Integrating Atmospheric Mercury Deposition and Aquatic Cycling in the Florida Everglades:

An approach for conducting a Total Maximum Daily Load analysis for an atmospherically derived pollutant

Integrated Summary

FINAL REPORT

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EXECUTIVE SUMMARY

Integrating Atmospheric Mercury Deposition with Aquatic Cycling in South Florida:

An approach for conducting a Total Maximum Daily Load analysis for an atmospherically derived pollutant

Florida Department of Environmental Protection
October, 2002
Revised November, 2003

Purpose:

The purpose of this project was to demonstrate the technical feasibility of conducting a Total Maximum Daily Load (TMDL) analysis for a system where the contaminant of interest is derived principally from atmospheric sources. Depending on the type of aquatic system, a number of contaminants may be categorized as significantly atmospheric in origin, including mercury, fixed nitrogen, PCB’s, and others. This study focuses on mercury, and incorporates extensive field data into a framework combining atmospheric mercury deposition and aquatic mercury cycling models to demonstrate the feasibility of the approach. The goal was to understand and simulate how changes in local atmospheric mercury emissions in south Florida would influence mercury concentrations in top predator fish, thus demonstrating the potential of combining air and water modeling approaches in TMDLs involving air deposition of mercury.

About 2 million acres of the south Florida Everglades ecosystem are currently under fish consumption advisories because of mercury contamination. The Clean Water Act requires that states list as impaired all waterbodies that do not meet water quality standards when the designated uses are not being met or because water quality criteria are being exceeded. Mercury-contamination fish consumption advisories represent an exceedance of water
quality standards because a designated use for the Florida Everglades ecosystem is not being met. Once a waterbody such as the Everglades is placed on the Clean Water Act 303(d) list, a TMDL study is conducted to determine how much the pollutant (i.e., mercury) loading must be reduced, and from what sources, to meet the water quality standards and designated use for the waterbody. A TMDL establishes the maximum amount of a given pollutant that a particular waterbody can assimilate without exceeding surface water quality standards. TMDL-type analyses for determining needed reductions in atmospherically derived pollutants have rarely been done due to the data needs and technical complexity of developing and linking atmospheric and aquatic cycling models.

Mercury is both a naturally occurring element and a pollutant that cycles, in a variety of chemical forms, through air, water and soil. Some forms of mercury are transported around the world through the air, others tend to deposit from the atmosphere at local or regional scales. Extensive monitoring of the Florida Everglades ecosystem has shown that the primary source of mercury loading is atmospheric deposition – over 95% of the mercury load to the Everglades each year comes from atmospheric deposition. Because some atmospheric mercury is transported into Florida from both local and distant sources, a difficulty in producing a TMDL is determining the relative contribution of these sources. To conduct a TMDL analysis for mercury, atmospheric models are needed to simulate the transport of local mercury emissions and deposition onto the Everglades water surface. In addition, once the mercury deposition is estimated using atmospheric models, this deposition must be used as input to an aquatic ecosystem model that will simulate mercury cycling in the Everglades and uptake through the food chain to top predator fish, such as largemouth bass.

To that end, this modeling project was sponsored by the Florida Department of Environmental Protection and US Environmental Protection Agency to combine atmospheric mercury deposition models with an aquatic mercury cycling model. The mercury deposition output from the atmospheric models was used as input to an aquatic mercury cycling model. The aquatic mercury cycling model was used to predict the change in largemouth bass mercury concentrations that might occur if mercury emissions were reduced. The goal is to provide data and models that can be used to conduct a Total Maximum Daily Load study for mercury in the Everglades. ¹

Results and Conclusions

The following results were obtained from using output of the atmospheric model as input to the aquatic ecosystem model:

1. The E-MCM model predicts a linear relationship between atmospheric mercury deposition and mercury concentrations in largemouth bass, with a small residual mercury concentration in fish at zero atmospheric mercury deposition (Figure 9). In other words, for any reduction in mercury inputs to the Everglades a slightly lesser

¹ For additional information about the Florida DEP Mercury Program, access the web address given below: http://www.floridadep.org/labs/mercury/index.htm
reduction in fish mercury concentrations may be anticipated. Furthermore, error analysis shows that the E-MCM predicts near equivalence between the percent decrease in atmospheric mercury deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury. The slight offset from a 1:1 relationship results from slow mobilization of historically deposited mercury from deeper sediment layers to the water column. Until buried below the active zone, this mercury can continue to cycle through the system. In addition, because mercury is a naturally occurring element, fish tissue mercury concentrations can never be reduced to zero.

2. In the absence of changes to the system other than mercury loading (e.g., changes in sulfur cycling, nutrient cycling, or hydrology), a reduction of about 80% of current total annual mercury atmospheric deposition rates would be needed for the mercury concentrations in a 3-year old largemouth bass at WCA 3A-15 to be reduced to less than Florida’s present fish consumption advisory action level of 0.5 mg/kg (parts per million).

3. Mercury concentrations in three-year-old largemouth bass are predicted to achieve 50% of their long-term, steady state response following sustained mercury load reductions within approximately 10 years and 90% within 30 years (Figure 10).

4. Despite the uncertainties identified, the progress represented in these demonstrations of a unique combination of atmospheric and aquatic cycling models is remarkable. There is every reason to believe that, with modest additional effort, the remaining uncertainties can be reduced to levels that will allow reliable, confident allocation of mercury emissions to protect the designated uses of the Everglades.

5. It is also evident that there is further potential for combining such air and water modeling approaches for TMDLs involving air deposition of mercury for other aquatic ecosystems. We believe the approaches presented here can be applied to other geographic areas and in other studies of air – water chemical interactions.

Combining Atmospheric and Aquatic Models

The atmospheric modeling approach used in this study was developed by the University of Michigan Air Quality Laboratory to simulate the atmospheric transport of mercury from local emission point sources in southern Florida to its deposition onto the Everglades. The aquatic model, the Everglades Mercury Cycling Model (E-MCM), was used to simulate how mercury was cycled in the Everglades and accumulated through the Everglades food chain to top-level predator fish (e.g., largemouth bass, a popular sport fish).

The Florida Everglades ecosystem extends over 3,000 square miles, thus it was not realistic to simulate the entire ecosystem. However, extensive monitoring studies in the Everglades by USEPA (1998) revealed a mercury “hot spot” in central Water Conservation Area 3. The US Geological Survey subsequently conducted several years of intensive field study at this ‘hot spot’ (WCA 3A-15). Data from this site were used to calibrate the E-MCM model. Deposition and aquatic cycling data were available for 1995-1996; as a result, this period (22
June 1995 to 21 June 1996) was selected as the period of study. Atmospheric deposition rate for 1995-1996 is referred to as “current” deposition rate in this report.

Because of limited information and tools available to support modeling of a global transport domain, source-receptor modeling relied primarily on local sources to estimate deposition to the Everglades. As discussed in detail in Section 5.4.5 of the report, several lines of evidence suggest that local sources were the predominant contributor to mercury deposition on south Florida.

We acknowledge the global-scale cycling of some forms of mercury, but paucity of data or models to quantify or simulate this potential source to Florida puts this phenomenon beyond the reach of this analysis. An analysis by the principals of the FAMS project, independent of this work, examined rainfall mercury deposition in relation to trace element signatures of common sources of air pollution. They concluded that most mercury deposited at long-term south Florida deposition collection sites did not originate from local sources. Further field measurements and modeling analyses are underway to resolve this seeming paradox.

To estimate the deposition load to WCA 3A-15 measured wet deposition at multiple FAMS sites was combined with modeled dry deposition in this analysis. Estimating total deposition to the TMDL study site required analysis of historical weather patterns in south Florida and selecting representative wind direction and rainfall patterns to use in estimating both wet and dry mercury deposition over the area based on local point source mercury emissions. The atmospheric model was calibrated to 1995-96 mercury deposition rates (both dry and wet deposition). Different mercury deposition reduction scenarios were simulated (75, 50, 30, and 15% of current levels) and provided as input to the aquatic mercury cycling model.

The aquatic mercury cycling model was run using the projected estimates of mercury deposition onto the marsh water surface at WCA 3A-15. The E-MCM model was run for 200 years so that steady-state conditions would be reached between atmospheric mercury deposition and largemouth bass mercury concentrations at current deposition rates. A relationship between atmospheric mercury deposition and largemouth bass mercury concentration was developed using the results from each of the different mercury emission/deposition scenarios. In addition, the time required for largemouth bass mercury concentrations to decrease to 50% and 90% of their long term, steady state mercury concentrations based on the reduced mercury deposition scenarios was estimated to be 10 and 30 years, respectively.

**Assumptions and Cautions**

This analysis demonstrates that atmospheric and aquatic mercury cycling models can be combined and used to estimate the reduction in fish mercury concentration associated with reduced mercury deposition. However, several assumptions and cautions must be considered when interpreting these results:
1. This report is not a fully formed mercury TMDL intended for implementation; that was not the goal of the present analysis. However, this report does demonstrate the technical feasibility of a combined modeling analysis to encompass the multi-media aspects of an air-water-biota pollutant problem. It establishes a method that furthers the goal of conducting a mercury TMDL study for the Florida Everglades.

2. The contribution of global mercury emissions to current atmospheric mercury deposition in southern Florida is poorly understood. After model testing and evaluation to assess the strengths of the assumption, the final model analysis of the relationship between mercury emissions and atmospheric deposition assumed that most of the mercury in deposition was from local sources. Although the comparison between observed and predicted wet deposition rates based on this assumption was good, this remains an area of scientific debate.

3. The processes affecting the transformation of mercury in the atmosphere were poorly understood or quantified at the time of this report. Therefore, the atmospheric modeling may not accurately reflect the properties of the actual mercury species that are being deposited onto the Everglades.

4. Not all the aquatic cycling processes affecting the transformation of inorganic mercury to methylmercury (which is the toxic mercury species that accumulates in fish) are represented in detail in the Everglades Mercury Cycling Model. For example, sulfate reduction is an important to the process of transforming inorganic to methylmercury. Some of the byproducts of sulfate reduction bind inorganic and methylmercury, making them less available for biological uptake. The details of these processes are not yet understood, thus cannot be modeled. Until the model is progressively refined and parameterized these limitations might affect the results reported here.

5. Although the measurement set is drawn from extensive, quantitative research, uncertainties remain in all field measurements, but this uncertainty is not included in the modeled output. The magnitude of the uncertainty is unknown, but it can affect the interpretation and conclusions drawn from the results.

6. Natural year-to-year variation in mercury deposition can be relatively large. This natural variability has not been included in the minimum loading calculations (although the effects of this variability were examined over long time-frames through Monte Carlo analysis). The 1995-1996 period was used as the basis for this analysis because it is the 12 month period for which extensive field monitoring and modeling data were available. It was not, however, a typical year as 1995 and 1996 were relatively wet years in southern Florida.

7. Only one area of the Everglades was considered in the simulation - WCA 3A-15. Other areas in the Everglades might not respond similarly because of different habitat, food web dynamics and water quality.

**Recommendations**

The following actions are recommended in order to allow a formal TMDL to be conducted for the Florida Everglades:
1. Obtain better estimates of local vs. regional and global mercury contributions to southern Florida. This is critical because estimates of regional plus global sources by various workers range from ca. 25 to >60% of the mercury deposition over southern Florida.

2. Incorporate the aquatic chemistry and cycling of sulfur into the Everglades Mercury Cycling Model. Sulfate is an important influence on the production of methylmercury, affecting not only mercury transformations, but also the biological availability of mercury for uptake. There is a strong sulfate gradient decreasing from north to south in the Everglades Protection Area that is an important cofactor controlling the severity of the mercury problem at any given site.

3. Apply the atmospheric and aquatic models to other areas of the Florida Everglades to see if similar changes occur in largemouth bass mercury concentrations following reduced atmospheric deposition of mercury.

4. Improve mercury emissions inventories and better describe mercury species’ transformations in the atmosphere. These are critical information needs to improve mercury transport and fate modeling.

5. Obtain better estimates of the uncertainty in the study. Uncertainty can affect the interpretation and conclusions drawn. Uncertainties that potentially affect decisions regarding controlling local mercury emission sources should receive highest priority.
Cover, counterclockwise from top left:
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Figure 3. Thunderstorm over the central Florida Everglades. Courtesy Dan Scheidt, USEPA Region 4.

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Figure 6. Wood storks feeding in the Florida Everglades. Courtesy SFWMD.

This project and the preparation of this report was funded in part by a Section 103 Air Pollution Control Grant from the U.S. Environmental Protection Agency (US EPA) through a contract with the Mercury and Environmental Science Program of the Florida Department of Environmental Protection. The total cost of the project was $543,351 of which $161,880 or 28 percent was provided by USEPA.
FOREWORD

This document presents the results of a pilot project designed to evaluate the technical feasibility, given the present state of knowledge of mercury cycling in the environment, of calculating an atmospherically driven total maximum daily load (TMDL) for mercury for the Florida Everglades. This is among the first efforts to integrate atmospheric and aquatic cycling of a pollutant in a combined modeling analysis, as would be required for use in pollutant TMDLs where an atmospheric sources may be important contributors to pollutant loads. This project is not being conducted by Florida DEP with the expectation that it will be used as the basis for implementing changes to source permits or other action. Its purpose is to provide a technical analysis to provide the basis for a more comprehensive approach to a full TMDL process to be conducted subsequently.

This analysis is built upon extensive results from research on the sources, transport and fate of mercury in south Florida, and focuses on modeling approaches that might be used in the context of a TMDL for mercury deposited from the atmosphere. Florida law specifies the process the state will use for developing TMDLs for implementation. This law directs development of rules for the method of designating impaired waters and for the TMDL analysis itself. Any future TMDL analysis intended to be used to support policy will have to
conform to these legal strictures. The Rule has been adopted but is subject to further review by the USEPA. As agreed between Florida DEP and USEPA Region 4, the schedule for TMDL implementation does not require completion of atmospheric TMDLs for mercury until 2010. The purpose of this project is to establish the technical basis for more definitive efforts in the future. This project is a collaborative, voluntary effort between DEP and USEPA.

This analysis was conducted for a portion of the Everglades known as Water Conservation Area 3A. This area was chosen because it offered a wealth of information gained from the extensive monitoring, modeling and research conducted by the cooperating agencies of the South Florida Mercury Science Program. This fruitful collaboration among state, federal and private groups has greatly illuminated the causes of the mercury problem in the Everglades, and by extension, the causes of the problem that exists across much of our country.

This and a similar effort being conducted by the Wisconsin Department of Natural Resources, represent an early effort to examine the issues that arise when a TMDL addresses atmospheric sources. As originally set forth in the Clean Water Act 30 years ago, TMDL analyses were conceived for direct discharge of wastes to a waterbody to address simple water quality problems such as low dissolved oxygen caused by excessive biological oxygen demand. However, it has since become apparent that pollutants from the atmosphere can represent significant loads to water bodies. Pioneering studies in Chesapeake Bay and the Great Lakes have demonstrated that the atmosphere can be a large source of nutrients or toxic substances to water bodies. Similarly, for the Florida Everglades, average annual atmospheric deposition rates for mercury outweigh surface water input by more than 20:1 (USEPA, 1998).

While the concept of an atmospheric TMDL may seem straightforward, the technical challenges in coupling air source pollutant emissions, chemistry and transport with the complex aquatic cycling and fate of mercury are daunting. At this time, significant uncertainties remain in our basic understanding of the atmospheric mercury cycle and modeling of mercury transport and fate, and likewise in our understanding of the aquatic cycling transformation processes and mercury bioaccumulation in aquatic food webs.

We wish to thank our many collaborators of the South Florida Mercury Science Program for their data, analyses, guidance, advice and efforts in the preparation of this document. We especially wish to thank William J. Bigler (DOH, retired), Forrest Ware (FWC, retired) and Thomas Savage (DEP, retired) who began the monitoring that led to the discovery of the mercury problem in Florida and which ultimately provided impetus for this work.

This document was developed by the Florida Department of Environmental Protection and its contractor, Tetra Tech, Inc. It was funded by appropriations from the Florida Legislature and in part by USEPA Region 4 by Cooperative Agreement No. X984123-97-0. The findings herein do not represent the policies or views of the USEPA. This project supported the efforts of the University of Michigan Air Quality Laboratory and Tetra Tech under DEP Contracts AQ-136 and SP-508, respectively.
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>ACME</td>
<td>Aquatic Cycling of Mercury in the Everglades study, USGS</td>
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<td>AT</td>
<td>Andytown monitoring site of the Florida Atmospheric Mercury Study (FAMS)</td>
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<td>CMAQ</td>
<td>Community Multiscale Air Quality Model, an USEPA/NOAA atmospheric chemistry, transport and deposition model</td>
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<td>CWA</td>
<td>Clean Water Act</td>
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<td>DEP</td>
<td>Florida Department of Environmental Protection</td>
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<tr>
<td>DOH</td>
<td>Florida Department of Health</td>
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<td>EAA</td>
<td>Everglades Agricultural Area</td>
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<td>ENP</td>
<td>Everglades National Park</td>
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<td>EPA</td>
<td>Everglades Protection Area (i.e. Water Conservation Areas and the Everglades National Park)</td>
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<tr>
<td>E-MCM</td>
<td>Everglades Mercury Cycling Model</td>
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<td>FAMS</td>
<td>Florida Atmospheric Mercury Study</td>
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<td>FEDDS</td>
<td>Florida Everglades Dry Deposition Study</td>
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<td>FS</td>
<td>Fakahatchee Strand State Park monitoring site of the Florida Atmospheric Mercury Study (FAMS)</td>
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<tr>
<td>FWC</td>
<td>Florida Fish and Wildlife Conservation Commission</td>
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<tr>
<td>GIS</td>
<td>Geographic Information System, computer mapping system</td>
</tr>
<tr>
<td>GMT</td>
<td>Greenwich Mean Time (5 hours earlier than USA east coast time)</td>
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<td>Hg</td>
<td>The chemical notation for the element mercury, derived from the Greek for liquid silver -Hydrargyrum</td>
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<td>Hg(0)</td>
<td>Elemental mercury, the silvery metal liquid at room temperature</td>
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<tr>
<td>Hg(II)</td>
<td>Divalent mercury, a form of inorganic mercury; mercuric ion, RGM</td>
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<td>Hg(p)</td>
<td>Atmospheric particulate-associated mercury</td>
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<td>Hg_t, Hg_tot</td>
<td>Total mercury, i.e. lab analysis of all forms of mercury</td>
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<tr>
<td>HYSPLIT_4</td>
<td>Hybrid Single Particle Lagrangian Integrated Trajectories Model, a NOAA atmospheric transport &amp; deposition model</td>
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<td>LMB</td>
<td>Largemouth bass</td>
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<tr>
<td>mb</td>
<td>Millibars of pressure in the atmosphere</td>
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<tr>
<td>MCM</td>
<td>Mercury Cycling Model</td>
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<td>MDN</td>
<td>Mercury Deposition Network, a sub-network of the National Atmospheric Deposition Program</td>
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<tr>
<td>mg/kg</td>
<td>Milligrams per kilogram, a unit of measure of concentration, ppm</td>
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<td>MeHg</td>
<td>Methylmercury</td>
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<td>METAALICUS</td>
<td>Mercury Experiment To Assess Atmospheric Loading in Canada and the United States</td>
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<td>Mercury Study Report to Congress (USEPA 1997)</td>
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<tr>
<td>MWC</td>
<td>Municipal Waste Combustors, (aka., Municipal Solid Waste Incinerator)</td>
</tr>
<tr>
<td>MWI</td>
<td>Medical Waste Incineration</td>
</tr>
<tr>
<td>NADP</td>
<td>National Atmospheric Deposition Program</td>
</tr>
<tr>
<td>ng/L</td>
<td>nanograms per liter, unit of measure of concentration, ppt</td>
</tr>
<tr>
<td>NCEP</td>
<td>NOAA National Center for Environmental Prediction</td>
</tr>
<tr>
<td>NGM</td>
<td>Nested Grid Model</td>
</tr>
<tr>
<td>NOAA – ARL</td>
<td>National Oceanic and Atmospheric Administration – Air Resources Lab</td>
</tr>
<tr>
<td>NPDES</td>
<td>National Pollutant Discharge Elimination System</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per billion, a unit of measure of concentration, ppb</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million, a unit of measure of concentration</td>
</tr>
<tr>
<td>ppt</td>
<td>parts per trillion, a unit of measure of concentration</td>
</tr>
<tr>
<td>RAMS</td>
<td>Regional Atmospheric Modeling System</td>
</tr>
<tr>
<td>RELMAP</td>
<td>Regional Lagrangian Model of Air Pollution</td>
</tr>
<tr>
<td>REMAP</td>
<td>Regional – Environmental Monitoring Assessment Program</td>
</tr>
<tr>
<td>RGM</td>
<td>Reactive Gaseous Mercury</td>
</tr>
<tr>
<td>SFMSP</td>
<td>South Florida Mercury Science Program</td>
</tr>
<tr>
<td>SFWMD</td>
<td>South Florida Water Management District</td>
</tr>
<tr>
<td>SoFAMMS</td>
<td>South Florida Atmospheric Mercury Monitoring Pilot Study</td>
</tr>
<tr>
<td>TGM</td>
<td>Total Gaseous Mercury</td>
</tr>
<tr>
<td>TMDL</td>
<td>Total Maximum Daily Load</td>
</tr>
<tr>
<td>TT</td>
<td>Tamiami Trail monitoring site of the Florida Atmospheric Mercury Study</td>
</tr>
<tr>
<td></td>
<td>(FAMS)</td>
</tr>
<tr>
<td>UMAQL</td>
<td>University of Michigan Air Quality Laboratory</td>
</tr>
<tr>
<td>USEPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>USFWS</td>
<td>U.S. Fish and Wildlife Service</td>
</tr>
<tr>
<td>USGS</td>
<td>U.S. Geological Survey</td>
</tr>
<tr>
<td>µg/L</td>
<td>micrograms per liter, a unit of measure of concentration, ppb</td>
</tr>
<tr>
<td>µeq/L</td>
<td>microequivalents per liter, a unit of measure of concentration</td>
</tr>
<tr>
<td>WCA</td>
<td>Water Conservation Area, a subdivision of the Everglades</td>
</tr>
</tbody>
</table>
1 BACKGROUND

Our understanding of the biogeochemical cycle of mercury has improved dramatically within
the past decade. Prior to the development of ‘clean’ sampling and ‘ultra-trace’ analytical
procedures, concentrations or pools of mercury in air, rain and surface waters, and the fluxes
between these compartments, were commonly overestimated, in some cases by two to three
orders of magnitude (Fitzgerald, 1986, 1989). Against this inflated backdrop, anthropogenic
sources of mercury to the atmosphere of all types appeared small, with estimates of natural
emissions accounting for 90 to 95 percent of total cycle. By the early 1990’s, application of
more accurate measurements of the global pools and fluxes of mercury overturned this view,
leading to the conclusion that natural emissions were “between 20 and 50 percent of the
direct and indirect anthropogenic sources” (Expert Panel, 1994). Present estimates tend
toward the lower end of this range. This new insight into the ‘natural vs. anthropogenic’
question, plus the finding that the accumulation of mercury in seepage lakes in remote areas
is largely attributable to atmospheric inputs (Watras, et al., 1994), has changed the way the
mercury problem is viewed. Attention now focuses beyond the problem of elevated mercury
in fishes in these lakes to the importance of deposition processes, atmospheric transport and
chemistry, and ultimately to sources of mercury to the atmosphere.

The view that anthropogenic sources of mercury to the atmosphere predominate is buttressed
by studies of long-term trends of mercury in the environment by examination of cores of
sediments and similar media. “Considered individually, these methods are subject to much
uncertainty. However, when considered as a whole they indicate that the total atmospheric
mercury burden has increased since the beginning of the industrialized period by between a
factor of two and five.” (Expert Panel, 1994). The significance of this increase is confounded
by lack of uniformity, both temporally and geographically. For example, in some areas it has
been shown that mercury deposition peaked between 1950 and 1970, at a level about three
times present deposition rates. (Engstrom and Swain, 1997; Zillioux, et al., 1993). Similar
analyses of sediment records in the Florida Everglades indicate an increasing trend up

The most recent data on mercury trends at a site broadly representative of the continental
U.S. was recently published by a team of USGS scientists (Schuster, et al., 2002). As shown in
Figure 1, mercury has accumulated in core records since the Industrial Revolution,
peaking in the 1960’s through the 1980’s and declining in the past decade or so.
A remaining area of great scientific uncertainty is how to incorporate the varying spatial scales of the atmospheric mercury cycle into an understanding of mercury bioaccumulation in aquatic systems. The differing chemical and physical forms of mercury found in the atmosphere vary greatly in their transport and deposition properties. Elemental mercury vapor \{Hg(0)\} is relatively inert and has an atmospheric half-life measured in months to years, exerting its effect worldwide. Particulate-associated mercury \{Hg(p)\} has a half-life of days to weeks, exhibiting a regional effect (several hundred kilometers). Reactive gaseous mercury \{RGM or Hg(II)\} has a half-life measured in hours and, if emitted in this form, is deposited on a local scale, i.e. largely within a few score kilometers.

When looking at atmospheric loading from the frame of reference of a particular waterbody, the ability to distinguish global vs. regional vs. local scales of air transport and deposition is crucial to formulation of control strategy. Because of the geographic distribution of regional sources, and the fact that south Florida is meteorologically disjunct from the continental US, the scales important to the Everglades are local and global. This leads to the question: Is the source of mercury contributing to deposition into the Everglades predominantly coming from emissions sources within south Florida, or is it coming from long distance transport from sources around the globe? This pilot study asks: To what extent could abatement of south Florida mercury emissions reduce deposition on the Everglades and subsequent bioaccumulation in Everglades biota? This effort uses available data and mesoscale air and water models to address this question about local sources.
gives no direct information about the significance of global sources, which could limit the
efficacy of local controls in reducing mercury concentrations in Everglades biota.

Although not directly relevant to the present analysis, which does not directly consider how
global sources of mercury may affect Florida, it should be noted that complementary studies
of mercury deposition in south Florida have yielded conflicting conclusions regarding the
magnitude of global mercury sources. The present inability to directly gauge the relative
importance of local vs. global sources, tells us that the scope of previous studies and some of
the methods of sampling and analysis were limited in their ability to provide conclusive
information. New, more specific and powerful methods have been developed, and are being
applied in a series of studies over the next two years to ultimately enable us to answer this
question with confidence.
2 PROBLEM STATEMENT

In 1989, monitoring by the Florida Fish and Wildlife Conservation Commission (FWC), the Florida Department of Environmental Protection (DEP), and the Florida Department of Health (DOH) revealed high levels of mercury in fish from the Everglades. Long known to be neurotoxic to humans, consumption of mercury-contaminated food had caused tragic illness and mortality in several episodes around the world. These findings led the Florida State Health Officer to issue Health Advisories urging fishermen not to eat some species of fish caught from the Everglades, and to limit consumption of largemouth bass and several other predatory fish species taken from many other fresh and coastal waters of Florida.

When extensive sampling was completed in the early 1990s, it was evident that approximately 1 million acres of the remnant Everglades system contained fish with high mercury burdens - largemouth bass averaged nearly 2.5 mg/kg mercury, which exceeded all health-based standards. More than another million acres of fresh waters in Florida contain largemouth bass with elevated but lesser levels of mercury. Were sampling to be comprehensive, we would expect mercury problems in bass to be found in one-half to two-thirds of Florida’s waters. Florida DEP and USEPA have determined that inability to consume one’s catch of sport fish at-will impairs recreation, a designated beneficial use of the affected waters.

This finding of excessive levels of mercury in fish is not limited to Florida. To date, over 40 states have issued health advisories restricting consumption of fish based on their mercury content, and similar problems are found broadly in North America, Europe and Asia.

2.1.1 Nature of the Everglades mercury problem

Mercury issues within the Everglades are extremely difficult to assess due to the size and heterogeneity of the Everglades, compounded by the complexity of mercury biogeochemistry. The gaps in scientific knowledge needed to control this problem are being addressed by a consortium of government and private agencies\(^2\) collaborating as the South

\(^2\) Florida Department of Environmental Protection, South Florida Water Management District, U.S. Environmental Protection Agency, Florida Electric Power Coordinating Group, Florida Fish and Wildlife Conservation Commission, and U.S. Geological Survey. Other SFMSP collaborators include the Academy of...
Florida Mercury Science Program (SFMSP). The SFMSP goal is to elucidate the processes governing the environmental cycle of mercury through monitoring, modeling and research and to recommend sound management strategies for the mercury problem.

It is now generally accepted that this widespread mercury problem is caused by human activities that result in air emissions of mercury. Major sources to the atmosphere are municipal waste combustors (MWC), medical waste incinerators (MWI), metals mining and smelting; coal-fired utilities and industry; and the mining, smelting, use and disposal of mercury itself. The unusually severe problem in the Everglades has many unique features, and may be the result of a combination of factors (SFWMD, 1999, 2000, 2001, 2002). Both long distance transport and localized deposition around certain types of sources are important. The principal concerns there focus on local effects of waste incinerators and other emissions sources in southeast Florida, increased release of mercury or other substances from the Everglades Agricultural Area promoted by drainage and soil disturbance, or hydrologic changes.

The SFMSP has sponsored a series of projects related to this issue such as the Florida Atmospheric Mercury Study (FAMS), South Florida Atmospheric Mercury Monitoring Pilot Study (SoFAMMS), Florida Everglades Dry Deposition Study (FEDDS), Speciated Atmospheric Mercury Study (SAMS), USEPA Regional Environmental Monitoring and Assessment Program (REMAP), Speciated Atmospheric Mercury Profiling Experiment (SAMPEX) and the USGS Aquatic Cycling of Mercury in the Everglades (ACME) program. Numerous publications have resulted. The South Florida Water Management District and the Florida Fish and Wildlife Conservation Commission (FWC) also have ongoing monitoring programs. Data from these programs were used extensively to develop and calibrate the models applied in this assessment.

2.1.2 Rationale for a TMDL approach

From its inception, the SFMSP approached the Everglades mercury problem as a multimedia one. The conceptual model encompassed three major processes – atmospheric sources and cycling, aquatic cycling, and bioaccumulation – and the linkages between them. Components addressed in this analysis include sources of mercury, and environmental media including air, water, sediments, and biota.

When renewed emphasis on the TMDL process emerged in the late 1990’s, the approach being taken by the SFMSP was compatible; thus further monitoring, modeling and research have been coordinated with the long-term goals of the TMDL approach. Because of the extensive data collected and models developed by the SFMSP through the 1990’s, USEPA in 1999 solicited Florida’s participation as one of two states for pilot studies of how to

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3 For a partial bibliography see: [http://www.floridadep.org/labs/mercury/index.htm](http://www.floridadep.org/labs/mercury/index.htm)
rationally incorporate deposition of air pollutants in the TMDL process. Thus began what is termed the Florida Mercury TMDL Pilot Study.

For this project, we chose a site within Everglades Water Conservation Area 3A, Site 3A-15, because of the richness of data from that region (3A-15 was one of the USGS ACME intensive study sites, and there existed an extensive water quality database for the region from the USEPA REMAP project). This site was also known to have high concentrations of mercury in fish. It is important to recognize that, although the Everglades is widely recognized as a large freshwater wetland, it is by no means homogeneous; rather, it comprises a host of diverse environments of different types of vegetative assemblages and environmental gradients. Likewise, mercury concentrations in water, sediments, and biota also are spatially heterogeneous. Thus, the results from this pilot analysis cannot and should not be extrapolated to any other portion of the Everglades.

This pilot TMDL evaluates various scenarios of atmospheric emissions from point sources in south Florida and simulates the effects of these atmospheric loadings on bioaccumulation in top predators in the Everglades aquatic system. Key to the approach is the linkage of atmospheric deposition models (Hybrid Single Particle Lagrangian Integrated Trajectories Model, version 4 [HYSPLIT\_4] and Regional Atmospheric Modeling System [RAMS]) with the Everglades Mercury Cycling Model (E-MCM) to estimate mercury concentrations in predatory fish (i.e., largemouth bass). Detailed reports containing the results of these models are provided as Appendices I and II to this document. A summary of the relevant results from the modeling efforts is provided in this report.

### 2.2 Description of TMDL Process

Water quality standards are established to protect the designated uses of Florida’s waters. When States, Tribes or local communities identify problems in meeting water quality standards, a TMDL can be a framework for addressing those problems. The purpose of this demonstration project is to explore the utility of using atmospheric and mercury-cycling models within the TMDL framework and to provide the stakeholders with technical information that may be used to develop a water quality plan to address mercury issues in the Everglades.

Section 303(d) of the Clean Water Act (CWA) requires states to identify the waters for which the effluent limitations required under the National Pollutant Discharge Elimination System (NPDES) or any other enforceable limits are not stringent enough to meet any water quality standard adopted for such waters. The states must also prioritize these impaired water bodies for TMDL development, taking into account the severity of the pollution and the beneficial uses of the waters.

A TMDL represents the maximum amount of a given pollutant that a particular waterbody can assimilate without exceeding surface water standards. The TMDL can be expressed as the total mass of pollutant that can enter the water body within a unit of time. For this pilot TMDL, it is the total mass of atmospherically and water-borne mercury that enters the Everglades. In most cases, the TMDL determines the allowable mass per day of a pollutant
and divides it among the various pollution sources in the watershed as waste load (i.e., point source discharge) and load (i.e., non-point source) allocations. The TMDL also accounts for natural background sources (e.g., atmospheric deposition derived from global sources) and provides a margin of safety.

Although this document is not a TMDL determination per se, we list the elements of TMDLs as described in USEPA guidance to put this pilot effort in context. Specifically, we discuss how this document compares with those elements, and in what additional elements work would be needed to fully develop a TMDL. Some of these elements are required under the Clean Water Act, while others are elements recommended in USEPA guidance. The following eight elements represent USEPA Region 4 TMDL guidance:

1. **Plan to meet State Water Quality Standards:** Although not explicitly required by the USEPA guidance for TMDL analyses, it is desirable to include a study and plan for the specific water and pollutants that must be addressed to ensure that applicable water quality standards are attained.

2. **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.

3. **Analyze/account for all sources of pollutants.** All significant pollutant sources are described, including the magnitude and location of sources.

4. **Identify pollution reduction goals.** The TMDL plan includes pollutant reduction targets for all point and non-point sources of pollution.

5. **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, do the recommended pollutant load allocations exceed the loading capacity of the receiving water?

6. **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 assurances that the appropriate load reductions will be implemented.

7. **Provide implementation recommendations for pollutant reduction actions and a monitoring plan.** The TMDL should provide a specific process and schedule for achieving pollutant reduction targets. A monitoring plan should also be included, especially where management actions will be phased in over time and to assess the achievement and validity of the pollutant reduction goals.
8. **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.

The elements of a TMDL required by statute are loading capacity, wasteload allocation, load allocation, margin of safety, and seasonal variation.

### 2.2.1 Current Status of addressing TMDL Elements

This analysis addresses 5 of the 8 elements of the TMDL process, described below:

1. **Describe quantified water quality goals, targets, or endpoints.** The present quantitative endpoints for mercury in Florida waters derive from its propensity for bioaccumulation in aquatic food webs, presenting chronic health risks to humans and wildlife that eat large amounts of fish. The quantitative endpoints for human health are the DOH guidelines for mercury health advisories to fishermen, detailed in section 3.3 of this report, specifically in Table 4. Florida Department of Health guidelines for mercury in fish consumption advisories.

2. **Analyze and account for all sources of pollutants.** The primary sources of mercury to the Everglades are storm water runoff via canal structures draining into the Everglades, and atmospheric deposition. The data given in Table 1 (USEPA, 2001) define the proximate sources of the mercury load to the Everglades Protection Area (i.e. the water conservation areas and ENP). However, until apportionment of the mercury deposition between local emissions and global background sources has been resolved, this element cannot be completed to the extent of formulation of source-specific controls.

<table>
<thead>
<tr>
<th>Year</th>
<th>Atmospheric Deposition</th>
<th>EAA Water Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1994</td>
<td>238 Hg kg/yr. (^4)</td>
<td>2 Hg kg/yr.</td>
</tr>
<tr>
<td>1995</td>
<td>206 Hg kg/yr.</td>
<td>3-4 Hg kg/yr.</td>
</tr>
</tbody>
</table>

3. **Identify pollution reduction goals.** The pollutant reduction goal here is the reduction of atmospheric mercury deposition necessary to achieve mercury deposition needed to achieve a concentration in Everglades fish of less than 0.5 mg/kg. Within the limitations of the assumptions of the air and water models, the pollutant reduction goal for atmospheric deposition from locally derived sources has been estimated.

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\(^4\) Annual deposition derived from Florida Atmospheric Mercury Study (FAMS), 1993 – 1996.

\(^5\) Derived from biweekly monitoring of ‘into’ structures discharging from the EAA into the Everglades Protection Area, USEPA, 1994 - 1996.
4. **Describe the linkage between water quality endpoints and pollutants of concern.**
   This is described by the modeling presented in Chapter 4 of this analysis, which suggests a strong direct relationship between inorganic mercury loads to the Everglades Protection Area from atmospheric deposition (Figure 9) and mercury concentrations in largemouth bass. In addition, modeling suggests a relatively rapid response of mercury in fish to changes in load (Figure 10).

5. **Develop margin of safety that considers uncertainties, seasonal variations, and critical conditions.** A margin of safety could be incorporated into the analysis as regards a human health reference dose for mercury, and in the atmospheric and aquatic modeling. This issue is discussed more fully in Section 5.3.

Because this is a pilot TMDL, none of the elements of the TMDL methodology has been completely resolved in this report. Key portions of Elements 2 - 6 are addressed, but these must be treated more exhaustively in later analyses. Addressing Element 7 awaits narrowing the uncertainties highlighted here. Both external and internal peer review of this pilot study have been completed; comments from various stakeholders — public, private and interested parties — have been incorporated herein. As this document is not a complete TMDL analysis, the stakeholder review for the pilot – Element 8 – was not intended to fulfill the public review requirements for a TMDL. Review comments and responses are summarized in Appendix III.

**2.3 Florida’s 303(d) Process**

Florida’s rivers, streams, and lakes are spectacularly beautiful and are essential natural resources, supplying water necessary for public consumption, recreation, industry, agriculture, and aquatic life (DEP, 2000). DEP is responsible for preserving and maintaining the quality of Florida’s waters. The TMDL program is a key component of a comprehensive approach to protecting water quality in Florida. As directed by Florida Statutes, rules have been developed to give specific guidance for implementing the TMDL process. Rule 62-303, F.A.C (Impaired Waters Rule) defines the data and methodologies required for placing waterbodies on the impaired list.

DEP has developed a five-phase approach to eliminating water quality impairment through its 303(d) Process (Table 2). This integrates monitoring and evaluation on a five-year cycle to assess quality of all waters. Waterbodies listed in earlier assessment cycles have been placed on a ‘planning list,’ whereby further monitoring is initiated to validate the original listing and determine probable sources of the stressors causing the listing. This monitoring step was added because waters often were originally listed based on nominal data and information. The data analysis step provides detailed documentation of the water quality and serves as the basis for the development of the TMDL for waterbodies on the validated list.

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6 The first draft of this report was submitted to an independent panel for review. Those reviewers were:
Dr. Mark Cohen, NOAA Air Resources Laboratory
Dr. Kent Thornton, Principal Ecologist, FTN Associates, Ltd.
Dr. Joseph V. DePinto, LimnoTech, Inc.
Dr. Donald B. Porcella, Environmental Science and Management, Electric Power Research Institute
Dr. Robert P. Mason, Associate Professor, Chesapeake Biological Laboratory, University of Maryland
The TMDLs and other basin related issues are incorporated into a Basin Management Plan in consultation with local stakeholders. When water quality impairment is found, TMDL assessments are initiated.

<table>
<thead>
<tr>
<th>Table 2. Steps in Florida’s 303(d) Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Initial Basin Assessment.</td>
</tr>
<tr>
<td>Identification of waterbodies requiring restoration, protection, or TMDL development.</td>
</tr>
<tr>
<td>2. Coordinated Monitoring.</td>
</tr>
<tr>
<td>Supplement existing data for TMDL development</td>
</tr>
<tr>
<td>3. Data Analysis and TMDL Development.</td>
</tr>
<tr>
<td>Document water quality and conduct TMDLs</td>
</tr>
<tr>
<td>Work with local stakeholders</td>
</tr>
<tr>
<td>Incorporate implementation of TMDLs</td>
</tr>
<tr>
<td>Address watershed goals</td>
</tr>
</tbody>
</table>

If additional data or closer examinations of existing data show that the water quality is impaired, then the most appropriate action to bring this water body back into compliance with its standard is pursued. Typically, this action would include completing a TMDL analysis for the drainage basin.

Changes in standards or the establishment of site-specific standards are the result of ongoing science-based investigations or changes in toxicity criteria from USEPA. Changes in designated uses and standards are part of the USEPA’s surface water standards triennial review process and are subject to public review. Standards are not changed simply to bring the water body into compliance, but are based on existing uses and natural conditions.

Seventeen areas of the Everglades are included on Florida’s 1998 Water Quality Limited Waters List (303(d) List) for violations due to fish consumption advisories for mercury, including WCAs 1, 2, 3, and Everglades National Park (ENP). The project study area, WCA 3A-15, is listed for fish consumption advisories for mercury (Figure 2).

### 2.4 Watershed

#### 2.4.1 Overview
The Everglades are a naturally occurring wetland system that historically (i.e., prior to 1855) occupied the lower third of the Florida peninsula south of Lake Okeechobee (Figure 2). Hydrologically, the Everglades are part of the greater Kissimmee River-Lake Okeechobee-Everglades system that conveyed water from central Florida southward towards Florida Bay.

During the 20th Century, the extent of the Everglades was significantly reduced and the spatial and temporal patterns in hydrology, fire, and nutrient supply altered (Davis and Ogden, 1994). Approximately half of the Everglades were drained for agriculture and urban development during the early to mid 20th Century. Presently, the north to south movement of water through the remnant Everglades is regulated by control structures at Lake Okeechobee and in the Water Conservation Areas (Figure 2).

GIS coverages for land use, land ownership, and vegetation types were obtained from BASINS2 (USEPA, 1998). Land usage is based on the Anderson Level 2 land classification system. Topographic information was obtained from BASINS2 (1:250,000 scale DEM).

2.4.2 Hydrology
The present Everglades system extends from the southern edge of Lake Okeechobee through the Everglades Agricultural Area (EAA), Water Conservation Areas and Everglades National Park to Florida Bay. The EAA has been diked and drained to supply land for agriculture. Water flows slowly in a southerly direction from Lake Okeechobee. The overall topographic gradient between Lake Okeechobee and Florida Bay is approximately 1 foot per 10 miles (0.3 m/16.1 km) (Davis and Ogden, 1994).

WCA-3A is contained by levees on three sides. On the western side it is only partially leveed to allow overland water flow from the Big Cypress swamp (Davis and Ogden, 1994). Major water inputs are from the S-11 structures (A, B, & C) and the S-8 and S-9 pump stations on the Miami Canal and the S-140 pump station that drains from Hendry County. Gravity drainage from the S-150 spillway also occurs at times. Within WCA-3A, ground elevation ranges from 7 to 10 feet above Mean Sea Level (Davis and Ogden, 1994).

Rainfall supplies approximately 70 percent of the annual water budget of the Water Conservation Areas (Davis and Ogden, 1994). The remainder comes from runoff from the EAA. Long-term average annual precipitation near WCA 3A ranges between 51.6 inches at a station near Lake Okeechobee, to 50.4 inches in the ENP (SERCC, 2000). During the period between 1970 and 1998, the station located at WCA 3A-S_R averaged 50.3 inches per year (SFWMD, 1999). The highest precipitation occurs from June through September with between 6 and 9 inches of rainfall per month. The winter months are considerably drier, with rainfall approximately 1 inch/mo.
Figure 2. Location of Everglades watershed, Water Conservation Area 3A, and study site 3A-15.
The annual ambient air temperature is between 72 and 75 °F (22 – 24 °C), varying from an average monthly temperature of 62 to 66 °F (16.7 - 19 °C) in January to an average of 80 to 83 °F (26.7 - 28 °C) in August (SERCC, 2000). Minimum temperatures for January averaged 52°F (11 °C), and maximum temperatures for August averaged 91°F (32.8°C) between 1961 and 1990 (SERCC, 2000).

2.4.3 Physiographic Characteristics
Land elevations change only subtly throughout the Everglades. The average slope between Lake Okeechobee in the north and Florida Bay in the south is approximately 1:53,700 (Davis and Ogden, 1994).

Everglades soils consist predominantly of peat soils underlain by limestone deposits.

2.4.4 Vegetation and Land Use
WCA-3A is predominantly composed of wetlands dominated by herbaceous plants (95%), of which approximately 50% is comprised of sawgrass and cattails, approximately 45% is wet prairies, and some forested wetland areas (3.5%) do occur. Evergreen forests, mixed rangeland, and localized built-up areas make up the remaining 1.5 percent of the area (BASINS2, USEPA, 1998).

WCA 3A provides flood protection and water supply to residents in southeast Florida. In addition, this area provides fish and wildlife habitat as well as recreational opportunities (e.g., fishing).

2.5 Existing Conditions and Summary of Monitoring Data
Several water quality parameters have been identified as having an impact on concentrations of total and methylmercury in freshwater systems. In particular, dissolved organic carbon, pH, sulfate (and sulfide), and chloride have received much attention. Table 3 shows the average values for water quality parameters at WCA 3A-15.

Mercury concentrations were measured in surface waters at WCA-3A-15 on 8 occasions between 1995 and 1998. Total mercury ranged from 1.05 ng/L to 2.70 ng/L and averaged 1.94 ng/L (Krabbenhoft, et al., 1998). Largemouth bass (Micropterus salmoides) were collected at WCA 3A-15 on 5 occasions between December 1996 and November 1998 by the FWC (Lange, et al., unpublished data). Fish ranged in length from 12 cm to 51 cm. Mercury concentrations in the tissue ranged from 0.45 mg/kg to 4.3 mg/kg (Figure 3).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved organic carbon</td>
<td>~ 16 mg/L</td>
</tr>
<tr>
<td>Surface water pH</td>
<td>~ 7.2</td>
</tr>
<tr>
<td>Surface water chloride</td>
<td>~ 5 mg/L</td>
</tr>
<tr>
<td>Surface water sulfate</td>
<td>100 μeq/L</td>
</tr>
<tr>
<td>Sedimentation rate</td>
<td>&lt; 1 cm/yr.</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>~ 2 mg/L</td>
</tr>
<tr>
<td>Fraction of marsh with open water</td>
<td>&lt;50%</td>
</tr>
<tr>
<td>Periphyton density</td>
<td>High</td>
</tr>
<tr>
<td>Macrophytes</td>
<td>Includes sawgrass, cattails, water lilies</td>
</tr>
</tbody>
</table>

Figure 3. Methylmercury concentrations in largemouth bass in WCA 3A-15. (Lange, et al. unpublished data).

2.6 Identification of Violated Water Quality Standards and Impaired Designated Uses

Under the federal Clean Water Act, states are responsible for establishing, reviewing, and revising water quality standards. The components of the surface water quality standards system include: classifications, water quality criteria, an antidegradation policy, and special protection of certain waters. Florida has five classes of waters with associated designated uses, which are arranged in order of degree of protection required:
Class I - Potable Water Supply
Fourteen general areas throughout the state including: impoundments and associated tributaries, certain lakes, rivers, or portions of rivers that are used as a drinking water supply.

Class II - Shellfish Propagation or Harvesting
Generally coastal waters where microbial water quality allows for commercial shellfish harvesting.

Class III - Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife
The surface waters of the state are Class III unless otherwise described in rule 62-302.400 of the Florida Administrative Code. These uses are also protected for all Class I and Class II waters.

Class IV - Agricultural Water Supplies
Generally located in agriculture areas around Lake Okeechobee.

Class V - Navigation, Utility and Industrial Use
Currently, there are no Class V water bodies.

To protect the present and future most beneficial uses of these waters, water quality criteria have been established for each classification. While some of these criteria are intended to protect aquatic life, others are designed to protect human health. Water quality standards, described in Rules 62-302.500 and 62.302.530, F.A.C, are expressed as either numeric (a specific concentration which cannot be exceeded) or narrative (used to describe a condition that is not desired). All of the Everglades, including Water Conservation Area 3A, is classified as a Class III water body. This designation means its waters are to be suitable for recreation, and propagation and maintenance of a healthy, well-balanced population of fish and wildlife.

Florida’s Class III water quality criterion of 12 ng/L for total, unfiltered mercury has not been exceeded in either the Everglades marsh, or in tributary waters. However, the Department of Health (DOH) fish tissue guidance concentration of 0.5 mg/kg is currently exceeded throughout areas of the marsh, prompting the issuance of fish consumption advisories by the Florida State Health Officer. DEP recognizes that health advisories impair recreation and that this means that the current water quality criterion, which is met, is of limited utility.

Furthermore, as regards protection of Everglades wildlife, risk assessments conducted by the SFWMD (Fink et al., 1999) as part of the South Florida Mercury Science Program have identified the potential for adverse effects from mercury for wading birds. A preliminary risk assessment for the Florida panther (Felis concolor coryi, a Federally-listed endangered species), indicates that this species may be at risk from methylmercury, particularly in areas where panthers consume prey that feed on fish-eating wildlife.

Detailed discussions of the atmospheric and aquatic fate and transport processes are provided in the modeling technical support documents (Keeler, et al., 2001; Tetra Tech, 2001) prepared to support this analysis. These documents are provided as Appendices I and II.
2.7 Identification of Pollutants Being Addressed and Why

This TMDL addresses the trace element mercury in its various environmental forms. The behavior of mercury in the environment is highly complex with each of the several chemical forms behaving differently. Methylmercury, formed from inorganic mercury by sulfate-reducing bacteria in the sediments is the most biologically active form. Once formed, methylmercury is readily taken up and retained by organisms and tends to increase in concentration in higher trophic levels (i.e., biomagnifies). Although at ambient levels methylmercury does not appear to significantly affect plants, invertebrates, or fishes, when biomagnified, as in the Everglades 1 to 10-million fold, it poses the risk of chronic neurotoxicity to birds and mammals, including humans.

Previous work in the Everglades has shown that the dominant input of mercury (95%) to the WCA 3A is from atmospheric sources (USEPA, 1998; SFWMD, 1999). The remainder of the mercury enters the system via overland flow from tributary watersheds.
3 NUMERIC TARGETS AND WATERSHED INDICATORS

This section identifies the selection of water quality targets for the TMDL. An objective of a TMDL is to define a safe concentration, in this case, of mercury. Additionally, this section develops a source allocation (air and water) that will allow the water quality goal to be met.

3.1 Numeric Targets

Because of the biogeochemical cycling of mercury between the earth and the atmosphere, and because many factors affect its availability and propensity for bioaccumulation, mercury poses unique problems in setting numeric targets. No simple relationship links mercury concentrations in water and mercury concentrations in fish; the relationship is site specific.

Using previous (1984) USEPA guidance, Florida in 1992 adopted a Class III water quality criterion for total (unfiltered) mercury of 12 ng/L, which was believed adequate at the time to prevent excessive mercury accumulation in fish such that these fish could be consumed without concern as regards human health effects. Subsequent studies have shown that mercury levels in fish exceed the DOH consumption advisory level of 0.5 mg/kg in many waters that met the Class III water quality criterion, including most of the Everglades. The Florida Department of Environmental Protection has determined that the inability of anglers to eat their catch at-will impairs recreation, a designated use of Class III waters. Through its participation in the SFMSP and this TMDL study, DEP is working to develop sufficient information to establish a mercury criterion that will protect all of the beneficial uses.

Since it is fish mercury levels rather than mercury concentrations in water that have the potential to impair both the recreational use and protection of fish and wildlife designated uses of Class III Florida waters, a fish mercury level is a more appropriate criterion for this pilot project. A fish mercury criterion integrates those site-specific biogeochemical and food web effects that result in bioaccumulation. While prediction of fish mercury levels from atmospheric loading is a complex endeavor, it is not significantly more complex that predicting mercury concentrations in water, and it is a far better indicator of effects on beneficial uses. In recognition of this, in 2000 the USEPA issued a new human health methylmercury criterion as a fish tissue criterion.
For this TMDL pilot project, a numeric target of 0.5 mg/kg total mercury in age 3 largemouth bass has been selected, as this is currently the level which Florida uses as the basis for fish consumption advisories. Whether this numeric target is protective of human health or wildlife populations awaits further review (see below).

3.2 Identification of Watershed Indicators

Mercury concentration in the edible flesh of fish determines whether the recreational use of a waterbody is impaired. Mercury concentration in prey fish determines whether the fish and wildlife use is impaired. The indication of impairment in wildlife is wildlife daily dietary mercury consumption in comparison to the maximum, safe daily dose. The maximum, safe daily dose is not known for any Everglades species, but is inferred with unknown uncertainty for wading birds from mallard duck feeding studies. Safe daily dose must be determined for the species of interest and compared with actual exposure. Without this information, there is no basis for establishing a margin of safety.

3.3 Identification of Target Levels to be Protective of Beneficial Uses

The Everglades Protection Area (i.e. the water conservation areas and ENP) are designated as Class III waters of the State, which are to be protected for recreation and for the propagation and maintenance of a ‘healthy, well-balanced population of fish and wildlife.’

Following the finding in 1989 of elevated levels of mercury, the Florida Department of Health, Toxicology and Hazard Assessment Section, surveyed the literature and consulted toxicologists in other states as to risks posed to fishermen and their families. DOH developed advisories to the public in general accord with exposure limits then recommended by the World Health Organization and other states. Since the late 1980’s, several studies, re-analyses and meta-analyses have been conducted to further refine estimates of acceptable human exposure to mercury.

In its Mercury Study Report to Congress (USEPA, 1997), USEPA proposed lowering its ‘reference dose’ for methylmercury from 0.3 µg/kg body weight/day to 0.1 µg/kg body weight/day. Congress referred this risk assessment to the National Research Council for independent review, and in 2000 the National Research Council gave substantial support to the new USEPA reference dose. Subsequently, in late 2000, USEPA published a new recommended water quality criterion for mercury of 0.3 mg/kg, expressed as methylmercury in fish flesh. This recommended criterion will be considered in due course by DEP through the Clean Water Act mandated Triennial Review process.
Pending reevaluation of standards, Florida DOH guidelines (Clewell, et al., 1998) for acceptable concentrations of total mercury in the edible portions of wild-caught fish are those given in Table 4.

<table>
<thead>
<tr>
<th>Advisory</th>
<th>Mercury Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>See information provided by USEPA below</td>
<td>Less than 0.5 mg/kg</td>
</tr>
<tr>
<td>Limited Consumption – fish should not be eaten more than once per month by women of childbearing age or children, nor more than once per week by other adults.</td>
<td>0.5 to 1.5 mg/kg</td>
</tr>
<tr>
<td>No Consumption – fish should not be eaten</td>
<td>Greater than 1.5 mg/kg</td>
</tr>
</tbody>
</table>

Note from Table 4 that fish tissue total mercury concentrations greater than 0.5 mg/kg result in the establishment of fish consumption advisories. (For high trophic level fish, such as largemouth bass, total mercury and methylmercury concentrations are essentially equivalent.) DEP has made the determination that recreational use necessitates that fish not only be present and available to anglers, but also that these fish must be safe to eat.

Mercury concentrations in fish tissue currently exceed the 0.5 mg/kg fish consumption advisory level throughout the Everglades/Big Cypress system, and exceed the 1.5 mg/kg level in parts of Water Conservation Areas 2, and 3, and in the freshwater portions of Everglades National Park.

Mercury bioaccumulates in the aquatic food chain. Therefore, top predators such as the largemouth bass can be expected to accumulate the greatest concentrations of mercury. This pilot TMDL uses the Florida DOH guideline for acceptable mercury concentration in fish of 0.5 mg/kg in 3-year-old largemouth bass as the numeric target, because this is currently the level that Florida uses as the basis for fish consumption advisories. Three-year-old (ca. 1000 g) bass were selected as the appropriate index of ingestion exposure because this size class is legally harvestable, abundant, and is the most prevalent cohort in the angler’s catch (F. Ware, personal communication).

The pilot TMDL study indicates that mercury from atmospheric deposition needs to be reduced to achieve the desired fish tissue concentration. The target range for mercury and possible strategies for attaining the desired levels of mercury are provided in Chapter 4 Air and Watershed Modeling and Chapter 6 Conclusions, Research Needs and Plans, of this report.

7 The USEPA recommends women of childbearing age eat no more than 8 ounces of freshwater fish caught by family and friends in a week’s time period; children under 10 should eat no more than 4 ounces. For further details on the EPA advisory see world wide web: [http://www.epa.gov/ost/fishadvice](http://www.epa.gov/ost/fishadvice)
3.4 Comparison of Numeric Targets and Existing Conditions

This section assesses how far the water quality parameters of concern for WCA 3A must change in order to comply with the stated water quality standards for the water body. Table 5 gives the existing water quality conditions, the desired water quality endpoints, and comments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Existing Value (Mean and range)</th>
<th>Water Quality Endpoint</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury in ambient water (ng/L)</td>
<td>1.94 (1.05 – 2.70)</td>
<td>Florida Class III Water Quality Standard: &lt; 12ng/L</td>
<td>This value is designed to ensure that water standards are met.</td>
</tr>
<tr>
<td>Mercury in edible sport fish tissue (mg/kg)</td>
<td>1.28 (0.45 – 4.3)</td>
<td>Florida DOH fish consumption advisory: &lt; 0.5 mg/kg</td>
<td>Concentrations greater than this value trigger the issuance of fish consumption advisories by DOH.</td>
</tr>
<tr>
<td>Mercury in whole prey fish (mg/kg)</td>
<td>0.1 mg/kg provisional USFWS standard</td>
<td>Safe tissue concentration for propagation and maintenance of a healthy, well-balanced population of fish and wildlife</td>
<td>This value is estimated to be protective of fish-eating wildlife and animals that feed on them.</td>
</tr>
</tbody>
</table>
4 AIR AND WATERSHED MODELING: SOURCE ANALYSIS FOR LOADINGS, MERCURY MASS BALANCE, LINKAGE OF STRESSORS TO WATER QUALITY ENDPOINTS

This section summarizes the methods and results of the atmospheric modeling (Keeler et al., 2001) and aquatic mercury cycling (Tetra Tech, 2001) modeling efforts used in this project. Full details of the modeling efforts can be found in the Technical Reports provided as Appendix I (Atmospheric Model) and Appendix II (E-MCM) of this report.

There are four primary forms of mercury considered in the models: three of these are methylmercury \(\{\text{MeHg}\}\), divalent mercury salts and compounds \(\{\text{Hg(II)}\}\) and elemental mercury \(\{\text{Hg(0)}\}\). Hg(II) is explicitly defined here as all divalent inorganic mercury (other than particulate associated divalent inorganic mercury). The fourth form is Hg(p) representing divalent inorganic mercury \(\{\text{Hg(II)}\}\) that is associated with suspended particulate matter in water or air. Provisions have also been made in the E-MCM for some of the particulate Hg(II) on non-living solids in water to exchange slowly, while the remainder is assumed to exchange rapidly enough to assume instantaneous partitioning.

4.1 Technical Approach

Two modeling components were employed for this project. The first modeling approach, developed by the University of Michigan Air Quality Laboratory (UMAQL), was used to simulate the atmospheric transport of mercury from point sources in southern Florida to its deposition onto the Everglades (Keeler, et al., 2001; Appendix I). The second model, the Everglades Mercury Cycling Model (E-MCM), was used to simulate the fate and transport of the mercury within the aquatic environment (Tetra Tech, 1998, 2001; Appendix II). The E-MCM provides estimates of the rates of mercury methylation and bioaccumulation through the food chain to a top-level predatory fish (largemouth bass). Detailed descriptions of these models and uncertainties are provided in the referenced technical support documents for this analysis.
4.1.1 Source Analysis of Loadings

Sources evaluated in this study include both atmospheric emissions and surface water inputs of mercury. The atmospheric source characterization was based on the emissions database used for the RELMAP (Bullock, et al., 1997) modeling simulations performed for the USEPA Mercury Study Report to Congress (USEPA, 1997). The USEPA mercury emissions database includes speciated data for both area- and point-source emissions, with a summary of the standard speciation profiles used for point-source emissions listed in Table 6. Figure 4 shows the location and relative magnitude of the 38 point sources considered in this analysis. The analysis of Dvonch, et al., (1999) utilizing receptor modeling and emissions inventory scaling techniques, estimated the importance of local mercury sources potentially impacting south Florida. That analysis indicated that approximately 92% of the total mercury deposition to south Florida could be accounted for by local sources alone. Thus, this analysis was limited to Florida sources and a complete listing of the point sources used in this study can be found in Table C1 of Appendix I. The USEPA mercury emissions database considered ‘area source’ emissions to be only mercury in the elemental form, Hg(0), and these accounted for only 2 percent of the total emissions. As a result, area sources were not considered in this study.

<table>
<thead>
<tr>
<th>Mercury Emission Source Type</th>
<th>Speciation Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg(0)</td>
</tr>
<tr>
<td>Municipal Waste Combustion</td>
<td>20</td>
</tr>
<tr>
<td>Medical Waste Incinerators</td>
<td>2</td>
</tr>
<tr>
<td>Electric Utility Boilers (coal, oil, gas)</td>
<td>50</td>
</tr>
<tr>
<td>Commercial and Industrial Boilers</td>
<td>50</td>
</tr>
<tr>
<td>Hazardous Waste Incinerators</td>
<td>As specified per location in USEPA database</td>
</tr>
</tbody>
</table>

Mercury inputs to WCA 3A-15 via surface water flow were based on data collected as part of the USGS ACME study (Krabbenhoft, et al., 1998, et al., 1998, Hurley, et al., 1998, Cleckner, et al., 1998). For these studies, surface water was collected at several sites, including site 3A-33, located ca. 50 km upstream of 3A-15, for analysis of total and methylmercury. The average concentrations of unfiltered Hg(II) and unfiltered methylmercury at 3A-33 were 2.14 and 0.27 ng/L respectively for 7 sampling dates between December 1996 and November 1999 [unfiltered Hg(II) is derived as the difference between measured Hg_{tot} and unfiltered MeHg]. These concentrations were assumed to be the surface inflow concentrations for site 3A-15.
4.2 Atmospheric Transport and Deposition Modeling

4.2.1 Approach Overview

The modeling conducted by UMAQL to link local emissions of mercury with deposition in south Florida and at site 3A-15 involved a ‘hybridized’ modeling approach (Figure 5). Two types of models were used to ultimately obtain estimates of the monthly and annual wet- and dry-deposition of speciated mercury \{Hg(0), Hg(II) and Hg(p)\} to the South Florida Water Management District’s Water Conservation Area 3A (SFWMD WCA-3A). The first was a mesoscale meteorological model (Regional Atmospheric Modeling System \{RAMS\}; Pielke, et al., 1983), which provided the meteorological components driving and influencing air parcel transport and mercury species deposition. The second was a Lagrangian air-pollution dispersion/deposition model to estimate average wet- and dry-deposition patterns and amounts (HYbrid Single Particle Lagrangian Integrated Trajectories Model Version 4 \{HYSPLIT_4\}; Draxler and Hess, 1997). Because simulating every day of the year-long study period would be prohibitively time- and resource-intensive, a clustering approach was adopted to identify distinct meteorological flow regimes which would likely lead to distinct wet- and dry-deposition patterns. Weighting each cluster by its annual frequency of occurrence in turn yielded an estimate of monthly and annual deposition.
Figure 5. Schematic depiction of hybridized meteorological-atmospheric dispersion, transport and deposition modeling approach used to simulate Hg deposition in the WCA-3A by UMAQL. RGM is reactive gaseous mercury, believed to be Hg(II).

The specific steps employed in this hybrid approach are as follows:

1. Compute daily back-trajectories (for air parcels arriving in Davie, FL) for each day of a one-year study period (22 June 1995 to 21 June 1996) during which precipitation was collected on an event (i.e., daily) basis at the University of Florida Agricultural Experiment Station in Davie, FL.

2. Identify meteorological clusters, or groups, of back-trajectories that represent the dominant atmospheric transport regimes that impacted south Florida during the one-year study period.

3. Select a number of representative days from each cluster and use RAMS to obtain hourly three-dimensional meteorological fields (U and V wind components, vertical velocity, temperature, specific humidity and pressure) and two-dimensional meteorological fields (terrain height, mean sea-level pressure, total precipitation, pressure, temperature, and micrometeorological parameters, which include u*, t* and q*) for the selected representative days.

4. Using the three-dimensional and two-dimensional meteorological fields computed in part (3) as input fields; use HYSPLIT_4 to estimate average wet- and dry-deposition patterns/amounts for each of these representative days, computing a cluster average deposition for each of the clusters. HYSPLIT_4 was modified by UMAQL to
incorporate both basic mercury physical parameters and chemical processes, and include the ability to simulate the fate of the various mercury species important in the atmospheric deposition of mercury.

(5) Weight the average daily wet- and dry-deposition estimates for each cluster by the number of days assigned to each cluster, and thus obtain an estimate of the speciated monthly and annual wet- and dry-depositional loading of mercury to the SFWMD WCA-3A.

As mentioned above, climatological records for the one-year period from 22 June 1995 to 21 June 1996 were used to characterize the climatological conditions in the Everglades. This period was chosen as the ‘year of record’ because precipitation chemistry for mercury had been collected on an event (i.e., daily) basis at the University of Florida Agricultural Experiment Station in Davie, FL. How representative this one-year meteorological record was relative to the overall meteorologic regime of the area was investigated as part of this study (Keeler, et al., 2001). The results indicated that the study year was indeed representative of meteorological conditions over the eight-year period from 1991-1999, in terms of the frequency of the 8 meteorological clusters. However, average precipitation depth for 3 south Florida FAMS sites was 156 cm, somewhat higher than the long-term average range of 125 – 140 cm.

The input data used for the calculation of the daily back-trajectories consisted of analysis of short-term forecasted meteorological fields from the National Center for Environmental Prediction’s (NCEP) Nested Grid Model (NGM). The standard NGM model domain encompasses the contiguous United States and Canada with a latitudinal and longitudinal grid spacing of approximately 90 km.

Early research suggested that the atmospheric deposition of mercury to south Florida is dominated by wet deposition, with the majority of this deposition associated with summertime convective precipitation events (Guentzel et al., 2001, Dvonch et al., 1999). The convective events responsible for the preponderance of wet deposition typically occur during the mid- to late-afternoon hours in south Florida and thus daily back-trajectories were calculated for 2000 GMT each day. The modeled analysis of dry deposition conducted as part of this study, however, suggests that dry deposition is important as well, comprising perhaps 34 to 40% of the total mercury deposition signal.

A number of previous regional atmospheric modeling studies have employed objective analyses of meteorological flow regimes to assess annual impacts from briefer intensive studies. Cluster analysis is an objective mathematical technique whereby large data sets can be divided into similar groups or clusters that reflect some underlying structure within the data set. For this analysis, the goal was to identify meteorological flow regimes which would likely lead to distinct wet- and dry deposition patterns. Weighting each cluster by its monthly and annual frequency of occurrence results in an estimate of the monthly and annual deposition without the necessity of modeling every day of the 1-year period studied.

Following the completion of the objective clustering of the back-trajectories, Daily Weather Maps from NOAA were used to evaluate each day of the year-long period to determine if the
clustering resulted in an accurate representation of meteorological flow regimes. This hand analysis of the daily maps provided independent validation of the trajectory clustering approach.

Eight different atmospheric transport clusters were obtained through this analysis procedure, and a summary of these is presented in Table 7. For each meteorological cluster, the measured rainfall depth, volume-weighted mean mercury concentration, and the total mercury wet deposition are given from the Davie Monitoring site. The efficacy of the clustering technique is evident, with Meteorological Clusters 3 & 6 resulting in the majority of wet deposition of mercury. This data provides impetus for continuation of the hybrid modeling using the clustering and aggregation approach described later. Plots showing the general nature of each of the clustered back-trajectory groups can be found in Appendix A of Appendix I. Maps of the surface meteorological features for days representative of each cluster can be found in Appendix B of Appendix I.
Table 7.
Summary of “clustered” atmospheric transport regimes and precipitation statistics associated with each cluster based upon data collected at Davie, Florida during the 1995-96 SoFAMMS study period.

<table>
<thead>
<tr>
<th>Cluster Number</th>
<th>Description of flow regime represented</th>
<th>No. of Days within cluster</th>
<th>No. of Days with Rainfall (Davie, FL)</th>
<th>Total Rainfall for Cluster (cm) (Davie, FL)</th>
<th>Volume Weighted Mean Hg Concentration for Cluster (ng/L) (Davie, FL)</th>
<th>Total Hg Wet deposition observed (µg/m²) (Davie, FL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weak local flow, variable in direction</td>
<td>65</td>
<td>18</td>
<td>12.1</td>
<td>31.8</td>
<td>3.84</td>
</tr>
<tr>
<td>2</td>
<td>Weak synoptic flow from north</td>
<td>35</td>
<td>5</td>
<td>2.7</td>
<td>29.2</td>
<td>0.79</td>
</tr>
<tr>
<td>3</td>
<td>Moderate local/synoptic flow from east</td>
<td>104</td>
<td>30</td>
<td>26.2</td>
<td>20.9</td>
<td>5.47</td>
</tr>
<tr>
<td>4</td>
<td>Strong synoptic flow from northeast.</td>
<td>48</td>
<td>8</td>
<td>22.1</td>
<td>10.8</td>
<td>2.39</td>
</tr>
<tr>
<td>5</td>
<td>Strong synoptic flow from northwest</td>
<td>32</td>
<td>9</td>
<td>6.9</td>
<td>10.6</td>
<td>0.73</td>
</tr>
<tr>
<td>6</td>
<td>Moderate synoptic flow from south</td>
<td>58</td>
<td>29</td>
<td>94.0</td>
<td>14.5</td>
<td>13.64</td>
</tr>
<tr>
<td>7</td>
<td>Moderate synoptic flow from southwest</td>
<td>11</td>
<td>4</td>
<td>8.7</td>
<td>12.8</td>
<td>1.12</td>
</tr>
<tr>
<td>8</td>
<td>Strong synoptic flow from north</td>
<td>13</td>
<td>1</td>
<td>0.1</td>
<td>7.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
For each cluster, two wet days and two dry days were selected for use in the modeling exercise (Table 8). Where possible, these days were chosen such that they represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster. It was believed that in doing so, potential biases from choosing two days with nearly identical deposition patterns would be minimized.

<table>
<thead>
<tr>
<th>Cluster Number</th>
<th>Wet Days</th>
<th>Dry Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29 MAY 1996</td>
<td>22 FEB 1996</td>
</tr>
<tr>
<td></td>
<td>09 SEP 1995</td>
<td>27 JUN 1995</td>
</tr>
<tr>
<td>2</td>
<td>13 MAY 1996</td>
<td>20 SEP 1995</td>
</tr>
<tr>
<td></td>
<td>16 AUG 1995</td>
<td>06 JUN 1996</td>
</tr>
<tr>
<td>3</td>
<td>11 SEP 1995</td>
<td>17 DEC 1995</td>
</tr>
<tr>
<td></td>
<td>13 JUN 1996</td>
<td>30 MAR 1996</td>
</tr>
<tr>
<td>4</td>
<td>11 MAR 1996</td>
<td>23 OCT 1995</td>
</tr>
<tr>
<td></td>
<td>29 SEP 1995</td>
<td>07 FEB 1996</td>
</tr>
<tr>
<td>5</td>
<td>19 MAR 1996</td>
<td>17 FEB 1996</td>
</tr>
<tr>
<td></td>
<td>09 APR 1996</td>
<td>21 MAR 1996</td>
</tr>
<tr>
<td>6</td>
<td>23 JUN 1996</td>
<td>13 APR 1996</td>
</tr>
<tr>
<td></td>
<td>27 MAY 1996</td>
<td>07 MAR 1996</td>
</tr>
<tr>
<td>7</td>
<td>02 MAR 1996</td>
<td>12 JAN 1996</td>
</tr>
<tr>
<td></td>
<td>15 OCT 1995</td>
<td>22 MAY 1996</td>
</tr>
<tr>
<td>8</td>
<td>Not Modeled*</td>
<td>03 MAR 1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23 DEC 1995</td>
</tr>
</tbody>
</table>

* No days with rain (>1mm) occurred during the year of record

### 4.2.2 Airshed Pollutant Loads

Atmospheric inputs of mercury to WCA 3A-15 were estimated for both wet and dry deposition as described above. The model estimates reported here were developed using the source-specific emissions rates and mercury speciation factors used in the USEPA Mercury Study Report to Congress. Two additional emissions scenarios were evaluated but not used in this analysis, as described in Appendix 1. Results from the dry deposition simulations were used, in conjunction with measured wet deposition rates, as input into E-MCM. Detailed discussions of the atmospheric modeling can be found in Appendix I.

### Wet Deposition

These model results predicted a total mercury wet deposition of $18.74 \pm 1.57 \, \mu g/m^2/yr.$ (± 1 standard deviation) to WCA 3A-15. The temporal variation in the wet deposition of
total mercury to the WCA 3A-15 is presented in Figure 6. As would be expected from the marked seasonality of rainfall in south Florida, the model indicates a significant seasonal trend in total mercury wet deposition to the area, predicting that over 80 percent of the wet deposition would occur from May through October.

![Figure 6](image_url)  

**Figure 6.** Comparison of the modeled monthly total mercury wet deposition to WCA 3A-15 and FAMS\(^8\) observed total mercury wet deposition (average of Tamiami Trail Ranger Station and Andytown sites).

The speciated mercury wet deposition is presented in Figure 7. From this figure, it can be seen that the predicted total wet deposition of mercury is dominated by deposition of reactive gaseous mercury (RGM), believed to be in the form of Hg(II). In contrast, model results suggest that the deposition of gaseous elemental mercury, Hg(0), is negligible. Once again, the seasonal nature of the deposition is apparent.

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\(^8\) The Florida Atmospheric Mercury Study (FAMS) measured mercury deposition (both bulk and wet-only rainfall collection), particulate-associated mercury and total gas-phase mercury (TGM) at 9 sites in Florida (i.e. panhandle, north-central Florida, marine background site, 4 sites near the Everglades, and 2 sites in the southwestern peninsula). Long-term integrated samples were collected (monthly precip, weekly TGM and Hg(p)). Operations began in 1993; all sites were operational by mid-1995 and operated through the end of 1996 (Pollman, *et al.*, 1995; Guentzel, 1997; Guentzel, *et al.*, 2001).
Figure 7. Modeled monthly speciated mercury wet deposition to WCA 3A-15.

**Dry Deposition**

The hybrid model estimates of the dry deposition of mercury to the WCA 3A-15 were performed for the same emissions inventory employed in the wet deposition modeling (Appendix I). As for the simulated wet deposition results, the results presented here use the emissions from the USEPA Mercury Report to Congress as input for the model.

The hybrid model estimate for dry deposition of mercury to WCA 3A-15 during the one-year period of record was $12.2 \pm 2.0 \, \mu g/m^2/yr. \ (\pm \ 1 \ \text{standard deviation}).$ While considerable variability was evident in the monthly deposition estimates, on average, dry deposition to the site showed a seasonal trend, with relatively greater deposition occurring during the climatological wet season. As was the case for the wet deposition to WCA 3A-15, dry deposition to this area is dominated by the Hg(II) fraction. Note that the dry deposition estimate derives from local source emissions alone and includes no contribution from global background.

Levels of Hg(II) calculated by the model were the result of the dispersion and deposition of Hg(II) emissions from the USEPA Mercury Study Report to Congress (USEPA, 1997), not the result of Hg(II) production from atmospheric chemical reactions. Measurements of Hg(II) species in the atmosphere were not available due to the limitations of measurement techniques. In addition, based on our understanding of the rates of conversion of Hg(0) to Hg(II) at the time, the conversion of Hg(0) to RGM during
passage from the coast to the Everglades was too slow to be significant, and therefore not included in these calculations.

By 1999 more robust techniques had been developed and field measurements were available for comparison with model results. Interestingly, the levels of Hg(II) predicted by the model were consistent with the values measured by the UMAQL and USEPA FEDDS and SAMPEX studies in south Florida during 1998 and 2000. Values of Hg(II) were measured and estimated by the model to range from 0 to 100 pg/m$^3$ and varied spatially and temporally across the eastern portion of the Everglades in Broward County.

Model-calculated total atmospheric deposition of mercury to WCA 3A, estimated as the sum of the wet and dry deposition, is approximately 30.94 ± 13.55.

One end point of the atmospheric modeling was selection of the appropriate loading term of mercury to the 3A-15 study site. While we had both measured and modeled wet deposition rate estimates, we chose a combination of measured wet deposition of 23.1 µg/m$^2$/yr. from the FAMS project (average of deposition rates for the Andytown, Fakahatchee Strand and Tamiami Trail sites) and the modeled estimate of dry deposition 12.2 ± 2.0 µg/m$^2$/yr., for a total of 35 µg/m$^2$/yr. For all ensuing aquatic cycling modeling efforts, this combined estimate was used.

### 4.3 Aquatic Mercury Cycling Modeling

A dynamic mercury cycling model has been developed to simulate the conditions found in marsh areas of the Florida Everglades. The Everglades Mercury Cycling Model (E-MCM) (Tetra Tech, 1999b) is an adaptation of the Dynamic Mercury Cycling Model for lakes (D-MCM) (Tetra Tech, 1996, 1999a). E-MCM accommodates unique features of Everglades marshes from the point of view of mercury cycling in aquatic systems. These features include shallow waters, a system of canals and managed water levels, a warm subtropical climate, high sun exposure, neutral to alkaline pH, high concentrations of dissolved organic carbon and sulfate, large biomass of aquatic vegetation including periphyton, sawgrass, cattails and water lilies, and a wide range of nutrient levels and primary productivity. Field data (USEPA, 1998) for parts of the Everglades have shown considerable spatial and temporal variability, with some locations apparently conducive to methylmercury production and bioaccumulation.

E-MCM also incorporates recent advances made by researchers investigating mercury cycling in freshwater systems and in the Everglades specifically. These advances include an improved understanding of the factors governing methylation, demethylation, Hg(II) reduction, food web mercury transfers, and the role of aquatic vegetation in the mercury cycle (e.g. Krabbenhoft, et al., 1998, Gilmour, et al., 1998a, Hurley, et al., 1998, Cleckner, et al., 1998).
4.3.1 Model Description
E-MCM is a mechanistic simulation model that runs on Windows™-based computers. The model uses a mass balance approach to predict time-dependent concentrations of the three primary forms of mercury [methylmercury, Hg(II), and elemental mercury (Hg(0))] in water and sediments (dissolved and particulate phases), vegetation, and a simplified food web (Figure 8).

Model compartments include the water column, three macrophyte species (cattails, sawgrass, water lilies), up to four sediment layers and a food web. The model has two types of particles in the water column: detritus and “other” suspended solids, plus solids in the sediments. For each type of particles - detrital, suspended and sediment solids - compartments have been set up for two types of Hg(II) exchange: (1) instantaneous and (2) slow exchange governed by the kinetics of adsorption and desorption.

Figure 8. Conceptual model of aquatic mercury cycling processes described in the Everglades Mercury Cycling Model (E-MCM).
The simplified food web consists of detritus, periphyton, phytoplankton, zooplankton, benthos, shrimp, *Gambusia* (mosquitofish), bluegill/warmouth sunfish, and largemouth bass. Fish mercury concentrations tend to increase with fish age, and are therefore followed in each year-class (up to 20 cohorts for each species). Bioenergetics equations developed for individual fish at the University of Wisconsin (Hewett and Johnson, 1992) are modified to consider temperature dependent growth and coupled to methylmercury fluxes (Harris and Bodaly, 1998). These fluxes for individual fish are then adapted to simulate year classes and entire populations (Tetra Tech, 1999b).

Major processes involved in the mercury cycle in an Everglades marsh are shown in Figure 8. These processes include surface inflows and outflows, vertical groundwater flow, instantaneous mercury partitioning between some binding sites on abiotic solids and dissolved complexes, slower adsorption/desorption kinetics for Hg(II) on other sites on abiotic solids (see Appendix A, Modeled Deposition of Mercury to Everglades Water Conservation Area 3A-15), particulate settling, resuspension and burial, macrophyte related fluxes (throughfall, litter, transpiration), atmospheric deposition, air/water gaseous exchange, *in-situ* transformations (e.g. methylation, demethylation, methylmercury photodegradation, Hg(II) reduction, Hg(0) oxidation), mercury kinetics in plankton, and methylmercury fluxes in fish populations (uptake via food and water, excretion, egestion, mortality, fishing).

Although the Everglades is shallow, significant temperature vertical gradients in the water column have been observed by ACME researchers (D. Krabbenhoft, unpublished data). The model allows for surface and bottom water layer compartments if desired.

### 4.3.2 Modelling Approach

The aquatic mercury cycling component of this project uses the site designated as WCA 3A-15 as the basis for the model calibration and calculations. Site WCA 3A-15 is in the northern portion of WCA 3A and was selected because it has elevated mercury concentrations in largemouth bass, and has been extensively studied by the USGS ACME program. The approach to aquatic modeling for the pilot mercury TMDL included the following key components:

- Calibration of E-MCM using estimates of typical long-term conditions at site WCA 3A-15 (e.g. after 100 years of simulation). The critical endpoint was mercury in largemouth bass, but the calibration examined total and methylmercury concentrations in each compartment for which data were available. The model calibration was performed using average wet deposition rates measured by the FAMS program between 1993 and 1996 at the FAMS sites located at Tamiami Trail, Fakahatchee Strand, and Beard Research Center in Everglades National Park (Guentzel, 1997; Guentzel, *et al.*, 2001; see Appendix II, Section 4.3). Dry deposition rates were obtained from the hybrid modeling conducted by UMAQL.
• Development of a long term steady-state dose-response curve relating predicted long-term average fish mercury concentrations to different levels of long term continuous atmospheric Hg(II) deposition. For example, if atmospheric deposition decreased to 50% of current levels and was maintained at the lower value for a long period, at what concentration would mercury in fish ultimately stabilize? Model runs were carried out for several mercury deposition scenarios to develop the curve.

• Assessment of the predicted timing of the response of fish mercury concentrations to different loadings of inorganic Hg(II).

• Sensitivity analysis of E-MCM predictions to various model input parameters, including atmospheric deposition rates of mercury.

• Assessment of the effects of year-to-year variations of atmospheric deposition under long-term constant mean annual loadings.

• Uncertainty analysis: Quantifying the effects of uncertainty regarding true current atmospheric deposition rates on model predictions and study conclusions.

General characteristics of site WCA 3A-15 are summarized in Table 9.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area modeled</td>
<td>1 km x 1 km</td>
</tr>
<tr>
<td>Surface water depth</td>
<td>0.2 to 0.7 m</td>
</tr>
<tr>
<td>Air temperatures (monthly means)</td>
<td>12 to 30 °C</td>
</tr>
<tr>
<td>Productivity</td>
<td>Low to Moderate</td>
</tr>
<tr>
<td>Flow pattern</td>
<td>Surface flow</td>
</tr>
<tr>
<td>Stratification</td>
<td>Intermittent</td>
</tr>
<tr>
<td>Anoxia</td>
<td>Yes</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>~ 16 mg/L</td>
</tr>
<tr>
<td>Surface water pH</td>
<td>~ 7.2</td>
</tr>
<tr>
<td>Surface water chloride</td>
<td>~ 5 mg/L</td>
</tr>
<tr>
<td>Surface water sulfate</td>
<td>100 µeq/L</td>
</tr>
<tr>
<td>Sedimentation rate</td>
<td>&lt; 1 cm/yr.</td>
</tr>
<tr>
<td>TSS</td>
<td>~ 2 mg/L</td>
</tr>
<tr>
<td>Macrophytes</td>
<td>Includes sawgrass, cattails, water lilies</td>
</tr>
<tr>
<td>Fraction of marsh with open water</td>
<td>&lt;50%</td>
</tr>
<tr>
<td>Periphyton density</td>
<td>dense</td>
</tr>
</tbody>
</table>
An important note on the model calibration is that, under ideal circumstances, E-MCM would have been calibrated to a long-term data set. Unfortunately, such long-term water chemistry and biota data sets do not exist, nor do high-quality, high-resolution mercury deposition and sediment accumulation rate data. This currently precludes a long-term, historical calibration, and was the impetus for choosing a calibration approach that assumed that current conditions reflect long-term dynamics – in essence, a quasi steady-state calibration. Further information on the approach to model calibration, sensitivity analysis, uncertainty analysis and assessment of year-to-year variations are provided below and discussed in detail in Appendix II.

**Model Inputs**

In response to the mercury issue in the Everglades, several agencies initiated research and monitoring programs in the 1990’s as the SFMSP. These began with the FAMS and USEPA Regional Environmental Monitoring and Assessment Program (REMAP) project. In 1993-1995 REMAP collected extensive data on the canal system, and in 1995-1996 sampled water, soil, vegetation and fish at 500 sites. Subsequently, in 1999, REMAP again sampled across the entire marsh system, examining the relationships between parameters and temporal trends. A joint study by USEPA and SFWMD sampled 9 surface water control structures over two years. (1993-1995) to determine surface water loads to the Everglades Protection Area (Table 1). FWC collects and maintains a long-term database on mercury in largemouth bass and other fishes. As a result, there are extensive air, water, soils and biota data on mercury at WCA 3A-15. From 1995 through the present, the USGS ACME Team has conducted intensive process-oriented research at 9 sites from north to south in the Everglades. Data from all these studies have been used to guide formulation and parameterization of the Everglades-Mercury Cycling Model, and subsequently its testing under a variety of Everglades conditions.

Estimates of atmospheric loading rates of mercury via wet deposition are available from three sources:

1. Direct estimates of wet deposition for three sites in the Everglades region obtained as part of the FAMS monitoring program conducted between 1992 and 1996;
2. Direct estimates of wet deposition for three MDN sites in the Everglades region between late 1995 and the present, and
3. Modeled estimates of wet deposition derived from the source-receptor modeling conducted by UMAQL as part of this study.

Dry deposition fluxes are difficult to measure directly with reasonable precision, and are usually inferred in part from modeling. Carefully conducted direct measurements of wet deposition such as those obtained during FAMS are inarguably more reliable than
estimates derived from source receptor modeling. For that reason, we elected to use the wet deposition fluxes directly measured during FAMS as input to E-MCM.\(^9\)

Input data types and sources for WCA 3A-15 long-term simulations are summarized in **Table 10**. Mercury concentrations from the atmospheric model were input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry deposition, deposition of reactive gaseous mercury). Additional information describing inputs used in simulations is provided in Appendix II.

### Table 10. Summary of Data Inputs by Major Data Type Category

<table>
<thead>
<tr>
<th>Data Type</th>
<th>Parameter Estimate and Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrologic Data</strong></td>
<td></td>
</tr>
<tr>
<td>Precipitation</td>
<td>Monthly means from FAMS sites AT, FS, and TT, 1992-1996 (Guentzel, ‘97; Gill, et al., ‘99)</td>
</tr>
<tr>
<td>Surface water elevations</td>
<td>Direct daily measurements (USGS, Miami Florida Sub District Office)</td>
</tr>
<tr>
<td>Surface Flow</td>
<td>Monthly means computed based on cell size configuration, assumed hydraulic retention time, and precipitation seasonality.</td>
</tr>
<tr>
<td><strong>Physical Data</strong></td>
<td></td>
</tr>
<tr>
<td>Temperature and incident light</td>
<td>Monthly means estimated from NOAA gauge data at West Palm Beach, 10/89 to 9/94 – HydroQual (1997)</td>
</tr>
<tr>
<td>Soil moisture content</td>
<td>Assumed 100% saturation at all times</td>
</tr>
<tr>
<td><strong>Mercury Loadings</strong></td>
<td></td>
</tr>
<tr>
<td>Wet Hg(II) deposition</td>
<td>Monthly means from FAMS sites AT, FS, and TT, 1992 –1996. Guentzel, 1997; Gill, et al., 1999,</td>
</tr>
<tr>
<td>Dry Hg(II) deposition</td>
<td>Model mean monthly estimates from Keeler, et al., (2001)</td>
</tr>
<tr>
<td>Leaf Area Index</td>
<td>3 (assumed)</td>
</tr>
<tr>
<td>Upstream Surface water concentrations – Hg(II)</td>
<td>Based on average for 3A-33 = 2.14 ng/L (n = 7) sampled by USGS</td>
</tr>
<tr>
<td>Upstream Surface water concentrations – MeHg (unfiltered)</td>
<td>Based on average for 3A-33 = 0.27 ng/L (n = 7) sampled by USGS</td>
</tr>
</tbody>
</table>

\(^9\) This is not to say that the modeled wet deposition fluxes have little or no value. First, the robustness of the simulated dry deposition fluxes that the E-MCM model relies upon as additional atmospheric input is reflected in part by how well the source-receptor modeling captures the relationship between sources and wet deposition. The extent that the modeled wet deposition fluxes match observed values (cf., Figure 6) provides some assurance that the modeled wet, and by extension, dry deposition relationships are reasonable. Second, the fact that a TMDL analysis requires quantifying the relationship between sources and the target metric also necessitates the modeling of the relationship between sources and wet deposition of mercury.
### Surface Water Chemistry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>ACME data (n = 8) (G. Aiken, USGS unpublished data)</td>
</tr>
<tr>
<td>pH and dissolved oxygen</td>
<td>Limno-Tech (1996)</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>$\sim 100 \ \mu\text{eq/L}$ (Gilmour, et al., 1998b)</td>
</tr>
</tbody>
</table>

### Hg Concentrations in Marsh

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water Hg$_{\text{tot}}$ and MeHg (filtered and unfiltered)</td>
<td>1995-1998 data from ACME (D. Krabbenhoft, unpublished data)</td>
</tr>
<tr>
<td>Elemental Hg (DGM)</td>
<td>20 – 40 pg/L (Krabbenhoft, et al., 1998)</td>
</tr>
<tr>
<td>Sediment Hg</td>
<td>Gilmour, et al., 1998b</td>
</tr>
<tr>
<td>Sediment porewater chemistry</td>
<td>Gilmour, et al., 1998b</td>
</tr>
</tbody>
</table>

### Food Web and Vegetation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish growth (largemouth bass) and Hg concentrations</td>
<td>T. Lange, Florida Fish and Wildlife Conservation Commission (unpublished data)</td>
</tr>
<tr>
<td>Mosquitofish Hg concentrations</td>
<td>D. Krabbenhoft (ACME unpublished data)</td>
</tr>
<tr>
<td>Fish diets</td>
<td>Cleckner and Gorski (ACME unpublished data)</td>
</tr>
<tr>
<td>Fish biomasses</td>
<td>Marsh-wide average = 40 kg/ha (wet) (Jordan, 1996 cited in Ambrose, et al., 1997)</td>
</tr>
<tr>
<td>Macrophyte and periphyton biomasses and turnover rates</td>
<td>Ambrose et al., 1997</td>
</tr>
<tr>
<td>Macrophyte Hg$_{\text{tot}}$ concentrations</td>
<td>USGS collected samples, DEP funded analyses by Frontier Geosciences</td>
</tr>
<tr>
<td>Shrimp and zooplankton MeHg concentrations</td>
<td>100 - 200 ng/g (dry) (Cleckner, personal communication)</td>
</tr>
<tr>
<td>Benthos MeHg and Hg$_{\text{tot}}$ concentrations</td>
<td>No data</td>
</tr>
<tr>
<td>Periphyton MeHg and Hg$_{\text{tot}}$ concentrations</td>
<td>(Cleckner, et al., 1998)</td>
</tr>
</tbody>
</table>

### Particle Dynamics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II) Sorption</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Sediment decomposition rates</td>
<td>Derived from litter turnover rates and net mass sedimentation.</td>
</tr>
</tbody>
</table>
4.3.3 Linkage of Mercury Loads to Fish Tissue Concentrations

A fundamental question to examine in this pilot TMDL study was the relationship between atmospheric Hg(II) deposition and long term fish mercury concentrations. Once the model was calibrated to the current atmospheric Hg(II) deposition estimate of 35 µg/m²/yr., simulations were also carried out with loadings at 75, 50, 25 and 15% of current levels. In these simulations, Hg(II) and methylmercury concentrations in inflows were adjusted in proportion to Hg(II) deposition. Atmospheric loadings of methylmercury also were changed proportionally. Predicted fish mercury concentrations were compared after each simulation had run 200 years, producing essentially steady state conditions. Annual cycles of site conditions and mercury deposition were repeated throughout the simulation period.

![Graph showing predicted Hg concentrations in age 3 largemouth bass as a function of different long term constant annual rates of wet and dry Hg(II) deposition. Predictions are based on calibration to current loading of 31 µg/m²/yr.](image)

Figure 9. Predicted Hg concentrations in age 3 largemouth bass as a function of different long term constant annual rates of wet and dry Hg(II) deposition. Predictions are based on calibration to current loading of 31 µg/m²/yr.

Figure 9 shows the predicted long term relationship between atmospheric mercury deposition and mercury concentrations in age 3 largemouth bass in WCA 3A-15. A linear relationship is predicted, but the slope is not 1.0 and the intercept is non-zero. This suggests that there is not an exact correspondence between relative reductions in Hg(II) loading and fish mercury response. Moreover, the figure suggests that, in the absence of any Hg(II) loading, there will still be some mercury accumulating in largemouth bass. The source of this mercury is, in essence, “legacy” mercury, historically deposited and
now lying deep within the sediments (5 to 20 cm below the sediment-water interface) that the model predicts is mobilized and brought into the water column by macrophyte roots. As Figure 9 illustrates, this source of mercury becomes important only if atmospheric sources are substantially reduced. Eventually this legacy mercury would become exhausted, but at current sedimentation rates, the model predicts that this would not occur for some hundreds of years.

Both the linearity and the deviation of the predicted relationship from unity are strongly influenced by model assumptions not verified by field data. These include:

1. We assumed that two limiting factors govern methylation and demethylation rates: the supply of available mercury and the rate of activity of the methylating and demethylating microbes. We also assumed that methylation occurred in sediments and that it was porewater Hg(II) or a fraction of it being methylated. We further assumed that no cinnabar (HgS) formation would occur for any of the loading scenarios tested. It is possible that cinnabar formation or other geochemical constraints could result in the current levels of porewater Hg(II) remaining unchanged over a range of Hg(II) loading conditions. In this case, methylation rates in sediments might not respond in a linear manner to a change in Hg(II) loading. Work is needed to clarify the location of methylation and demethylation in the system and whether the concentrations of mercury available for the reactions change in response in a linear way to different Hg(II) loading to the system. Stable isotope addition studies conducted by the ACME team using enclosures in the Everglades are expected to yield considerable insight towards these issues. These experiments, which are supported by USGS and DEP, are currently underway.

2. We also assumed that microbial methylation and demethylation rates were limited only by their respective mercury substrates. It is possible that at some point these reactions could be limited by other factors such as the availability of carbon or a micronutrient in short supply.

3. We assumed that Hg(II) and MeHg concentrations in inflows would respond linearly to changes in atmospheric deposition. In fact, if other factors emerge which suggest that Hg(II) or MeHg concentrations in surface waters of the cell being modeled do not respond linearly to changes in atmospheric Hg(II) deposition, then the assumed linear relationship for inflowing mercury would not be appropriate either. This would further contribute to a non-linear response in the cell being modeled.

A second fundamental question addressed by the pilot mercury TMDL was: How fast will fish mercury concentrations change following reductions in mercury loading? This question was examined by running simulations for 200 years to reach steady state conditions, then instantaneously reducing atmospheric deposition as a step function and continuing the simulation for an additional 200 years. Surface water inflowing Hg(II) and MeHg concentrations were reduced as well but, unlike the reductions in atmospheric
loading rates, a time lag was imposed on the inflows to reflect the time expected for upstream areas to respond to load changes (see Appendix II, Section 6.3). The results for load reductions of 25, 50, 75 and 85% from the current deposition estimate of 35 µg/m²/yr. are shown in Figure 10.

![Figure 10](image_url)

Figure 10. Predicted dynamic response of Hg concentrations in largemouth bass in WCA 3A-15 following different reductions in Hg(II) deposition. Predictions are based on calibration to current loading of 35 µg/m²/yr.

Figure 11 shows that the number of years required for the system to approach a new steady state is effectively independent of the actual magnitude of the change. Two phases are illustrated by the curve: the first is a period of comparatively rapid response driven by the decline of Hg(II) loading and the hydraulic residence time of the system; the second phase is far slower, and is governed by the turnover rate of labile Hg(II) in the sediments supporting methylation. Because the simulated concentrations of mercury in largemouth bass ultimately reflect net methylation rates in the sediments, the response of largemouth bass is prolonged. For example, the time required to achieve 50 percent of the ultimate response in fish tissue mercury concentrations is approximately 10 years for all load reduction scenarios tested with the base calibration with atmospheric Hg(II) deposition = 35 µg/m²/yr. Within 30 years, approximately 90 percent of the ultimate predicted response is projected to occur.
Figure 11. Comparison of the rate at which age 3 largemouth bass concentrations approach steady state following different reductions in Hg(II) deposition (simulations all based on calibration with current Hg(II) deposition = 35 µg/m²/yr.).
5 UNCERTAINTY ANALYSIS

Assumptions – The limits of our knowledge

Our understanding of the biogeochemical cycle of mercury has advanced greatly in the past decade but a number of features of that cycle remain obscure. In any modeling analysis such as this, the degree of realism in the simulations and the ability of the models to reliably predict future reality (i.e., response to changes or management actions) is based on the degree to which the fundamental processes involved are properly represented in the models. Where these processes are not well understood or can only be represented by empirical data, the results therefrom grow in uncertainty. Several areas where this analysis outpaces the desired level of scientific understanding are discussed below.

5.1.1 The Atmospheric Cycle of Mercury:

The general features of the atmospheric portion of the mercury cycle have been understood for some decades. However, it is only more recently that the importance of speciation as it controls the transport and deposition of mercury has been appreciated. Since 1998 sampling methods have been developed and tested that can measure the relevant gaseous and particulate forms of mercury in both emissions and in the free atmosphere with greater precision and less bias than previously. The key unknowns at this time are the chemical and physical transformations that occur in the atmosphere. Several attempts have been made at construction of global mercury models but all lack key information on the atmospheric reactions of mercury and their rates.

As demonstrated in this analysis, we have achieved a measure of sophistication in measuring and modeling the local transport of emissions, but we lack the context of the overarching global cycle against which to compare local mercury emissions. For example, there is almost no information on ambient concentrations of reactive gaseous mercury in the troposphere, and likely fluxes of reactive gaseous mercury originating from local and hemispheric sources. Yet, it is this chemical species that largely governs wet and dry deposition rates.

The relationship between local emissions and deposition also is very sensitive to our assumptions regarding emission rates and the speciation of emissions. Speciated measurements from three different source types in south Florida performed during SoFAMMS (Dvonch, et al., 1999) evinced large (4 to 10x) differences from the emissions
Uncertainty Analysis

inventory compiled by USEPA for south Florida as part of it’s 1997 Mercury Study Report to Congress (MSRTC). Subsequent evaluation of the mercury emissions for south Florida, supported by Florida DEP, found similar emissions (within 20% for the large point sources) to those reported in the MSRTC. The speciation results from SoFAMMS clearly indicated that the fraction of reactive gaseous mercury leaving municipal and medical waste incineration facilities was higher than the USEPA inventory reported. The sensitivity of all atmospheric deposition model estimates to the speciation of mercury emitted, and in the ambient air, is currently the greatest source of error. This uncertainty ultimately speaks to our ability to mitigate the problem of high mercury concentrations in fish in the Everglades by controlling local sources. Clearly, the need remains for more substantial and fundamental research on: (1) the nature and magnitude of emissions in south Florida; (2) the magnitude of sources beyond south Florida; and (3) the atmospheric reactions of mercury and their rates.

5.1.2 The Aquatic Cycling of Mercury:
There are many assumptions and parametric uncertainties in the E-MCM. To produce accurate fish mercury concentrations, the model must be calibrated with the actual atmospheric load, including global background. Nevertheless, error analysis shows that this model predicts equivalence between the percent decrease in atmospheric deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury.

5.1.3 Mercury Bioaccumulation and Risk:
The prey fish mercury concentrations that will protect wildlife populations are not accurately known at this time. However, the means of measuring these values are well understood and it is only a matter of finding the resources to carry out these studies.

5.2 Uncertainty
In a complex scientific endeavor, explicit, detailed treatment of the uncertainties inherent in any program of measurement, modeling or analysis is a part of the scientist’s duty to be self critical of one’s own analyses. Uncertainty is an attribute of all measurements – sampling, analytical, etc. – and, in a complex analytical and modeling paradigm, uncertainties may add or compound at each step. It is axiomatic in science that the data must support the conclusions; uncertainty analysis is a requisite for understanding how confident one may be in any particular conclusion.

One goal of this TMDL Pilot Study is to take the present state of the art of mercury research – as exemplified by the SFMSP – and attempt a comprehensive, multimedia integrated analysis. The treatment of the uncertainties herein will give us an indication of the power of our present knowledge and, more constructively, guidance for the final phase of SFMSP studies to constrain these uncertainties to acceptable levels.

5.2.1 The Aquatic Cycling of Mercury
Although considerable research on mercury cycling in aquatic systems is embodied in the E-MCM, several gaps regarding model inputs and the state of knowledge became apparent during the pilot TMDL study which impose uncertainty in the aquatic modeling results. The following recommendations would reduce uncertainty in future model applications:

1. The processes of methylation and demethylation and their rates require further research to improve our understanding and ability to more reliably characterize them. In particular, the environmental factors governing both these processes need to be better understood. For example, the link between sulfur cycling and methylation/demethylation needs to be clarified, including the roles of sulfate reduction and sulfide concentrations. Likewise, the role of periphyton in methylation and demethylation needs to be clarified, including the effects of different periphyton types. The end product of biological demethylation should be elucidated, i.e. (Hg(0) vs. Hg(II)).

2. The sorptive (both adsorption and desorption) characteristics of Hg(II) and MeHg on sediment solids need to be better understood. Sorption helps dictate the amount of Hg(II) in solution and available for methylation; it also has implications regarding response times of the system to changes in atmospheric loading rates of mercury. There are currently experiments underway using stable mercury isotopes to address this issue for a site in the Experimental Lakes Area, Ontario. Similar experimental work is in progress using substrates from the Everglades.

3. Mercury fluxes associated with macrophytes, water column solids, and sediment solids appear to play an important role in mercury cycling in the Everglades. Mercury concentrations in macrophytes (Hg\text{tot} and MeHg) should be better quantified, as should the mercury fluxes associated with litter, throughfall, and transpiration. In the current model representation of mercury cycling in macrophytes, we assumed accumulation of RGM and dry particle mercury deposition onto leaves, but did not include any uptake of Hg(II), MeHg, or elemental mercury from the atmosphere directly into the plant material. Better information is needed on the sources of mercury accumulated by macrophytes to test this assumption. Furthermore, our approach to Hg(II) uptake by macrophytes suggests that porewater uptake of mercury is incapable of sustaining the high rates of mercury evasion over macrophytes reported by Lindberg, et al. (1998). Measurements should be made to confirm the reported flux rates, and research is needed to explain the source of this mercury, i.e. whether it is atmospheric in origin or from the sediments. Clarification also is needed regarding the depths from which most water is drawn into macrophytes and the potential for mercury in deeper sediments to be remobilized via root uptake.

4. We do not have species-specific bioenergetics and growth data for Gambusia. This information should be obtained from the literature if available. If such information is not available, experimental work is needed to obtain it.

5. As discussed in the next section, we addressed uncertainty associated with actual Hg(II) deposition rates and year-to-year variability in deposition. We did not address, however, the combined uncertainty and natural variability associated with other
model inputs. A Monte Carlo version of E-MCM has been developed and will be used in future assessments.

6. E-MCM was calibrated assuming site 3A-15 was essentially at steady state relative to current inputs of mercury. As evidenced by recent analyses of both mercury in fish fillets and in wading bird feathers collected in the Everglades – there is a strong indication that declines in the mercury burden for both types of biota have occurred since ca. 1990 — this steady-state assumption is in all likelihood incorrect. Ideally, the model calibration would have been time-dependent, and would be able to reproduce historical trends of mercury accumulation in the sediments. Such a calibration relies on independent estimates of the trends in emissions and deposition over approximately the past 100 years that are not available.

7. Finally, we calibrated E-MCM to a single site in this study. We were therefore unable to compare model predictions to observations in terms of the effects of different site conditions such as pH, DOC, fish growth rates, sulfate and sulfide levels, and other site conditions that vary systematically across the Everglades. As part of continuing E-MCM modeling support work funded by DEP and SFWMD, the model is currently being applied to at least five other sites located widely across the Everglades. This will allow testing of the predicted effects of changing site conditions.

5.3 Margin of Safety

A Margin of Safety determination is a requisite component of a TMDL analysis to account for the uncertainty in the understanding of the relationship between pollutant loadings and water quality impacts. Typically, this is incorporated explicitly by setting aside a fraction of the calculated maximum acceptable load as an unallocated source, or incorporated implicitly by utilizing a set of appropriately conservative (protective) assumptions in the analysis.

For this analysis, the Margin of Safety can be separated into three components: (1) that associated with the Florida Health Department consumption advisory level of 0.5 mg/kg mercury in fish; (2) that associated with the modeled relationship between atmospheric sources and atmospheric loadings; and (3) that associated with the modeled relationship between loadings and biotic response. To put this pilot effort in context, we describe some aspects of margin of safety that would need to be considered when developing a TMDL involving atmospheric deposition of mercury. These elements are discussed below.

5.3.1 Health risk margin of safety

In light of recent findings, a Margin of Safety is not incorporated in the water quality endpoint for this pilot TMDL. That endpoint is the 0.5 mg/kg mercury concentration in fish flesh, fish consumption advisory limit, as issued by the Florida DOH. Concentrations greater than this value trigger the issuance of fish consumption advisories by DOH. This number had been considered protective of human health for exposure to mercury from fish consumption. The 0.5 mg/kg advisory limit was based on the Provisional Tolerable Weekly Intake value proposed by the World Health Organization (WHO) in 1972. However, the
mercury reference dose used by the WHO of 0.43 µg/kg body weight-day exceeds the recent USEPA recommended and National Research Council confirmed reference dose of 0.1 µg/kg body weight-day. As well, the Florida relative source contribution for mercury from human consumption of marine and estuarine fish is in need of recalculation based on new data which indicate that fish consumption by Floridians is higher than the national average. This, along with the recent USEPA issuance of a guidance mercury water quality criterion for protection of human health of 0.3 mg/kg mercury concentration in fish flesh, suggests that the Florida 0.5 mg/kg limit is not conservative. The Florida 0.5 mg/kg advisory limit is currently under review.

5.3.2 Atmospheric modeling margin of safety
The manner in which atmospheric sources were considered and used in the source-receptor modeling must be considered non-conservative at this juncture. The current state of the art in atmospheric source-receptor modeling used in the analysis does not allow for background sources beyond the immediate model domain to be considered explicitly. Since the model considers only local sources as the forcing function controlling mercury deposition in the Everglades and, since local sources are the only inputs that have a reasonable likelihood of control, this makes the allocation of an acceptable load inherently non-conservative. Given that we cannot control background sources, to the extent that mercury fluxes into the Everglades are derived from global or regional sources, the benefit of controls on local sources would be minimized proportionately.

5.3.3 Aquatic cycling model margin of safety
The aquatic cycling modeling does not incorporate any margin of safety explicitly. The model was calibrated to our best estimates of current conditions to try and accurately simulate both existing and likely future behavior of mercury at Site 3A-15. A margin of safety could be incorporated into the analysis that considers the inherent uncertainty in the model predictions, but is not reasonably possible until the Monte Carlo capabilities are completed in E-MCM.

In summary, a margin of safety was initially built into the analysis by virtue of using the Florida Health Department consumption advisory level of 0.5 mg/kg, however the revised USEPA fish methylmercury criterion of 0.3 mg/kg eliminates that margin of safety. Given that controlling global sources is infeasible, however, our inability to resolve the contributions of global and local sources to deposition at Site 3A-15 suggests that we have underestimated the likely requisite local load reduction. When reasonable lower limits of global loadings are considered, our results indicate that virtually complete elimination of local sources is likely required to approach or achieve reductions in mercury concentrations in largemouth bass consistent with achieving a target level of 0.5 mg/kg.
5.4 Sources of Uncertainty

5.4.1 Aquatic Mercury Cycling Model – Conceptual Issues
One element of uncertainty analysis as applied to models is sensitivity analysis, i.e. understanding, in the present case, which variables in the E-MCM most affect predicted fish mercury concentrations at WCA 3A-15. Two types of sensitivity analyses were conducted to address this question. The first approach was to conduct a traditional type of analysis where each parameter is varied by the same relative amount, without regard to whether this value is actually likely to occur or is appropriate for the system of interest. The second approach considered the range of actual or (if such information was not available) likely values a parameter can assume. This latter approach is essentially a "minimum-maximum" analysis that examines sensitivity in the context of likely or actual parameter distributional ranges. It thus defines the bounds of uncertainty in model response related to a given variable. Details of the approaches and a presentation of the input parameter values used in the analyses are presented in Appendix II.

5.4.2 Traditional Sensitivity Analysis Results
Simulations were run varying inputs in isolation by a given amount, for example plus and minus 50%. In cases where a 50% change did not make physical sense, a lesser change was made, e.g. 10% or 25%. In addition, there were some inputs such as the fraction of fish in the diet that did not make sense to change in isolation. The following simultaneous changes were simulated:

- Fish growth rates and spawning sizes for all fish species were changed by the same percentage simultaneously.

- The areal coverage of the three macrophyte species, periphyton coverage, and quantities of suspended solids and detrital material in the water column were varied simultaneously. It is expected that a change in vegetation cover would affect the amount of settling material. Burial rates would be affected by these changes, since burial is calculated based on sources and sinks of particulate matter to the sediments.

- When the diet of largemouth bass was altered to increase or decrease the fraction of fish in the diet, it was necessary to also alter the fractions of the diet represented by other food items. The fractions added or subtracted from fish consumption were distributed evenly amongst other food items.

- Surface inflow and outflow rates (Qin and Qout) were varied simultaneously since it was assumed these rates were equal in simulations. This assumption is reasonable, given that estimated average flows in and out of WCA-3A over a 31-year period agreed within 12% (SFWMD, 2000).

- When atmospheric Hg(II) deposition was altered, surface inflowing Hg(II) and MeHg loads also were varied proportionately. Because the rates of atmospheric methylmercury
deposition are so low compared to other major fluxes, atmospheric methylmercury
deposition was not altered for this particular analysis.

To provide a common basis for comparing the effects of changes to model inputs on fish
mercury, the concentrations in age 3 largemouth bass were used as the endpoint (Figure 12).
Results are presented as absolute value of the ratio of the percent change in fish mercury
centration divided by the percent change in the input:

\[
\text{Ratio} = \left| \frac{\text{Percent change in fish Hg}}{\text{Percent change in input value}} \right|
\]

Predicted mercury concentrations in age-3 largemouth bass were most sensitive to factors
associated with particle and vegetation fluxes, Hg(II) loading, methylation rates, and factors
affecting fish diets and growth.

Figure 12. Predicted sensitivity of age 3 largemouth bass mercury concentrations in WCA 3A-15 to changes in various input values.
Another important conceptual issue is whether the relationship between biota response and external mercury loading rates to the system is linear. E-MCM predicts long term responses of fish mercury concentrations to changes in atmospheric Hg(II) deposition rates are virtually linear (but with a non-zero intercept) over practical time scales. The model predictions are governed, and to some extent made uncertain, by our current understanding of mercury cycling and the resulting assumptions in the model. Specifically, the following assumptions had a significant impact on the shape of the dose-response curve:

- Methylation occurs primarily in the sediments;
- Methylation depends on a bioavailable fraction of porewater Hg(II);
- Porewater Hg(II) concentrations are not currently at saturation. For example, it is plausible that additional Hg(II) loading could result in precipitation of the excess Hg(II) as cinnabar, with no change in porewater Hg(II). We do not have cinnabar forming in any of the loading scenarios we examined with our calibration; and
- Atmospheric methylmercury deposition, inflowing methylmercury loads, and inflowing Hg(II) loads were assumed to be reduced by the same percentage as Hg(II) deposition in scenarios with load reductions. In other words, no watershed-based upstream sources, i.e. geologic or anthropogenic, within the watershed are assumed to exist. In effect this means all upstream surface water loadings are derived from atmospheric deposition influenced to the same extent by variations in emissions as direct atmospheric inputs to WCA 3A-15. To put this assumption in perspective, given that atmospheric deposition to the Everglades constitutes >95% of the annual mercury load, the upper bound of watershed based sources is at most only a second order consideration.

Thus, we interpret the predicted response of fish mercury concentrations to load reductions in this study to reflect the current level of understanding. This level of understanding is currently inadequate, however, to support strong confidence in the absolute values of predicted fish mercury levels. Nonetheless, we are relatively confident in our ability to predict the percentage change in fish mercury concentrations from the percentage change in atmospheric loading. We recognize, of course, that the relationship between emissions and atmospheric deposition is dictated by a number of factors, including speciation of emissions and other source characteristics. Thus, while we can state that our analysis indicates that a desired percentage reduction requires a commensurate reduction in atmospheric loadings, the desired percentage change in atmospheric loadings does not necessarily equate to a similar reduction in overall emissions.

5.4.3 “Minimum-Maximum” Sensitivity Analysis Results
To conduct the “minimum-maximum” analysis, E-MCM was first run for the $i^{th}$ parameter at its high and low limits, while all other parameters were held constant at their nominal values. As in the more traditional sensitivity analyses presented earlier, the end-point for the analysis was the MeHg concentration in age 3 largemouth bass. The sensitivity index for the $i^{th}$ parameter ($S_i$) (Hoffman and Gardner, 1983) is calculated as:

$$S_i = 1 - \frac{E_{i,\text{low}}}{E_{i,\text{high}}}$$
where $E_{i,\text{low}}$ and $E_{i,\text{high}}$ are the predicted age 3 largemouth bass mercury concentrations for the low and high estimates for the $i^{th}$ parameter respectively. Note that, as $SI_i$ approaches 1 (i.e., the larger the difference between the high and low results), the model is increasingly more sensitive to the range in parameter uncertainty.

Results from the “minimum-maximum” analysis are shown in Figure 13. The analysis demonstrated that predicted concentrations of mercury in age 3 largemouth bass at WCA 3A-15 are most sensitive to uncertainties associated with inputs related to the in situ production and destruction of methylmercury. This is because: (1) in situ methylation is predicted to be a major source of MeHg for fish at WCA 3A-15; and (2) there is considerable uncertainty regarding true rates. This result is consistent with previous assessments indicating that future R&D efforts need to better elucidate factors affecting fish mercury concentrations in Everglades marshes, and aquatic systems in general.

In addition, uncertainties associated with particle-based mercury fluxes also significantly affected predicted fish mercury levels. There is a need to better constrain/estimate the production and fate of particulate matter via macrophytes and periphyton for the purposes of better constraining E-MCM predictions. Uncertainties regarding hydrologic inputs had a
moderate effect on predicted fish mercury concentrations. Because these parameters were altered individually, this result was anticipated and the full impacts of hydrological changes and uncertainties are likely not reflected in this analysis.

Figure 14. The effects of parameter error on predicted mercury concentrations in largemouth bass (LMB) following a reduction in current atmospheric loading rates by 17.7 $\mu$g/m$^2$/yr. (assumed current rate = 35 $\mu$g/m$^2$/yr.). Analysis assumes that the initial predicted concentration in LMB in the absence of error is 1 mg/kg. See text for explanation.
5.4.4 Effects of Parameter Uncertainty

The sensitivity index approach, as currently used, treated only one parameter at a time. An improvement to this approach would be to simultaneously vary groups of interdependent inputs to their minima or maxima (positive or negatively correlated).

Figure 14 presents an example of Monte Carlo analysis. In this analysis, the estimated uncertainty in modeled atmospheric deposition was combined with the uncertainty of a single parameter set within E-MCM – vegetative cover and settling solids. For the sake of simplicity, the analysis assumes that current largemouth bass concentrations average 1 mg/kg in the absence of error. In the upper panel, the effect of parameter error on LMB concentrations is delineated by reference lines showing the standard deviation of the predicted LMB concentrations. For example, the X-axis shows via dotted lines the relative standard deviation in predicted largemouth bass (LMB) mercury concentrations due to an assumed variability in vegetation turnover rate of 10%. Resultant variability in predicted LMB due to this factor alone is approximately 23%. Likewise, the Y-axis shows the relative standard deviation in predicted LMB mercury concentrations due to errors in the total deposition rate (8.3%).

The effects of the joint error distribution in these two parameters can be readily calculated by assuming the effects of the two errors are multiplicative which, based on model testing, is a reasonable assumption. The resulting uncertainty can then be used to assess the uncertainty in predicted largemouth bass mercury concentrations given a particular atmospheric load reduction. This is illustrated in the lower panel of Figure 14, which shows the resultant probabilistic distribution of predicted LMB mercury concentrations for a load reduction of 17.7 µg/m²/yr. (and a current assumed rate of 35 µg/m²/yr.).

Note that as more dimensions of parameter uncertainty are included, the likely predicted steady state or long-term response of largemouth bass to the given mercury load reduction becomes increasingly more uncertain.

5.4.5 Atmospheric modeling – Conceptual Issues

The Florida Everglades ecosystem extends over 3,000 square miles and is comprised of many habitat types, thus it was not realistic use the E-MCM to simulate the entire ecosystem. Because the extensive and intensive monitoring studies in the Everglades by USEPA and the US Geological Survey have focused on a mercury “hot spot” in central Water Conservation Area 3, this site was also chosen as the deposition receptor for this analysis. Extensive data were available for 1995-1996; as a result, this period (22 June 1995 to 21 June 1996) was selected as the period of study. Atmospheric deposition rate for 1995-1996 is referred to as “current” deposition rate in this report.

The atmospheric modeling did not attempt to deal with the inferred but ill-characterized long-distance transport of mercury from the global background into Florida. Clearly, long-
distance transport from the global background must be presumed to be non-zero, but neither present-day models nor measurements are adequate to estimate the magnitude of this source of mercury to Florida. Only local emissions sources were modeled.

As described in Appendix 1 and in recognition that there are limits to our understanding, tools and data available to support modeling of the global transport of a pollutant, source-receptor modeling relied primarily on local sources to estimate deposition to the Everglades. This has led to no little controversy and comment over the contributing role of local emissions in south Florida to wet deposition rates in the Everglades, and has fueled debate as to whether the estimate of the global or ‘long distance transport’ source to the total deposition signal is too uncertain to conclude that local sources are indeed important. The widely divergent estimates of the ‘local vs. global’ contributions to deposition derived from the FAMS (Guentzel, et al., 2001) and SoFAMMS (Dvonch, et al., 1998) have both illuminated and fueled this debate. It is, however, possible to draw upon the several lines of evidence available to set reasonable bounds around the likely contributions of mercury in Florida.

- Using multivariate receptor modeling, Dvonch, et al. (1998) concluded that 71 ± 8% of the wet deposition signal measured at five sites in the Everglades could be accounted for by local sources. Conversely, Guentzel, et al. (2001) based on their analysis of seasonal patterns in wet deposition of mercury and the uniform nature of summertime mercury concentrations in rain across the south Florida, as well as source apportionment calculations based on a relatively simple mass balance box model on atmospheric fluxes of reactive gaseous mercury in south Florida, concluded that local sources can account for only 30 to 46% of the wet deposition signal.

- An Everglades-wide sediment coring study begun in 1992 (Rood, et al., 1995) yielded estimates of historical mercury accumulation rates in Everglades soils spanning the period 1900 through ca. 1990. Comparison with recent deposition estimates (as µg/m²/yr) among comparable Everglades sites from that time to the present are given in the table below:

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>WCA-1</td>
<td>79</td>
<td>ENR Project</td>
<td>21</td>
</tr>
<tr>
<td>WCA-2</td>
<td>59</td>
<td>NA</td>
<td>--</td>
</tr>
<tr>
<td>WCA-3</td>
<td>39</td>
<td>Andytown</td>
<td>24</td>
</tr>
<tr>
<td>ENP</td>
<td>40</td>
<td>ENP</td>
<td>18</td>
</tr>
</tbody>
</table>

The average mercury accumulation rate in sediment Everglades-wide was 53 µg/m²/yr ca.1990 vs. 21 µg/m²/yr from atmospheric deposition in 2001. These data suggest a decline in deposition of ~ 60% overall since ca. 1990.

- Everglades largemouth bass (fillet) and great egret (feather) mercury concentrations have declined ca. 75% from the mid-1990’s to the year 2002.
Data on potential trends in the ‘global background’ indicate a “very small downward trend from 1995 through 2000” at Alert, Canada (Schroeder, Pers. Comm., 2002) and there are similar results from Mace Head, Ireland (Ebinghaus, from Schroeder, Pers. Comm., 2002). Both are relatively remote background sites. Published data indicate a decline over the northern Atlantic of ca. 20% by the mid-1990’s. (Langer & Slemr, 1991; Slemr, et al., 1995; Slemr, 1996; Slemr & Scheel, 1998; Ebinghaus & Slemr, 2000). It is apparent that long-term trends of elemental mercury in the atmosphere at background sites are not of similar magnitude to the declines evident in the Everglades ecosystem.

An independent analysis by the Florida Electric Power Coordinating Group on trends of mercury emissions and concentrations in south Florida biota (per above) concluded that at this juncture “…it is clear that the fundamental hypothesis that changes in local emissions of mercury [in southeast Florida] have been the primary agent for recent biota changes in mercury concentrations in the Everglades cannot be rejected.” (Pollman & Porcella, 2002).

Receptor modeling applied to source and ambient data during the intensive SoFAMMS field study in 1995 indicated that 92 (± 30)% of the total mercury deposition measured at the Davie site near Ft. Lauderdale could be accounted for by local sources (Dvonch, et al., 1998).

The approximate magnitude of the global background contribution can be bounded from the ca. 300 rain samples from 17 sites in Dade and Broward counties during the August 1995 SoFAMMS project. Observed minima in background rainfall mercury concentrations at coastal sites in south Florida approximated 5 ng/L. Assuming annual rainfall rates of 130 cm/yr., these concentrations would result in background deposition rates of about 6.5 µg/m²/yr., or about 21% of rainfall deposition.

As reported in herein, comparative model analyses of transport of mercury from all point sources in Florida and adjoining states vs. the 38 point sources in the south Florida modeling domain alone, indicated a contribution to the Everglades from regional sources within the southeastern US of less than 5% of total deposition.

Contrastingly, the FAMS investigators (Landing, et al., 1995, Guentzel, et al., 1997, 2001) concluded from the weak trace element signatures in rainfall samples and a box model of mercury fluxes into and over Florida, that local sources alone could not account for the amounts of mercury in measured in rain.

We view the FAMS and SoFAMMS projects as having been complementary, not contradictory. Combined with other information they support the notion that the dominant source term signal contributing to total mercury deposition in south Florida are local emissions.

By our analysis, estimated total deposition for June 1995 – June 1996 was 35.3 µg/m²/yr (DEP, 2002), of which 23 µg/m²/yr was measured by FAMS as wet deposition and 12.2 µg/m²/yr modeled as derived from dry deposition. Dry deposition in south Florida expectedly is greatly dominated by RGM. Since the removal rate of RGM from the
lower troposphere is rapid, and because the production rate is low, it is reasonable to assume that the predominant fraction of the dry deposited mercury in the Everglades is local in origin. If we assume that this fraction is 80%, then this equates to a local contribution of 9.8 µg/m²/yr. We then take the lowest estimate of 30% from Guentzel, et al. (2001) to describe the local emissions contribution to the annual wet deposition of 23.12 µg/m²/yr. This equates to a lower limit contribution of 6.9 µg/m²/yr from local emissions.

Combined, the total estimated contribution from local emissions to wet and dry mercury deposition is 16.7 µg/m²/yr, or 47% of the total signal. If we ascribe a contribution of 6.5 µg/m²/yr to the global background (as described above), then the maximum that other regional and larger scale sources other than global background can contribute is 34%. If we use the midpoint of the Guentzel, et al. (2001) estimate of local contributions to wet deposition (38%), the contributions of each major source category to total deposition are:

- Local sources – 52.5%
- Global background – 18.4%
- Other regional sources – 29.1%

Regardless of whether the FAMS or SoFAMMS analyses discussed above ultimately proves to be closer to the truth, we can use their combined results to constrain a lower limit for the likely contribution of local sources to total deposition. It is our conclusion that the sum of these various lines of argument suggest that at a minimum local sources account for more than 50% of mercury deposited in southern Florida, and several other analyses suggest that the contribution may be substantially greater. Narrowing of these divergent estimates is one of the remaining goals of the SFMSP.

This issue, i.e. not explicitly treating global sources, was the subject of several review comments. The authors maintain, however, that given the present state of understanding of the global mercury cycle, it would be unduly speculative to attempt this. At this time, there are few data at present to constrain a global mercury modeling analysis! For example, it is only within the last two years that the phenomenon of mercury depletion events at polar sunrise has been convincingly established. The magnitude of this sink has been speculated to be important to the global cycle, and the recent nature of its discovery reveals how little we understand atmospheric mercury cycling on the global scale.

To address questions about the potential importance of global background contributions to mercury to south Florida, the UMAQL group evaluated two model scenarios to aid in bounding the potential magnitude. By modeling two regional emissions source scenarios: one included all sources within the Southeastern US (including Florida), the other included only the 38 sources in southern Florida. By difference between the two scenarios, this modeling analysis estimated that sources outside the south Florida region contributed approximately 5% to deposition at the receptor site in near Fort Lauderdale. Because of its estimated small size, sources in the Southeast region outside south Florida were excluded from subsequent analyses.
Three main sources of uncertainty are present in the atmospheric modeling component of this project: source characterization, meteorological variation, and the input parameters specified in the model.

The source emissions inventory is the major source of uncertainty in the atmospheric model. The inventory used was that developed for the USEPA Mercury Study Report to Congress (USEPA, 1997), which was the only comprehensive, self-consistent emissions scenario available. Other emission and speciation scenarios were examined to evaluate their effects on total deposition (see Appendix I). Incorporation of point-source specific data on emission rates and mercury speciation for only two sources in the south Florida region would result in a significantly lower annual deposition rate (Appendix I, Figure 12). The apparent discrepancies among emissions data and the emissions scenarios evaluated in all likelihood reflect the rapid decline in mercury emissions occurring during the period of 1985 – 1995. Figure 15 shows the results of various emissions scenarios on the resulting wet deposition estimates.

Meteorological variation also represents an important source of uncertainty in the model. In the modeling, for each meteorological cluster, two wet days and two dry days were selected for use in the modeling exercise (Table 8). Where possible, these days were chosen such that they represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster. It was believed that in doing so, potential biases from choosing two days with nearly identical deposition patterns would be minimized.
Figure 15. Comparison of the modeled monthly wet deposition to SFWMD WCA 3A-15 as a function of emissions scenario. Scenario #1 corresponds to the emissions inventory derived from the USEPA Mercury Study Report to Congress; Scenarios #2 and #3 reflect adjustment for measured MWC & MWI speciation.

Figure 16 presents the modeled 24-hour total wet deposition estimates for WCA 3A, as a function of atmospheric transport cluster (similar data are discussed in Appendix I for dry deposition). Clusters with predominant offshore flows result in little wet or dry deposition. In contrast, clusters with onshore flows – where the air mass moves over the southeast Florida metropolitan area – produce significant, although variable, deposition. Lack of precision in estimates of wind direction and wind speed could lead to relatively larger errors in estimated deposition to a specific location such as WCA 3A-15. Another factor in the between-cluster variability is the location and magnitude of the emission sources relative to WCA 3A.

Other sources of uncertainty are the values used as inputs for dry deposition rates and the Henry’s Law constant. These parameters were used to calibrate the model. Their effects and use in the calibration procedure are discussed in Section 4 of Appendix I.
5.4.6 Effects of Uncertainty on Endpoint Predictions

As stated earlier in this section, the treatment of the uncertainties will give us an indication of the power of our present knowledge and, more constructively, guidance for the final phase of SFMSP studies to reduce these uncertainties to acceptable levels. To reiterate, uncertainties in this analysis can be lumped into three broad categories: (1) characterization of emission source rates and speciation, including both local sources and background (hemispheric and global) inputs; (2) the transport, reaction, and deposition of mercury from source to receptor; and (3) the aquatic cycling and fate of mercury once it enters the Everglades.

We evaluated the effects of uncertainty in the estimated wet and dry deposition rates to determine whether errors in the deposition rate used in model calibration to current conditions would fundamentally change the response between assumed changes in atmospheric loading and the endpoint of greatest interest, concentrations of mercury in 3-year old largemouth bass. There is uncertainty inherent in our estimates of average annual wet and dry Hg(II) deposition arising from (but not limited to) analytical and field collection errors, errors induced from extrapolating from sites where mercury wet deposition has been measured to site 3A-15, and errors in modeling source-receptor relationships, including errors in emission estimates and errors in simulating meteorological conditions.
To accommodate uncertainty in the current Hg(II) deposition rates, we calibrated E-MCM separately for three loading scenarios:

- The current mean annual load estimated from the UMAQL hybrid modeling analysis: 31 µg/m²/yr. (modeled wet + modeled dry).
- The upper and lower limits encompassing 95% of the likely estimates for the current modeled total deposition rates: 36.7 and 25.1 µg/m²/yr., respectively.

The UMAQL modeled estimates of total deposition were used for the purposes of this analysis because of the availability of uncertainty in the deposition estimates from the UMAQL analysis. This range of values encompasses the current estimates of total deposition derived from measured wet deposition and modeled dry deposition used in E-MCM simulations, and was thus considered adequate for the purposes of this exercise.

Table 11 summarizes the annual (propagated) uncertainties in wet, dry, and total deposition modeled by UMAQL. These uncertainties were coupled with uncertainties inherent in the estimates of annual wet deposition derived from the FAMS to develop an estimate of the total uncertainty in the wet and dry deposition rates, viz., 9.6% (Appendix II, Section 5.6)

<table>
<thead>
<tr>
<th>Flux Component</th>
<th>Deposition (µg/m²/yr.)</th>
<th>σ (µg/m²/yr.)</th>
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</thead>
<tbody>
<tr>
<td>Modeled Wet Deposition (UMAQL)</td>
<td>18.74</td>
<td>1.57</td>
</tr>
<tr>
<td>Modeled Dry Deposition (RGM &amp; particles, UMAQL)</td>
<td>12.20</td>
<td>2.03</td>
</tr>
<tr>
<td>Total Deposition</td>
<td>30.94</td>
<td>2.57</td>
</tr>
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</table>

For each of the three loading rates, E-MCM was calibrated to achieve the current observed total and methylmercury concentrations in the marsh, including fish. Thus, the predicted fish mercury concentrations were nearly identical in each calibration, but some rate constants by necessity were altered between scenarios to yield reasonable calibrations. Once the model was calibrated for each of the loading scenarios, we tested whether different calibrations yielded substantially different response curves. The comparisons were based on examining whether the same fractional reductions in deposition yielded the same long-term response. As shown in Figure 17, the uncertainty regarding the true loading rate has little effect on the timing or magnitude of the response of age 3 largemouth bass to load reductions of 50%. Results were similar for load reductions of 15% and 75%.
The effects of uncertainty in our current modeled estimates of atmospheric deposition of mercury thus appear to have little or no effect when we examine how changing the total atmospheric load by a fractional amount will influence the dynamics and magnitude of biotic response. It is important to realize that this conclusion is only valid within the framework of the underlying assumptions used to conduct the analysis. Perhaps most important is the assumption that upstream loads are changed fractionally in the same way and at the same rate as the atmospheric load. Clearly, the temporal response of the watershed is slower than the atmospheric pool to changes in emissions and loading. As of this writing, there are currently few data from dose-response experimental studies on catchments and wetlands (including the Everglades) in North America. Studies to elucidate the likely temporal response to changes in loading will be a major focus of the Mercury Experiment To Assess Atmospheric Loading in Canada and the United States (METAALICUS) in the

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10 To reiterate, the focal point of this conclusion is that depending upon the assumed atmospheric deposition rate used to calibrate the model, E-MCM will yield different responses in fish tissue mercury to identical (i.e., mass) magnitudes of reductions of mercury loading. Thus reducing regional emissions by 10 µg/m²/yr for the low deposition estimate scenario would result in a larger percentage reduction in fish tissue mercury than that predicted for the high deposition estimate scenario.
Experimental Lakes Area in northwestern Ontario, and the stable isotope mesocosm studies conducted in situ by ACME in the Everglades. Both studies are currently underway. Preliminary data for the Everglades indicate that an increase in Hg(II) loading produces a linear increase in MeHg in surface sediments and in fish. However, the slope of the response was highly variable among sites. Finally, this analysis does not resolve the question of how our uncertainty about the nature of all the sources contributing to mercury deposition in the Everglades affects the local source-receptor relationships developed in this analysis.

This analysis also illustrates another issue reflecting the state-of-the-art of calibration of E-MCM: viz., given that nearly identical simulation results can be obtained for three significantly different source loading rate scenarios (the upper loading rate estimate differed from the lower estimate by a nearly a factor of 50%), the model is not as well-constrained or robust as desired. The greatest difficulty when calibrating the Hg(II) component of the model lies in our uncertainty of sedimentary mercury accumulation rates. Once the Hg(II) component of the model is calibrated, the methylmercury cycle is not as well constrained as desired. For example, the rates of methylation and demethylation are still inadequately quantified, and different combinations of these two fluxes could still be combined to ultimately result in the same concentrations in fish. The major removal mechanism for total mercury from the study site was burial in the deep sediments, and our uncertainty in these rates based on available measurements is easily greater than 50%. Other variables in the model help constrain the calibration, but there is still too much uncertainty in this key loss pathway to ensure a more robust calibration.

5.4.7 Effects of Annual Variability in Atmospheric Deposition Rates on Endpoint Predictions

Even if the relationship between emissions and deposition was known exactly, and emissions remained unilaterally constant with time, year-to-year variability in mercury deposition will occur due to changing meteorological and precipitation patterns. This in turn expectedly would produce year-to-year variations in largemouth bass mercury concentrations. To address the effects of this variability, an artificial data set of atmospheric deposition of mercury was synthesized based on annual variability observed at three Everglades sites during FAMS (Appendix II, Section 4.5 describes the approach and Section 6.5 describes the results). These sites had comprehensive deposition data spanning 2 - 4 year periods. The synthesized data set, which comprised 500 annual values for total mercury deposition, had log normal distribution characteristics with the desired mean and standard deviation values derived from the FAMS sites.

Inherent in this approach were several key assumptions:

- Deposition is constant over the long-term but varies annually about some mean value, and can be described statistically as a lognormal distribution.
- Wet deposition rates measured at the Florida Atmospheric Mercury Study (FAMS) south Florida sites between 1993 and 1996 are adequate to describe the variance of this distribution.
- The coefficient of variation for total deposition is similar to values measured for wet deposition rates.
• Inflowing (upstream) MeHg and Hg_{tot} loads vary in proportion to wet Hg_{tot} deposition.

An average coefficient of variation of 26.4% was calculated for the three FAMS sites. The synthetic total deposition data set was then constructed based on the estimated annual average total mercury deposition rate of 35 \mu g/m^2/yr. (FAMS wet + modeled dry) developed in Appendix I. Variations in largemouth bass mercury concentrations were then computed by first running E-MCM with a fixed deposition rate of 35 \mu g/m^2/yr. for 200 years to achieve steady state conditions. Using the synthesized total deposition data set to simulate annual deposition variability, the model was then run an additional 500 years, with fish mercury concentrations recorded each year.

![Graph showing input annual atmospheric Hg(II) deposition rates and predicted Hg concentrations in age 3 largemouth bass for 500 year simulation.](image)

**Figure 18.** Input annual atmospheric Hg(II) deposition rates and predicted Hg concentrations in age 3 largemouth bass for 500 year simulation.

**Figure 18** gives the results from a long-term simulation. Under current deposition, the model calibrated concentration for mercury in 3-year old large mouth bass is 1.81 mg/kg, with a coefficient of variation of 3.6%. Compared to the variance in the deposition rates, the response of the bass was considerably damped, and reflects: (1) buffering against short-term changes by the sediment pool of mercury, which greatly exceeds the amount of mercury entering the system on an areal basis any given year; and (2) the fact that fish tissue concentrations reflect an integrated response over the 3 years of varying exposure, rather than simply reflecting the current year deposition rate.
6 CONCLUSIONS, RESEARCH NEEDS AND PLANS

The primary objective of this pilot study was to explore how a TMDL or critical loading analysis could be conducted when the pollutant of interest enters aquatic ecosystems largely through atmospheric deposition. In brief, a hybridized approach concatenating an atmospheric model with an aquatic mercury cycling model was used to predict the relationship between local emissions, deposition and, ultimately, mercury concentrations in largemouth bass at an Everglades site known to have elevated mercury concentrations in fish tissue.

This study synthesizes and integrates data from arguably one of the most comprehensive field measurement and monitoring programs conducted on the fate and transport of an environmental pollutant. Nonetheless, we recognize that numerous areas of uncertainty remain in the models’ formulations and the data they rely on, and both the model and data uncertainties identified in this report are guiding future research of the South Florida Mercury Science Program.

This combined modeling analysis successfully integrated a multimedia modeling approach with extensive field data to produce simulations that reasonably agree with conditions and changes seen in the south Florida region. For example, since the mid-1980’s emissions of mercury have declined dramatically. Similarly, monitoring data from the mid-1990’s to the present show significant declines in mercury in Everglades fish and wading birds. The timing of trends and rapidity of response seen in the biota appear consistent with: (1) the role of local sources as an important driver of atmospheric deposition as indicated by the UMAQL modeling; (2) the apparent decline in local emissions in south Florida inferred from limited municipal solid waste incinerator emissions data compiled by DEP; and (3) E-MCM modeling of the timing of change.

Overall, E-MCM was calibrated to fit observations for total and methylmercury at WCA 3A-15. Regarding the model simulations:

1. The E-MCM model predicts a linear relationship between atmospheric mercury deposition and mercury concentrations in largemouth bass, with a small residual mercury
concentration in fish at zero atmospheric mercury deposition (Figure 9). In other words, for any reduction in mercury inputs there may be a near 1:1 reduction in fish mercury concentrations. Furthermore, error analysis shows that the E-MCM predicts equivalence between the percent decrease in atmospheric mercury deposition rate and the percent decrease in largemouth bass mercury concentration over the likely range for current estimates of atmospheric deposition of mercury. The slight offset from a 1:1 relationship is a result of movement of historically deposited mercury from deeper sediment layers to the water column. Until this mercury is buried below the active zone, it can continue to cycle through the system. In addition, because mercury is a naturally occurring element, fish tissue mercury concentrations can never be reduced to zero.

2. In the absence of changes to the system other than mercury loading (e.g., changes in sulfur cycling, nutrient cycling, or hydrology), a reduction of about 80% of current total (1995-96) annual mercury atmospheric deposition rates would be needed for the mercury concentrations in a 3-year old largemouth bass at WCA 3A-15 to be reduced to less than Florida’s present fish consumption advisory action level of 0.5 mg/kg (parts per million). This modeling did not attempt to deal with long distance transport of mercury from the global background into Florida. Clearly, long-distance transport from the global background must be presumed to be non-zero, but neither present-day models nor measurements are sufficient to estimate the magnitude of this source of mercury to Florida. From the 1995 SoFAMMS project, we can estimate that background mercury concentrations in rainfall at coastal sites in south Florida approximate 5 ng/L. Assuming annual rainfall rates of 130 cm/yr., these concentrations would result in background deposition rates equal to 6.5 µg/m²/yr. If, as predicted by the UMAQL hybrid model/FAMS analysis, current loading rates are indeed ca. 35 µg/m²/yr., this rate of background deposition (i.e., 21% of total loading) suggests that to reach a target of age-3 largemouth bass average concentrations not exceeding 0.5 mg/kg wet muscle for an average year would require virtually complete elimination of local atmospheric deposition sources of mercury.

3. Mercury concentrations in age-3 largemouth bass are predicted to achieve 50% of their long-term, steady state response within approximately 10 years and 90% within ca. 30 years following sustained mercury load reductions. The time it should take to reach 50% or 90% of final steady-state fish mercury concentrations following a reduction in mercury deposition is independent of the actual magnitude of the decrease. In other words, it takes about 10 years and ca. 30 years to reach about 50% and 90% of the ultimate steady-state fish mercury concentration, respectively, whether the reduction is 85% or 25% of the current mercury deposition rates. The time scale of this response is quite sensitive to the turnover rate of mercury in the surficial sediments. Factors which increase the flux of detrital material to the sediments (e.g., eutrophication) will result in a faster response time as elevated mercury in the sediment pool is buried deeper and more rapidly.
6.1 Further Work in Progress or Planned

There are a number of research efforts underway or planned to improve the capability of the combined atmospheric modeling and aquatic modeling approach.

The mercury contribution from background (hemispheric or global) sources is unknown, and directly affects both the estimates of atmospheric deposition to the study site, and the response of the system to given changes in the magnitude of the current load. The present analysis excludes consideration of long-distance transport of mercury into Florida because the present state of global models and measurements do not give us any basis for doing so. When this modeling study was performed, there were no measurement data of mercury species at several altitudes to incorporate long-distance transport in a quantitative manner. Until measurements or models allow us to constrain the uncertainties in the long-distance transport phenomenon, there is no objective basis for addressing this question.

Note: USEPA, DEP and NOAA-ARL conducted winter and summer aircraft campaigns to measure the relevant mercury species in and above the marine boundary layer off the east coast of Florida which should allow parameterization of this source term. Results of this investigation should be completed in 2002.

Previous research has suggested that the atmospheric deposition of mercury to south Florida is dominated by wet deposition, with the majority of this deposition associated with summertime convective precipitation events (Guentzel et al., 1995, 2001; Dvonch et al., 1999). The modeled analysis of dry deposition conducted as part of this study, however, suggests that dry deposition is important as well, comprising perhaps 34 to 40% of the total mercury deposition signal. Currently, only very limited data are available to assess this component more directly.

Note: The Florida Everglades Dry Deposition Study (FEDDS) conducted winter and summer field campaigns in 1999 and 2000, respectively, and, when data analysis and modeling is completed, these results should improve both knowledge of depositional processes and parameterization of models.

If all current atmospheric loadings of Hg(II) to the marsh surface were eliminated, regardless of source, our analysis suggests that fish mercury concentrations would still be ca. 6% of current values, at least over the next 100 years. Only a fraction of this is due to continued deposition of MeHg, which, based on limited measurements, appears to comprise less than 1% of the estimated current total atmospheric mercury load. Most of the continued supply of mercury appears to be internal through remobilization of Hg(II) and methylmercury from deep sediment layers via porewater uptake by macrophytes. Over the course of 100 years, Hg(II) and methylmercury concentrations in these deeper sediments are not significantly affected by changes in atmospheric mercury deposition in the simulations. This in essence adds another source of mercury to the overlying active marsh system, a source which would slowly diminish in the absence of atmospheric
Conclusions, Research Needs and Plans

Hg(II) deposition. This assumption should be critically reviewed in any future assessments.

Note: DEP and USEPA have initiated further analyses of potential sources of MeHg in rain and of MeHg in rainfall at multiple sites in the Everglades to confirm initial estimates of rainfall MeHg from FAMS. This will allow better parameterization of this term in future assessments. The stable isotope mesocosm studies currently conducted by USGS ACME team (Krabbenhoft & Gilmour, 2002) should further identify the nature of the dose-response relationship and the role of internal remobilization of legacy mercury on recovery.

A second major objective of this study is to identify major sources of uncertainty in our model predictions that would adversely influence our ability to reliably assess the relationship between local mercury emission sources and biotic response. Excluding errors relating to source characterization, modeled annual total mercury deposition rates had an estimated error of 8.3%. As illustrated earlier, the large uncertainties in source emission characterization (quantity and speciation) have a very pronounced effect on modeled deposition rates.

Note: It is clear that one of the most critical areas for future investigation is resolving the divergences in present mercury emissions inventories. Further work in this area is underway.

A number of aquatic cycling process and other factors presently are not well understood and are not fully developed in the E-MCM. For example, the sulfur cycle, e.g. sulfide-mercury interactions, in the Everglades is anthropogenically perturbed and poorly understood. Proper representation of sulfur chemistry in sediments could change the shape and the slope of the atmospheric loading-biotic response curve. The response curve slope produced in this analysis differs from unity regarding relative response to relative changes in loading largely because the model predicts that “legacy” mercury stored deep in the sediments (5 to 20 cm below the sediment-water interface) is mobilized and brought into the water column by macrophyte roots. Based on current sedimentation rates, this material will not be removed from the system for perhaps hundreds of years.

Note: An improved representation of sulfur cycling and chemistry is presently being developed for the E-MCM and will be available for subsequent analyses.

The E-MCM model also has inherent uncertainties that affect the predicted response of largemouth bass to changes in mercury loadings. Sensitivity analysis identified a number of key parameters to which the model is quite sensitive, including particulate fluxes relating to vegetation cover and suspended solids, sediment methylation and demethylation rates, and factors affecting fish diets and growth. Based on current limits of uncertainty in parameter values, the E-MCM is most sensitive to the uncertainty in parameters that relate to methylation and demethylation. However, to fully assess the effect of parameter uncertainty in E-MCM, including inputs for mercury loading from
atmospheric deposition, a Monte Carlo analysis ideally would be conducted in which each model parameter is varied according to its likely distribution. Such capabilities in E-MCM were not available for this study. Nonetheless, the joint or combined effect of uncertainty in just two parameters (Figure 14) can be illustrated for predicted responses of largemouth bass to changes in atmospheric loading.

Note: Monte Carlo analysis routines are being developed for the E-MCM and will be available for subsequent analyses.

Based on the analyses presented herein it is evident that there is great potential for combining such air and water modeling approaches for TMDLs involving air deposition of mercury for other aquatic ecosystems. Although mercury was used as the ‘model’ pollutant for exploring how this type of TMDL analysis could be conducted, many of the limitations and successes that emerged in the application of the method for mercury likely are applicable to analyses that may be conducted for other impaired waters where the pollutants of concern are significantly of atmospheric origin (e.g. NOx, PCBs).

The progress represented in these demonstrations of a unique combination of atmospheric and aquatic cycling models is gratifying. Because this document represents the drawing together of many elements of monitoring and research programs, the preceding discussion has identified and dwelt on a number of areas where uncertainty remains. There is reason to believe that, with modest additional effort, these remaining uncertainties can be reduced to levels that will allow reasonable allocation of mercury emissions so as to protect the designated uses of affected waters.

6.2 Conclusions

This study has demonstrated the utility of using linked atmospheric and aquatic mercury cycling models to evaluate critical loading rates for an atmospherically derived pollutant (i.e., mercury). Important, if preliminary, information from this modeling indicates that the aquatic cycling of mercury is strongly influenced by changes in the atmospheric load, and that the ecosystem responds in a direct and rapid fashion to changes in load. This study also constructively reveals where uncertainties remain in the state-of-the-art for both the atmospheric and aquatic cycling models, and show what additional information is needed to improve subsequent analysis:

1. Based on the E-MCM model, the fundamental response of largemouth bass to long-term changes in atmospheric deposition of mercury appears insensitive to estimation errors of current levels of wet and dry deposition used during model calibration. This lack of sensitivity largely reflects our uncertainty in actual sedimentary mercury burial rates, coupled with the fact that this pathway is the major removal mechanism for mercury in the system. The predicted response is essentially linear, with calibrations to different assumed current atmospheric deposition rates yielding equivalent responses to imposed fractional reductions in deposition.

2. Sensitivity analyses indicate that E-MCM predictions are most sensitive to uncertainties associated with methylation and demethylation rates, particle and
vegetation fluxes, loading rates of Hg(II), and factors affecting fish diet and growth. Although the exercise of using differing calibrations based on uncertainties in current atmospheric deposition rates produced essentially equivalent mercury loading-largemouth bass response curves, we cannot extend that conclusion further. For example, changes in the assumed particle and vegetation fluxes may render model calibration problematic, and may suggest that other pathways for removing mercury from the system must be operating. The final calibration for E-MCM indicates that the primary removal mechanism for mercury at site 3A-15 is burial, and that sediment turnover rates govern the response time. Changing model calibrations that result in changes in sediment dynamics likely will have a profound effect on the predicted rate of response of the system to changes in atmospheric loading. Thus, further research on these model-sensitive parameters is required to more adequately define the relationship between loading and biotic response.

3. Year-to-year variations in atmospheric deposition to the Everglades are expected to be large (coefficient of variation = 26.3%), even if local emission rates remain essentially constant, due to year-to-year variations in meteorological and precipitation patterns. The impact of these variations on age 3 (and higher ages) largemouth bass mercury concentrations likely will be considerably dampened, both because of sediment buffering and because the concentrations of mercury in older fish reflect long-term integration of varying exposure levels. The lack of a long term Hg(II) deposition data set required us to synthesize a data set to estimate the effects of year-to-year variations in Hg(II) deposition. Longer periods of record will be helpful for any future assessments.

4. The E-MCM model was calibrated by assuming current conditions reflect a quasi-steady state. There is accumulating evidence from studies both on mercury concentrations in largemouth bass and wading birds in the Everglades that this is not true – that the system appears to be undergoing a declining trend in mercury concentrations in fish and birds. Under ideal circumstances, E-MCM would have been calibrated to a long-term data set. Unfortunately, such long-term water chemistry and biota data sets do not exist, nor do high-quality, high-resolution mercury deposition and sediment accumulation rate data. This currently precludes a long-term, historical calibration, and was the impetus for choosing a quasi steady-state calibration.

5. Local emission rates and speciation used to predict atmospheric loading rates to the Everglades have a profound effect on the predicted results. The hybrid model simulations (which used south Florida point source emissions derived from the USEPA Mercury Study Report to Congress emissions database) resulted in a modeled total deposition rate of 31 µg/m²/yr. Simply changing the emission rate of the two significant sources in Dade county to reflect actual stack testing speciation and rate data measured by Dvonch, et al. (1999) resulted in a 43% lowering of the modeled total deposition rate. These results would suggest that any attribution of hemispheric and global sources is very sensitive to parameterization of emissions speciation and atmospheric conversion. This uncertainty has obvious implications regarding the efficacy of controlling local sources to mitigate the current mercury problem in the Everglades. Thus, additional efforts to both assess source magnitudes and speciation,
and to characterize background rates of deposition, are critical if the TMDL process is to be successful.
7 RECENT TRENDS IN MERCURY EMISSIONS, DEPOSITION AND CONCENTRATIONS IN BIOTA

Over the past decade, progressive, statistically significant declines in mercury concentrations have been observed in both largemouth bass and great egret nestlings in a number of sites located throughout the Everglades (Pollman et al., 2002; Frederick et al., 2001). Coincident with these declines have been marked declines in local emissions of mercury (RMB Consulting & Research, 2002; Husar and Husar, 2002). Given that atmospheric deposition is the major source of Hg to the Everglades (Stober et al., 2001), and because local emissions have been postulated as the predominant source of mercury deposited in south Florida rainfall, including the Everglades (Dvonch et al., 1999), the question arises whether the observed declines in biota Hg concentrations can be related to declines in local emissions. This chapter reviews the existing data on mercury emissions, deposition, and biota trends in south Florida in order to address this question. Much of this discussion is based on work previously published by Pollman et al. (2002) and Pollman and Porcella (2003), but extends that work by including more recently available, longer time series for biota concentrations, as well as incorporating new analyses on wet deposition trends for mercury and some exploratory model hindcasting to examine the relationship between emissions and deposition, and aquatic biota response.

7.1 Trends in Mercury Emissions

Two fundamentally different types of analyses have been conducted to reconstruct recent trends of mercury emissions in south Florida. The first was a direct approach where a historical emissions inventory was compiled for the period 1980 to 2000 for Broward, Dade and Palm Beach Counties (RMB Consulting & Research, 2002). Emissions were estimated from plant operational data and emission factors typical for the source under consideration. These three counties were selected as the region containing sources most likely to be important local contributors to mercury deposition in the Everglades and south Florida. The second approach was an inferential or indirect approach, where the trend in local emissions was inferred by reconstructing a mass balance on the flows of Hg ascribed to various use categories or major economic sectors (Husar and Husar, 2002). This latter analysis first focused on Hg use on a national scale, beginning in 1850 and
continuing to 2000, then reduced the scale of analysis to the state level for Florida, and finally concluded with a regional analysis for the Broward, Dade, and Palm Beach counties for the period 1950 through 2000.

The emissions estimates compiled by RMB Consulting & Research (2002) indicated very large changes occurred between 1980-2000 as a function of the major combustion sources in south Florida (power generation, sugar industry, incineration of municipal and medical wastes; Figure 19). Total emissions were quite low between 1980-1982, and then increased in 1983 by 3.5 times above 1982 levels as both municipal waste combustors (MWC’s) and medical waste incinerators (MWI’s) came on line. Local emissions continued to increase through the 1980’s until 1991, when a peak emission flux of nearly 3,100 kg/yr of total Hg was estimated. Throughout the peak emission period of 1983-1991, local Hg emissions originated primarily from MWI’s (54 to 76% of the total), and MWI’s and MWC’s combined comprised 92 to 96% of the total. Power generation was never above 0.4%, while sugar processing accounted for 4 to 8% of the estimated emissions.

As more stringent regulatory requirements took effect in mid-1992, many MWI’s ceased operations, and medical waste was either sent offsite for processing, autoclaved, or landfilled rather than incinerated. As a result, local emissions declined sharply through 1993 (65% compared to 1991 levels), followed by a slower and nearly monotonic rate of decline through 2000. The total estimated decline in local emissions between 1991 and 2000 is 2,846 kg/yr, which equates to a total reduction of 93%.
Figure 19. Annual atmospheric mercury emissions in south Florida, 1980 – 2000, estimated by RMB Associates & Consulting (2002) as a function of major combustion source category. Sources include power generation facilities (Utility), municipal waste combustors (MWC), medical waste incinerators (MWI), and sugar refineries (Sugar).

Figure 20 shows the results from the materials flows analysis conducted by Husar and Husar (2002) for Broward, Dade, and Palm Beach counties. Use categories that contributed most greatly to the flow of mercury through south Florida included electrical (e.g., batteries, lighting, and switches), laboratory use, and control (measuring and control instruments) categories. Although coal is the largest source (45%; 65 Mg/yr) of Hg emissions for the US (total 144 Mg/yr), no coal combustion occurs in south Florida and only oil and product-related emissions occur.

The total mercury mobilization from electrical, laboratory use, and control categories is depicted in Figure 20 as a solid line ranging from a high of about 18,000 kg/yr in the 1980s and decreasing to <2,000 kg/yr in 1997. A somewhat uncertain fraction of this mobilized mercury is emitted to the atmosphere and, as a result, inferred emission fluxes based on assumed incineration rates of 15 and 30% of the total usage flux are included in the analysis. Also shown in Figure 20 are the direct emission estimates for MSW’s and the combined flux from MWC’s and MWI’s from the RMB analysis. Both analyses
show large declines in local emissions approximating 90% relative to peak emissions and the conclusion that local emissions have declined significantly appears reasonably robust. Estimated emissions from both studies agree well after 1993, but differ with respect to the timing of peak emissions.

![Graph](image)

**Figure 20.** Waste incineration emissions for Dade, Broward, and Palm Beach counties inferred from analysis of mercury usage, 1980 to 1997. Upper line shows annual total mercury usage based on different usages. Emission fluxes are based on 30% and 15% incineration rates (complete mobilization of combusted fraction). Plot also shows emissions for MSW and combined MSW and MWI sources estimated by RMB Associates & Consulting (2002). From Pollman et al. (2002).

### 7.2 Trends in Atmospheric Deposition of Mercury

An essentially continuous record of wet deposition fluxes and concentrations are available from November 1993 through December 2002 for samples collected from the Beard Research Center in Everglades National Park as part of the Florida Atmospheric Mercury Study (FAMS, 1993-1996) and the Mercury Deposition Network (MDN, 1996-2002; [http://nadp.sws.uiuc.edu/mdn](http://nadp.sws.uiuc.edu/mdn)). The FAMS data consist of integrated monthly wet deposition measurements (Guentzel et al., 2002), while the MDN data consist of integrated weekly samples. During 1996, monitoring from both studies overlapped for the entire year, and comparison of monthly results demonstrated excellent agreement between the two programs (Pollman and Porcella, 2002). As a result, we combined the two studies to form a period of record of eight full years.

Smoothed time series were constructed for Mercury deposition, rainfall depth, and volume weighted mean (VWM) Mercury concentrations in wet deposition using 12-month running averages derived from the integrated FAMS-MDN data set (Figure 21 and Figure 22). As illustrated in Figure 21, rainfall depth and deposition flux are very closely
related\textsuperscript{11}, and it is difficult to discern without further analysis whether any declines in wet deposition fluxes have occurred unrelated to changes in precipitation. Changes in VWM Mercury concentrations are a less ambiguous indicator of whether changes in the atmospheric mercury signal have occurred, although precipitation depth does exert some influence on wet deposition concentrations through washout, particularly when the sample integration period is short. Plotting the running average annual VWM as a function of time indicates that VWM Mercury concentrations have declined by 25\% since late 1993 (Figure 21).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dep_vpm.png}
\caption{Annual precipitation depth and wet deposition fluxes of mercury measured at Beard Research Station in Everglades National Park, 1993 – 2002. Data are plotted on a monthly basis as the 12-month running total flux or depth. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network.}
\end{figure}

An alternative analytical approach using analysis of variance (ANOVA; SAS, 1995) was used to eliminate possible confounding effects of both rainfall depth and seasonal dynamics on wet deposition concentrations. Guentzel et al. (2002) demonstrated that very strong seasonal dynamics consistently underlie wet deposition mercury concentrations in Florida within any given year; as a result, a seasonal dummy variable(D\textsubscript{month}) based on a sinusoidal transformation on the month of year the sample was collected was created and input to the model. The dummy variable had the following form:

\begin{itemize}
\item \textsuperscript{11} This is, of course, because deposition fluxes are the product of the weekly volume-weighted mean concentration and the rainfall depth.
\end{itemize}
Recent Mercury Trends in Florida

Figure 22. Annual volume weighted mean (VWM) Mercury concentration in wet deposition at Beard Research Station in Everglades National Park. Plotted on a monthly basis is the 12-month running average VWM concentration. Data are from the FAMS study (Guentzel et al., 2002) and the MDN network.

\[ D_{\text{month}} = A \cdot \sin\left(\frac{M^* \cdot \pi}{12}\right) + B \]

where \( A \) and \( B \) are fitted using non linear least squares regression (SAS, 1995) and are equal to 8.8827 and 6.6954, respectively, and \( M^* \) is the number of the month (\textit{v}iz., 1 through 12), adjusted using a one month offset so that predicted and observed peak values occurred during the same month. Residuals from the ANOVA model for VWM Mercury plotted as a function of time are shown in Figure 23 and demonstrate that a statistically significant decline (\( p = 0.0413 \)) in VWM Mercury concentrations occurred over the period of record. Between 1994 and 2002, the analysis indicates that VWM Mercury concentrations declined by approximately 3 ng/L due to factors other than seasonal dynamics and precipitation.
Figure 23. Plot of monthly residuals of ANOVA model of Mercury deposition as a function of time. Slope of regression line is significant at $p = 0.0413$.

The declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions estimated to have occurred since the late 1980’s and early 1990’s (Figure 19 and Figure 20). However, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993 (Figure 24).
7.3 Trends in Mercury Concentrations in Biota

Two data sets are available to examine recent trends in mercury concentrations in biota in the Everglades: (1) the unpublished data of Lange et al. (T. Lange, pers. comm.), who have collected and analyzed largemouth bass for tissue concentrations of Mercury from sites throughout Florida; and (2) the data of Frederick et al. (2001), who examined Mercury concentrations in the feathers of great egret chicks, also throughout Florida and including seven sites in south Florida. Pollman et al. (2002) analyzed the significance of biota temporal trends using the Mann-Kendall Slope Test-of-Sign. This method is a non-parametric test for zero slope that calculates the slope for each possible pairwise combination of observations in the data set, and then ascribes a value of 1, 0, or −1 to the result based on the whether the slope is positive, zero, or negative.

Largemouth bass mercury concentrations for 12 sites across Florida (including 9 sites in the Everglades) were analyzed for trend significance. The period of record analyzed extended from as early as 1988 to as late as 2000. The data were stratified according to age class since different age classes in any given year reflect different exposure histories. Of a possible 120 categories (i.e., 10 age classes x 12 sites), 66 had sufficient data to test for sign significance (Table 12). The results were split relatively evenly between a
Recent Mercury Trends in Florida

significant decline at the 95% confidence level (29 site-cohort combinations) and no trend (34 site-cohort combinations). Significant declines were observed across the state, suggesting a regional effect (e.g., atmospheric deposition), with the most consistent declines across cohorts observed for the two Everglades canal sites, L-67A and L-35B (and East Lake Tohopekaliga). The three sites in WCA-3A near site 3A-15 (located near the so-called “hot spot” of high fish tissue mercury concentrations in WCA-3A) also showed some cohorts with significant declines, although nearly as many site-cohort combinations also showed no change. Only three site-cohort combinations showed a significant increasing trend, and these all were observed at the U3 site in WCA-2A. This increase likely reflects a highly localized effect both in time and space, such as peat burning and oxidation that occurred in the Everglades following the intense drought and drydown in May and June 1999 (Pollman et al., 2002). This period of peat oxidation induced a series of short-term but substantial changes in Mercury biogeochemistry, including large scale increases in mosquitofish Mercury concentrations at site U3, while the response at 3A-15, which remained wet during this period, was more muted (Krabbenhoft and Fink, 2001).

Table 12. Summary of Mann-Kendall Slope Test-of-Sign for trends in mercury concentrations in largemouth bass. Test results are given for individual sites and age cohorts. (-) indicates significant declining trend; (0) indicates no significant trend; and (+) indicates significant increasing trend. Site-cohort combinations with insufficient data are left blank. All results reported at the 95% significance level.

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Figure 25. Tissue concentrations of mercury (wet weight) in largemouth bass in the L-67A and L-35B canals in the Florida Everglades. Filled circles show the geometric mean for each year; filled triangles show ± one standard error of the mean.
Great egret chick feather data from all seven sites studied by Frederick et al. (2001) were tested for trend significance. When Pollman et al. (2002) conducted their trend significance analysis, the time frame spanned by the great egret study extended from 1994 to 2001. Additional data have since been collected, and the full period of record now extends to 2003 (Figure 27). Four sites (Alley, Hidden, JW1, and L67) showed significant downward trends through 2001 based on both the Mann-Kendall test and Sen’s median slope analysis. The data from 2002 and 2003 further substantiate the overall robustness of the downward trend. Consistent with the largemouth bass results from the same region, results from great egret colonies located in the mid-Everglades indicate over an 80% decrease in Mercury concentrations over the period of 1994-2003.
Figure 27. Mercury concentrations in great egret nestlings at various colony locations in the Florida Everglades, 1994 – 2003. Discontinuities in the period of record reflect years when a colony site was abandoned or otherwise not used. Unpublished data courtesy of P. Frederick (2003).

7.4 Model Hindcasting

The E-MCM was used to predict changes in age 3 largemouth bass mercury concentrations in response to assumed changes in atmospheric loadings of mercury to site 3A-15. A simplified trajectory of changing deposition rates from 1900 through 2000 was developed with several assumptions or constraints imposed:

1. Based on Mercury accumulation rates measured in soil cores in WCA-2A (Rood et al., 1995), an increase in modern deposition rates of 7.4-fold (1985 to 1991) over “pre-industrial” (ca. 1900) was assumed. Rood et al. measured an average accumulation rate of 8 µg/m²-yr for ca. 1900 compared to 59 µg/m²-yr for 1985-1991.

2. We assume that, superimposed upon the long-term background deposition of 8 µg/m²-yr inferred from Rood et al., there has been a deposition signal derived from anthropogenic sources (local and larger geographic scale) that tracks the 1970-2000 Mercury trend in the municipal solid waste (MSW) inventory compiled by Kearney and Franklin Associates (1991). This inventory shows that Mercury in MSW peaked between 1985 and 1990, with a comparatively sharp decline through 1995, followed by relatively stable inventory quantities. As a first order analysis, we also assumed that anthropogenic emissions and associated deposition fluxes increased linearly from 1900 through 1985.
3. After emissions and deposition reached peak levels in 1985, we assumed that deposition declined linearly until 1996, with total mercury deposition reduced to 35 µg/m²-yr. Following 1996, we assume that anthropogenic emissions remained constant (although there is evidence of continuing emissions declines). Figure 28 shows the mercury deposition trajectory that resulted from these assumptions.

![Figure 28. Total (wet + dry deposition) mercury deposition trajectory used in E-MCM model hindcast.](image)

The mercury deposition trajectory was then used as the input forcing function to reconstruct a predicted time series of biotic (largemouth bass) response in south Florida using the E-MCM model. E-MCM had previously been calibrated for a site (site 3A-15) in the Florida Everglades regarded as a “hot spot” for high fish Mercury concentrations (Appendix 2). E-MCM was initially run at pre-1900 deposition conditions until steady-state was achieved in all the model compartments (water, sediments, biota). The model then was perturbed by imposing the reconstructed deposition time series, and the predicted biota response compared to the observed trends for ca. 1990-2000. Results are shown in Figure 29. The hindcast simulation predicts a monotonic decline in largemouth bass concentrations on the order of 20% beginning ca. 1989 and continuing through 2000. Although the timing of the response is generally consistent with the observed biota, the magnitude is only about 1/3 the observed decline of ca. 60% (average of all data for south Florida).
Mesocosm experiments currently underway in the Everglades indicate that mercury methylation rates and transfer to the aquatic food chain respond very rapidly in response to new inputs of Hg(II) (D. Krabbenhoft, pers. comm.). These experiments are being conducted using isotopic tracers to elucidate the magnitude and timing of changes in mercury cycling to changes in mercury inputs. Similar results are emerging from the Mercury Experiment To Assess Atmospheric Loading in Canada and the United States (METAALICUS; R. Harris, pers. comm.), which also is using isotopic tracers. E-MCM predicts that the primary pathway for introducing Mercury into the food chain at site 3A-15 is via methylation in the sediments and the benthic food web. Thus, the magnitude of the predicted response is governed by the residence time of bioavailable Mercury in the sediments, which in turn is governed largely by the mixed depth of actively exchanging surficial sediments. The current assumption is 3 cm and, in light of the recent isotopic tracer experimental results, may prove to be a large overestimate of the size and residence time of the Hg(II) pool available for methylation.
To test the effect the assumed size of the pool of bioavailable Mercury in the sediments exerts on the timing and magnitude of biotic response, we ran an additional simulation where the sediment exchange depth was reduced by an order of magnitude to 0.3 cm. The resultant hindcast agrees extremely well with the observed trends in largemouth mercury concentrations, both with respect to timing and the magnitude of change.

Figure 30. Same as Figure 29, except that the depth of surficial sediments actively exchanging Hg(II) is 0.3 cm.

7.5 Discussion and Conclusions

Local atmospheric emission rates of mercury in south Florida appear to have declined by over 90% since peak levels occurring in the late 1980’s to early 1990’s. This estimate is supported by two completely different approaches towards estimating emissions. Whether these changes in emissions have had a corresponding effect on local deposition rates of mercury in part is a function of the chemical speciation of the emissions. There are two major types of gas phase Mercury species present in emissions from combustion sources: elemental Mercury or Hg(0), and reactive gaseous mercury (RGM) or Hg(II). Speciation of emissions is critical because it influences greatly how far emitted Mercury likely will be transported. Hg(0) reacts in and is deposited from the atmosphere only very slowly, and has a characteristic residence time in the troposphere on the order of 1 year. RGM, on the other hand, is highly reactive, and is scavenged rapidly from the lower troposphere by either wet deposition or by adsorption to settling particles and surfaces. If, for example, there had been a decline in Hg(0) emissions from south Florida, but RGM emissions remained constant, we would expect little or no change in
Recent Mercury Trends in Florida

biota mercury concentrations in the Everglades as a result. On the other hand, if local RGM emissions have declined, but Hg(0) emissions have remained constant, one would expect to see more of a biotic response. By not considering speciation, we risk misinterpreting the true significance of the relationship between local emissions and biotic response. This would be particularly true if Hg(0) emissions greatly predominate. Unfortunately only limited data are available on the speciation of Mercury emissions as a function of source, including speciation measurements conducted by Dvonch et al. (1999) from a municipal waste incinerator (8 measurements), a medical waste incinerator (3 measurements) and a cement kiln (3 measurements) in Dade and Broward counties. The fraction of Hg(II) emitted ranged from 25% of the total (cement kiln) to nearly 95% for the medical waste incinerator. The fraction of Hg(II) emitted by the municipal waste incinerator averaged ca. 75%. Since the local emissions inventory for Dade and Broward counties in 1995-96 was dominated by municipal waste and medical waste incineration (ca. 86% of total emissions), it appears likely that Hg(II) emissions were predominant, at least for 1995-96. If these speciation results are similar for historical emission patterns (and there is no reason to expect that Hg(0) emissions were more important), then our approach of examining total emissions and linking the trends to local biota response appears reasonable.

Coupled with changes in local emission rates is evidence that mercury concentrations in wet deposition (annual VWM) in south Florida have declined by about 25% since late 1993. Statistical analysis indicates that the trends are significant, and are due to factors other than seasonal dynamics and changes in precipitation rates. Although the declines in measured VWM concentrations are considerably smaller than the overall decline in local emissions, most of the decline in emissions occurred prior to late 1993 when monitoring of mercury concentrations in wet deposition first began. Indeed, the relatively modest change in VWM concentrations agrees reasonably well with the emissions declines after 1993.

Statistically significant declines in mercury concentrations in both largemouth bass and great egret chicks have been observed for a number of sites in the Everglades. Declines over approximately the past decade for both species are on the order of 80%. Model hindcasting using the E-MCM model calibrated for site 3A-15 indicates that changes in atmospheric deposition inferred from sediment core analyses may account for the recent changes in largemouth bass mercury concentrations, both in terms of timing and magnitude of change. For this to be true, however, requires modifying the current model paradigm with respect to the size of the pool of Hg(II) that is readily bioavailable in surficial sediments for methylation (viz., reducing the size and residence time of the Hg(II) pool). Such a paradigm shift is consistent with recent isotopic tracers experiments indicating that mercury cycling in aquatic systems responds very rapidly to recent inputs.

Further research, analyses and model application will explore the present uncertainties in the model with the aim of better constraining this key parameter. Additional improvements will be pursued to refine the E-MCM to improve it as a tool to support TMDL analyses throughout Florida.
8 REFERENCES


Appendix I

Modeled Deposition of Speciated Mercury to the SFWMD Water Conservation Area 3A:
22 June 1995 to 21 June 1996

Project Description and Results

Submitted by:
Gerald J. Keeler, Principal Investigator
Frank J. Marsik, CO- Investigator
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1. INTRODUCTION

The University of Michigan Air Quality Laboratory (UMAQL) has participated in a number of studies aimed at gaining a better understanding of the potential causes of elevated mercury levels observed in fish and other wildlife within the Florida Everglades. These UMAQL studies have included the measurement of ambient gaseous and particulate forms of mercury, as well as the wet- and dry-depositional fluxes of total mercury. One such study included event-based precipitation sample collection at Davie, Florida from 22 June 1995 to 21 June 1996 to investigate the daily variability and seasonality in the mercury wet-deposition at this site in South Florida (Dvonch 1998).

![Figure 1. Temporal variation in event wet-deposition of total mercury at Davie, Florida for the period 22 June 1995 to 21 June 1996.](image)
The total mercury wet-deposition to the site for the year was 30.1 µg/m². Statistical analysis of the one-year event precipitation database indicated that differences in observed rainfall depth accounted for only 14 percent of the variability in the observed event mercury concentration at the Davie site (Dvonch, 1998). On an annual basis, a distinct seasonal pattern in total mercury wet-deposition was observed (Figure 1), with elevated levels being associated with the climatological “wet season” in South Florida (Spring/Summer). During this Spring/Summer period, approximately 80 percent of the annual total mercury wet-deposition at the site was reported.

The UMAQL was subsequently funded by the State of Florida and the US Environmental Protection Agency to determine the feasibility of extending the use of the Davie event-precipitation database to provide a preliminary estimate of the total mercury wet-deposition to all of South Florida (henceforth referred to as the EPA Aggregation Study). Application of a comprehensive meteorological-chemical process model that could be run for each day of the one-year study period to obtain the annual deposition estimate was not a viable option. The spatial and temporal resolution required to adequately model the complex meteorological conditions observed in South Florida dictated that an alternative modeling approach be used to estimate the total mercury wet-deposition to South Florida.

Past studies investigating acid deposition in the United States noted that considerable variability in observed precipitation chemistry (up to 40 percent) could be attributed to differences in the atmospheric transport regimes impacting a given site. Experience gained through these studies allowed the UMAQL to develop a hybrid modeling approach which first determined the dominant atmospheric transport regimes
impacting our Davie site. A high-resolution mesoscale meteorological model was then coupled to a Lagrangian transport/dispersion model to obtain estimates of the wet-deposition of total mercury to South Florida for the obtained atmospheric transport regimes. Finally, the deposition estimates for each transport regime were calculated according the their annual frequency of occurrence to obtain an annual estimate of the total mercury to South Florida. The final results of the project are being prepared for submission to the Journal of Applied Meteorology (In Preparation).

Following the completion of our hybrid-modeling effort in South Florida, it was evident that a more complete and comprehensive Hg model was needed. The UMAQL entered into a Cooperative Research Agreement with the State of Florida and the US Environmental Protection Agency to develop a full-scale meteorological-chemical process model that will combine: (1) a high resolution meteorological processes model capable of adequately describing relevant pollutant transport and cloud/precipitation-scavenging processes and (2) a chemical model incorporating the most up-to-date mercury chemistry and gas-particle interactions. This first phase I of the CMAQ model development will be completed in Calendar Year 2001. It has been apparent to all that the CMAQ Hg Model would provide a more comprehensive treatment of the important meteorological and chemical processes that strongly influence the deposition and cycling of Hg to S. Florida. However, this was not feasible for the Pilot TMDL study.

The Florida Hg Pilot Total Maximum Daily Load (TMDL) Study was initiated to help the agencies determine the feasibility of performing TMDL analyses and to identify scientific methods and modeling gaps that may add to the uncertainty in the final analysis. The UMAQL Tasks for the Florida Pilot TMDL Study focused on providing
Tetra Tech, Inc. with estimates of the monthly and annual wet- and dry-deposition of speciated mercury \([\text{Hg}(0), \text{Hg}(\text{II}) \text{ and } \text{Hg}(p)]\) to the South Florida Water Management District’s Water Conservation Area 3 (SFWMD WCA3) for the same one-year period modeled for the EPA Aggregation Study (22 June 1995 to 21 June 1996). These atmospheric deposition estimates were to be used as input into Tetra Tech’s Everglades Mercury Cycling Model (E-MCM). Since the CMAQ Hg Model being developed by the UMAQL was not available for this TMDL Pilot Study, a simpler hybrid modeling approach employed for the EPA Aggregation Study was employed. This approach aimed to capture the most critical meteorological features observed in S. Florida using a comprehensive mesoscale meteorological model (RAMS) to drive the transport and deposition model (HYSPLIT) together with a proven aggregation technique to arrive at annual wet and dry deposition loadings to WCA3.

The Davie Monitoring site (assumed to be representative of Southeastern Florida) was impacted by eight different atmospheric transport regimes (or clusters) during the period studied, each representing a particular synoptic meteorological flow regime. Representative days from each transport regimes (or clusters) were modeled and average deposition patterns and estimates were obtained for each cluster. The annual estimates were calculated by weighting cluster average deposition amounts by the frequency of occurrence of each cluster, resulting in annual total mercury wet- and dry-deposition fluxes to the SFWMD WCA3.

The TMDL atmospheric transport and deposition modeling was performed using the 1996 Hg emissions inventory developed for the USEPA Mercury Study Report to Congress (US EPA, 1997). Details of the methodologies used in developing that Hg
emissions database can be found in the USEPA Report and are not repeated here. The EPA database was the best available information at the time and does not include recent findings that the Hg(II) compounds dominate incinerator emissions or that motor vehicles (an area source) may be an important source category for Hg emissions. Never-the-less, using the USEPA emissions and finely resolved meteorology resulted in a total mercury wet-deposition to SFWMD WCA3 estimated at $18.74 \pm 6.15 \mu g/m^2/\text{year}$, with the annual speciated wet-deposition estimated to be $0.01 \pm 0.00 \mu g/m^2/\text{year}$ for Hg(0), $14.40 \pm 4.51 \mu g/m^2/\text{year}$ for Hg(II) and $4.33 \pm 1.65 \mu g/m^2/\text{year}$ for Hg(p). The greatest monthly total mercury wet-deposition was estimated for the month of July 1995, $3.98 \pm 0.61 \mu g/m^2$.

Dry-deposition modeling results suggested an annual total mercury dry-deposition of $12.20 \pm 7.4 \mu g/m^2/\text{year}$, with the annual speciated dry-deposition estimated to be $0.06 \mu g/m^2$ for Hg(0), $11.20 \pm 6.80 \mu g/m^2$ for Hg(II) and $0.94 \pm 0.53 \mu g/m^2$ for Hg(p). The greatest monthly total mercury dry-deposition was estimated for the month of September 1995, $1.29 \pm 0.72 \mu g/m^2$. Seasonal trends were noted for both total mercury wet- and dry-deposition.

### 2. METHODOLOGY AND MODEL DESCRIPTION

The UAQL employed a hybrid modeling approach to obtain estimates of the monthly and annual wet- and dry-deposition of speciated mercury [Hg(0), Hg(II) and Hg(p)] to the South Florida Water Management District’s Water Conservation Area 3 (SFWMD WCA3). The specific steps employed in this hybrid approach are as follows:

1. Compute daily back-trajectories (for parcels arriving in Davie, FL) for each day of a one-year study period (22 June 1995 to 21 June 1996) during which precipitation was collected on an event (i.e., daily) basis at the University of Florida Agricultural Station in Davie, FL.
(2) Identify meteorological clusters, or groups, of back-trajectories that represent the dominant atmospheric transport regimes that impacted South Florida during the one-year study period.

(3) Select a number of representative days from each cluster and use a mesoscale meteorological model to obtain three-dimensional meteorological fields (U and V wind components, vertical velocity, temperature, specific humidity and pressure) and two-dimensional meteorological fields (terrain height, mean sea-level pressure, total precipitation, pressure, temperature, and micrometeorological parameters, which include ustar, tstar and qstar) for the selected representative days.

(4) Using the three-dimensional and two-dimensional meteorological fields computed in part (3) as input fields, use a Lagrangian air-pollution dispersion/deposition model to estimate average wet- and dry-deposition patterns/amounts for each of these representative days, computing a cluster average deposition for each of the clusters.

(5) Weight the average daily wet- and dry-deposition estimates for each cluster by the number of days assigned to each cluster, and thus obtain an estimate of the speciated monthly and annual wet- and dry-depositional loading of mercury to the SFWMD WCA3.

The tools used to perform the above tasks are outlined below:

**Determination of 72-hour back-trajectories**

Daily back-trajectories were computed using the HYbrid Single Particle Lagrangian Integrated Trajectories Model Version 4 (HYSPLIT_4) (Draxler and Hess, 1997). HYSPLIT_4 is a complete modeling system that can be used for a range of meteorological/air quality applications ranging from the calculations of simple forward- and/or backward-trajectories to the performance of complex dispersion/deposition simulations. The initial version of the model (Draxler and Taylor, 1982) used rawinsonde observations as the meteorological input data and the dispersion calculations performed with the model assumed uniform mixing during the daytime and no mixing during the nighttime. In time, the model was updated to include the use of gridded meteorological data from either analyses or short-term forecasts as input data, and was
updated to include the use of a temporally and spatially varying diffusivity profile for use in the dispersion and deposition calculations.

For this study, the input data used for the calculation of the daily back-trajectories consisted of analysis and short-term forecasted meteorological fields from the National Center for Environmental Prediction’s (NCEP) Nested Grid Model (NGM). The data was obtained from a standard data archive maintained by the National Oceanic and Atmospheric Administration’s Air Resources Laboratory (NOAA-ARL). NOAA-ARL routinely archives this NGM data in a format that can be read by HYSPLIT_4. The standard NGM model domain encompasses the contiguous United States and Canada with a latitudinal and longitudinal grid spacing of approximately 90 km. Due to storage space considerations, the NOAA-ARL’s archived NGM data set contains information from only every other grid point in the domain and thus has a reduced resolution of approximately 180 km by 180 km. There are ten vertical levels in the model, stretching from the surface to 300 mb. At each gridpoint, data is available for the following variables: the U and V wind components, vertical velocity, temperature, specific humidity, and pressure. The following variables are available at the surface: terrain height, mean sea-level pressure, convective precipitation, total precipitation, exchange coefficient at the surface, upward turbulent flux of sensible heat, upward turbulent flux of latent heat and surface pressure. The data from the NOAA-ARL archive is available in two-hour intervals.

Previous research has reported that the atmospheric deposition of mercury to South Florida is dominated by wet-deposition, with the majority of this deposition associated with summertime convective precipitation events (Guentzel et al. 1995;
Given that these latter precipitation events typically occur during the mid- to late-afternoon hours, it was assumed that the air masses that deliver pollutants to these convective storms would moving into South Florida during the middle to late afternoon. Thus, back-trajectories were calculated using an arrival time in South Florida of 2000 GMT.

**Clustering of atmospheric transport back-trajectories**

A number of previous studies have been conducted that employ objective analyses of meteorological flow regimes. Moody and Samson (1989) used a statistical technique to perform a cluster analysis of two-dimensional mixed layer back-trajectories in an effort to determine what fraction of chemical variability in acidic precipitation composition could be related to differences in atmospheric transport. Their results suggested that from 10 to 40 percent of the precipitation chemistry variability could be accounted for by differences in atmospheric transport regimes. Similar objective statistical techniques linking atmospheric transport regimes with precipitation chemistry variability have been employed by Fernau and Samson (1990), Dorling et al. (1992 a, b), Dorling and Davies (1995) and Brook et al. (1995).

In short, cluster analysis is an objective mathematical technique whereby large datasets can be divided into similar groups or clusters, hopefully reflecting some underlying structure that is within the dataset. The goal is to have within-cluster members differ from each other as little as possible, while having each cluster as distinct from the other clusters as is possible. For this analysis, the goal was to identify distinct meteorological flow regimes which would likely lead to distinct wet- and dry-deposition patterns. By weighting each cluster by its annual frequency of occurrence, an estimate of
monthly and annual deposition could be obtained without the time-consuming and resource intensive task of modeling every day of the year-long period studied.

Following the calculation of the daily 72-hour back-trajectories, resulting data was analyzed using the SAS statistical analysis package (SAS Institute, Cary, NC). The SAS CLUSTER procedure was used to hierarchically cluster the observations using the Ward’s Minimum Variance Method. This method is based upon the concept that the greatest amount of information is available when a set of \( n \) members is ungrouped. Therefore, the grouping starts with \( n \) member acting as \( n \) separate groups. The initial step is to select two of these \( n \) separate groups which when united, will reduce the number of groups to \( n-1 \), while resulting in the least amount of lost information. If desired, the process may be continued until only one group, with \( n \) members, remains. Specific details on the method can be found in Ward (1963).

In its implementation of Ward’s minimum variance method, the SAS CLUSTER procedure determines the distance between two clusters as the ANOVA sum of squares between the two clusters added up over all of the variables. In this study, the variables are the observed precipitation amount and trajectory end points, the latter of which correspond to air parcel locations at \( T_0 \) (trajectory arrival time, 2000Z), \( T_0-1 \) hour, \( T_0-2 \) hours, etc. With each new generation (or iteration) of the analysis program, a squared multiple correlation coefficient, \( R^2 \), is calculated. In this case, \( R^2 \) represents that portion of the variance accounted for by the current number of clusters. By monitoring the decrease in \( R^2 \) following iterations of the program, one can determine the degree of information loss that is acceptable, beyond which further clustering of the data does not provide useful information. During our analysis, a considerable degradation in the
amount of variance explained by the remaining clusters became evident for generations in
which the data set was grouped into fewer than eight clusters ($R^2 < 0.80$). For this
reason, we felt that the use of eight clusters would reduce the data set to a manageable yet
representative number of atmospheric transport regimes that could be modeled, without
sacrificing a large amount of statistical information. Eder et al. (1994), among others,
have suggested the use of Average Linkage Techniques in the objective clustering of
meteorological data. Both the Ward’s Minimum Variance Method and the Average
Linkage Technique were tested for this study, with the Ward’s Minimum Variance
Method doing a superior job of producing clusters that could be attributed to distinct,
meteorological atmospheric flow regimes. For this reason, the output from the Ward’s
Minimum Variance Method was used.

Clustering of back-trajectories typically includes hourly the endpoints for the
entire 72-hour history of the air parcel back-trajectories. However, due to the proximity
of South Florida to the southern boundary of the NGM domain the back-trajectories for a
number of days originated from locations out of the NGM model domain. As a result, the
full 72-hour length of these back-trajectories could not be computed. The SAS
CLUSTER procedure removes back-trajectories with missing data points prior to
clustering, resulting in a large number of days being eliminated from the analysis. After
reviewing the back-trajectory database in conjunction with detailed meteorological
analysis of each day, it was determined that 12 hours of back-trajectory information
would allow us to adequately characterize the atmospheric flow regime impacting South
Florida on a given day while maximizing the number of clusters included in the objective
clustering routine. The use of only 12 hours of back-trajectory data still resulted in
approximately 60 days being removed from the clustering analysis due to missing data points. Days not objectively grouped due to missing data were placed into the obtained clusters after detailed analysis of the Daily Weather Maps from the National Oceanic and Atmospheric Administration (NOAA).

An analysis of the potential bias resulting from using 12-hour trajectories vs 48 or 72-hour trajectories was conducted for days where complete 72-hour back trajectories were available. For the analysis in S. Florida it was determined that using the 12-hour trajectories did not significantly influence the objective clustering procedure and hence, did not significantly impact the meteorological frequencies calculated or the final modeling results. It should be emphasized that the 12-hour trajectories were not used in the transport and deposition modeling from which the loadings calculations were derived. This is because the RAMS high temporal and spatial resolution meteorological inputs were used to drive the HYSPLIT transport and deposition model, and not the trajectories.

Mesoscale modeling of representative cluster days

Detailed modeling of the three-dimensional meteorological fields across S. Florida was performed for input to the HYSPLIT dispersion and deposition calculations. Two representative days from each of the objectively obtained clusters where chosen for modeling. The days were chosen such that they represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster. This approach was used to minimize potential biases that could be introduced by choosing two days with nearly identical deposition patterns. The days chosen for modeling are presented in Table 1. It should be noted that the sensitivity of the final deposition estimates to the days chosen from each cluster was investigated. The HYSPLIT Model was run using the
NGM Model output as input to the transport and deposition model for each day of the study period from June 1995 – July 1996. The wet and dry deposition calculated for S. Florida was output to a file which allowed us to select two days from each cluster and to use the deposition estimates for these days instead of the estimates that were derived using the RAMS derived meteorology. The result of this exercise provided the degree of uncertainty in the estimates obtained using the 2 extreme days chosen. Using the daily deposition estimates and selecting the most representative two-days from each cluster only changed the annual deposition estimates by 8%.

**TABLE 1**

<table>
<thead>
<tr>
<th>Cluster Number</th>
<th>Wet Days</th>
<th>Dry Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29 MAY 1996</td>
<td>22 FEB 1996</td>
</tr>
<tr>
<td></td>
<td>09 SEP 1995</td>
<td>27 JUN 1995</td>
</tr>
<tr>
<td>2</td>
<td>13 MAY 1996</td>
<td>20 SEP 1995</td>
</tr>
<tr>
<td></td>
<td>16 AUG 1995</td>
<td>06 JUN 1996</td>
</tr>
<tr>
<td>3</td>
<td>11 SEP 1995</td>
<td>17 DEC 1995</td>
</tr>
<tr>
<td></td>
<td>13 JUN 1996</td>
<td>30 MAR 1996</td>
</tr>
<tr>
<td>4</td>
<td>11 MAR 1996</td>
<td>23 OCT 1995</td>
</tr>
<tr>
<td></td>
<td>29 SEP 1995</td>
<td>07 FEB 1996</td>
</tr>
<tr>
<td>5</td>
<td>19 MAR 1996</td>
<td>17 FEB 1996</td>
</tr>
<tr>
<td></td>
<td>09 APR 1996</td>
<td>21 MAR 1996</td>
</tr>
<tr>
<td>6</td>
<td>23 JUN 1996</td>
<td>13 APR 1996</td>
</tr>
<tr>
<td></td>
<td>27 MAY 1996</td>
<td>07 MAR 1996</td>
</tr>
<tr>
<td>7</td>
<td>02 MAR 1996</td>
<td>12 JAN 1996</td>
</tr>
<tr>
<td></td>
<td>15 OCT 1995</td>
<td>22 MAY 1996</td>
</tr>
<tr>
<td>8</td>
<td>Not Modeled</td>
<td>03 MAR 1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23 DEC 1995</td>
</tr>
</tbody>
</table>

Due to the geographical characteristics of South Florida, the transport, dispersion and deposition (both wet and dry) of pollutants across this region are controlled by circulation patterns that range from the meso- to synoptic-meteorological scales. For this
reason, the modeling performed for this project required the use of a mesoscale meteorological model to accurately describe the three-dimensional meteorological fields across South Florida during the study period. The Regional Atmospheric Modeling System (RAMS) (Pielke et al. 1983) was selected for use in our study, given its previous successful use in investigations involving lake-/sea-breeze circulations for a number of coastal areas across the United States. As an example, Eastman and Pielke (1995) used RAMS to study lake breeze circulations by comparing RAMS model output with tracer data. Lyons et al. (1995a) used RAMS to provide input to a photochemical model for the Lake Michigan Ozone Study (LMOS). Lyons et al. (1995b) also used RAMS to investigate wind flow/sea breeze regimes across Florida.

The present study took advantage of the nested grid-structure capability that is available in RAMS. The first grid shown in Figure 2 encompassed the eastern United States, with a mesh size of c. The second grid (nested within Grid One) encompassed the southeastern U.S. with a mesh size of 20 km using a 62 x 62 horizontal grid points is shown in Figure 3. Figure 3 also displays the third grid (nested within Grids One and Two) encompassed South Florida, with a mesh size of 5 km using a 50 x 50 horizontal grid points. All three grids used 34 levels in the vertical with a vertical grid spacing of 50 m near the surface, with vertical grid spacing stretching to 850 m near the model top at approximately 15 km.

The RAMS model was initialized with meteorological fields derived once again from the NCEP’s NGM. Given that the mesoscale convective features that play an important role in mercury wet-deposition in South Florida can extend beyond the 300mb,
Figure 2. RAMS Grid #1 used 60 km mesh and 50 x 50 horizontal grid points.

Figure 3. RAMS Grid #2 (left) with 62 x 62 grids with a 20 km mesh and nested Grid#3 (right) used 50 x 50 horizontal grid points and a 5 km mesh.
the NGM data fields archived by the NOAA-ARL could not be used, since this data does not extend beyond the 300mb vertical level. As a result, NGM data fields archived by the University of Michigan were used to initialize the RAMS model. The data fields archived by the University of Michigan had a horizontal resolution of 250 km (E-W) by 125 km (N-S) with a vertical extension to 100 mb. Surface and rawinsonde observations within the modeling domain were blended to the NGM (first-guess fields) data to create input files for initialization, boundary conditions and FDDA (Four Dimensional Data Assimilation) for RAMS. Also, given the importance of land-ocean temperature differences in controlling the occurrence and magnitude of land/sea-breeze circulations, weekly average sea-surface temperature data was obtained from NCEP to be used as input fields for the RAMS simulations. This data is satellite derived and has a global 1° by 1° resolution.

Deposition estimates for each of the days listed in Table I were calculated using the 36-hour RAMS model simulations. Each simulation period represented essentially the day listed in Table I plus the previous 12-hour period. This was done to insure that the model had stabilized prior to the start of the 24-hour period for which wet- and dry-deposition estimates were desired. The first 12-hours of simulation was performed using only Grid One. During the remaining 24-hours of simulation, Grids Two and Three were included and hourly meteorological fields resulting from Grids Two and Three were saved for use as input for the wet- and dry-deposition calculations to be performed using HYSPLIT_4 (Draxler and Hess, 1997) during the next stage of the analysis.
Dispersion and deposition modeling

The dispersion and depositional modeling portion of this project used the HYSPLIT_4 Modeling System (Draxler and Hess, 1997). As noted earlier, HYSPLIT_4 is a complete modeling system that can be used for a range of meteorological/air quality applications ranging from the calculations of simple forward- and/or backward-trajectories to the performance of complex dispersion/deposition simulations. For this portion of our study, HYSPLIT_4 was executed using the medium resolution (20 km x 20 km) meteorological output fields from the RAMS simulations discussed in the previous section (Grid Two). The HYSPLIT_4 domain shown in Figure 4, and displays an example of a dry deposition field for a 24-hour simulation performed for the project.

![Figure 4. HYSPLIT_4 domain used deposition modeling for this project.](image-url)
The model allows the user to specify the number of emissions sources to be studied, the location of each source in the x, y and z directions, the emission rate and duration of emission. HYSPLIT_4 can treat both particles and gaseous pollutants for either continuous or puff releases, with the model simulations presented in this paper using the continuous release option.

The emissions database used for this work is the data used for the RELMAP (Bullock et al., 1997) mercury model simulations performed for, and discussed in, the United States Environmental Protection Agency (US EPA) Mercury Study Report to Congress (US EPA 1997). The US EPA mercury emissions database includes speciated information for both area- and point-source emissions, with a summary of the standard speciation profiles used for point-source emissions listed in TABLE 2. A complete listing of the point sources used in this study can be found in TABLE C1 of Appendix C. Also given in the Appendix C is Figure C1 showing the location of all of the regional point sources that were used in modeling deposition with Grid #2. The US EPA mercury emissions database considered area source emissions to be only in the elemental form, Hg(0), and accounted for only 2 percent of the total emissions. As a result, area sources were not considered in this work. The uncertainty in the magnitude, and form, of the mercury emitted from point sources in S. Florida was much greater than the impact of omitting the area sources in this modeling effort. Future evaluations should consider all sources and their differential impacts on the deposition to sensitive ecosystems.
TABLE 2
Mercury Emissions Inventory Used In Current Study

<table>
<thead>
<tr>
<th>Mercury Emission Source Type</th>
<th>Speciation Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg(0)</td>
</tr>
<tr>
<td>Municipal Waste Combustion</td>
<td>20</td>
</tr>
<tr>
<td>Medical Waste Incinerators</td>
<td>2</td>
</tr>
<tr>
<td>Electric Utility Boilers (coal, oil, gas)</td>
<td>50</td>
</tr>
<tr>
<td>Commercial and Industrial Boilers</td>
<td>50</td>
</tr>
<tr>
<td>Hazardous Waste Incinerators</td>
<td>As specified per location in EPA database</td>
</tr>
</tbody>
</table>

Once released, particulate and vapor phase pollutant transport, dispersion and deposition are explicitly calculated. HYSPLIT_4 has three different pollutant removal mechanisms: dry-deposition, wet-deposition and radioactive decay (not relevant to this work). For the simulations presented in this report, dry-deposition processes were addressed by explicitly defining both particle and vapor phase dry-deposition velocities. The deposition values used, for daytime and nighttime periods respectively, were set at 0.025 and 0.013 cm/s for Hg(0), 2.50 and 1.25 cm/s for Hg(II) and 0.45 and 0.23 cm/sec for Hg(p).

The daytime deposition velocities noted above were based upon those suggested by Shannon and Voldner (1995). However, the nighttime deposition values suggested by Shannon and Voldner (1995) were lower than those measured by the University of Michigan Air Quality Laboratory during the 1999 Florida Everglades Dry-Deposition Study (FEDDS). During the 1999 FEDDS, surrogate surface measurements of total mercury dry-deposition were made during the two-week study period, as were ambient measurements of particulate and vapor phase mercury. These datasets were used to obtain estimates of nighttime deposition velocities for Hg(II). These results suggested...
that the nighttime deposition velocities were approximately one-half of the daytime velocities. As a result, this study assumed that the nighttime deposition velocities for all species were one-half of their daytime values. For our modeling study, the daytime period corresponded to 0900 to 1600 LT.

Within HYSPLIT_4, the wet-deposition of particulate and gaseous species follows that of Hicks (1986) and is divided into two distinct processes: those in which the pollutants are continually ingested into a cloud from the polluted boundary layer (within cloud scavenging) and those in which rain falls through the polluted boundary layer (below cloud scavenging). Particle wet removal coefficients for both within- and below-cloud removal processes are typically explicitly set, using values suggest by Draxler and Hess (1997). Gaseous wet-removal of Hg(0) and Hg(II) is related to the solubility of each species using the relationship:

\[ V_{\text{gas}} = H R T P, \]

where \( H \) is the Henry’s Law Coefficient, \( R \) is the universal gas constant (0.082 atm M K), \( T \) is temperature, and \( P \) is the precipitation rate. For our simulations, the Henry’s Law constants used for Hg(0) and Hg(II) were 0.112 M atm\(^{-1}\) and 2.1 \( \times \) 10\(^5\) M atm\(^{-1}\), respectively.

During initial model simulations, we obtained unrealistically high values of mercury wet-deposition to the Davie site when compared with our observed event wet-deposition data set. Our investigation of this issue led us to the conclusion that the major reason for unrealistically high values of mercury wet-deposition at Davie was likely the simplified representation of the wet-removal process within HYSPLIT_4 (as described above). Pandis and Seinfeld (1990) emphasize the importance of considering the
interaction between equilibrium processes (vapor/water drops/particles) when modeling wet- and dry-depositional processes. Pandis and Seinfeld (1990) point out that the solubility of a species that dissociates (e.g., HNO₃, SO₂) varies as a function of pH. Presently, there is a great deal of uncertainty regarding the dissolution of reactive mercury (mostly likely in the form of HgCl₂), and how this process may vary as a function of the chemical content and/or pH of cloud/rain droplets.

Modeling of the complex vapor/water drops/particle interactions was beyond the scope of this Florida Pilot TMDL Study. As a result, in lieu of modifying the wet-removal parameterization within the HYSPLIT_4 model, we ran sensitivity analysis on the model by varying the removal coefficient by several orders of magnitude. Initially, an optimal value for the coefficient was determined by comparing the observed wet-deposition results from our Davie site with the modeled wet-deposition for this site. Interestingly, significant changes in the removal coefficient did not significantly change the average deposition to South Florida as a whole or to WCA3. The main impact of changing the removal coefficient was to lessen the wet-removal of mercury within the grid cells containing the major emissions point sources. The Davie site was located in one of the grid cells that contained had several major point sources. Since the variation in the Henry’s Law constant had little impact on the estimate of total Hg deposition to WCA3, the exact value of the coefficient was unimportant. The modeled wet deposition amounts provided to Tetra Tech Inc., and presented in this report, therefore, were derived from the use of the literature derived removal coefficients. However, the sensitivity analysis remains in this report to illustrate the need for better models with more detailed treatments of the wet and dry removal processes for mercury.
TABLE 3. Summary of “clustered” atmospheric transport regimes and precipitation statistics associated with each cluster based upon data collected at Davie, Florida during the 1995-96 SoFAMMS study period.

<table>
<thead>
<tr>
<th>Cluster Number</th>
<th>Description of flow regime represented</th>
<th>No. of Days within cluster</th>
<th>No. of Days with Rainfall (Davie, FL)</th>
<th>Total Rainfall for Cluster (cm) (Davie, FL)</th>
<th>Volume-Weighted Mean Hg Concentration for Cluster (ng/L) (Davie, FL)</th>
<th>Total Hg Wet-deposition Observed (µg/m²) (Davie, FL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weak local flow, variable in direction</td>
<td>65</td>
<td>18</td>
<td>12.1</td>
<td>31.8</td>
<td>3.84</td>
</tr>
<tr>
<td>2</td>
<td>Weak synoptic flow from north</td>
<td>35</td>
<td>5</td>
<td>2.7</td>
<td>29.2</td>
<td>0.79</td>
</tr>
<tr>
<td>3</td>
<td>Moderate local/synoptic flow from east</td>
<td>104</td>
<td>30</td>
<td>26.2</td>
<td>20.9</td>
<td>5.47</td>
</tr>
<tr>
<td>4</td>
<td>Strong synoptic flow from northeast.</td>
<td>48</td>
<td>8</td>
<td>22.1</td>
<td>10.8</td>
<td>2.39</td>
</tr>
<tr>
<td>5</td>
<td>Strong synoptic flow from northwest</td>
<td>32</td>
<td>9</td>
<td>6.9</td>
<td>10.6</td>
<td>0.73</td>
</tr>
<tr>
<td>6</td>
<td>Moderate synoptic flow from south</td>
<td>58</td>
<td>29</td>
<td>94.0</td>
<td>14.5</td>
<td>13.64</td>
</tr>
<tr>
<td>7</td>
<td>Moderate synoptic flow from southwest</td>
<td>11</td>
<td>4</td>
<td>8.7</td>
<td>12.8</td>
<td>1.12</td>
</tr>
<tr>
<td>8</td>
<td>Strong synoptic flow from north</td>
<td>13</td>
<td>1</td>
<td>0.1</td>
<td>7.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
3. CLUSTER ANALYSIS RESULTS

Eight distinct atmospheric transport clusters were obtained through the cluster analysis procedure. Given that the distributions of total mercury wet-deposition for each cluster exhibited departures from normality, and given the unbalanced nature of the clusters due to their small size in terms of the number of wet-deposition events per cluster, it was necessary to use a non-parametric test for statistical comparisons between clusters. Moody and Samson (1989) indicated that significant differences among transport groups could be reported when the null hypothesis of no difference in distributions could be rejected at the 95 percent confidence level using the Kruskal-Wallace test, a non-parametric one-way analysis of variance test. Using this test and the clusters obtained during our analysis, the null hypothesis of no differences in distributions was rejected at the 95 percent confidence level.

A summary of the eight atmospheric transport clusters obtained in this analysis is presented in Table 3. The general nature of these clustered back-trajectory groups is described below, with plots of each cluster found in Appendix A. Surface meteorological maps for days representative of each cluster can be found in Appendix B.

The first cluster identified by this analysis is presented in Figure A1 and can best be described as characterizing days with weak, local flow. An analysis of daily surface weather maps indicated that the flow regimes included in this cluster were generally associated with weak centers of high pressure centered over South Florida. The second cluster identified is presented in Figure A2. This cluster is again characterized by weak flow, but of a synoptic influence. Days included within Cluster 2 generally were influenced by both weak high and low-pressure systems over and near the Florida
peninsula. Stronger flow is evident for those days included as part of Cluster 3 (Figure A3). The days included in this cluster were characterized as having moderate flow from the east, typically associated with varying extents of influence from the semi-permanent Bermuda High. Initially, attempts were made to separate the easterly flow into those days with easterly synoptic flow and those days with mainly locally produced sea-breeze circulations. However, it was found to be very difficult to separate a purely “sea-breeze” day (when no significant synoptic forcing was present) from those days when the sea-breeze forcings were superimposed over weak easterly synoptic flow. As a result, no separation was performed for this analysis.

Cluster 4 (Figure A4) is characterized by strong synoptic flow, northeasterly in direction, which was generally associated with strong high-pressure centers over the East Coast of the United States. Days included in this cluster category often followed days that had experienced a cold frontal passage across South Florida. Strong synoptic flow was also a characteristic of those days included in Cluster 5 (Figure A5). These days were characterized as having strong northwesterly flow, generally associated with the advance of a strong Southern Plains high-pressure area following a cold frontal passage across South Florida. Clusters 6 and 7 (Figure A6 and A7, respectively) were also associated with flow patterns influenced by passing cold frontal boundaries. The days in Cluster 6 were characterized by southerly flow, typically in advance of cold frontal boundaries. Cluster 7 days were those that were influenced either by nearly stationary cold frontal boundaries, weak residual troughs or multiple frontal boundaries positioned across South Florida so as to result in southwesterly flow. Finally, Cluster 8 (Figure A8) was
characterized by moderate to strong synoptic flow from the north, generally associated with advancing areas of high-pressure in the Central and Southern Plains.

As seen in Table 3, the clusters with the highest observed volume-weighted mean Hg concentrations were Clusters 1-3, despite the fact that these clusters experienced some of the largest rainfall totals. However, these clusters were characterized by weak to moderate atmospheric transport patterns. These weaker flow regimes likely resulted in relatively low boundary-layer ventilation rates (the product of the horizontal wind speed and the boundary layer height) compared to the other cluster categories. Such conditions would be consistent with a relatively higher pollutant burden from local sources remaining in South Florida, resulting in a relatively higher concentration of pollutants (including Hg) in rainfall. The data presented in Table 3 also indicates that elevated volume-weighted mean Hg concentrations alone did not explain the observed total Hg wet-deposition at the Davie, FL site on a cluster-by-cluster basis. Despite having relatively low volume-weighted mean Hg concentrations, Clusters 4 and 6 reported relatively high total Hg wet-deposition fluxes, likely due to relatively high amounts of observed precipitation.

The climatological representativeness of the transport regimes obtained for the 1995-96 study period were investigated by comparing the atmospheric flow patterns across South Florida for the eight-year period from 1991-1999. A second cluster analysis was performed on an ensemble data set that contained trajectory data for the Davie site for each day for the period 1991-1999. Using this eight-year database, the number of days grouped in each meteorological cluster was determined. Atmospheric transport from these sectors would have the greatest likelihood of impacting WCA3. The results of this analysis are presented in Table 4. In brief, this analysis suggests that the atmospheric transport regimes
obtained for the one-year period studied, 1995-96, were representative of the recent climatological mean, and were indistinguishable when considering the year-to-year variability implicit in the 6-year means presented below. If anything the 1995-'96 period had a slightly lower frequency of transport from the local source region which would result in lower deposition estimates for the study period relative to the typical deposition in most of the 1990s, given that the emissions stayed constant during the last decade.

Table 4
Prevalence of Atmospheric Transport from the East through Southwest Sector

<table>
<thead>
<tr>
<th>Period</th>
<th>Frequency of Occurrence (As % of all days)</th>
<th>Frequency of Occurrence of Days with Rainfall (As % of all rain days)</th>
<th>Percentage of Annual Rainfall Accounted For By E – SW Sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995-1996</td>
<td>47 %</td>
<td>61 %</td>
<td>75 %</td>
</tr>
<tr>
<td>1991-1999</td>
<td>59 %</td>
<td>65 %</td>
<td>74 %</td>
</tr>
</tbody>
</table>

4. DEPOSITION MODELING STUDY RESULTS

In this section, the final results are presented for the atmospheric modeling runs performed as part of this Florida TMDL Pilot Project. The modeling scenario presented here was performed using the emissions inventory developed for the RELMAP modeling exercises performed as part of US EPA’s Mercury Study Report to Congress [USEPA RTC] (1977), which were based upon the estimated emissions for the year 1995. The USEPA RTC emissions inventory contained three mercury speciation categories (standard, 50% control and 85% control) for both medical waste combustors and municipal waste combustors, with each category have a separate relative speciation for mercury. The speciation percentages used were those categorized by the USEPA RTC under the standard emissions control category. These speciation percentages were presented earlier in TABLE 2 of this document. The actual sources used during the modeling exercise are
presented in Appendix C. Changes in the speciation of the mercury emissions across the major categories (Medical Waste Incinerators, Municipal Waste Incinerators) have a significant effect on the modeling estimates derived.

**Modeled Mercury Atmospheric Loadings**

**Monthly Wet-deposition of Speciated Mercury**

The scenario presented here incorporates the standard source specific mercury speciation used in the US EPA Mercury Study Report to Congress. These model results predict a total mercury wet-deposition of $18.74 \pm 6.15 \, \mu g/m^2$ to the SFWMD WCA3. The temporal variation in the wet-deposition of total mercury to the SFWMD WCA3 is presented in Figure 5. Not surprising, the model estimates suggest a significant seasonal trend in total mercury wet-deposition to the area, predicting that over 80 percent of the wet-deposition should occur during the months of May through October.

![Graph showing monthly wet-deposition of mercury](image)

**Figure 5.** Modeled monthly total mercury wet-deposition to SFWMD WCA3.
The speciated mercury wet-deposition is presented in Figure 6. From this figure, it can be seen that the total wet-deposition of mercury estimated was dominated by deposition of reactive gaseous mercury, believed to be in the form of Hg (II). In contrast, model results suggest that the deposition of gaseous elemental mercury, Hg(0), is relatively negligible. Once again, the seasonal nature of the deposition is apparent.

![Figure 6. Modeled monthly speciated mercury wet-deposition to SFWMD WCA3.](image)

**Monthly Dry-deposition of Speciated Mercury**

The hybrid model estimates of the dry-deposition of mercury to the SFWMD WCA3 are presented below. All dry-deposition estimates are presented in tabular form in Appendix D. The hybrid model’s estimate for the total mercury dry-deposition to SFWMD WCA3 during the one-year study period was 12.2 ± 7.4 µg/m². Monthly estimates of the total mercury dry-deposition to the SFWMD WCA3 are presented in
Figure 7. While considerable variability exists in the monthly deposition estimates, inspection of Figure 7 indicates that on average, dry-deposition to the site does show a seasonal trend, with relatively greater deposition occurring during the climatological wet season. The general trends noted in the total mercury dry-deposition can be seen in Figure 8, as well. Figure 8 presents the results for the speciated dry-deposition of mercury to SFWMD WCA3. As can be seen, as was the case for the wet-deposition to SFWMD WCA3, dry-deposition to this area is dominated by the Hg(II) fraction.

Figure 7. Modeled monthly total mercury dry-deposition to SFWMD WCA3.
Figure 8. Modeled monthly speciated mercury dry-deposition to SFWMD WCA3.

Model Validation Results

Calculation of Monthly Averages and Uncertainties for Wet-Deposition of Total Mercury

As part of an initial quality assurance check on the model’s performance, a comparison was made between the monthly total mercury wet-deposition estimates obtained from the hybrid model and the observed monthly wet-deposition measured at two nearby sites that were part of the Florida Atmospheric Mercury Study (FAMS) (Guentzel et al., 1997). The results of this comparison are presented in the next section.

The monthly estimates of total mercury wet-deposition to the SFWMD WCA3 obtained from the hybrid model (and their associated uncertainties) were computed as follows. First, the cluster average total mercury wet-deposition was computed using the following relationship:
\[
\overline{Hg_j} = \frac{Hg_{j, \text{Day1}} + Hg_{j, \text{Day2}}}{2}
\]  \hspace{1cm} (1)

where \(Hg_{j, \text{Day1}}\) and \(Hg_{j, \text{Day2}}\) represent the modeled total mercury wet-deposition at the SFWMD WCA3 for the two representative days that were modeled for a given cluster, \(j\).

Monthly total mercury wet-deposition estimates for the site were then obtained by multiplying the average total mercury wet-deposition for a given cluster, \(j\), by the number of occurrences of that cluster during the \(k^{th}\) month, then summing over all clusters:

\[
[Hg^k] = \sum_{j=1}^{8} Hg_j \cdot n_j
\]  \hspace{1cm} (2)

Finally, to provide some measure of the uncertainty in the model estimates of monthly total mercury wet-deposition, the standard deviation of the total mercury wet-deposition estimates for each cluster was computed. While it is fully understood that one does not typically calculate a standard deviation based upon two numbers, it does provide some measure of the variability in the model estimates for each cluster at the site. The weighted monthly uncertainty for the site was computed as:

\[
\sigma_k = \frac{\sum_{j=1}^{8} \sigma_j \cdot n_j}{\sum_{j=1}^{8} n_j}
\]

where \(\sigma_j\) is the standard deviation in the cluster estimate of total mercury wet-deposition for cluster “\(j\)” at the site and \(n_j\) is the number of occurrences of cluster \(j\) events during the \(k^{th}\) month.
Comparison of Model Estimates vs Observed Wet-Deposition Data

As noted above, as an initial quality assurance check on the ability of the modeling approach to accurately estimate the monthly wet- and dry-deposition of mercury across South Florida, modeled estimates of the monthly total Hg wet-deposition to the SFWMD WCA3 were compared with an average of the monthly observed total mercury wet-deposition to South Florida for the period studied, as represented by observations obtained from the Florida Atmospheric Mercury Study (FAMS) (Guentzel et al., 1997). The FAMS sites used for this comparison were the Tamiami Trail Ranger Station and the Andytown site. These sites were selected for use in the validation exercise given that they border the SFWMD WCA3 to the south and north, respectively.

The comparison of the average observed monthly total mercury wet-deposition at the two FAMS sites versus the modeled total mercury wet-deposition to SFWMD WCA3 for the study period is presented in Figure 9. Overall, the hybrid modeling approach accurately portrays the very seasonal nature of the total mercury wet-deposition to South Florida. In terms of annual deposition, the modeled annual deposition of total mercury for the study period to the SFWMD WCA3 was $18.7 \pm 6.2 \, \mu g/m^2$, compared with an average for the two FAMS sites of $19.2 \, \mu g/m^2$. On a monthly basis, it can be seen that the model and observed data do not compare well during the months of July and August 1995. This disagreement is likely a result of the large uncertainty associated with Cluster #3 transport events (Figure 9), which occur with a relatively high frequency during these two months. The uncertainty derives from the choice of the two days modeled with RAMS to represent the entire cluster. One of the two days had a more northerly orientation in the onshore flow and hence, resulted in a lower deposition estimate for Cluster #3 than would have
been derived using a more “typical day” in that cluster (See Figure 11). However, during the remaining months of the year, the modeled total mercury wet-deposition values show good general agreement with the observed FAMS data. As a result, for the purposes of this Pilot TMDL Study, the hybrid model provides reasonable estimates of mercury wet-deposition to the SFWMD WCA3 for the period studied.

![Figure 9. Comparison of the modeled monthly total mercury wet-deposition to SFWMD WCA3 for Scenario #1 and FAMS observed total mercury wet-deposition (average of Tamiami Trail Ranger Station and Andytown sites) (Guentzel et al., 1997).](image)

**Model Sensitivity Analysis**

The hybrid-model estimates of speciated mercury wet- and dry-deposition are sensitive to a number of uncertainties associated with both model input parameters and model descriptions of important processes. Three important areas of uncertainty include: meteorological input fields, emissions estimates (mass rate and speciation) and model
description of the scavenging of ambient gaseous species (related to the wet-deposition of these species). In this section, a number of analyses are discussed that were made in order to better understand the impact associated with changes and/or variations in these factors.

**Sensitivity of Total Mercury Deposition to Meteorological Variability**

To investigate the variability of the hybrid model’s wet- and dry-deposition estimates as a function of varying meteorology the daily mercury deposition data was employed. Figures 10 and 11 present the modeled 24-hour total mercury dry- and wet-deposition estimates for SFWMD WCA3 as a function of atmospheric transport cluster category. The 24-hour deposition estimates for each day listed in Table 1 are presented in an effort to show the within-cluster variability, as well as the between-cluster variability. It should be noted that to avoid biasing model results toward a given flow pattern, the days chosen to represent a given cluster were chosen to represent spatial extremes in the deposition pattern associated with that cluster. It was felt that this would result in a more realistic “average deposition” for a given cluster.

Inspection of Figure 10 indicates that there is considerable variability in the modeled 24-hour dry-deposition to SFWMD WCA3 as a function of atmospheric transport cluster. Some clusters, such as Clusters 5 and 7, show little deposition to SFWMD WCA3 given that most of the local source emissions are transported away from the site. In contrast, Clusters 2-4 and 6 showed relatively greater dry-deposition due to the onshore nature of the flow. The degree of within-cluster variability differed as a function of cluster, as well. For Clusters 1,5 and 7 (for which one would expect less impact from local sources), there was good agreement between Day 1 and Day 2 estimates, suggesting relatively little variability on a day to day basis under these flow conditions. One could
infer that errors in wind input data for these three clusters would not likely contribute significantly to deposition errors by the model, since variations in atmospheric transport within these cluster groups do not result in much variation in deposition estimates. For Clusters 2, 3, and 4 (for which one would expect greater impact from local sources), there was relatively poorer agreement between Day 1 and Day 2 estimates. These relatively large “within-cluster” differences suggest that slight changes in flow can greatly impact the extent to which SFWMD WCA3 is impacted by a source plume. For this reason one could infer that errors in wind input data for these three clusters could contribute significantly to deposition errors by the model, since variations in atmospheric transport within these cluster groups result in significant variation in deposition estimates.

A comparison of the variability in model estimates of the 24-hour wet-deposition of total mercury to the SFWMD WCA3 is presented in Figure 11. As was true for dry-deposition (discussed above), model results suggest that there is considerable between-cluster, as well as within-cluster, variability. For Clusters 5 and 7, the wet-deposition estimates for both days are quite similar, albeit low. Again, these two clusters represent atmospheric transport regimes that consist of offshore flow (taking local emissions away from SFWMD WCA3) and thus changes (and/or errors) in specified wind direction/transport have little impact on wet-deposition to WCA3. For clusters with predominant onshore transport, significant within-cluster can again be noted. This suggests that for these clusters, slight changes in the predominant flow can lead to noticeable differences in wet-deposition to SFMWD WCA3. For this reason, errors in the estimation of wind direction and speed could lead to larger errors in estimated wet-deposition to WCA3.
Figure 10. Comparison of modeled 24-hour dry-deposition to SFWMD WCA3 as a function of atmospheric transport cluster (and day within cluster).

Figure 11. Comparison of the modeled 24-hour wet-deposition to SFWMD WCA3 as a function of atmospheric transport cluster (and day within cluster).
Sensitivity of Total Mercury Deposition to Emissions Variability

As one might expect, the estimates of total mercury wet- and dry-depositional loading to the SFWMD WCA3 are highly sensitive to the magnitudes of emissions used in our simulations, as well as to the relative speciation of mercury [Hg(0), Hg(II) and Hg(p)] used for simulations. In this section, we present findings regarding the sensitivity of total mercury deposition to changes in both of these factors.

Comparison of Different Total Mercury Emission Rates

Figure 12 presents the estimates of the total mercury dry-deposition to SFWMD WCA3 for the three emissions scenarios. Scenario #1 represents the emissions from the 1997 USEPA Mercury Report to Congress. In Scenario #2, a modified emissions database was utilized that incorporated the results of 1995 in-field stack emission measurements (Dvonch et al. 1999) performed at two large Dade County mercury emission point sources. In accordance with these stack measurements, the total mercury emissions from a Dade County medical waste incineration facility (MedX, Inc.) was changed from 9.2 kg/year to 100.4 kg/year and the total mercury emissions from the Dade County Resource Recovery Facility (municipal waste incinerator) was changed from 1,156.1 kg/year to 255.0 kg/year. In Scenario #3, the fractional changes made in Scenario #2 were applied to all medical and municipal waste incineration sources in the modeling domain. The last two scenarios were run to provide the model estimate of the changes that one would expect to see in the deposition with significant reductions in the emissions from 1) only two large sources and 2) all of the incinerators in S. Florida.
Figure 12. Comparison of the modeled monthly dry-deposition to SFWMD WCA3 as a function of emissions scenario.

Inspection of Figure 12 shows that significant differences are apparent for the monthly total mercury dry-deposition to WCA3 for the three scenarios used in this work. In terms of annual differences, the estimated annual dry-depositional loadings of total mercury to WCA3 for Scenarios 1-3 are 12.2, 7.3 and 4.1 \( \mu g/m^2/\)year, respectively. These results suggest that uncertainties in the actual mass emissions of mercury from only two large point sources (Scenario #2) can have a pronounced impact on the modeled estimates of the total mercury dry-depositional loading to WCA3.

Similarly, pronounced differences between the three emission scenarios can be seen in the modeled estimates of the total mercury wet-depositional loading to WCA3,
presented in Figure 13. The estimated annual wet-depositional loadings of total mercury to WCA3 for Scenarios 1-3 are 18.7, 10.3 and 7.1 µg/m²/year, respectively.

![Figure 13](image.png)

**Figure 13. Comparison of the modeled monthly wet-deposition to SFWMD WCA3 as a function of emissions scenario.**

**Comparison of Different Mercury Speciation Scenarios**

Given that each of the different mercury species have unique characteristics (in terms of dry-deposition velocities and solubility in water), it is important to investigate how variations in the relative abundances of each of these species in the effluent from the different mercury sources might affect both the wet- and dry-depositional loading to WCA3. To simplify the analysis, we modeled only those days associated with Cluster #3, the cluster for which local sources most impact WCA3. The first speciation profile included in this analysis was that used for the 1997 US EPA Mercury Report to Congress (shown in Table 2). The second profile was a slight modification of the Report to
Congress Profile (and is thus referred to as the modified profile). The modifications included changing the medical waste incinerators which were characterized as having 98 percent Hg (II) and 2 percent Hg (0) and municipal waste incinerators which were characterized as having 80 percent Hg (II) and 20 percent Hg (0). The results of this comparison are shown in the Figure.

![Comparison of modeled total mercury deposition](image)

**Figure 14. Comparison of the modeled total mercury deposition to SFWMD WCA3 for days within Cluster #3, using two different mercury speciation profiles.**

Figure 14 shows that for both dry- and wet-deposition to WCA3, the modified speciation profile resulted in an increase in the total mercury loading to WCA3. For total mercury dry-deposition, the modified speciation profile resulted in an increase from $6.6 \pm 4.7 \, \mu g/m^2$ to $8.0 \pm 5.8 \, \mu g/m^2$, an increase of roughly 22 percent. For total mercury wet-deposition, estimates using the modified speciation profile resulted in an increase from $12.8 \pm 0.2 \, \mu g/m^2$ to $13.3 \pm 0.1 \, \mu g/m^2$, an increase of roughly 4 percent. The relative impact of such difference in emissions speciation will likely depend on location of the receptor site relative to sources and source types. However, these results (particularly those of dry-deposition) suggest that uncertainties in the mercury speciation from different
source types is an important source of uncertainty in this and future modeling efforts. As such, the development of improved speciation profiles for relevant mercury point source-types should be a major research priority.

**Sensitivity of Total Mercury Deposition to Model Parameterizations**

The HYSPLIT_4 model used in the estimation of both wet- and dry-deposition of mercury to SFWMD WCA3 allows for the specification of a number of parameters influencing the rates of dry- and wet-removal of mercury from the atmosphere. In this section, we present results of tests looking into the sensitivity of our results to changes in these removal rates.

**Comparison of Different Mercury Dry-Deposition Velocities**

As noted in Section 2d of this document, daytime deposition velocities for the three modeled species of mercury were set to those suggested by Shannon and Voldner (1995). The nighttime deposition velocities suggested by Shannon and Voldner (1995), however, were considerably lower than those observed during the 1999 FEDDS intensive. Preliminary results from the FEDDS measurements suggested that the nighttime deposition velocities were approximately one-half of the daytime velocities. As a result, this modeling study assumed that the nighttime deposition velocities for all three mercury species were one-half of their daytime values. The results presented in Figure 15 show the differences in the modeled total mercury dry-deposition to WCA3 for the case using solely the Shannon and Voldner (1995) specified dry-deposition velocities and for the case in which the nighttime dry-deposition velocities were set to one-half of their respective daytime values (denoted as “This Report”). Figure 15 indicates that the use of the Shannon and Voldner (1995) dry-deposition velocities results in total mercury dry-
deposition estimates that are considerable lower than those using nighttime values of one-half daytime values. Annualized, the former results in annual total mercury dry-deposition to WCA3 of 7.6 µg/m², while the latter results in annual total mercury dry-deposition to WCA3 of 12.2 µg/m². These results suggest that present uncertainties in the dry-deposition velocities associated with the different species of mercury [particularly Hg (II)] can have a significant impact on modeled dry-deposition loading estimates. More research is needed to narrow the uncertainties in these dry-deposition velocities.

Figure 15. Comparison of the modeled monthly dry-deposition to SFWMD WCA3 using two sets of speciated dry-deposition velocities.

Comparison of Different Wet-Removal Rates

As discussed in Section 2d, initial model simulations were compared with the Davie event-precipitation dataset to investigate the model performance for these simulations. The initial model simulations produced estimates of mercury wet-deposition
to the Davie site that were unrealistically high when compared with the observed data set. Since the development of an improved analytical representation of wet-removal process for use within the HYSPLIT_4 model was beyond the scope of this project, the effective Henry’s Law coefficient was varied by a factor of $10^{-2}$ which was used for the wet-deposition calculations presented in this report. This change was determined by comparing the observed wet-deposition results from our Davie site with the modeled wet-deposition for the Davie site.

![Image of graph showing comparison of modeled monthly total mercury wet-deposition to SFWMD WCA3 using two different values for the Hg(II) wet removal rate.]

Figure 16. Comparison of modeled monthly total mercury wet-deposition to SFWMD WCA3 using two different values for the Hg(II) wet removal rate.

Figure 16 shows a comparison of the modeled monthly total mercury wet-deposition for the SFWMD WCA3 using both the standard and reduced Hg(II) removal rates. In this case, the model results suggest that decreasing the removal rates used for Hg(II) resulted in a very slight but insignificant increase in the amount of total mercury wet-deposited to SFWMD WCA3. Theoretically, a reduction in the amount of Hg(II)
removed by wet-removal processes closer to the source regions allows more Hg(II) to be available for wet removal at SFWMD WCA3 and other downwind locations. While the lowering of the removal rate did decrease the deposition in the grid cells containing the sources, it had no significant impact on the estimates for WCA3. These results suggest the importance of further research focused two areas: (1) narrowing the uncertainty associated with the solubility of reactive gaseous mercury and (2) developing improved descriptions of wet-removal processes for used in dispersion/deposition models.

**Sensitivity of Results to 24 versus 48 hour model simulations**

To investigate the sensitivity of the model estimates of wet and dry deposition to S. Florida due to the model simulation time, 24 and 48 hours of HYSPLIT simulations were performed. Cluster 2 was chosen to investigate the 24 and 48-hour simulations. Two RAMS simulations were performed for 48 hours for each of the dry days selected. Similarly, two RAMS simulations were performed for the wet days selected. Output from each of the RAMS simulations were then input to HYSPLIT to produce the dry and wet deposition fields over South Florida for this comparison.

First, the HYSPLIT model was run for each of the dry and wet days for the 24 and 48 hours of simulation with local sources only. Next, the HYSPLIT model was executed for each of the dry and wet days for 24 and 48 hours, but with the regional sources added. Results for the dry and wet deposition were calculated and are shown in Tables 5 and 6, which represent the results for the average of the 2 days for Cluster 2 for the dry and wet simulations, respectively. In general, the total deposition is nearly doubled when comparing a 24-hour to a 48-hour simulation, which is what you would expect if the
simulation time was not significantly impacting the deposition estimates. This was true for both the dry and wet deposition.

For the dry day model simulations, results shown in Table 5, the total dry deposition from local sources after 24 hours is 0.823 kg and the contribution from all sources was 0.825 kg. The contribution of the regional sources to the dry deposition to south Florida using the 24-hour simulation was only 0.24%. However, the dry deposition after 48 hours from local sources was 1.8 kg, and 2.2 kg from all sources. The regional sources contributed 14% to the dry deposition to south Florida for this cluster, which is relatively small compared to the remaining 86% contributed by local sources alone. While on the surface this may appear to be a significant finding, one must remember that the contribution of this cluster to the overall dry deposition must be considered before interpreting the regional source input to be important. Since Cluster 2’s modeled dry deposition was relatively small, less than 5% of the total, the 14% increase would translate into less than 1% increase in the total deposition to all of South Florida.

The wet deposition to south Florida from local sources, as shown in Table 6, is 4.8 kg and 4.9 kg from all sources. Regional sources have contributed 1.6% to the wet deposition within a 24-hour period. The accumulated wet deposition after 48 hours from local sources is 9.965 kg, and 10.135 kg from all sources. The regional sources have contributed to 1.7% of the wet deposition to south Florida within a 48-hour period. Contribution of wet deposition to south Florida within a 24 or 48-hour period is small and almost identical.
Table 5. Summary of 24 to 48 hours of HYSPLIT Dry simulations for Cluster 2 (over South Florida land).

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<th>Duration of simulation (hrs)</th>
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<th>Local Sources only</th>
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<tr>
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<td>Average (ng/m³)</td>
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Table 6. Summary of 24/48 hours of HYSPLIT Wet simulations for Cluster 2 (over South Florida land area).

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<th>Duration of simulation (hrs)</th>
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<th>Local Sources only</th>
</tr>
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<tbody>
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<td></td>
<td>Average (ng/m³)</td>
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To further explain this finding and to better understand the meteorological significance of the 24 vs 48-hour simulation times, as well as the impact on the local/regional sources contributions, a set of forward trajectories was plotted for the days modeled moving away from the sources for 24 and 48 hours. One trajectory from each
source was calculated starting at a height of 500 m above the ground. The RAMS’s Grid One output was used to generate the trajectories because it covered a large domain sufficient to generate forward trajectories for 48 hours. Figures 17.a and 17.b represent the 24 and 48-hour forward trajectories for one of the wet days simulated for cluster 2 respectively. Figures 18.a and 15.b represent the 24 and 48 hours forward trajectories for one of the dry days for cluster 2, respectively. It is evident from the trajectory plots that few of the trajectories from regional sources to the north make it to south Florida, and extending the trajectories from 24 to 48 hours has a negligible impact. This results was not unexpected as past research has also noted that S. Florida is meteorologically cut-off from the continental meteorological flow patterns that influence northern Florida and the southern U.S.
Figure 17a. Twenty-four hour forward trajectories for all sources for a wet day.

Figure 17b. Forty-eight hour forward trajectories for all sources for a wet day.
Figure 18a. Twenty-four hour forward trajectories for all sources for a dry day.

Figure 18b. Forty-eight hour forward trajectories for all sources for a dry day.
5. Conclusions

As part of the Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study, a hybrid modeling approach was used to provide monthly and annual estimates of the atmospheric loadings (wet and dry) of speciated mercury to the South Florida Water Management District Water Conservation Area 3 (SFWMD WCA3). These atmospheric loading estimates were used as input to an Everglades Mercury Cycling Model (E-MCM). The hybrid modeling approach incorporated a mesoscale meteorological model and a dispersion/deposition model to obtain estimates of the monthly and annual wet- and dry-deposition of speciated mercury [Hg(0), Hg(II) and Hg(p)] to the South Florida Water Management District’s Water Conservation Area 3 (SFWMD WCA3). Daily back-trajectories were computed for the study period and then grouped into eight, statistically distinct clusters which represented eight meteorologically distinct atmospheric transport regimes that impacted South Florida during the one-year period studied. These clusters were found to be representative, in terms of frequency of occurrence, of the meteorological clusters over a longer period from 1991-1999. Days representative of each of the meteorological clusters were modeled using RAMS to obtain high-resolution meteorological fields that were then used to determine cluster average estimates of speciated mercury wet- and dry-deposition fluxes. These cluster averages were weighted by the monthly frequency of occurrence of each cluster to obtain the monthly and annual deposition estimates for the one-year period studied.

Prior to using the model to obtain the depositional loading estimates for SFWMD WCA3, preliminary tests were performed to investigate the sensitivity of the hybrid model to a number of model inputs and parameterizations. A large variability in the
meteorological conditions within a few of the identified clusters resulted in relatively large uncertainty in the monthly estimates for WCA3, but were less important when looking at the annual deposition estimates. The dry-deposition estimates were found to be sensitive to the deposition velocities chosen for each mercury species, as well as to the speciation of the stack emissions used in the modeling.

An attempt was also made to evaluate the performance of the hybrid modeling approach through the comparison of the monthly total mercury wet-deposition estimates for WCA3 obtained from the model and those obtained from observed data. The total mercury wet-deposition estimates were found to be in good agreement with the measured wet-deposition values from the FAMS project (Guentzel et al., 1997). With respect to the dry-deposition estimates produced by the hybrid model, model estimates agreed quite well with the dry-deposition measurements obtained during the 1999 Florida Everglades Dry-Deposition Study, where the first actual dry-deposition measurements were made in the Everglades near the Water Management Districts S-151 structure.

Monthly and annual wet-/dry-deposition estimates were obtained to better understand how emissions inventories and/or changes in local mercury emissions might impact future wet- and dry-depositional loading of mercury to the SFWMD WCA3. Based upon the emissions inventory provided by the USEPA, local sources accounted for the majority (>95%) of the wet-deposition regardless of the uncertainties in the modeling approach. Local sources also accounted for the majority (>86%) of the dry-deposition to WCA3 with a slightly larger uncertainty in the estimates due to the model sensitivity to the dry-deposition velocities, and the meteorological flow conditions used.
The hybrid modeling approach used in this study provided reasonable estimates for the atmospheric deposition of speciated mercury to the SFWMD WCA3. As the mercury TMDL modeling process becomes more refined and is implemented within Florida and other states, efforts must continue to develop a more comprehensive pollutant transport/transformation/deposition model for use in obtaining atmospheric deposition estimates for these TMDL efforts. The University of Michigan Air Quality Laboratory is presently working under a cooperative agreement with the US EPA and the State of Florida DEP to develop a CMAQ Mercury Model. However, this is not enough! Significant efforts must be made to improve mercury emissions inventories (both in terms of total mass emitted and speciation), to improve the descriptions of physical and chemical transformation processes that likely occur during transport, and to narrow the uncertainties associated with background levels of the relevant species. The research completed here clearly identified data gaps and areas for model improvements for the deposition of reactive mercury forms and the chemistry of mercury emitted into the atmosphere.

6. Acknowledgements

The authors would like to thank Dr. Tom Atkeson of the Florida Department of Environmental Protection and Mr. Kenneth P. Larson of the Broward County Department of Natural Resource Protection for their efforts in the collection of the precipitation data used in this report. We would like to thank Mr. Christopher Gleason for his assistance in the data analysis associated with this project. Finally, we would also like to thank Dr. Curt Pollman, TetraTech, for providing insight into the precipitation chemistry data from the Florida Atmospheric Mercury Study used in this work.
7. References


APPENDIX I, Addendum A

ATMOSPHERIC BACK-TRAJECTORIES BY CLUSTER
Figure A1. Cluster 1: Weak local flow, variable in direction, generally associated with a weak high pressure center located over South Florida.

Figure A2. Cluster 2: Weak synoptic flow from northerly direction, generally associated with both weak high and low pressure systems.

Figure A3. Cluster 3: Weak synoptic or enhanced sea breeze flow from easterly direction, generally associated with the influence of the Bermuda High.

Figure A4. Cluster 4: Strong synoptic flow from northeasterly direction generally associated with strong high pressure over eastern U.S.
Figure A5. Cluster 5: Strong synoptic flow from northwesterly direction, generally associated with the advance of a strong southern Plains high-pressure area after a cold frontal passage.

Figure A6. Cluster 6: Moderate synoptic flow from southerly direction, generally associated with the approach of a cold frontal boundary from the northwest.

Figure A7. Cluster 7: Moderate synoptic flow from west to southwesterly, generally associated with the weak troughs or multiple frontal boundaries.

Figure A8. Cluster 8: Moderate to strong synoptic flow from north to northwesterly, generally associated with strong high pressure areas in central and southern Plains.
APPENDIX I, Addendum B

SURFACE WEATHER MAPS
Figure B1. Surface map features representative of atmospheric transport associated with Cluster #1.

Figure B2. Surface map features representative of atmospheric transport associated with Cluster #2.
Figure B3. Surface map features representative of atmospheric transport associated with Cluster #3.

Figure B4. Surface map features representative of atmospheric transport associated with Cluster #4.
Figure B5. Surface map features representative of atmospheric transport associated with Cluster #5.

Figure B6. Surface map features representative of atmospheric transport associated with Cluster #6.
Figure B7. Surface map features representative of atmospheric transport associated with Cluster #7.

Figure B8. Surface map features representative of atmospheric transport associated with Cluster #8.
APPENDIX I, Addendum C

MERCURY POINT SOURCE EMISSIONS INVENTORY
### TABLE C1. Local Source Emissions Employed in Hybrid Modeling

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<th>HgO (Fraction of Total)</th>
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Addendum C, Continued

Figure C1. Location of point sources in Grid #2 used in the regional HYSPLIT Modeling.
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SUMMARY OF MONTHLY SPECIATED WET- AND DRY-DEPOSITION ESTIMATES FOR THE SOUTH FLORIDA WATER MANAGEMENT DISTRICT’S WATER CONSERVATION AREA 3
TABLE D1. Hybrid Model Estimates and Uncertainties for Wet-deposition to SFWMD WCA using USEPA RTC Emissions.
All units are in micrograms per square meter.

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<th>Hg (0) Unc.</th>
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TABLE D2. Hybrid Model Estimates and Uncertainties for Dry-deposition to WCA3 using USEPA RTC Emissions.
All units are in micrograms per square meter.

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APPENDIX II

Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study: Application of the Everglades Mercury Cycling Model (E-MCM) to Site WCA 3A-15

Prepared for the Florida Department of Environmental Protection

Submitted by Reed Harris, Curtis D. Pollman, David Hutchinson and Don Beals Tetra Tech Inc. Lafayette, CA October 2001
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Summary

The Clean Water Act Section 303(d) requires States to (1) identify and list waterbodies where State water quality standards are not being met and (2) establish “Total Maximum Daily Loads” (TMDLs) for those waters. A pilot project is currently underway to test methods relevant to the development of TMDLs for mercury from air sources. It combines field information with atmospheric and aquatic modeling of mercury transport and fate from source to receptor, in this case fish. We selected age 3 largemouth bass as our standard. The project is a cooperative, voluntary effort between the USEPA and the States of Wisconsin and Florida.

The pilot study is being conducted on a portion of the Florida Everglades within Water Conservation Area 3A (site 3A-15), 50 km west of Fort Lauderdale, and Devil’s Lake in Wisconsin (a small lake near Madison). Both of these waterbodies are on their States’ lists of impaired waterbodies, and have fish consumption advisories due to high levels of mercury in fish. The sites also were selected because of previous extensive mercury studies on-site.

This document describes aquatic modeling undertaken with the Everglades Mercury Cycling Model (E-MCM) in support of the Florida pilot activities. This final document reflects the initial results of the study in the spring of 2000, as well as the many useful comments received during the peer review process in the spring of 2000. Changes to model simulations related to the peer review process are detailed in Appendix A.

The basic objective for aquatic modeling in the Florida pilot mercury TMDL study was to predict the magnitude and timing of the relationship between changes in atmospheric Hg(II) deposition and fish mercury concentrations in Everglades marsh area Water Conservation Area (WCA) 3A-15. Since this was a pilot exercise, an important component was to identify the strengths and weaknesses of the process.

E-MCM is a mechanistic simulation model that runs on Windows™-based computers. Using a mass balance approach, the model predicts time-dependent concentrations for three forms of mercury in water and sediments (dissolved and particulate phases), vegetation and a simplified food web that includes three fish populations.

Overall, our modeling approach was designed to allow us to predict the magnitude and timing of the response of fish mercury concentrations to changes in atmospheric Hg(II) deposition, while considering the model sensitivity to different inputs and year to year variations in mercury deposition in the absence of a long-term record of mercury deposition at the site.

To calibrate the model, we used an estimate of 35.32 µg m⁻² yr⁻¹ for the mean annual atmospheric Hg(II) deposition (23.18 wet, 11.2 reactive gaseous mercury, 0.94 dry particles), based on observations from three sites studied from 1993-96 during the Florida Atmospheric Mercury Study (FAMS) (Guentzel, 1997; Guentzel et al., in review). The predicted long-term average mercury concentration for age 3.0 largemouth bass at WCA 3A-15 was 1.80 µg g⁻¹ wet muscle. Once the model was calibrated, simulations were run to predict the response of fish mercury concentrations to long-term sustained reductions in atmospheric Hg(II). We assumed that atmospheric methylmercury deposition and inflowing methylmercury and Hg(II) concentrations would also drop in response to the lower deposition rates. Simulations were run with Hg(II) and MeHg deposition reductions of 25, 50, 75 and 85%. The relationship between loading changes and system response (e.g. Hg concentrations in age 3 largemouth bass) is nearly linear, although the slope is less than 1 (i.e., a 50% reduction in loading produces something less than a 50% response). The deviation of the slope from unity and non-zero intercept is a direct consequence of longer-term re-supply of Hg(II) and methylmercury from deeper sediments to the overlying system via macrophyte roots. Because of the depth to which
Macrophytes may take up Hg from the sediments, coupled with the time required to bury so-called legacy mercury from the rooting zone, this re-supply is present even when the system is allowed to adjust to load reductions for 200+ years in our simulations. Based on a linear interpolation of model results, a load reduction of 77% is needed for predicted long-term average mercury concentrations in age 3 largemouth bass to drop from 1.80 to 0.5 µg g⁻¹ wet muscle.

There is a lack of long-term mercury deposition data (e.g. 10 years or more) in the Everglades. To make initial estimates of the effects of year-to-year variations in Hg(II) deposition, we used the characteristics of monthly sampled data from 3 sites included in the Florida Atmospheric Mercury Study (FAMS) from 1993-96 to synthesize a 500 year set of annual Hg(II) deposition rates. The results of this simulation predict the mercury concentration in age 3 largemouth bass exceeded 1.92 µg g⁻¹ wet muscle 5% of the years. To reduce mercury concentrations of an age 3 largemouth bass from 1.92 to 0.5 µg g⁻¹ wet muscle, E-MCM predicts a required decrease in atmospheric Hg(II) deposition of 78-79%. It is also possible that, while reductions in Hg(II) loading to WCA 3A-15 may significantly reduce fish mercury concentrations, there may continue to be some fish over 0.5 µg g⁻¹ wet muscle, even if all anthropogenic contributions to Hg(II) deposition are eliminated, unless additional remedial options are developed.

Regardless of the magnitude of the load reduction, fish mercury concentrations were predicted to change by 50% of the ultimate response within 8-9 years. Within 25-30 years, 90% of the ultimate predicted response has occurred. The actual magnitude of the change in fish Hg is of course still dependent on the magnitude of the load reduction.

Predicted mercury concentrations in age 3 largemouth bass were most sensitive to factors associated with particle and vegetation fluxes, Hg(II) loading, methylation rates, and factors affecting fish diets and growth. While the dataset for model calibration for E-MCM at WCA 3A-15 was extensive in most regards, it would be useful to have improved mercury concentration data for the lower food web and vegetation. Furthermore, the lack of a long-term dataset for Hg(II) deposition required us to synthesis a dataset from limited data to assess the effects of normal year-to-year variations in rainfall and Hg loading rates on fish mercury dynamics. There are also gaps in the state of knowledge of mercury cycling in the Everglades that resulted in modeling assumptions and impose uncertainty on the relationship between mercury deposition and fish mercury concentrations. These gaps should be addressed in future studies and include the location of and governing factors for methylation and demethylation, and mercury fluxes associated with vegetation and particles (litter, throughfall, transpiration, sedimentation, decomposition).

Overall, this study indicates that mechanistic modeling of the aquatic Hg cycle is a useful component of the TMDL process, but is currently limited by scientific gaps. The nearly linear predicted response of fish mercury concentrations to changes in atmospheric Hg deposition is driven significantly by assumptions regarding the bioavailability of mercury for various reactions, particularly methylation. Similarly the predicted response dynamics of fish mercury concentrations are affected by estimated sedimentation rates, which had significant uncertainty, and assumptions regarding the bioavailable Hg pools participating in various reactions. On a positive note, mercury researchers are actively investigating several key knowledge gaps and it is expected that over the next few years the predictive strength of the MCM models will improve.
1. Introduction

1.1 Background on the Florida Pilot Mercury TMDL

The Clean Water Act Section 303(d) requires States to (1) identify and list waterbodies where State water quality standards are not being met and (2) establish “Total Maximum Daily Loads” (TMDLs) for those waters (USEPA 1999). TMDLs specify the amount of a pollutant that may be present in the water and still allow the waterbody to meet State water quality standards. Pollutant loads are allocated among point and non-point pollution sources, and include a margin of safety that accounts for uncertainty in the relationship between pollutant loads and characteristics of the waterbody. The allocations for water sources in TMDLs typically are implemented through existing Federal, State, Tribal, and local authorities. Year 2000 is the next year that States are required to develop their lists of impaired waterbodies, schedule for developing TMDLs, and submit them to the Environmental Protection Agency (USEPA) for review and approval.

A pilot project is currently underway to test methods relevant to the development of TMDLs for mercury from air sources. It combines field information with atmospheric and aquatic modeling of mercury transport and fate from source to receptor, in this case fish. The project is a cooperative, voluntary effort between the USEPA and the States of Wisconsin and Florida. The pilot study is being conducted on a portion of the Florida Everglades known as Water Conservation Area 3A-15 (WCA 3A-15, 30 miles west of Fort Lauderdale), and Devil’s Lake in Wisconsin (a small lake near Madison). Both of these waterbodies are on their States’ lists of impaired waterbodies, and have fish consumption advisories due to high levels of mercury in fish.

Separate draft TMDL documents are being written for the studies in Wisconsin and Florida. Each draft TMDL will have supporting documents describing the atmospheric and aquatic modeling efforts. This document has been prepared in support of the Florida pilot mercury TMDL effort, and describes the associated aquatic modeling activities. The atmospheric deposition model used for the Everglades is called the Regional Meteorological Pollutant Chemistry and Transport Model, developed at the University of Michigan. Atmospheric modeling for the Everglades TMDL pilot work is described in a supporting document (Keeler et al., 2000).

2. Aquatic Modeling Objectives

The overall objective of the aquatic modeling component of the pilot mercury TMDL for the Florida Everglades was:

To predict the magnitude and timing of the relationship between changes in atmospheric Hg(II) deposition and fish mercury concentrations in Everglades marsh area WCA 3A-15.

Specific sub-objectives included:

- Prediction of the reduction in Hg(II) loading to WCA 3A-15 necessary to maintain mercury concentrations in age 3 largemouth bass below 0.5 µg/g wet.

- Development of an Hg deposition – fish Hg response curve showing the effects of changing atmospheric Hg(II) deposition on long-term average mercury concentrations in largemouth bass in WCA 3A-15.
Via sensitivity analysis, identification of the most important factors affecting fish mercury concentrations in WCA 3A-15.

Estimation of the effects of year to year variability in Hg(II) deposition on fish mercury concentrations

Identification of scientific gaps and needs in order to reduce uncertainty regarding the links between atmospheric Hg(II) deposition and fish mercury concentrations in Everglades marsh areas.

3. Overview of the Everglades Mercury Cycling Model (E-MCM)

A mercury cycling model has been developed to simulate the conditions found in marsh areas of the South Florida Everglades. The Everglades Mercury Cycling Model (E-MCM) (Tetra Tech 1999b) is an adaptation of the Dynamic Mercury Cycling Model for lakes (D-MCM) (Tetra Tech 1999a). E-MCM accommodates unique features of Everglades marshes. Such features include shallow waters, a system of canals and managed water levels, a warm subtropical climate, high sun exposure, neutral to alkaline pH, high concentrations of dissolved organic carbon, large biomass of aquatic vegetation including periphyton, sawgrass, cattails and water lilies, and a wide range of nutrient levels and primary productivity. Field data (e.g. Gilmour et al., 1998a, Gilmour et al., 1998b, Krabbenhoft et al., 1998) for parts of the Everglades have shown considerable spatial and temporal variability, with some locations apparently more conducive to methylmercury production and bioaccumulation.

E-MCM also incorporates recent advances made by researchers investigating mercury cycling in freshwater systems and in the Everglades specifically. These advances include an improved understanding of the factors governing methylation, demethylation, HgII reduction, food web mercury transfers, and the role of aquatic vegetation in the mercury cycle. Much of this work was done through the Aquatic Cycling of Mercury in the Everglades (ACME) project (e.g. Krabbenhoft et al., 1998, Gilmour et al., 1998a, Hurley et al., 1998, Cleckner et al., 1998).

E-MCM is a mechanistic simulation model that runs on Windows™-based computers. Using a mass balance approach, the model predicts time-dependent concentrations for three forms of mercury in water and sediments (dissolved and particulate phases), vegetation and a simplified food web (see Figure 1 and Table 1).
3.1 Mercury Forms

There are three primary mercury forms in the E-MCM: methylmercury, Hg(II) and elemental mercury. Hg(II) is defined here as all mercury which is neither methylmercury nor elemental mercury. Provisions have also been made for some of the particulate Hg(II) on non-living solids to exchange slowly, while the remainder is assumed to exchange rapidly enough to assume instantaneous equilibrium partitioning.

3.2 Model Compartments

Model compartments include the water column, three macrophyte species (cattails, sawgrass, water lilies), four sediment layers and a food web (Table 1). The model has two types of particles in the water column: detritus and other suspended solids. For detritus, suspended solids and sediment solids, provisions have been made for two types of Hg(II) exchange: (1) instantaneous and (2) slowly exchange governed by the kinetics of adsorption and desorption.

Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry particle deposition, deposition of reactive gaseous mercury).
Table 1. Compartments and Mercury Forms in E-MCM

<table>
<thead>
<tr>
<th>Compartment</th>
<th>MeHg</th>
<th>Hg(II)</th>
<th>Elemental Hg</th>
<th>Solid HgS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water Column (abiotic)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Non-living suspended particles*</td>
<td>●</td>
<td>●</td>
<td></td>
<td>●</td>
</tr>
<tr>
<td><strong>Sediments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment Porewater</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Sediment Solids*</td>
<td>●</td>
<td>●</td>
<td></td>
<td>●</td>
</tr>
<tr>
<td><strong>Vegetation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattails</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sawgrass</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water lilies</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Food Web</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Detritus*</td>
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</tr>
<tr>
<td>Periphyton</td>
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<td>Phytoplankton</td>
<td>●</td>
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<tr>
<td>Benthos</td>
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<td></td>
</tr>
<tr>
<td>Shrimp</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-Piscivore Fish Cohorts (up to 20)</td>
<td>●</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Omnivore Fish Cohorts (up to 20)</td>
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<td>●</td>
<td></td>
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<tr>
<td>Piscivore Fish Cohorts (up to 20)</td>
<td>●</td>
<td>●</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Includes slowly and rapidly exchanging components for Hg(II).

The simplified food web consists of detritus, periphyton, phytoplankton, zooplankton, benthos, shrimp, mosquitofish (*Gambusia*), bluegill/warmouth sunfish (grouped together), and largemouth bass. Fish mercury concentrations tend to increase with age, and are therefore followed in each year class (up to 20 cohorts) for each species. Bioenergetics equations developed for individual fish at the University of Wisconsin (Hewett and Johnson 1992) were modified to consider temperature dependent growth and coupled to methylmercury fluxes (Harris and Bodaly 1998). These fluxes for individual fish are then adapted to simulate year classes and entire populations (Tetra Tech 1999b).

### 3.3 E-MCM Processes

A detailed description of model processes and equations in E-MCM is provided in the user’s guide (Tetra Tech 1999b). Major processes involved in the mercury cycle in an Everglades marsh are shown in Figure 1. These processes include surface inflows and outflows, vertical groundwater flow, instantaneous methylmercury partitioning between abiotic solids and dissolved complexes, instantaneous and slower adsorption/desorption kinetics for Hg(II) on abiotic solids, particulate settling, resuspension and burial, macrophyte related fluxes (throughfall, litter, root uptake, transpiration), atmospheric deposition, air/water gaseous exchange, in-situ transformations (methylation, demethylation, MeHg photodegradation, Hg(II) photoreduction), mercury kinetics in
plankton, and methylmercury fluxes in fish populations (uptake via food and water, excretion, egestion, mortality, fishing).

4. Aquatic Modeling Approach

Overall, our aquatic modeling approach was designed to allow us to predict the magnitude and timing of the response of fish mercury concentrations to changes in atmospheric Hg(II) deposition, while considering the model sensitivity to different inputs, uncertainty regarding true Hg(II) loading rates, and year to year variations in mercury deposition in the absence of a long-term record of mercury deposition at the site.

Aquatic modeling for the Everglades pilot mercury TMDL included the following key components:

- Selection of a site known to have elevated fish mercury concentrations, as well as a high quality dataset: Water Conservation Area 3A-15
- Data assembly
- Calibration of E-MCM using estimates of long-term average annual conditions at site WCA 3A-15. The critical end point was mercury in largemouth bass, but the calibration examined total and mercury concentrations in each compartment for which data were available.
- Development of a long-term steady-state dose-response curve relating predicted long-term average fish mercury concentrations to different levels of long-term continuous atmospheric Hg(II) deposition. For example, if atmospheric deposition decreased to 50% of current levels and was maintained at the lower value, one question that immediately arises is at what levels would fish mercury concentrations ultimately stabilize? Model runs were carried out for several mercury deposition rates to develop the steady-state response curve.
- Assessment of the predicted timing of the response of fish mercury concentrations to different loadings of inorganic Hg(II).
- Sensitivity analysis of E-MCM predictions to various model input parameters, including atmospheric deposition rates of mercury.
- Assessment of the effects of year-to-year variations of atmospheric Hg(II) deposition.

Further information on the approach to model calibration, sensitivity analysis, and assessment of year-to-year variations is provided below. Site selection is described in the overall draft TMDL document. Data assembly, model calibration and modeling results are presented in later sections of this document.

4.1 Approach to Model Calibration:

The model was initially calibrated on the basis of estimated long-term average conditions. Most of the data for the calibration were collected over a period of several years in the 1990’s.
Atmospheric mercury deposition data were based on measurements of wet deposition conducted at the following south Florida FAMS sites: Tamiami Trail, Fakahatchee Strand, and the Beard Research Center in Everglades National Park. Wet deposition measurements between 1993 and 1996 were used to derive the loading estimates. On-site mercury concentrations (except sport fish Hg) and fluxes were largely measured from 1995-99 during the ACME studies (e.g. Krabbenhoft et al., 1998, Gilmour et al., 1998a, Gilmour et al., 1998b, Hurley et al., 1998, Cleckner et al., 1998). Mercury in largemouth bass, warmouth, and bluegill was measured by the Florida Fish and Wildlife Conservation Commission (T. Lange unpublished data).

For the purposes of this component of the study we assumed that these datasets reasonably encompassed current mercury fluxes and concentrations at WCA 3A-15. Secondly we assumed these conditions were reasonably stable. We then ran simulations for 100 years with annual deposition patterns and site conditions repeating year over year, often with monthly frequencies for inputs. We examined the resulting mercury concentrations and fluxes once the system had effectively stabilized (i.e. concentrations were not changing year to year). These results were reported on a weekly basis for the 101st year of the simulation, so we could examine the seasonality of the predictions.

### 4.2 Approach to Developing an Hg(II) Dose - Fish Response Curve

One of the central questions for the pilot mercury TMDL exercise was to predict the relationship between atmospheric Hg(II) deposition and long-term fish mercury concentrations. To make these predictions, we ran simulations with different Hg(II) loads maintained for a period of 200 years until fish mercury concentrations were at a quasi steady-state year-over-year. Simulations focused on the potential effects of Hg(II) load reductions on fish mercury concentrations, with predictions made for reductions of 25, 50, 75 and 85% of current estimates of total atmospheric Hg(II) deposition (wet and dry combined). These results were then combined in plots to show the shape of the Hg(II) dose – long-term fish Hg response curve. We chose age 3 largemouth bass as a benchmark standard for our analyses.

When running simulations with Hg(II) deposition rates other than current loadings, we had to make assumptions about other external mercury sources. For the simulations examining long term predicted fish Hg concentrations for different loads, we adjusted atmospheric methylmercury deposition, inflowing methylmercury and inflowing Hg(II) concentrations in proportion to the reduction in atmospheric Hg(II) deposition.

### 4.3 Approach to Predicting the Timing of the System Response

To examine the time required for fish mercury concentrations to respond to load reductions, we ran simulations for 200 years with Hg(II) deposition held constant at current levels, then instantaneously reduced the atmospheric Hg(II) and MeHg in a step function manner to a constant lower load. Inflowing Hg(II) and MeHg concentrations were also reduced in proportion to atmospheric deposition, but with a lag time introduced. To estimate this lag effect, the model was first run with all external Hg(II) and MeHg loads reduced in a step function manner along with atmospheric deposition. The temporal responses of Hg(II) and MeHg in the 3A-15 model cell were then used as estimates of the response dynamics for inflows responding to reduced atmospheric deposition. We examined fish Hg response dynamics for load reductions of 25, 50, 75 and 85% from current atmospheric deposition rates to develop the response curve.
4.4 Approach to Sensitivity Analysis

It is important to understand which inputs in the model have the greatest influence on predicted fish mercury concentrations. A standard approach is the use of a sensitivity analysis, varying selected input parameters a given amount, in this case plus or minus 50%. In some cases, a change to an input value of 50% did not make physical sense; for example one could not increase the fraction of the marsh covered by vegetation from 80 to 130 percent. In such cases, a lesser increase was tested. To allow a common basis to compare the effects of different inputs, results were plotted as the percent change in fish mercury concentration versus percent change in the input variable ($\Delta \text{Hg}_{\text{fish}} \%/\Delta \text{Input}\%$).

It should be noted that this type of traditional sensitivity analysis does not account for the actual variability/uncertainty associated with each input. Some inputs may vary proportionately more than others. It also does not account for the fact that some inputs co-vary, such as DOC concentration and light extinction. These limitations can be accommodated via a Monte Carlo approach that uses probabilistic distributions for key inputs and includes relationships between inputs, but is beyond the scope of the current exercise. A Monte Carlo version of E-MCM has been developed and currently is undergoing testing.

An alternative approach that considers the actual limits that a model parameter can assume provides a means for defining the bounds of uncertainty in model response related to that variable. This so-called “minimum-maximum” analysis examines sensitivity in the context of likely parameter distributional ranges. It differs from pure sensitivity analysis insofar as the latter is typically conducted in isolation, with all parameters perturbed by the same relative amount without any regard to the likelihood of that magnitude of perturbation for each given parameter. The former is based on the actual measured limits of uncertainty for the parameter or, if the limits are not well defined, an estimate of what the likely limits are.

Both the traditional or classical and the “minimum-maximum” types of sensitivity analyses were applied to the E-MCM model. To conduct “minimum-maximum” analysis, E-MCM was first run for the $i^{th}$ parameter at its high and low limits, while all other parameters were held constant at their nominal values. As in the more traditional sensitivity analyses presented earlier, the end-point for the analysis was the MeHg concentration in age 3 largemouth bass. The sensitivity index for the $i^{th}$ parameter ($SI_i$) (Hoffman and Gardner, 1983) is calculated as:

$$SI_i = 1 - \frac{E_{i,\text{low}}}{E_{i,\text{high}}}$$

where $E_{i,\text{low}}$ and $E_{i,\text{high}}$ are the predicted age 3 largemouth bass mercury concentrations for the low and high estimates for the $i^{th}$ parameter respectively.

As $SI_i$ approaches 1 (i.e., the larger the difference between the high and low results), the model is increasingly more sensitive to the range in parameter uncertainty. This simple technique reflects both classical sensitivity (the partial derivative of output $Y$ with respect to parameter $X$), and the range of variability of the input parameter. This latter feature brings us closer into the realm of uncertainty analysis.
4.5 Approach to Year-to-Year Variations of Atmospheric Deposition

It is also important in a TMDL study to consider year-to-year variability in mercury deposition. No long-term dataset (e.g., 20 years or more) is available in terms of atmospheric deposition on-site. An approach was therefore used whereby we synthesized an artificial set of 500 mean annual wet Hg\textsubscript{t} deposition rates based on data from three of the FAMS sites in the region. These sites had comprehensive deposition data spanning 2-4 year periods. The 500 point synthesized dataset had lognormal distribution characteristics with the desired mean and standard deviation values.

Inherent in this approach were several key assumptions:

1. Deposition is constant over the long-term but varies annually about some mean value, and can be described statistically as a lognormal distribution.

2. Wet Hg\textsubscript{t} deposition rates measured at the Florida Atmospheric Mercury Study (FAMS) south Florida sites between 1993 and 1996 are adequate to describe the variance of this distribution.

3. The coefficient of variation for total deposition is similar to values measured for wet Hg\textsubscript{t} deposition rates.

4. Wet Hg(II) deposition, dry Hg(II) deposition, RGM deposition and wet MeHg deposition vary in proportion to wet Hg\textsubscript{t} deposition.

5. Inflowing MeHg and Hg(II) loads vary in proportion to wet Hg\textsubscript{t} deposition.

Data for analysis were restricted to years (within each site) that had $\geq$ 9 months data. The FAMS marine background site Crawl Key was precluded from analysis because its rainfall and deposition patterns were clearly dissimilar from the interior Everglades sites. Three sites had sufficient year-to-year data to compute standard deviations for wet Hg\textsubscript{t} deposition: Everglades National Park (EG), Fakahatchee Strand (FS), and Tamiami Trail (TT) (Table 2). For each site, wet Hgt deposition was summed for each year with greater than 8 months of data, and then divided by the number of months within each year to yield a “normalized” monthly deposition rate for each year. Assuming that annual deposition is lognormally distributed, each normalized monthly deposition rate was then log-transformed, and the standard deviations ($\sigma$) and coefficients of variation (c.v.) across the years were computed for each site. This resulted in an average c.v. of 26.4% for the three sites.

The synthetic total deposition dataset was then constructed based on the estimated annual average total Hg deposition rate of 35.32 $\mu$g/m\textsuperscript{2} yr\textsuperscript{-1} estimated from FAMS data. A normally distributed data set was first produced ($n = 500$) with a mean value of 1.0 and $\sigma$ of 0.264. This data set was then exponentially transformed and scaled to produce a data set with an arithmetic mean value of 35.32 $\mu$g/m\textsuperscript{2} yr\textsuperscript{-1}.

Variations in largemouth bass concentrations were then computed by first running E-MCM with a fixed deposition rate of 35.32 $\mu$g m\textsuperscript{-2} yr\textsuperscript{-1} for 200 years to achieve pseudo steady state conditions. Using the synthesized total deposition data set to simulate annual deposition variability, the model was then run an additional 500 years, with fish mercury concentrations recorded each year.
Table 2. Standard deviation and coefficient of variation of “normalized” average monthly wet Hg deposition rates in South Florida. Data derived from Gill et al., (1999).

<table>
<thead>
<tr>
<th>Site</th>
<th>N (years)</th>
<th>Ln-transformed Average Normalized Monthly Deposition</th>
<th>Standard Deviation</th>
<th>Coefficient of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Everglades National Park</td>
<td>3</td>
<td>0.627</td>
<td>0.085</td>
<td>0.136</td>
</tr>
<tr>
<td>Fakahatchee Strand</td>
<td>4</td>
<td>0.672</td>
<td>0.209</td>
<td>0.311</td>
</tr>
<tr>
<td>Tamiami Trail</td>
<td>2</td>
<td>0.605</td>
<td>0.208</td>
<td>0.344</td>
</tr>
</tbody>
</table>
5. Scenario Development

5.1 Water Conservation Area 3A -15

Water Conservation Area 3A (WCA 3A) in the Everglades is located about 50 km west of Fort Lauderdale (USEPA 1999) and has an area of approximately 1,800 km² (Figure 2). Water Conservation Area 3A-15 was selected because it has elevated mercury concentrations in largemouth bass, and has been extensively studied in terms of mercury cycling.

![Figure 2. Location of WCA 3A-15.](image-url)
Characteristics of WCA 3A-15 are summarized in Table 3.

<table>
<thead>
<tr>
<th>Table 3. Water Conservation Area 3A-15 Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Area modeled</td>
</tr>
<tr>
<td>Surface water depth</td>
</tr>
<tr>
<td>Air Temperatures (monthly means)</td>
</tr>
<tr>
<td>Productivity</td>
</tr>
<tr>
<td>Flow pattern</td>
</tr>
<tr>
<td>Stratification</td>
</tr>
<tr>
<td>Anoxia</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>Surface water pH</td>
</tr>
<tr>
<td>Surface water chloride</td>
</tr>
<tr>
<td>Surface water sulfate</td>
</tr>
<tr>
<td>Sedimentation rate:</td>
</tr>
<tr>
<td>TSS</td>
</tr>
<tr>
<td>Macrophytes</td>
</tr>
<tr>
<td>Fraction of marsh with open water</td>
</tr>
<tr>
<td>Periphyton density</td>
</tr>
<tr>
<td>Top predator fish</td>
</tr>
</tbody>
</table>

5.2 Model Inputs for Long-term Average Conditions

In response to the mercury issue in the Everglades, several agencies initiated research and monitoring programs in the 1990's. These include the ACME studies (1995-present), FAMS (Guentzel et al., 1995; Gill et al., 1999). A USEPA Regional Environmental Monitoring and Assessment (REMAP) project in 1994-1995 at approximately 200 canal stations, in 1995-96 across the entire marsh system with data on water, soil, vegetation and fish at 500 sites, and again in 1999 to explore relationships between certain parameters and determine trends. A study by the South Florida Water Management District sampled 9 surface water control sites over three years (1993-1995) to determine surface water loads to the EPA. The FWC has collected and maintains a long-term database on mercury in largemouth bass and other fishes, overseen by Ted Lange of the Eustis Fisheries Research laboratory. As a result, there are extensive air, water, soils, and biota data on mercury at WCA 3A-15. Input data types and sources for WCA 3A-15 long-term simulations are summarized in Table 4.
<table>
<thead>
<tr>
<th>Data Type</th>
<th>Parameter Estimate and Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrologic Data</strong></td>
<td></td>
</tr>
<tr>
<td>Precipitation</td>
<td>Monthly means from FAMS sites AT, FS, and TT, 1992-1996 (Guentzel, 1997; Gill <em>et al.</em>, 1999)</td>
</tr>
<tr>
<td>Surface water elevations</td>
<td>Direct daily measurements (USGS, Miami Florida Sub District Office)</td>
</tr>
<tr>
<td>Surface Flow</td>
<td>Monthly means computed based on cell size configuration, assumed hydraulic retention time, and precipitation seasonality.</td>
</tr>
<tr>
<td><strong>Physical Data</strong></td>
<td></td>
</tr>
<tr>
<td>Temperature and incident light</td>
<td>Monthly means estimated from NOAA gauge data at West Palm Beach, 10/89 to 9/94 – Hydroqual (1997)</td>
</tr>
<tr>
<td>Soil moisture content</td>
<td>Assumed 100% saturation at all times</td>
</tr>
<tr>
<td><strong>Mercury Loadings</strong></td>
<td></td>
</tr>
<tr>
<td>Dry Hg(II) deposition</td>
<td>Model mean monthly estimates from Keeler <em>et al.</em>, (2000)</td>
</tr>
<tr>
<td>Leaf Area Index</td>
<td>3 (assumed)</td>
</tr>
<tr>
<td>Upstream Surface water concentrations – Hg(II)</td>
<td>Based on average for 3A-33 = 2.14 ng/L (n=6) sampled by USGS</td>
</tr>
<tr>
<td>Upstream Surface water concentrations – MeHg (unfiltered)</td>
<td>Based on average for 3A-33 = 0.27 ng/L (n=6) sampled by USGS</td>
</tr>
<tr>
<td><strong>Surface Water Chemistry</strong></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>ACME data (n = 8) (G. Aiken, USGS unpublished data)</td>
</tr>
<tr>
<td>pH and dissolved oxygen</td>
<td>Limno-Tech (1996)</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>~100 µeq/L (Gilmour <em>et al.</em>, 1998b)</td>
</tr>
<tr>
<td><strong>Hg Concentrations in Marsh</strong></td>
<td></td>
</tr>
<tr>
<td>Surface water Hg$_{\text{total}}$ and MeHg (filtered and unfiltered)</td>
<td>1995-1998 data from ACME (D. Krabbenhoft, unpublished data)</td>
</tr>
<tr>
<td>Elemental Hg (DGM)</td>
<td>20 – 40 pg/L (Krabbenhoft <em>et al.</em>, 1998)</td>
</tr>
<tr>
<td>Sediment Hg</td>
<td>Gilmour <em>et al.</em>, 1998b</td>
</tr>
<tr>
<td>Sediment porewater chemistry</td>
<td>Gilmour <em>et al.</em>, 1998b</td>
</tr>
<tr>
<td><strong>Food Web and Vegetation</strong></td>
<td></td>
</tr>
<tr>
<td>Fish growth (largemouth bass) and Hg concentrations</td>
<td>T. Lange, Florida Fish and Wildlife Conservation Commission (unpublished data)</td>
</tr>
</tbody>
</table>
Table 4. Summary of Data Inputs by Major Data Type Category

<table>
<thead>
<tr>
<th>Mosquitofish</th>
<th>Hg concentrations</th>
<th>D. Krabbenhoft (ACME unpublished data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish diets</td>
<td></td>
<td>Cleckner and Gorski (ACME unpublished data)</td>
</tr>
<tr>
<td>Fish biomasses</td>
<td></td>
<td>Marshwide average = 40 kg/ha (wet) (Jordan, 1996 cited in Ambrose et al., 1997)</td>
</tr>
<tr>
<td>Macrophyte and periphyton biomasses and turnover rates</td>
<td>Ambrose et al., (1997)</td>
<td></td>
</tr>
<tr>
<td>Macrophyte Hg_{tot} concentrations</td>
<td>USGS collected samples, DEP funded analyses by Frontier Geosciences</td>
<td></td>
</tr>
<tr>
<td>Shrimp and zooplankton MeHg concentrations</td>
<td>100 - 200 ng/g (dry) (Cleckner, personal communication)</td>
<td></td>
</tr>
<tr>
<td>Benthos MeHg and Hg_{tot} concentrations</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>Periphyton MeHg and Hg_{tot} concentrations</td>
<td>(Cleckner et al., 1998)</td>
<td></td>
</tr>
</tbody>
</table>

**Particle Dynamics**

| Hg(II) Sorption | Calibrated |
| Sediment accumulation rates | Derived from Delfino et al., (1993 and 1994) |
| Sediment decomposition rates | Derived from litter turnover rates and net mass sedimentation. |

Additional information describing inputs used in simulations is provided below:

### 5.2.1 Cell Configuration:

Unlike a lake, an Everglades marsh does not have defined boundaries. Dimensions for a marsh “cell” must therefore be selected. We chose a 1 km x 1 km cell size to represent an area of homogeneous conditions within WCA 3A-15; this size is consistent with the spatial resolution of other hydrologic and aquatic cycling models such as the Everglades Landscape Model (ELM) (Fitz et al., 1996) currently under development or currently applied to the Everglades. This choice is somewhat arbitrary insofar as there are few data available to define the appropriate dimensions of a homogeneous cell in this system, particularly with respect to mercury dynamics. The choice of cell size also has significant implications for the relative importance of atmospheric, inflowing, and in-situ loadings of total and methylmercury to the cell. For a square cell shape, a smaller the cell area results in a greater importance of inflows relative to other sources. The effects of different inflow rates were tested during the sensitivity analysis and are discussed below.

Four sediment layers were included in the model, similar to Ambrose et al., 1997. The layer thicknesses were 3, 5, 20, and 20 cm respectively, starting with the surficial layer.

### 5.2.2 Water Temperature and Incident Light

Water temperatures were assumed to be the same as air temperatures. Daily data for air temperature and incident light were available from NOAA data collected at West Palm Beach, from October 1989 to September 1994 Hydroqual (1997). From these data, mean monthly temperatures and incident light were estimated as shown in Figures 3 and 4.
Figure 3. Estimated Mean Monthly Water Temperatures for WCA 3A-15. Estimated from Hydroqual (1997).

Figure 4. Mean Monthly Incident Light for WCA 3A-15. Source: Estimated from HydroQual (1997).
5.2.3 Hydrology

Precipitation data were averaged from three sites: FAMS data for Tamiami Trail (TT), Fakahatchee Strand (FS), and Andytown (AT) from 1992-96.

![Bar chart showing estimated mean monthly precipitation for WCA 3A-15. Data from proximal Everglades FAMS sites, 1992-1996. Source: Guentzel, 1997; Gill et al., (1999).](image)

Field data are lacking for the surface flow rates at WCA 3A-15. The following approach was therefore taken to estimate mean monthly surface flows:

- Assume cell size of interest: 1 km x 1 km, 0.5 m average depth for surface water;
- Assume hydraulic residence time: \( \tau_w = 48 \) days (similar to Ambrose et al 1997);
- Compute average annual flow and water velocity through cell based on hydraulic residence time;
- Compile average monthly precipitation from FAMS sites AT, FS, and TT for 1992-1996 (annual average = 142.9 cm);
- Assume seasonality of surface flow mimics precipitation;
- Scale mean monthly flows to match pattern of observed precipitation.

The result of the above exercise is shown in Figure 6. There are distinct dry and wet seasons in the winter and summer/fall respectively. Inflows were assumed equal to outflows.
Water depths were measured directly at WCA 3A-15 by the USGS, Miami Florida Sub District Office. Data for complete calendar years of daily data were available for 1996 and 1997 and were averaged to estimate daily water levels, shown in Figure 7.
5.2.4 External Mercury Loadings

Mean monthly wet Hg(II) deposition rates were estimated using precipitation and mercury concentration data from the FAMS study for three sites from 1992-96: Tamiami Trail (TT), Fakahatchee Strand (FS), and Andytown (AT). Direct empirical measurements of long-term dry deposition rates of RGM and Hg(II) associated with aerosols are not available. Estimates were obtained from local source-receptor modeling conducted as part of the TMDL pilot exercise (Keeler et al., 2000). The deposition rates used in the simulations with current atmospheric Hg(II) deposition are shown in Figures 8 and 9.

Figure 8. Monthly wet Hg(II) deposition rates used in long-term E-MCM calibration. Source: FAMS data (Guentzel, 1997) for Tamiami Trail (TT), Fakahatchee Strand (FS), and Andytown (AT) from 1992-96.

Figure 9. Monthly dry/RGM Hg(II) deposition rates used in long-term E-MCM calibration. Source: Model estimates from Keeler et al., 2000)
Methylmercury concentrations in wet deposition were assumed to equal 0.02 ng/L. Limited data collected during FAMS at several Everglades sites showed that methylmercury concentrations in monthly-integrated bulk deposition samples were equal to or below 0.020 ng/L (Guentzel et al., 1995). Sensitivity analyses demonstrate that the model is insensitive to variations in concentrations at these comparatively low levels. Dry deposition rates for methylmercury were assumed to be negligible.

The USGS ACME study collected surface water concentrations of total and methylmercury at several sites, including 3A-33, a location upstream of 3A-15. The average concentrations of Hg(II) and methylmercury were 2.14 and 0.27 ng L\(^{-1}\) respectively for 8 sampling dates between December 1996 and November 1999. These concentrations were assumed to be the surface inflow concentrations for site 3A-15.

### 5.2.5 Water Chemistry Inputs

Several water quality parameters have been identified as having an impact on concentrations of total and methylmercury in freshwater systems. In particular, dissolved organic carbon, pH and chloride have received much attention. Table 5 shows the values used for these parameters during WCA 3A-15 simulations.

### 5.2.6 Food Web Inputs

The food web in the Everglades is complex. For the purposes of this study, a simplified nine-compartment food web was selected as shown in Figure 10. These compartments are anticipated to be those most involved in the transfer of methylmercury through the food web to our endpoint, largemouth bass.

![Figure 10. Food Web Compartments in E-MCM](image-url)

In the above food web scheme, largemouth bass could eat any combination of food items desired from the other compartments. Bluegill and warmouth were combined as a single omnivorous fish category called sunfish, but could not eat largemouth bass. Mosquitofish (Gambusia) were assumed not to eat other fish, relying instead on plankton, periphyton and benthos. Tables 5 through 7 and
Figure 11 show the diets used in the E-MCM calibration for each of the three fish populations at different ages. These diets were developed based on discussions with ACME researchers investigating the food web on-site (L. Cleckner, P. Garrison, pers. comm.).

<table>
<thead>
<tr>
<th>Dietary Item</th>
<th>Fraction of diet by wet weight for largemouth bass at different ages (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Benthos (Crayfish)</td>
<td>0.26</td>
</tr>
<tr>
<td>Shrimp</td>
<td>0.37</td>
</tr>
<tr>
<td>Fish</td>
<td>0.37</td>
</tr>
<tr>
<td>Total</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5. Preferred dietary pattern of largemouth bass used for final calibration

Figure 11. Fractions of largemouth bass diet (by weight) represented by *Gambusia* and Sunfish in final calibration (Source: T. Lange unpublished data).
### Dietary Item Fraction of diet by wet weight for sunfish at different ages (years)

<table>
<thead>
<tr>
<th>Dietary item</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoplankton</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Periphyton</td>
<td>0.15</td>
<td>0.20</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Invertebrates</td>
<td>0.30</td>
<td>0.15</td>
<td>0.20</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Benthos</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Shrimp</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Gambusia</td>
<td>0.10</td>
<td>0.25</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6. Dietary pattern of sunfish used for final calibration.

### Dietary Item Fraction of diet on wet weight basis

<table>
<thead>
<tr>
<th>Dietary Item</th>
<th>Fraction of diet on wet weight basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Periphyton</td>
<td>0.25</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>0.40</td>
</tr>
<tr>
<td>Benthos</td>
<td>0.25</td>
</tr>
<tr>
<td>Shrimp</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 7. Dietary pattern of mosquitofish (Gambusia) used for final calibration.

Fish growth rates can also significantly affect mercury concentrations. Growth data provided by the Florida Fish and Wildlife Conservation Commission (T. Lange, unpublished data) were used for largemouth bass as shown in Figure 12.

![Figure 12](image-url)  

Figure 12. Observed and Calibrated Growth Rates for Largemouth Bass. Source for observations: T. Lange, unpublished data. Largemouth bass data derived from 1996 – 1998 collections caught from the wild at WCA 3a-15 study site.
The relationship between fish length and weight is also important in E-MCM since there is a preferred prey size range for piscivory, based on fish lengths. Data provided by the Florida Fish and Wildlife Conservation Commission (T. Lange, unpublished data) were used for largemouth bass as shown in Figure 13. Largemouth bass were assumed to prefer prey ranging from 15 to 40% of their own length. On occasions where sunfish were piscivorous, they were assumed to prefer fish ranging from 5 to 33% of their own length. These preferences resulted in largemouth bass and sunfish fish consumption patterns shown earlier in Tables 5 and 6.

![Figure 13. Length versus Weight relationship for Largemouth Bass at WCA 3A-15.](image)

5.2.7 Particle Dynamics

Growth and turnover of vegetation such as sawgrass, cattails and lilies, settling, decomposition and burial of particles play an important role in mercury cycling in the Everglades (Ambrose et al., 1997, this study). Table 8 shows mean annual values associated with E-MCM inputs for vegetation particle fluxes in the water column.
Table 8. Vegetation-related particle fluxes in the water column: E-MCM inputs

Figure 14 shows the particle budget calibrated for the surficial sediment layer (0-3 cm). The mean annual bulk burial velocity at the bottom of the surficial sediment layer (3 cm) was 2.87 mm yr⁻¹.

![Calibrated particle fluxes for surficial sediments.](image-url)
6. Results

6.1 Model Calibration to Current Loadings

The calibration of long-term average concentrations at WCA 3A-15 to the estimated current annual atmospheric Hg(II) deposition rate of 35.32 µg m\(^{-2}\) yr\(^{-1}\) (wet and dry deposition combined) are shown in Table 9 and Figures 15 through 20. Mercury observations in water and sediments are based on sampling programs from 1995-98 by the ACME research team (e.g. Krabbenhoft et al., 1998, Gilmour et al., 1998a, Hurley et al., 1998, Cleckner et al., 1998). Fish mercury observations by the Florida Fish and Wildlife Conservation Commission (T. Lange unpublished data) spanned a period from December 1996 through November 1998. Predicted long-term average concentrations were developed by running E-MCM for one hundred years with repeating annual cycles of site conditions and mercury loadings, to effectively reach a stable situation. The model was then run for one more year saving results on a weekly basis.

Table 9 shows observed and predicted mean concentrations for total mercury and methylmercury in surface waters and sediments at WCA 3A-15. Predicted concentrations of total and methylmercury in surface waters and sediments are within observed ranges for the most part (Figures 15 and 16).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Predicted Mean</th>
<th>Observed Mean</th>
<th>Observed Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfiltered total Hg in water</td>
<td>ng L(^{-1})</td>
<td>2.23</td>
<td>1.94</td>
<td>Krabbenhoft et al., (unpublished data)</td>
</tr>
<tr>
<td>Unfiltered MeHg in water</td>
<td>ng L(^{-1})</td>
<td>0.59</td>
<td>0.50</td>
<td>Krabbenhoft et al., (unpublished data)</td>
</tr>
<tr>
<td>Total Hg on sediment solids</td>
<td>ug g(^{-1}) dry</td>
<td>0.14</td>
<td>0.114</td>
<td>Gilmour et al., (1998b)</td>
</tr>
<tr>
<td>MeHg on sediment solids</td>
<td>ug g(^{-1}) dry</td>
<td>0.003</td>
<td>0.004</td>
<td>Gilmour et al., (1998b)</td>
</tr>
</tbody>
</table>
Figure 15. Predicted long-term concentrations of total mercury in WCA 3A-15 surface waters for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m2/yr. Observations: Krabbenhoft et al., (unpublished data)

Figure 16. Predicted long-term methylmercury concentrations in WCA 3A-15 surface waters for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m2/yr. Observations: Krabbenhoft et al., (unpublished data)
Figure 17. Predicted long-term Hgt concentrations in WCA 3A-15 surface sediments for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m²/yr. Observations: Gilmour et al., 1998b

Figure 18. Predicted long-term MeHg concentrations in WCA 3A-15 surface sediments for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m²/yr. Observations: Gilmour et al., 1998b

Predicted mercury concentrations for Gambusia, sunfish and largemouth bass were also consistent in magnitude with observations. Predicted Gambusia mercury concentrations were 0.13 and 0.23 µg/g
wet whole body at age 3 months and 6 months respectively. Mean values reported for 3 sampling periods in 1997 to 1998 ranged from 0.057 to 0.166 µg/g wet whole body (D. Krabbenhoft, unpublished data). Predicted and observed mercury concentrations for warmouth, bluegill and largemouth bass are shown in Figures 19 and 20. The model has three fish populations: non-piscivores, omnivores and piscivores. Bluegill and warmouth were treated as a single omnivorous fish type, referred to as sunfish. While the data showed significant variability, the model calibration predicted sunfish concentrations well within the range of observations (Figure 19). Mercury concentrations in largemouth bass were also reasonably predicted (Figure 20).

![Figure 19. Predicted long-term methylmercury concentrations in sunfish in WCA 3A-15 for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m2/yr. Observations: Lange et al., unpublished data](image)

Figure 19. Predicted long-term methylmercury concentrations in sunfish in WCA 3A-15 for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m2/yr. Observations: Lange et al., unpublished data
Figure 20. Predicted long-term methylmercury concentrations in largemouth bass in WCA 3A-15 for calibration with current atmospheric Hg(II) deposition = 35.32 µg/m²/yr. Observations: Lange et al., unpublished data

Predicted long-term average annual Hg(II) and MeHg fluxes after 100 years of simulation are shown in Figures 21 and 22 respectively. Hg concentrations in the deeper two sediment layers are still adjusting after 100 years of simulation and fluxes in these compartments should not be taken as steady state. Atmospheric deposition is the dominant source of Hg(II) to the marsh, but to some extent this result depends on the cell size and configuration chosen (see discussion of results).

The dominant predicted source for methylmercury is in-situ production (7.6 µg m⁻² yr⁻¹, 87% of total MeHg load to the marsh), which in our simulations for WCA 3A-15 was calibrated to occur in the sediments.

Elemental mercury was produced in simulations via photoreduction of Hg(II), photodegradation of methylmercury, and to a minor extent by reduction within macrophyte roots and biological demethylation. We assumed the primary product of biological demethylation was Hg(II) (95%). Volatilization of elemental mercury from the water surface was predicted at an annual rate of 6.9 µg m⁻² yr⁻¹, while transpiration of elemental mercury produced by reduction of Hg(II) with macrophytes was only 0.12 µg m⁻² yr⁻¹.
Figure 21. Predicted long-term annual Hg(II) fluxes in $\mu g m^{-2} yr^{-1}$ for calibration to annual atmospheric Hg(II) deposition rate of 35.32 $\mu g m^{-2} yr^{-1}$

Figure 22. Predicted long-term annual MeHg fluxes $\mu g m^{-2} yr^{-1}$ for calibration to annual atmospheric Hg(II) deposition rate of 35.32 $\mu g m^{-2} yr^{-1}$
6.2 Long-term Hg(II) Deposition – Fish Hg Response Curve

A fundamental question to examine in this pilot TMDL study was the relationship between atmospheric Hg(II) deposition and long-term fish mercury concentrations. Once the model was calibrated to the current atmospheric Hg(II) deposition estimate of \(35.32 \mu g \text{ m}^{-2} \text{ yr}^{-1}\), simulations were also carried out with load reductions of 25, 50, 75 and 85% of current levels. In these simulations to predict long-term fish Hg concentration, atmospheric methylmercury deposition, inflowing Hg(II) loads, and inflowing MeHg loads were adjusted in proportion to Hg(II) deposition. Predicted fish mercury concentrations were compared after each simulation had run 200 years using repeating annual cycles of site conditions and mercury deposition.

Figure 23 shows the predicted long-term relationship between atmospheric mercury deposition and mercury concentrations in age 3 largemouth bass in WCA 3A-15.

![Graph showing the predicted Hg concentrations in age 3 largemouth bass as a function of different long-term constant annual rates of wet and dry Hg(II) deposition. Predictions are based on calibration to current loading of 35.32 \(\mu g \text{ m}^{-2} \text{ yr}^{-1}\).](image)

Figure 23. Predicted Hg concentrations in age 3 largemouth bass as a function of different long-term constant annual rates of wet and dry Hg(II) deposition. Predictions are based on calibration to current loading of \(35.32 \mu g \text{ m}^{-2} \text{ yr}^{-1}\).

Figure 24 is based on the same modeling results as Figure 23, but presents information as fractions of current fish mercury concentrations and atmospheric Hg(II) deposition. A linear relationship is predicted, but the slope is not 1.0 and the intercept in both Figures 23 and 24 is non-zero. This indicates that there is not an exact correspondence between relative reductions in Hg(II) loading and fish Hg response. Furthermore, the figure suggests that in the absence of any Hg(II) loading from any sources, there will still be some mercury accumulating in largemouth bass. This latter consequence can occur only if sources other than atmospheric inputs of Hg(II) become important. In our simulations, macrophyte roots mobilized Hg(II) and methylmercury from all sediment layers to
differing degrees, including the deeper layers (layers 2-4) which extended down as much as 48 cm from the surface. We chose to look at results after 200 years of simulation, at which time the deep layers had not fully adjusted to changes in mercury loadings in the system, and continued to supply Hg(II) and methylmercury to the overlying system. If we had carried the simulations out for very long periods, e.g., thousands of years, it is expected that the deeper layers would eventually adjust to overlying loads, and the predicted fish mercury concentrations would be closer to a direct proportional response to loadings. While this Hg(II) and methylmercury “source” from deep macrophyte roots is secondary under current conditions, it takes on greater importance when other methylmercury sources are heavily reduced.

![Graph of predicted fraction of current Hg concentration in age 3 largemouth bass as a function of long-term reductions in Hg(II) deposition (wet and dry). Predictions are based on calibration to current loading of 35.32 µg m⁻¹ yr⁻¹.]

**Figure 24.** Predicted fraction of current Hg concentration in age 3 largemouth bass as a function of long-term reductions in Hg(II) deposition (wet and dry). Predictions are based on calibration to current loading of 35.32 µg m⁻¹ yr⁻¹.

### 6.3 Timing of the System Response

A second fundamental question of the pilot Hg TMDL exercise was: How fast will fish mercury concentrations change following reductions in Hg loading? We examined this question by running simulations for 200 years with current loads to approximate steady state and then reducing atmospheric deposition as a step function and continuing the simulation for an additional 200 years. Atmospheric methylmercury deposition was reduced in proportion to Hg(II) deposition. Inflowing Hg(II) and methylmercury concentrations were reduced, but not as instantaneous step functions following cuts to atmospheric deposition. Instead, a lag time was introduced for inflows to reflect the time expected for upstream areas to respond to load reductions. To estimate this lag effect, the model
was first run with all external Hg(II) and MeHg loads reduced in a step function manner along with atmospheric deposition. The temporal responses of Hg(II) and MeHg in the 3A-15 model cell were then used as estimates of the response dynamics for inflows responding to reduced atmospheric deposition.

The results for load reductions of 25, 50, 75 and 85% from the current deposition estimate of 35.32 $\mu$g m$^{-1}$ yr$^{-1}$ are shown in Figure 25.

![Figure 25. Predicted dynamic response of Hg concentrations in largemouth bass in WCA 3A-15 following different reductions in Hg(II) deposition. Predictions are based on calibration to current loading of 35.32 $\mu$g m$^{-1}$ yr$^{-1}$.](image)

We also wanted to test whether the rate at which fish mercury concentrations approached a new steady state situation following a load reduction depended on the magnitude of the load change. Figure 26 shows that the number of years for the system to approach a new steady state is effectively independent of the actual magnitude of the change. For example, the numbers of years predicted to achieve 50% of the ultimate response in fish Hg is approximately 8-9 years, for all load reduction scenarios tested with the base calibration with atmospheric Hg(II) deposition = 35.32 $\mu$g m$^{-2}$ yr$^{-1}$. 

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Figure 26. Comparison of the rate at which age 3 largemouth bass concentrations approach steady state following different reductions in Hg(II) deposition (simulations all based on calibration with current Hg(II) deposition = 35.32 µg m⁻² yr⁻¹)

6.4 Sensitivity Analysis

It is important to understand which variables most affect predicted fish mercury concentrations in E-MCM at WCA 3A-15. Two types of sensitivity analyses were conducted to address this question. The first approach was to conduct a traditional type of analysis where each parameter is varied by the same relative amount, without regard to whether this value is actually likely to occur or appropriate for the system of interest. The second approach considered the range of actual or (if such information is not available) likely values a parameter can assume. These limits then are used to help define the bounds of uncertainty in model response related to a given variable. This latter approach is essentially a "minimum-maximum" analysis that examines sensitivity in the context of likely or actual parameter distributional ranges.

6.4.1 Traditional Sensitivity Analysis Results

Simulations were run varying inputs in isolation by a given amount, for example plus and minus 50%. In cases where a 50% change did not make physical sense, a lesser change was made, e.g. 10% or 25%. In addition, there were some inputs such as the fraction of fish in the diet that did not make sense to change in isolation. The following simultaneous changes were simulated:

- Fish growth rates and spawning sizes for all fish species were changed by the same percentage simultaneously.
The areal coverage of the three macrophyte species, periphyton coverage and quantities of suspended solids and detrital material in the water column were varied simultaneously. It is expected that a change in vegetation cover would affect the amount of settling material. Burial rates were affected by these changes, since burial is calculated on the basis of sources and sinks of particulate matter to the sediments.

When the diet of largemouth bass was altered to increase or decrease the fraction of fish in the diet, it was necessary to also alter the fractions of the diet represented by other food items. The fractions added or subtracted from fish consumption were distributed evenly amongst other food items.

Surface inflow and outflow rates (Qin and Qout) were varied simultaneously since it was assumed these rates were equal in simulations.

When atmospheric Hg(II) deposition was altered, we also altered surface inflowing Hg(II) and MeHg loads proportionately. Atmospheric methylmercury deposition was not altered.

To provide a common basis for comparing the effects of changes to inputs on fish Hg, results are presented as absolute value of ratio of the percent change in fish Hg divided by the percent change in the input:

$\left| \frac{\% \text{ change in fish Hg}}{\% \text{ change in input value}} \right|$

Mercury in age 3 largemouth bass was used as the end point of interest. Results of the traditional sensitivity analysis are shown in Figure 27. Predicted mercury concentrations in age 3 largemouth bass were most sensitive to factors associated with particle and vegetation fluxes, Hg(II) loading, methylation rates, and factors affecting fish diets and growth.
Figure 27. Predicted sensitivity of age 3 largemouth bass mercury concentrations in WCA 3A-15 to changes in various input values. Results are based on calibration with current atmospheric Hg(II) deposition = 35.32 µg m⁻² yr⁻¹

6.4.2 Minimum-Maximum Sensitivity Analysis Results

Results from the “minimum-maximum” sensitivity analysis are shown in Figure 28, while parameter descriptions, minima and maxima are shown in Table 10. Most of the parameters included in the analysis were evaluated for only one minimum and maximum value without perturbing any other variables. There are, however, two parameters that were evaluated simultaneously: fish maximum weight and RA, which is a fish respiration multiplier. RA and fish maximum weight are matrix-type inputs and it was both convenient programmatically and appropriate to vary all three trophic levels of fish (herbivorous, omnivorous, and piscivorous fish) simultaneously at their minima and maxima (see Table 11). The appropriateness owes to the fact that all three fish types share similar environmental conditions and would be dependent on the same driving forces. For example, a particular environmental regime may cause all three fish types to expend more energy hunting for food and have a higher respiration level. This in turn would produce higher tissue mercury concentrations for each trophic level.
Figure 28. Calculated SI values for different E-MCM model parameters analyzed using the "minimum-maximum" sensitivity analysis approach.

Similarly, minimum and maximum fish weights were varied simultaneously for all species. This follows because, for example, a nutrient-rich environment implies greater food availability and would likely result in higher maximum weights in all three fish species.
<table>
<thead>
<tr>
<th>Ranking/Parameter Name</th>
<th>Units</th>
<th>Description</th>
<th>Sensitivity Index</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methylation Efficiency</td>
<td>g MeHg/g TOC labile</td>
<td>Methylating efficiency of microbes, per unit of carbon flux and unit available Hg(II) concentration. If you wish to calibrate the methylation rate, use this input. To adjust the temperature sensitivity of methylation, see Q10meth.</td>
<td>0.864135</td>
<td>0.008575</td>
<td>0.1715</td>
</tr>
<tr>
<td>2-MeHg photodegradation</td>
<td>ng/m3/day</td>
<td>MeHg photodegradation) rate constant at waterbody surface per unit of surface light intensity. There is ongoing research into the wavelengths associated with this process. See also Ke (light extinction) in the physical input category.</td>
<td>0.821421</td>
<td>0.00006</td>
<td>0.006</td>
</tr>
<tr>
<td>3-Demethylation efficiency</td>
<td>g ElemHg/g TOC lab</td>
<td>Demethylating efficiency of microbes, per unit of carbon flux and unit available MeHg concentration. If you wish to calibrate the demethylation rate, use this input. Demethylation does not depend on temperature in this version of the model.</td>
<td>0.734534</td>
<td>0.009</td>
<td>0.18</td>
</tr>
<tr>
<td>4-Detritus conc in water</td>
<td>mg/L</td>
<td>Bulk concentration of detritus in water. This is a time series input.</td>
<td>0.627215</td>
<td>7.56</td>
<td>15</td>
</tr>
<tr>
<td>5-Surface outflow</td>
<td>m3/day</td>
<td>Flow rate for surface outflow from epilimnion This is a time-series input.</td>
<td>0.41634</td>
<td>0.35</td>
<td>1.4</td>
</tr>
<tr>
<td>6-Macrophyte fraction</td>
<td>fraction</td>
<td>Fraction of total area covered by macrophyte species #1</td>
<td>0.413694</td>
<td>0.01</td>
<td>0.77</td>
</tr>
<tr>
<td>7-Partitioning coefficient MeHg Benthos</td>
<td>g dry/g wet</td>
<td>Ratio of MeHg concentrations in benthos and sediments = (ug MeHg/g wet benthos) / (ug MeHg/g sed)</td>
<td>0.411652</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>8-Fish respiration multiplier</td>
<td>none</td>
<td>RA from Wisconsin Respiration equation, from Hewett and Johnson 1992. Increases or decreases fish respiration multiplicatively</td>
<td>0.388929</td>
<td>See Appendix 1</td>
<td>See Appendix 1</td>
</tr>
<tr>
<td>9-Precipitation</td>
<td>m/d</td>
<td>Daily precipitation equivalent in meters of rainfall per day.</td>
<td>0.371396</td>
<td>0.35</td>
<td>1.4</td>
</tr>
<tr>
<td>10-Partitioning MeHg Detritus</td>
<td>m3/g dry part</td>
<td>MeHg partitioning between detritus particles and dissolved inorganic Hg(II) = [ug Hg(II) /g dry seston]/[ug dissolved inorganic MeHg/m3].</td>
<td>0.367028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11-Partitioning MeHg Shrimp</td>
<td>g dry/wet</td>
<td>Ratio of MeHg concentrations in shrimp and detritus = (ug MeHg/g wet shrimp) / (ug MeHg/g detritus)</td>
<td>0.364331</td>
<td>6</td>
<td>24</td>
</tr>
</tbody>
</table>
Table 10. Sensitivity indexes, descriptions, minima and maxima for parameters used in analysis (see Table 11 for minima and maxima for matrix parameters).

<table>
<thead>
<tr>
<th>Ranking/Parameter Name</th>
<th>Units</th>
<th>Description</th>
<th>Sensitivity Index</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-Hg(II) photoreduction</td>
<td>ng/m3/day</td>
<td>Hg(II) photoreduction rate constant at waterbody surface per unit of surface light intensity. There is ongoing research into the wavelengths associated with this process. See also Ke (light extinction) in the physical input category.</td>
<td>0.363948</td>
<td>0.0004</td>
<td>0.04</td>
</tr>
<tr>
<td>13-DOC in epilimnion</td>
<td>mg/L</td>
<td>Dissolved organic carbon in the epilimnion. This parameter is used in calculations of mercury complexation and bioavailability for methylation and demethylation in the epilimnion.</td>
<td>0.29317</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>14-Frac detritus decompose</td>
<td>fraction</td>
<td>Fraction of detrital particles that decompose upon settling without being incorporated into the sediments</td>
<td>0.27106</td>
<td>0.05</td>
<td>0.2</td>
</tr>
<tr>
<td>15-DOC in porewater</td>
<td>mg/L</td>
<td>Dissolved Organic Carbon in the porewater of sediment zone 1. DOC is used in calculations of mercury complexation and bioavailability for uptake by the food web and bioavailability for mercury methylation and demethylation.</td>
<td>0.212892</td>
<td>37.5</td>
<td>81.25</td>
</tr>
<tr>
<td>16-Zoo Bioconcentration</td>
<td>dimensionless</td>
<td>Bioconcentration factor for MeHg in zooplankton. The model uses this to estimate zooplankton MeHg on the basis of phytoplankton MeHg.</td>
<td>0.201915</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>17-Inflow MeHg conc</td>
<td>ng/L unfilt</td>
<td>Inflow MeHg concentration. This includes dissolved, SS, and planktonic MeHg (i.e. all MeHg in the water column of the inflow). This time-series input is treated as a step function.</td>
<td>0.19325</td>
<td>0.05</td>
<td>0.48</td>
</tr>
<tr>
<td>18-Inflow Hg(II) conc</td>
<td>ng/L unfilt</td>
<td>Inflow Hg(II) concentration. This includes dissolved, SS, and planktonic Hg(II), and solid HgS in the inflow. (i.e. all Hg(II) in the water column of the inflow).</td>
<td>0.159199</td>
<td>0.84</td>
<td>3.44</td>
</tr>
<tr>
<td>19-Chloride in epilimnion</td>
<td>mg/L</td>
<td>Concentration of chloride in the epilimnion. This parameter is used in thermodynamic speciation calculations</td>
<td>0.150649</td>
<td>14</td>
<td>56</td>
</tr>
<tr>
<td>20-SO4 in sediment</td>
<td>ueq/L</td>
<td>Sulfate in porewater of sediment zone 1. sulfate is optionally used in estimates of methylation rates. See also the input called KSO4 in the input category called Hg Rate Constants.</td>
<td>0.142424</td>
<td>43</td>
<td>172</td>
</tr>
<tr>
<td>21-Fish max weight</td>
<td>grams</td>
<td>Maximum weight of fish for weight equation. Note that this is just used in an equation. The fish often never actually gets to this ultimate weight. A fish cannot exceed this weight.</td>
<td>0.124899</td>
<td>See Table 11</td>
<td>See Table 11</td>
</tr>
<tr>
<td>22-Precipitation Hg(II)</td>
<td>ng/L</td>
<td>Concentration of Hg(II) in precipitation. Dry deposition of MeHg.</td>
<td>0.058535</td>
<td>0.926</td>
<td>1.074</td>
</tr>
<tr>
<td>Ranking/Parameter Name</td>
<td>Units</td>
<td>Description</td>
<td>Sensitivity Index</td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------</td>
<td>------------------------------------------------------------------------------</td>
<td>-------------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>23-Partitioning Hg(II) Detritus</td>
<td>ug Hg(II)/g dry seston/ug dissolved inorganic Hg(II)/m3.</td>
<td>0.049309</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24-Macrophyte transpiration g H2O/g biomass/day</td>
<td>Transpiration rate for macrophyte species #1 (g H2O/g dry Biomass/day)</td>
<td>0.03067</td>
<td>7</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>25-RGM atmosphere pg Hg/m3</td>
<td>RGM (reactive gaseous mercury) in the atmosphere. (pg Hg/m3)</td>
<td>0.029178</td>
<td>0.926</td>
<td>1.074</td>
<td></td>
</tr>
<tr>
<td>26-Mass trans coeff water to Sed m/day Epilimnion/sediment MTC (Mass transfer coefficient). (e.g. 0.01-0.1 m/day). This is used to calculate diffusion across the sediment/water column boundary in the epilimnion. Assumed to be the same for Hg(II) and MeHg.</td>
<td>0.027242</td>
<td>0.015</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27-Water depth m</td>
<td>Elevation is the distances in metres from the deepest point in the waterbody to the surface (e.g. 0 metres is the bottom). Input is a time series.</td>
<td>0.001655</td>
<td>0.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>28-MeHgWetDeposit ng/L Concentration of MeHg in precipitation. Dry deposition of MeHg.</td>
<td>0.000549</td>
<td>0.01852</td>
<td>0.02144</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29-Partitioning MeHg Solid m3/g dry sed</td>
<td>Hg(II) partitioning between non-living seston and dissolved inorganic Hg(II) = [ug Hg(II)/g dry seston]/[ug dissolved inorganic Hg(II)/m3].</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variable Name</td>
<td>Units</td>
<td>Description</td>
<td>Trophic Type</td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
<td>-------------</td>
<td>--------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Fish respiration multiplier</td>
<td>RA from Wisconsin Respiration equation</td>
<td>Piscivore</td>
<td>2.23E-03</td>
<td>3.35E-03</td>
<td></td>
</tr>
<tr>
<td>Fish respiration multiplier</td>
<td>RA from Wisconsin Respiration equation</td>
<td>Omnivore</td>
<td>1.23E-02</td>
<td>1.85E-02</td>
<td></td>
</tr>
<tr>
<td>Fish respiration multiplier</td>
<td>RA from Wisconsin Respiration equation</td>
<td>Non-Piscivore</td>
<td>8.64E-03</td>
<td>1.30E-02</td>
<td></td>
</tr>
<tr>
<td>Fish maximum weight</td>
<td>grams</td>
<td>Maximum weight of fish for weight equation. Note that this is just used in an equation. The fish often never actually gets to this ultimate weight. A fish can not exceed this weight.</td>
<td>Piscivore</td>
<td>2.00E+03</td>
<td>3.69E+03</td>
</tr>
<tr>
<td>Fish maximum weight</td>
<td>grams</td>
<td></td>
<td>Omnivore</td>
<td>1.50E+02</td>
<td>2.10E+02</td>
</tr>
<tr>
<td>Fish maximum weight</td>
<td>grams</td>
<td></td>
<td>Non-Piscivore</td>
<td>1.50E+00</td>
<td>2.50E+00</td>
</tr>
</tbody>
</table>

There are two key points to highlight in terms of the interpretation of the results of this phase of the sensitivity analysis:

1. The “minimum-maximum” analysis provides an indication of how sensitive model predictions are to uncertainties associated with various input parameters. It does not necessarily indicate which input parameters can have the most impact on predictions. For example, the concentration of Hg(II) in wet deposition can have a large impact on predicted fish Hg levels, particularly in systems such as 3A-15 where the primary input of Hg is atmospheric deposition. In other words, the model predictions are influenced strongly by changes in the magnitude of this parameter. Since, however, the concentration of Hg(II) in wet deposition is well-quantified and does not appear to vary substantially from year-to-year (i.e., there is little uncertainty in the parameter), our analysis indicates that the model predictions are comparatively insensitive to the inherent uncertainty in this parameter. Thus, the approach used in this study provides insight into where future efforts to reduce input parameter uncertainties will produce the greatest benefit towards reducing uncertainty in model predictions.

2. The sensitivity index does not address model parameter interdependencies – that is, each parameter is treated as a separate entity and is evaluated at its minimum and maximum value. In reality, groups of dependent parameters will move in concert with each other. For example, one input, DOC, affects light extinction, a second input. The current approach does not address these types of interdependent relationships between site conditions. Another example considers inputs involved in overall reactions comprising both forward and backward reaction paths – methylation/demethylation and photochemical oxidation/reduction in surface waters are two such examples. Different combinations of these inputs can result in the same net result – e.g., a combination of two very fast forward and backward reaction rate constants can be selected to produce precisely the same rate of net production as two very slow forward and backward rate constants. Until our understanding of the true unidirectional or gross (i.e., forward and backward,
rather than net) reaction rates is improved, the model sensitivity to these types of paired inputs is subject to the rates assumed in the model.

All parameters in Figure 28 and Table 10 are numerically ranked. The numbers in the following text refer to these codes. For the most part the parameters can be divided into four main categories:

1. Rate constants involving the production or destruction of methylmercury;
2. Inputs related to particle/macrophyte budgets and associated Hg fluxes;
3. Hydrology; and
4. Fish mercury uptake.

Parameter sensitivities for the four categories are discussed below:

**Rate Constants Involving The Production Or Destruction Of Methylmercury**

Overall, the first three most sensitive model parameters are related to the production or degradation of methylmercury within the system. Predicted largemouth bass MeHg levels at WCA 3A-15 are sensitive to the uncertainty associated with rate constants used for bacterial methylation and demethylation because: (1) in situ methylation is predicted to be a major source of MeHg for fish at WCA 3A-15; and (2) there is considerable uncertainty regarding true rates. This result is not surprising, and is consistent with previous assessments of R&D needs to better understand factors affecting fish mercury concentrations. We chose minimum and maximum values that were 0.5 and 10.0 times the mean values for both methylation and demethylation rate constants.

Uncertainty in rates of photochemical reduction of Hg(II) also emerged as important in the analysis. This was to some extent affected by the relatively wide range between minimum and maximum values tested (0.1 and 10.0 times the mean rate constant respectively). The mean calibrated rate of photoreduction had a significant but not dominant effect on fish Hg levels, converting about 10% of the external Hg(II) load to the marsh to elemental mercury, which then left the system rapidly through volatilization. The mean value was calibrated to provide reasonable overall volatilization rates when combined with MeHg photodegradation. Since the true rate for either process is unknown, we assumed equal contributions of elemental mercury production between these two processes. Furthermore, we assumed no photo-oxidation of elemental Hg back to Hg(II), and our calibrated Hg(II) photo-reduction rate is really a better measure of net reduction/oxidation than gross Hg(II) reduction. All of these uncertainties associated with Hg(II) reduction/oxidation (and MeHg photodegradation) should receive further attention.

**Inputs related to particle budgets and associated Hg fluxes**

Fluxes associated with particles are predicted to be very important at WCA 3A-15 for both Hg(II) and MeHg cycling. These fluxes include macrophyte and periphyton production, turnover, settling, and decomposition, all of which affect the ultimate rate of sediment accretion. The current minimum/maximum analysis indicates that uncertainties associated with particle fluxes can significantly affect predicted fish mercury concentrations (see Figure 28): e.g., (4) detritus concentration in water; (6) fraction of marsh covered by macrophytes; (10) MeHg partitioning on detritus; (14) mineralization of detritus at sediment/water interface. There is a need to better constrain/estimate the production and fate of particulate matter via macrophytes and periphyton for the purposes of better constraining E-MCM predictions.

**Hydrology**

Uncertainties regarding hydrologic inputs had a moderate effect on predicted fish mercury concentrations (e.g. Figure 28): (5) Surface water outflow; (9) Rainfall rate; (17) and (18) Inflowing MeHg and Hg(II) concentrations, respectively). Note that because these parameters were altered
individually, the full impacts of hydrological changes and uncertainties are likely not reflected in this analysis. For example, we expect that changes in hydrology could simultaneously affect inflowing Hg, outflowing Hg, macrophyte production or type of assemblage, trophic structure, fish diets, fish growth, and in situ methylation via changes in water chemistry or the effects of dry/wet cycles on sediment oxidation and release of mercury or constituents affecting methylation such as sulfate. A Monte Carlo approach with appropriate dependencies between inputs might better estimate the overall effects of hydrology on fish mercury concentrations, although setting up these dependencies would not be a simple task. Finally, the effects of flow rates are directly impacted by the assumed size and resulting hydraulic retention time of the marsh cell modeled. The estimated hydraulic residence time at 3A-15 was 48 days. Uncertainties associated with flow rates would have more importance at sites such as F1 and U3 with faster water throughput.

Fish Mercury Uptake
Uncertainties associated with model inputs affecting fish mercury uptake moderately affected predicted fish mercury concentrations (Figure 28): (7) MeHg partitioning to benthos; (8) fish respiration rate; (11) MeHg BCF in shrimp; (16) MeHg BCF for zooplankton). This is not to say that factors affecting uptake of MeHg by fish are unimportant; rather the analysis indicated that predicted fish Hg was only moderately sensitive to the limited uncertainty we assigned to these inputs. BCF’s for shrimp and zooplankton were varied from 0.5 to 2.0 times the mean value, while the BCF for MeHg in benthos was varied from 0.25 to 1.6 times the mean value, and fish respiration rates were varied from 0.8 to 1.2 times the mean (all three fish types varied simultaneously).

Conclusions
1. Predicted concentrations of mercury in age 3 largemouth bass at WCA 3A-15 are most sensitive to uncertainties associated with inputs related to the in situ production and destruction of methylmercury. This is because: (1) in situ methylation is predicted to be a major source of MeHg for fish at WCA 3A-15; and (2) there is considerable uncertainty regarding true rates. This result consistent with previous assessments of R&D needs to better understand factors affecting fish mercury concentrations in Everglades marshes, and aquatic systems in general.
2. Uncertainties associated with particle-based mercury fluxes also significantly affected predicted fish mercury levels. There is a need to better constrain/estimate the production and fate of particulate matter via macrophytes and periphyton for the purposes of better constraining E-MCM predictions.
3. Uncertainties regarding hydrologic inputs had a moderate effect on predicted fish mercury concentrations. Because these parameters were altered individually, this result was anticipated and the full impacts of hydrological changes and uncertainties are likely not reflected in this analysis.
4. The sensitivity index approach, as currently used, treated only one parameter at a time. An improvement to this approach would be to simultaneously vary groups of interdependent inputs to their minima or maxima (positive or negatively correlated). Such an effort to modify the current model setup structure expectedly would be only moderate.

6.5 Year-to-Year Variability in Atmospheric Hg(II) Deposition

To address year-to-year variations in atmospheric Hg(II) deposition, we synthesized a set of 500 annual Hg(II) deposition rates as discussed in Section 4.5. A simulation was run for 200 years with constant Hg deposition rates, and then continued for an additional 500 years with year-to-year variations in Hg loadings based on observed variations in wet Hg(II) deposition rates. By assuming that the coefficient of variation of total deposition is similar to the measured coefficient of variation for wet deposition, a synthesized data set for total deposition that varies each year about a mean value
of 35.32 µg m\(^{-2}\) yr\(^{-1}\) was derived. We simultaneously varied wet Hg(II) deposition, dry Hg(II) deposition, RGM deposition and wet MeHg deposition as step functions from year to year. Figure 29 shows the distribution of annual deposition rates used in the simulation. A description of the development of this lognormal distribution is provided in Section 4.5. We also varied inflowing MeHg loads and inflowing Hg(II) loads in proportion to the changes in atmospheric deposition.

![Figure 29](image)

**Figure 29. Distribution of annual atmospheric deposition rates used for 500 year simulation. Distribution synthesized from FAMS data as described in Section 4.5.**

The results of the 500 year simulation are shown in Figure 30. Concentrations in age 3 largemouth bass varied from a low of 1.67 to a high of 1.97 µg g\(^{-1}\) wet muscle. The mean concentration for the distribution was 1.81 µg g\(^{-1}\) wet muscle.
Figure 30. Input annual atmospheric Hg(II) deposition rates and predicted Hg concentrations in age 3 largemouth bass for 500 year simulation.

Figure 31 shows the distribution of predicted fish mercury concentrations for the 500-year simulation. Table 12 presents synoptic statistics for the distribution of 500 predicted fish mercury concentrations for age 3 largemouth bass.

Figure 31. Distribution of predicted Hg concentrations in age 3 largemouth bass for 500 year simulation. Bin size = 0.02 µg/g.
Table 12. Summary Statistics for predicted Hg concentrations in age 3 largemouth bass for 500 year simulation (µg g⁻¹ wet muscle)

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7. Discussion

7.1 Predicted Mercury Concentrations

Predicted surface water concentrations of total and methylmercury were very dynamic, capable of changing significantly within days. Field data show surface water mercury concentrations in fact to be capable of changing significantly on a within-day basis (Krabbenhoft et al., 1998), although simulations on this short a time scale were not undertaken during this study. Figures 15 and 16 indicate the long-term average model calibration is reasonably predicting the magnitude of observed concentrations of total and methylmercury in surface waters at WCA 3A-15. Since surface water Hg concentrations are very dynamic and responsive to recent site conditions and Hg loading patterns, it was not expected that the simulations of long-term average conditions (typically with inputs entered on a monthly basis) would match precisely the observations on specific dates sampled from 1995-98.

Observed concentrations of total and methylmercury in surface waters at WCA 3A-15 tend to be higher in the wet season (summer/fall) and lower in the dry season (winter) (D. Krabbenhoft, pers. comm.). E-MCM predictions suggested slightly lower concentrations of total mercury in surface waters in the wet season however. This result was significantly influenced by the assumed seasonality of macrophyte litter production that resulted in increased scavenging of mercury from the water column in the wet season. In view of the discrepancy between observed and predicted seasonal trends for mercury in surface waters, the seasonality of vegetation biomasses and turnover rates should be reassessed in future work.

Predicted concentrations of total and methylmercury in surficial sediments (0-3 cm) also reasonably reflected observations (Figures 17 and 18). Significant variability existed for mercury concentrations in cores sampled on different dates and even for cores sampled on the same dates. Given the expertise of the field teams, this variability is likely real and due to natural variations between cores.

Observations of methylmercury concentrations in the lower food web (zooplankton, shrimp, periphyton, benthos) were limited but when combined with observed dietary patterns in fish, reasonable concentrations were predicted for mosquitofish (*Gambusia*), sunfish and largemouth bass (Figures 19 and 20). Mosquitofish predictions are treated as tentative because:

- We did not find bioenergetics information specific to mosquitofish for our simulations. We therefore used bioenergetics information for finescale dace.
- We did not have information on the growth rates for mosquitofish at WCA 3A-15. Thus a growth rate pattern was assumed.
- Mosquitofish populations spawn several times during a 12 month period. E-MCM can only have spawning once per year, and is not set up for multiple cohorts within a year.

Thus while the predicted mosquitofish concentrations were of the correct order of magnitude, we believe additional efforts are needed to locate literature values or measure mosquitofish bioenergetics and growth rate information in the field/laboratory.

Good data were available for mercury concentrations in bluegill and warmouth at WCA 3A-15. As mentioned earlier, E-MCM has three fish populations so we combined bluegill and warmouth into a single omnivore category called sunfish. Table 6 shows the assumed sunfish dietary pattern which
was primarily invertebrates, shrimp and benthos from ages zero to three, with some piscivory occurring at ages 4 and higher. Figure 19 shows a reasonable agreement between observations and predictions. Many of the warmouth observations exceeded 0.5 µg g⁻¹ whole body, and would likely be even higher if determined on a muscle basis.

Predicted largemouth bass mercury concentrations in the long-term average simulations also agreed reasonably with observations (Figure 20), but the field dataset had some atypical features for fish mercury concentrations versus length. Fish mercury concentrations usually increase with length, but at WCA 3A-15 observed largemouth bass mercury concentrations show little obvious increase between 10-30 cm in length, ranging from approximately 0.5 to 1.5 µg g⁻¹ wet muscle. The model similarly showed little increase in mercury concentration in the 20-30 cm length range. In fact predicted concentrations dropped slightly from 20-27 cm. The reason in the model, and perhaps in the observations, was that the bass were assigned a preference for crayfish in this length range (Figure 11 and Table 5). Beyond 35 cm in length, there were few observations (n=3) but the largemouth bass concentrations increased rapidly and were at or above 3 µg g⁻¹ wet muscle in all cases. We achieved this result when the largemouth switched to primarily sunfish above age 3. This is consistent with field observations (T. Lange, pers. comm.).

Figure 31 suggests that if the annual variability in Hg(II) deposition at WCA 3A-15 is approximated by the FAMS dataset characteristics, the concentration exceeded 5% of the years would be 1.92 µg g⁻¹ wet muscle. The highest simulated mercury concentration in an age 3 largemouth bass at WCA 3A-15 for the 500 simulation was 1.97 µg g⁻¹ wet muscle.

The standard deviation in annual Hg(II) deposition was 16.97 % of the mean rate, but the standard deviation for Hg concentration in age 3 largemouth bass was less, only 3.5% of the mean concentration. This occurred due to dampening that occurs simply because age 3 fish are continuously integrating their mercury accumulation over a three period, rather than responding instantaneously to varying conditions in the water column. Also, it takes time for changes in loading to translate into different exposure to the fish because of the steps involved between Hg(II) deposition and mercury concentrations in the diet of fish. The dynamics of the system response to a change in load are examined in the next section.

7.2 How fast does the WCA 3A-15 marsh respond to changes in atmospheric Hg(II) deposition?

Figure 26 shows that WCA 3A-15 is predicted to respond significantly within the first decade following Hg(II) loading reductions. Regardless of the magnitude of the load reduction, fish mercury concentrations are predicted to change by 50% of the ultimate response within 8-9 years (Figure 26). Within 30 years, 90% of the ultimate predicted response has occurred. Figure 31 shows that these predictions are not significantly altered because of uncertainty regarding true current Hg deposition rates and the effects of recalibration to different estimates of current deposition. The actual magnitude of the change in fish Hg is of course dependent on the magnitude of the load reduction, as shown in Figures 23 through 25.

Mercury concentrations in the marsh do continue to change very slightly beyond 100 years after a load reduction. We tested this by comparing the predicted fish mercury concentrations after 100 years with those 1000 years after a load reduction. Total mercury concentrations in water changed by less than 0.5% from 100 to 1000 years, while mercury concentrations in age 5 largemouth bass changed by less than 1.5% during the same period.
7.3 Processes Controlling Hg Concentrations and Dynamics at WCA 3A-15

Hg(II)

Figures 21 and 22 show the predicted long-term average annual fluxes for Hg(II) and methylmercury at WCA 3A-15 respectively. Since concentrations in any given compartment depend on both sources and sinks, it is important to look at both the loading and removal aspects of the mass balances.

Hg(II) in WCA 3A-15 surface waters is very dynamic, due to the shallow waters and relatively rapid kinetics of some processes relative to lake environments. Hg(II) loading was primarily atmospheric in the simulations, but this is affected somewhat by the size and geometry assigned to the marsh cell being modeled. Similar to Fitz et al. (1996) in their modeling of nutrient dynamics in the Everglades, we chose a 1 km x 1 km area as representative of conditions at 3A-15. Segregating the modeled system unit of interest into a set of smaller cells to better represent spatial heterogeneity, a smaller cell size would result in water flowing through the individual cell in a shorter time period than the entire system unit, although the overall hydrologic characteristics of the system unit would not change. When comparing fluxes on an areal basis, this in turn would increase the relative importance of surface inflows as a mercury source for a given cell. The sensitivity analysis (Figures 27 and 28) suggested that the surface flow rate and hydraulic residence times were significant but secondary, and suggests that our choice of cell size is probably adequate. Future work funded by DEP with E-MCM will involve setting up the model as a series of linked cells, thus enabling us to test the effects of cell size more explicitly and rigorously.

Wet and RGM deposition were both important sources of Hg(II) to the marsh (Keeler et al., 2000). We used a leaf area index of 3.0 and backed out the concentrations of atmospheric RGM that would generate the monthly RGM deposition rates provided by Keeler et al., (2000). These monthly atmospheric RGM concentrations ranged from 10.8 to 22.5 pg m\(^{-3}\).

In our calibration, most of the macrophyte related Hg(II) loading occurred as throughfall which in turn derived most of its mercury from the atmosphere rather than root uptake. The relative magnitude of throughfall versus litter was influenced by the ability of rain to wash off mercury from macrophyte leaves. This washoff effect is unquantified and should receive future attention.

The predicted total load of Hg(II) to the marsh via combined litter and throughfall was 10.81 µg m\(^{-2}\) marsh yr\(^{-1}\). Only 17% of this total (1.81 µg m\(^{-2}\) marsh yr\(^{-1}\)) originated from root uptake of Hg(II) via transpiration. To achieve higher mercury transpiration rates, we would need one or both of the following: (1) higher predicted porewater concentrations of Hg(II), which ranged from 1.4 to 3.6 ng L\(^{-1}\) in the four sediment layers and were of the same general magnitude as measurements by Gilmour et al., (1998b), and/or (2) higher water transpiration rates. Our transpiration rates were on the order of 10 g H\(_2\)O per g dry biomass per day, equivalent to approximately 1.5 to 2.0 m yr\(^{-1}\). These initial results suggest that most of the Hg(II) in litter and throughfall (combined) is derived from the atmosphere and represents a new source of mercury rather than recycling of mercury from roots. Alternatively a mechanism other than transpiration would have to transport surface water or subsurface mercury into the plant leaves.

Furthermore, predicted root uptake of porewater Hg(II) on an annual basis (1.93 µg m\(^{-2}\) marsh yr\(^{-1}\) = 50% macrophyte areal coverage * 3.86 µg m\(^{-2}\) macrophyte covered area yr\(^{-1}\)) was incapable of supporting volatilization rates over macrophytes suggested by Lindberg et al., (1999), which were orders of magnitude higher. The disagreement between our simulated and Lindberg et al.’s measured volatilization rates over macrophytes may suggest an alternative mechanism unaccounted for in the
model which could result in the localized reduction of Hg(II) at the root interface and subsequent flux through the plant to the atmosphere.

The primary removal mechanism for Hg(II) at WCA 3A-15 is predicted to be burial (Figure 21), accounting for 63% of total Hg(II) load to the system. Predicted concentrations of Hg(II) in sediments were sensitive to the rate of particle sedimentation. The predicted response dynamics of the marsh were also significantly influenced by burial. Faster sedimentation rates would lead to faster system responses. The particle budget for the marsh is therefore important in terms of loadings, predicted concentrations and predicted response dynamics for Hg(II).

**Methylmercury**

The dominant predicted source for methylmercury at WCA 3A-15 is in-situ production (7.6 µg m⁻² yr⁻¹), representing 87% of total MeHg load predicted for the marsh. In our simulations for WCA 3A-15 we calibrated methylation to occur in sediments, and there was no methylation by periphyton, although these are both ongoing topics of investigation. Atmospheric deposition of methylmercury appears to be a minor source – less than 1% of the total methylmercury load to the marsh. The prediction that local production of methylmercury is the major source to WCA 3A-15 is consistent with the hypothesis that local site factors are driving the variability and “hot spots” observed for methylmercury across the Everglades. Several significant loss mechanisms were predicted for methylmercury, including photodegradation, outflow, biological demethylation, and to a lesser extent burial.

The response of methylmercury concentrations in the marsh to changes in Hg(II) loadings depends on the rate at which methylation responds to changes in Hg(II) loading, and the rate at which existing methylmercury concentrations in the system can adjust to changes in methylmercury supplied. We did not resolve within our study which of these two rates controls the response of methylmercury concentrations to changes in Hg(II) loading.

### 7.4 Effects of Atmospheric Hg Deposition on Fish Mercury Concentrations

Figures 23 and 24 illustrate that in the longer term, fish mercury concentrations are predicted to respond significantly to changes in atmospheric Hg(II) deposition. A near linear relationship between atmospheric Hg(II) deposition and fish mercury concentrations is predicted, but the slope is not 1.0, i.e. the relationship has a non-zero intercept that indicates a continuing supply of methylmercury under quasi “steady-state” conditions when all external inputs of Hg(II) have been eliminated. A load reduction of 77% is needed for long-term average mercury concentrations in age 3 largemouth bass to drop to 0.5 µg g⁻¹ wet muscle. If we use the age 3 largemouth bass concentration exceeded 5% of the years as a standard (1.92 µg g⁻¹ wet muscle), a decrease in atmospheric Hg(II) deposition of 78-79% is needed to reduce mercury concentrations from 1.92 to 0.5 µg g⁻¹ wet muscle.

As mentioned above, the long-term simulations predict that mercury concentrations in age 3 bass would still be 0.11 µg g⁻¹ wet muscle even without any atmospheric (HgII) deposition. This is because there is some remobilization of Hg(II) and methylmercury from deep sediment layers via porewater transpiration by macrophytes. Over the course of 100-200 years, Hg(II) and methylmercury concentrations in these deeper sediments are not significantly affected by the recent changes in atmospheric mercury deposition imposed in the simulations. Transpiration of this legacy mercury effectively becomes an added source of mercury to the overlying active marsh system, a source which would continue for long periods in the absence of atmospheric Hg(II) deposition. If we had carried the simulations out for very long periods, e.g., thousands of years, it is expected that the
deeper layers would eventually adjust to overlying loads, and the predicted fish mercury concentrations would be closer to a direct proportional response to loadings.

The predicted long-term response of fish mercury concentrations to changes in atmospheric Hg(II) deposition and concentrations (i.e. linear but with a non-zero intercept), is governed by, 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 had a significant impact on the shape of the long-term dose-response curve:

- Methylation occurs primarily in the sediments.
- Methylation depends on a bioavailable fraction of porewater Hg(II)
- Porewater Hg(II) concentrations are not currently at saturation. For example it is plausible that additional Hg(II) loading could result in precipitation of the excess Hg(II) as cinnabar, and no change in porewater Hg(II). We do not have cinnabar forming in any of the loading scenarios we examined with our calibration.
- Atmospheric MeHg deposition, inflowing methylmercury loads and inflowing Hg(II) loads were assumed to be reduced by the same percentage as Hg(II) deposition in scenarios with load reductions.

Thus we interpret the predicted response of fish Hg to load reductions in this study to reflect the current level of understanding. This level of understanding is currently inadequate however to place strong confidence in the predictions. The validity of the above assumptions needs resolution.

Furthermore, uncertainty and natural year-to-year variability associated with input values for E-MCM is not reflected in the analysis, with the exception of Hg(II) and MeHg loading rates. This uncertainty would be best accommodated through a Monte Carlo approach. A Monte Carlo version of E-MCM was under development at the time this analysis was prepared.

It is important to recognize that fish mercury concentrations in largemouth bass are sufficiently elevated for some larger fish that it may not be practical or even theoretically possible to bring concentrations below 0.5 µg g\(^{-1}\) wet muscle on the basis of local anthropogenic Hg(II) load reductions alone. For example, the field measurements of muscle Hg concentrations for larger bass over 35 cm are limited (n=3), but exceeded 3 µg g\(^{-1}\) wet muscle in all cases (Figure 20). Assuming at best a 1:1 response to a change in atmospheric Hg(II) deposition, concentrations in these fish would need to drop by a factor of six to reach 0.5 µg g\(^{-1}\). This decrease is roughly equivalent to the estimated increase in mercury loading to the Everglades over pre-industrial loadings derived by Delfino et al. (1994) from sediment cores. Assuming that these inferred increases are from both local and larger scale sources, it is plausible that reductions in Hg(II) loading to WCA 3A-15 may significantly reduce fish mercury concentrations, but still be inadequate to reduce concentrations below 0.5 µg g\(^{-1}\) wet muscle, even if all anthropogenic contributions to Hg(II) deposition are eliminated.
8. Conclusions

Overall, E-MCM was calibrated to reasonably fit observations for total and methylmercury at WCA 3A-15. The model predicts a linear, but not 1:1 long-term response in fish mercury concentrations to sustained reductions in atmospheric Hg(II) deposition. The departure from a simple 1:1 relationship between changes in loadings and relative response becomes more pronounced as external Hg input reductions approach 100% and reflect principally resupply of Hg(II) and MeHg from deep sediments for long periods (200+ years).

Mercury concentrations in age 3 largemouth bass are predicted to achieve 50% of the ultimate response within 8 to 9 years and 90% within 25 to 30 years following sustained load reductions. To reach a target of age 3 largemouth bass concentrations not exceeding 0.5 µg g⁻¹ wet muscle for 95% of the years, a reduction of approximately 78-79% in atmospheric Hg(II) deposition is needed. Some larger largemouth bass at WCA 3A-15 may stay above 0.5 µg g⁻¹ wet muscle on a long-term average basis regardless of reductions in Hg(II) emissions.

There are several gaps in the state of knowledge of mercury cycling in aquatic systems which resulted in modeling assumptions and impose uncertainty regarding the predicted magnitude and timing of the relationship between mercury deposition and fish mercury concentrations. These gaps should be addressed in future studies and include the location and governing factors for methylation and demethylation, and fluxes associated with vegetation and particles (litter, throughfall, sedimentation, decomposition). Furthermore, uncertainty and natural year-to-year variability associated with input values for E-MCM should be included in future analyses via a Monte Carlo approach. Finally, the lack of a long-term Hg(II) deposition dataset required us to synthesize a dataset to estimate the effects of year-to-year variations in Hg(II) deposition. Longer periods of record will be helpful for any future assessments.

Acknowledgments

We wish to thank the agencies funding this work and the exceptional team researching mercury cycling in the Everglades who provided information essential to our modeling efforts. In particular we thank the funding and support of Tom Atkeson and Don Axelrad of the Florida Department of Environmental Protection, Larry Fink of the South Florida Water Management District and Ruth Chemerys and Rochelle Araujo of the USEPA. It was our good fortune to work with the ACME research team led by Dave Krabbenhoft (USGS) and including Cynthia Gilmour, Andrew Heyes and Jani Benoit (Academy of Natural Sciences), Jim Hurley (Wisconsin DNR/University of Wisconsin), Lisa Cleckner and Sue King (University of Wisconsin), Paul Garrison (Wisconsin DNR), Mark Marvin DiPasquale, George Aiken and Mike Reddy (USGS), and Ted Lange (Florida Fish and Wildlife Conservation Commission).
9. References


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Limno – Tech 1996


The initial draft report was based on simulations carried out up to February 14th, 2000. A subsequent peer review of the draft report resulted in many useful suggestions that were incorporated in the final simulations. Key changes are documented below:

1. **Atmospheric wet Hg(II) deposition**: Atmospheric wet Hg(II) deposition rates were changed from the values generated by the Keeler et al. (2000) modeling exercise, to values based on field observations. Based on data collected from FAMS sites which were most proximal to site 3A-15, annual precipitation and Hg(II) concentrations in precipitation were revised. These sites included Tamiami Trail (TT), Andytown (AT), and Fakahatche Strand (FS), and had the advantage of circumscribing 3A-15. Deposition estimates were derived from observations beginning in late 1992 (FS) and extending through 1996. This revision resulted in an increase in mean annual precipitation to 142 cm yr\(^{-1}\) from 134 cm yr\(^{-1}\), and an increase in the annual wet deposition Hg(II) load to 23.1 µg m\(^{-2}\) yr\(^{-1}\), 23% higher than the previous simulated value of 18.74 µg m\(^{-2}\) yr\(^{-1}\). RGM and dry particle deposition rates for Hg(II) remained the same, based on the Keeler et al. model results, at 11.2 and 0.94 µg m\(^{-2}\) yr\(^{-1}\) respectively. The total Hg(II) atmospheric load increased to 35.32 µg m\(^{-2}\) yr\(^{-1}\), 14% higher than the original total of 30.94 µg m\(^{-2}\) yr\(^{-1}\).

2. **Atmospheric MeHg deposition**: The concentration of methylmercury in precipitation was changed to 0.02 ng L\(^{-1}\) from 0.15 ng L\(^{-1}\) based on limited wet and bulk deposition measurements conducted by Guentzel (1997) at several south Florida sites during FAMS. Combined with the above revised annual precipitation rates, annual wet MeHg deposition decreased from 0.20 to 0.028 µg m\(^{-2}\) yr\(^{-1}\).

3. **Inflow mercury concentrations**: Initial simulations used Hg(II) and MeHg inflow concentrations based on WCA 2BS. For final simulations, WCA 3A-33 was used as the basis to estimate inflow mercury concentrations. The result was a 12.6% increase in mean annual Hg(II) surface inflow concentration from 1.90 to 2.14 ng L\(^{-1}\), and a 32% decrease in the mean annual MeHg surface inflow concentration from 0.40 to 0.27 ng L\(^{-1}\).

4. **Largemouth bass diet**: The diet of largemouth bass was adjusted based on unpublished field data provided by Ted Lange of the Florida Fish and Wildlife Conservation Commission. In particular, largemouth bass at WCA 3A-15 are atypical of other Everglades sites, relying more heavily on crayfish when the bass are in the 200-300 mm length range. The dietary preferences in this length range were set to 24% grass shrimp, 63 crayfish, and 12% fish by weight. The concentrations of largemouth bass in the field data showed an atypical pattern of little increase between 1-3 years of age. This may have been due in part to a switch to a lower mercury exposure diet through crayfish in the 200-300 mm length range.
5. **Long term Hg load/fish Hg response curves:** The original simulations of the response of long term fish Hg concentrations to sustained reductions in atmospheric mercury deposition included reductions in Hg(II) but not methylmercury deposition. For the final simulations, methylmercury atmospheric deposition, inflowing Hg(II) load and inflowing MeHg load were all reduced by the same proportion as Hg(II) deposition.

6. **Timing of the system response:** In the original set of simulations which examined the timing of the system response, we reduced both atmospheric Hg(II) deposition and inflow loads of MeHg and Hg(II) simultaneously, as step functions, by the same proportions. For the final set of simulations we introduced a lag time to the reductions in inflowing Hg(II) and MeHg loads. This was designed to reflect the time it would take for upstream conditions and Hg export to respond to a change in atmospheric deposition. To estimate this lag effect, the model was first run with all external Hg(II) and MeHg loads reduced in a step function manner along with atmospheric deposition. The temporal responses of Hg(II) and MeHg in the 3A-15 model cell were then used as estimates of the response dynamics for inflows responding to reduced atmospheric deposition. The result of this modification was a slightly slower predicted system response half-life, increasing from 6-7 years up to 8-9 years.

7. **Year to Year Variability:** In the original 500 year simulation to examine year to year variability, we changed atmospheric Hg deposition from year to year, but not inflowing loads of Hg(II) or MeHg. For the final 500 year simulation, we varied all external Hg(II) and MeHg loads (atmospheric deposition and inflows) simultaneously as step functions, by the same proportions.
APPENDIX III

Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study: Response to Reviewer Comments

In addition to those from the Peer Reviewers\(^1\), comments were received from EPA, DEP, SFWMD and the Utility Industry. We appreciate the time, effort and thoughtful consideration that went into these comments. In response, many changes were made to the summary and support documents. Many comments were concerned with deficiencies in the available information and these will guide future work. Our responses are organized in three sections: the aquatic cycling model, the atmospheric transport and deposition model and comments related to policy.

A few themes appeared repeatedly. Some reviewers thought that this pilot study looked too much like a TMDL; others thought it did not go far enough towards being a TMDL that could be implemented. DEP considers this study an important step along the way to creating a TMDL for atmospheric mercury, but does not consider it a TMDL. The intent was to synthesize our current knowledge by combining atmospheric and aquatic models so as to define those areas where additional information is required. In our view, a TMDL must result in a margin of safety that is not unnecessarily large and also result in a fair apportionment of abatement responsibility. More information is required for this. We chose to follow an EPA Region IV process for defining a TMDL in order to better see the missing information. Because it was not intended to produce a TMDL, this study did not follow the process prescribed by Florida Law for producing a TMDL. For those in other states who may wish to apply some of the results reported here to TMDL development, we urge caution. The atmospheric model used for this study lacks chemical and physical transformations that may be essential to predicting accurate deposition rates. The aquatic cycling model used for this study is very site specific in its dependence upon the characteristics of Everglades. The same is true of dry deposition velocities.

\(^1\) The first draft of this report was submitted to an independent panel for review. Those reviewers were:

- Dr. Mark Cohen, NOAA Air Resources Laboratory
- Dr. Kent Thornton, Principal Ecologist, FTN Associates, Ltd.
- Dr. Joseph V. DePinto, LimnoTech, Inc.
- Dr. Donald B. Porcella, Environmental Science and Management, Electric Power Research Institute
- Dr. Robert P. Mason, Associate Professor, Chesapeake Biological Laboratory, University of Maryland

Informal review comments on various drafts from many commenters are included here in as well.
Another common theme concerned the absence a “global background” contribution to deposition. Some reviewers expressed the view that an estimate of should have been included even if its reliability was unknown; others suggested that nothing useful had been produced because of the absence of a global background term. Two groups of researchers differ about the significance of global background to South Florida deposition for the period modeled. One group arrived at the conclusion that the background contribution was less than 20% using both receptor and dispersion modeling approaches. Both research groups rely on somewhat uncertain source inventories for their conclusions. It appears that only direct measurement can resolve the question. A technique has been developed for measuring low levels of Reactive Gasous Mercury in the atmosphere. Two sets of measurements have been made in South Florida under conditions that may reveal the levels of RGM in the atmosphere during periods with trans-Atlantic trade winds. These data are being analyzed. It is evident that deposition cannot be modeled with certainty until the contribution of global background is known. However, we believe that introduction of a speculative value for global background would make the results of this study more difficult, or impossible, to understand and did not include it for that reason.

Many reviewers pointed out the absence of one or another process in the models. Examples are the absence of a sulfur cycle in the aquatic cycling model and the absence of gas-particle and chemical transformations in the atmospheric model. There are many others. These are not willful omissions, but reflect current knowledge. The modelers are aware of these deficiencies and, for the most part, they are noted in the support documents. The results of this pilot study will help set research priorities for the missing process information.

What follows is a list of comments and responses. In many cases, reviewers’ comments have been combined and paraphrased.

**AQUATIC CYCLING MODEL**

1. **COMMENT:** References to the MCM manual should be specific. Lack of detail about the specific processes modeled and the adjustable parameters is a general criticism. Information about the rate equations is lacking, as is their seasonal variability. **RESPONSE:** We intend to update the manual for the E-MCM and make it available on the World Wide Web. The model will also be made available.

2. **COMMENT:** The hydrologic treatment of the box in the model is not adequately explained. **RESPONSE:** Additional discussion has been included in the support document.

3. **COMMENT:** The water model appears to treat all atmospherically deposited species as equally bioavailable and similar to upstream inputs. How does the model treat particulates of atmospheric origin, which vary seasonally? How would changes in input speciation (from source reduction) affect results in the water? **RESPONSE:** Seasonal and temporal variation in the deposition of Hg(p) may affect the bioavailability of Hg(II). This is noted for future consideration. No information is available about this subject.

4. **COMMENT:** The importance of periphyton to methylation in the model requires more discussion. **RESPONSE:** The ability of periphyton to support methylation occurs only with those species found in the areas of the Everglades made eutrophic by stormwater runoff and not to the modeled area, WCA-3A-15.

5. **COMMENT:** There is no discussion of controlling the bioaccumulation of mercury through control of water quality in tributary inflows. Sulfate, DOC and organic particulates may
affect bioaccumulation and should be discussed in relation to limitations on emissions control. RESPONSE: The sulfur cycle will be incorporated into the E-MCM as the necessary information becomes available, as will the effects of DOC and organic particulates. These constituents are not just in tributary inflows, but are a feature of the entire Everglades. With so little quantitative knowledge about their effects on bioaccumulation it would premature to consider them in relation to air source abatement.

6. COMMENT: Several questions were raised about the ability of the model to predict fish bioaccumulation. These concerned the choice of food consumption scenarios, and whether the model can actually predict weight vs. age in bass. There were comments such as the predicted *Gambusia* mercury levels are twice those measured and the model does not predict scatter in sunfish and only appears to fit bass data because of three high concentration fish. RESPONSE: The food web modeled is simplified. In addition, because interannual variations in rainfall affect marsh hydrology and temperature, they are likely to affect food web structure and possibly growth rate. Many of the food web data used were collected over periods of extremes in Everglades rainfall, which may have affected their applicability. The error in predicting mercury in three-year old bass is a combination of diet variability, diet bioaccumulation variability, a simplified food web and growth rate variability. Further studies are needed to ensure that the error in predicting bass concentration is quantitatively understood.

7. COMMENT: There is no rationale given for holding MeHg deposition constant in model while reducing Hg(II) loads in different scenarios. RESPONSE: This was changed in the model to make MeHg deposition constantly proportional to total reactive mercury deposition.

8. COMMENT: The modeled deposition rate is far too uncertain to be used as input into the E-MCM. This is a critical flaw. RESPONSE: Uncertainty in deposition is not a critical flaw for this pilot study, which was intended to determine the additional information needed to produce an implementable TMDL.

9. COMMENT: The linear relation between the fractional change in bass mercury concentration and fractional change in deposition needs to be discussed more completely. RESPONSE: This requires further investigation. The linearity suggests that the process that limits the rate of bioaccumulation in bass in the model has a rate proportional to deposition rate. How this comes about remains to be learned.

10. COMMENT: How is it that the E-MCM can be calibrated with different deposition rates and still give the same fractional response in fish to deposition changes? RESPONSE: That model calibration can take place over the range of deposition rates examined reflects the limited constraints on the model, which are caused by lack of more detailed process information. This problem is discussed in the support document. The model yields the same fractional change in three year old bass concentration for the same fractional change in deposition rate when calibrated to different initial deposition rates. This is discussed in the preceding comment.

11. COMMENT: What is the origin of the methylmercury deposition rate assumed? RESPONSE: In FAMS, amounts of methylmercury near the minimum detection limit were measured in rainfall. The origin of this methylmercury is unknown. At the low concentration modeled, it has little effect on bass bioaccumulation.
12. COMMENT: What use is made of interannual variability? If the interannual variability is due to rainfall, does it make sense to assume the same coefficient of variation for the dry deposition? RESPONSE: Ultimately, interannual variability in deposition will be a consideration in establishing the margin of safety. Nothing is known about the interannual variability of dry deposition.

13. COMMENT: The role of temperature not adequately explained in discussing the model. RESPONSE: Water and sediment temperature were assumed to be that of the air. In fact, both will vary with incident light, DOC and suspended material and both will vary diurnally. Stratification does occur in some circumstances. These details were not modeled and the consequence of leaving them out awaits further investigation.

14. COMMENT: Is the 5% from tributary inflow relocation of deposited mercury or from a terrestrial source? RESPONSE: The tributary inflow refers to the Everglades as a whole and not to the modeled cell. As no discharges of anthropogenic mercury or geological sources are known, mercury in tributary inflows almost certainly had its origin from atmospheric deposition.

15. COMMENT: There was no discussion of the assumption that concentrations flowing into the cell vary linearly with deposition rate. RESPONSE: This is a reasonable assumption, but it requires field verification. As modeled, the inflow flux into the cell was about one-third of the wet deposition, which makes it a significant term.

16. COMMENT: The addition of a scenario in which all external loads are zeroed out will highlight the contribution of internal cycling from the peat soil. This would also give the clearance rate of the soil. RESPONSE: This is a good idea that will be tried when the opportunity becomes available.

17. COMMENT: Many comments were directed toward processes or effects that were or were not included in the E-MCM. RESPONSE: The E-MCM is being designed to model a subtropical marsh system that is extremely complex both biogeochemically and ecologically. Discovering what we don’t know is an arduous and ongoing task. Much remains to be known. As new process information becomes available, it is incorporated into the E-MCM. The utility of this model obviously depends upon its ability to predict fish mercury levels. Among other things, deposition is uncertain, which makes calibration problematical. Efforts to constrain the calibration and conduct validation at more subtle levels are ongoing. Some of the questions raised by reviewers are answered in the revision (see Appendix A of the support document); the others could not be answered. As of the date of publication, all of the information we have and are seeking, is described in the report and appendices. Electronic copies of the model and the user’s manual are available. The following is a quotation from the E-MCM support document: “Thus we interpret the predicted response of fish Hg to load reductions in this study to reflect the current level of understanding. This level of understanding is currently inadequate however to place strong confidence in the predictions.”

The following comments are included without specific responses in the belief that they may be useful. Some of these comments were addressed above or in the revisions of the aquatic cycling model support document or in the summary report; others were not, often because information was lacking. In some cases, reviewers’ comments have been combined and paraphrased.
1. Calibration, capabilities and limitations of E-MCM are not adequately discussed. A table summarizing the values of all input parameters and calibrated input parameters would be helpful – the source should be fully referenced and estimated error should be given.

2. It would be useful to see a table that lists the E-MCM state and input variables and the source of information used to provide that information and the update intervals. I’m not exactly sure which state variables are included in E-MCM. For example, Cl is listed in the characteristics table for 3A-15, but it does not appear as a state or input variable in the E-MCM Table 7. In the TMDL study document, sulfate is included as an input variable, but in Section 5.2.5 Water Chemistry Inputs (p. 19, Appendix II), it states that DOC, pH, and Cl have received considerable attention, and therefore, are the important constituents to consider. Is Cl a state variable? There is no mention of sulfate in Section 5.2.5. It should be added to the text. Sulfate is included in the input tables and sulfate and chloride are listed in the Table 1, General Characteristics of 3A-15 (p. 11, TMDL Study), but there is only one average concentration given. (As an aside, it would be useful to express sulfate in mg/L rather than ueq/L). Adding a table would answer these questions and clarify which constituents are included in the model.

3. Can model hindcast the trend in fish mercury caused by the 67% reduction in emissions from 1989 to 1994?

4. More discussion of the linear response is needed.

5. Predicted *Gambusia* levels were twice those measured; the model cannot predict the scatter in concentration for the sunfish and the model only appears to fit the bass data because of three high concentration fish. A close examination of the model results for bass in the 10-30 cm range suggests that the model under-predicts the fish concentration at the smaller lengths and fails to predict the apparent lack of change in concentration across this size range. If fish concentration prediction is the “flagship” of the model, then it does not appear to have produced a viable result.

6. The food web portion of the model is sketchy at best and the results presented not very convincing. The food consumption scenarios are presented with little convincing justification for their choice. The model does not even appear to predict the weight versus age relationship for bass. The model line is halted at age 7, but clearly further extrapolation would lead to significant errors in the model’s ability to predict fish growth. How then can the model provide a good estimation of Hg bioaccumulation?

7. The details of the bottom sections of the food web are sketchy. Nine compartments are in the model. Answers to the following questions would be helpful: What, if any, is the link between the detritus, periphyton and phytoplankton compartments and do they all exchange with the water column in a similar way, i.e., slow and fast dynamics? Or are they sinks? How was phytoplankton and periphyton uptake modeled? What fraction of these compartments is consumed by the food chain and what fraction is removed by other processes?

8. Figure 2: The three large fish Hg levels suggest a change in diet to include another trophic level. If this is the case, use of a linear relationship beyond the diet change is inappropriate.

9. Sensitivity analysis with the E-MCM shows the importance of vegetation, but how are changes in vegetation linked to the rest of the system?
10. Not enough is said about vegetation characteristics and particle settling when these have the greatest influence.

11. It is intriguing that given the variability in inputs over the season, and the non-similar variability in temperature and light - two factors that likely control to a large degree microbial and photochemical processes - that the model predicts a constant MethylHg concentration in sediments over the season. In another study in the shallow ecosystem of Lavaca Bay, TX (e.g. Bloom et al., 1999) there was a dynamic change in MethylHg concentration in sediments seasonally. Why does the model not predict such changes? The lack of any variability in MethylHg concentration in sediments. Again, why the lack of data for comparison when Gilmour et al and others have been studying the region for a number of years? or are the data points the average of many values. If so, show error bars. The water temperature varies from 15 °C in Feb to 30° C in July yet we see no effect of this on a compound that is produced and decomposed biologically? This is not believable. The report should discuss this and provide an explanation or rationale for this.

12. Water column concentration does not follow total flux in model (Fig 15). Why?

13. Why not use literature values of H(II) sorption instead of calibrating? There is no unique solution with Hg(II) distributed among multiple phases.

14. Was MeHg sorption calibrated or measured?

15. Is there a link between detritus, periphyton and phytoplankton in the model – do they exchange in the water?

16. In scaling for different loading rates, the report states “some rate constants were altered”. The information provided is insufficient on what constants were changed, why they were and how these changes are justified. Much more information is needed in this regard. Were the same constants changed in each case?

17. Why is product of demethylation Hg(II) in model – contradicts literature. Need more information on methylation and demethylation processes – how parameterized in the model? Sensitivity analysis should include partition coefficients and depth of maximum methylmercury production. Why was methylation only allowed to occur in sediments?

18. Figure 21 from model shows different dry deposition than Base case in Keeler because leaves were included. Explanation needed.

19. Fig 21 shows the overall fluxes with Hg(II) dry deposition that are different than the Base case Keeler model, as the Keeler model does not include leaves. Why is leaf index area assumed to be 3?

20. More details are required as to how the assessment of the dominance of atmospheric deposition as a source of Hg to plants must be given.

21. The estimated inflows to the box are modeled as proportional to deposition depth. This is okay, but would not water depths also be related to these inputs and outputs, or is there a larger hydrologic control. Could not water depths, a measured parameter, be used to estimate input/output fluxes? If there is changing water depth seasonally, does this not mean that
inflows and outflow are not always necessarily the same i.e. at low precipitation, outflow exceeds inflow and water depth drops; at high flow, the opposite occurs. Perhaps the model has these changes included in it but it not apparent in the text, and the caption for Fig 6 implies that inflow= outflow at all times.

22. It is clear that the E-MCM application assumes that Hg(II) and MeHg concentrations in the surface inflows varies in a direct linear fashion with changes in atmospheric deposition, but the rationale for this assumption is not explained nor is it justified by any observations in this or other systems. Also, the rationale for assuming that atmospheric MeHg concentrations do not change with deposition rate changes is not clear.

23. There are a great many assumptions made in this analysis, and, in general, the authors have done a very good job of stating them. They have not always justified the assumptions. For example, one assumption is that surface inflow = outflow and hence the water column depth of the systems remains constant. I would like to see a long-term record of depth (or inflow vs. outflow – there must be good records from the control structures); in other words, how variable is the annual cycle of depth shown in Figure 7 of App II. My concern here is how the long-term response will be affected by periods of very wet or very dry years, especially in a system that is this shallow (has a relatively small overflow rate). Many processes and environment conditions are correlated with water column depth. Depth can have a major impact on the importance of interfacial transport (air-water and sediment-water exchange) fluxes on concentrations in the water column.

24. Back of the envelope or order of magnitude calculations should be performed on selected processes or relationships to see if these are consistent with observations or first principles. For example, methylmercury concentrations in water and fish mercury concentrations are being predicted by the model. Simple BAFs can be calculated and compared with average methyl mercury concentrations and 3 year old largemouth bass mercury concentrations measured at the site. Are the BAFs similar? Are the ratios of annual average total to methyl mercury measured at the site consistent with the ratios predicted in the model? There are a number of simple calculations that can be performed comparing model output to observed field measurements to increase confidence in model performance. Weight of evidence is ultimately going to be the determinant of confidence. The more information that can be provided to indicate that the relative direction and magnitude of the responses are reasonable, the greater the possible contribution to, and consideration in, management decisions.

25. I really think it would be instructive and useful from a TMDL perspective to investigate the shape of this curve if surface inflows were not a function of atmospheric load reduction (i.e., bound the question) by producing a plot where the atmospheric load is reduced by selected intervals but the surface water inflow loads are held constant. This should produce a load-response curve that will start out linear but will begin to level off as atmospheric loads are reduced to a level that ultimately represents the steady-state fish response to current surface water inflow loads (i.e., the curve will begin to become non-linear at low atmospheric loading).

**ATMOSPHERIC TRANSPORT AND DEPOSITION MODEL**

Concerns that were stated by several reviewers are discussed below. Comments without specific responses follow. Many reviewers were concerned about the exclusion of global background from this modeling effort. This was discussed above.
Several reviewers saw exclusion of gas-particle and chemical transformations as a shortcoming of this study. Following the completion of the hybrid-modeling effort in South Florida, it was evident that a more complete and comprehensive Hg model was needed. The UMAQL entered into a Cooperative Research Agreement with the State of Florida and the USEPA to develop a full-scale meteorological-chemical process model that will combine: (1) a high resolution meteorological processes model capable of adequately describing relevant pollutant transport and cloud/precipitation-scavenging processes and (2) a chemical model incorporating the most up-to-date mercury chemistry and gas-particle interactions. This first phase I of the CMAQ model development will be completed in calendar year 2001. It has been apparent to all that the CMAQ Hg Model would provide a more comprehensive treatment of the important meteorological and chemical processes that strongly influence the deposition and cycling of Hg to South Florida. However, this was not feasible for the Pilot TMDL study. However, the use of RAMS for providing the high-resolution meteorological data in the Pilot study was felt to be an excellent intermediate step in capturing the most important temporal and spatial meteorological phenomenon in S. Florida.

Several reviewers were concerned about the clustering technique employed. The technique is widely accepted in the modeling community and is used extensively by US EPA in their Aggregation Approach. Here, the 365 study days were objectively clustered into eight meteorological flow patterns based on trajectory endpoints and whether precipitation had occurred on that day. From each cluster, subsets of wet and dry back trajectory flow patterns were selected. Wet and dry were defined by whether or not it rained at Davie, the endpoint of the back trajectory. For the wet days in each cluster, two days with flow patterns representing extremes were selected and modeled. The deposition fields for the two days were averaged to represent the specific cluster’s deposition. The same was done for the dry subset of days. Thus, each cluster was represented by the average of two dry and two wet days. The purpose of the aggregation approach, which employed the clustering technique, was to limit computational time required for detailed simulations of the meteorology and deposition on small spatial scales in S. Florida. The principal concerned raised about the clustering technique was that it was not possible to determine from the supporting document how well the average of the selected wet and dry days represented the corresponding wet and dry days of the entire cluster. A comparison of the wet and dry deposition estimates calculated using the two days selected is given in Figures 7 and 8 in the Atmospheric Modeling document. The selection of two “extreme days” in each cluster was done to allow us to give an upper estimate in the uncertainty for the Hg deposition values. Subsequent to this work we decided to take a different approach to answering the question of how representative the days selected were to the final deposition estimates. The HySPLIT 4 model was run using coarse meteorological input data from the NGM Model as supplied by NOAA. The model simulated the emissions, transport and deposition of Hg to S. Florida for each day of the study.

First, the wet and dry deposition totals (better than 8%) compared extremely well with the values estimated using the aggregation approach. Next, we looked at the wet and dry deposition for each day of the year and looked at how much variability would result in our choice of the days used in the aggregation modeling. It turns out that our choice of days was not as important as we thought it might be. For the two clusters (#2 and 3) the days selected were extremes but choosing them in place of other days resulted in less than 5% differences in the total annual deposition. In other words, if we averaged the wet and dry deposition from all of the days in each cluster instead of taking just two of them we would have not had a significant impact on the annual deposition. Stated more strongly the aggregation approach used was robust in terms of providing a representative estimate of the deposition of Hg to S. Florida. It should be noted that for the Pilot Project we felt that the high-resolution meteorological files were much more important to getting the spatial deposition patterns correct than including detailed chemistry considering the spatial domain and time scales of less than
12 hours that are important for transport in S. Florida. To allow us to model the deposition for each day we sacrificed the spatial and temporal resolution of the input data, which resulted in a spatial average of the deposition fields, which had less definition than the previous approach.

Some reviewers’ were also concerned about the selection of the base-case scenario to compare the model to field measurements. Three different scenarios were modeled, which differed only in the emissions of the same modeled sources. The base-case scenario used inventory values from the EPA Report to Congress. The second scenario used the base-case inventory except that recently measured values were substituted for a medical waste incinerator and a municipal waste incinerator. The third scenario proportioned all modeled medical and municipal waste incinerators to the corresponding values of the recent measurement to provide a “future emissions” scenario. After considerable investigation and scrutiny of the emissions data the UMAQL finally concluded that the US EPA data was the best data available for S. Florida for the period modeled. Other emissions work by Roberson and others suggested that the EPA had underestimated the incinerator category and this would have resulted in greater emissions from the largest point sources in the domain. The base-case scenario also gave close agreement with wet deposition measurements of FAMS. The other two scenarios gave annual wet deposition values that were successively lower than FAMS by significant amounts. What is apparent from this analysis is that no implementable TMDL for atmospheric mercury can be created without an accurate source inventory.

Change of the model term containing the Henry’s Law constant concerned several reviewers. In writing the original version of the modeling support document we did not effectively communicate the point that our changes to the constant were for sensitivity analysis of the model and not to calibrate it. The results of the sensitivity analysis suggested that the parameterization for wet removal in the grid squares with the point sources over-estimated the wet deposition, as it did for the Davie site. Since the Henry’s Law constant did not have a significant impact on the wet deposition to WCA 3A, the wet deposition values provided were those obtained using the original values given in the model. We should have been clearer as to our objectives with presenting these sensitivity results.

The final area of concern to several reviewers was dry deposition. The values used by other modelers were not based upon measurements but were simply estimated based upon other work done previously for sulfur and nitrogen species. Although disagreement with data was given as the reason for changing published values for night deposition velocities, no experimental data were given in the report for either the Davie Site or for the FEDDS Site in the Everglades marsh. This was largely due to the timing of the deadline for the report and the dates of the field studies. The dry deposition results from the SoFAMMS and the FEDDS have been presented at the South Florida Annual Mercury Science Meetings. The values obtained during the two-week to a month intensives were within a factor of two of the modeled results. Taking the seasonal intensives and estimating the annual dry deposition resulted in values slightly higher but with the uncertainties of the modeled results. Reasonable estimates of dry deposition suggest that it is significant compared to wet deposition and must be modeled accurately to obtain total deposition.

It is particularly important to understand the interaction of RGM with emergent vegetation in the Everglades marsh. If RGM binds tightly to emergent vegetation, the manner and location of the decay of senescent vegetation may play an important role in the availability of Hg(II) for methylation. The fate of the RGM deposited is still not well understood at this time. While it is true that the RGM might bind to the vegetation it can also be washed off with precipitation and may also be photoreduced and evade back into the atmosphere. The FEDDS results are currently being prepared for publication. It is likely that more field work on dry deposition will be required. In the meantime, dry deposition is a significant source of uncertainty in modeling total deposition.
As was done for the aquatic cycling model, the following comments are included without specific responses in the belief that they may be useful. Some of these comments were addressed above or in the revisions of the atmospheric model support document or in the summary report; others were not, often because information was lacking. In some cases, reviewers’ comments have been combined and paraphrased.

MODELING TECHNIQUES

1. It is not clear that the choice of days to model representing “extremes in the spatial nature of the atmospheric transport” will result in the most reasonable estimate. At least at first glance, one might presume that selection of the most representative days – i.e., “average days” – would be most appropriate. Perhaps the reasoning behind this assumption could be explained in more detail. This question was addressed in the section above. The selection of the days was not a significant source of uncertainty or error in the estimates.

2. It is noted that the simulations result in a large amount of within-cluster variability. Two days were used to create an average for each cluster. However there were sometimes dramatic differences in the predicted deposition between those two days. Thus, it would seem that the validity of the “average” developed from these two widely varying days needs to be examined.

   This was also addressed in the section above.

3. It is stated that: “Reactive gaseous mercury {RGM or Hg(II)} has a half-life measured in hours and, if emitted in this form, is deposited on a local scale, i.e., within a few tens of kilometers.” Although the deposition of RGM is quite efficient, and, substantial deposition does occur locally, it is not likely that all of the RGM is deposited locally. It would be interesting in future studies to include a mass budget of the emitted mercury, e.g., to estimate the proportion of the emitted mercury that was deposited locally, the proportion that was deposited in the study area, the proportion leaving the modeling domain, etc.

   It is obviously true that not all RGM is deposited within a few tens of kilometers but the fraction that does deposit is a function of the meteorology and the stack heights of the sources. In Florida where the stack heights are relatively low compared to Midwestern power plants, for example, the RGM emitted will likely dry deposit with the 10s of kilometers scale or get introduced into clouds where it will rapidly go into solution and be available for wet deposition. It is felt that RGM emitted above the boundary layer at night will likely be transported long distances. Emissions in Florida that are transported off-shore at night will also be transported longer distances.

4. The time frame of 1 year to obtain clusters of different atmospheric transportation regimes is too short to adequately represent the South Florida/study area. As meteorologists we were not comfortable in extending the one-year of modeling results to represent a climatological deposition to S. Florida. The one year from 1995-1996 was chosen as it was the only year with daily event precipitation results and was not chosen to be representative. For this project we attempted to determine just how representative the 1995-’96 year was in terms of flow patterns and precipitation. We calculated trajectories for S. Florida for an eight-year period from 1992-2000 and performed the objective cluster analysis on each year. What we found was the 95-’96 year was actually representative of the 8 year period and not one of the extreme years. The clusters calculated for the 8 years were
compared to those calculated for the one-year and the variation in the frequency of each cluster varied by no more than 6-10%. This would have had a very small impact on the annual deposition estimates for S. Florida.

5. The spatial scale of the analysis needs to be described. There should be a series of maps that overlay the basic horizontal grid structure. The first should show the NGM data points used by RAMS (i.e., 180-km resolution). The second should be the grid structure of RAMS (i.e., 5-km). The third should be the RAMS data points that feed HYSPLIT (i.e., 20-km). This would give the reader a feel for the density of data from which trajectories for the clusters are derived and from which source-receptor data in HYSPLIT are derived. Figures showing the nested grid system used in the modeling will be added to the Appendix of the modeling document.

6. The report states: "The current state of the art in atmospheric source-receptor modeling used in the analysis does not allow for background sources beyond the immediate model domain to be considered explicitly." While this may be true for the choices made by the authors, it is not generally true. Other choices could have been made (e.g., using an eulerian-based regional scale model) which would have allowed a consideration of broader scales of influence, other sources, and background. If the argument, as made elsewhere in the report, is that there is no basis to constrain these other tools, the same is true for the tools chosen. The statement was written to reflect our belief that the state of the art in atmospheric Hg chemical modeling and the lack of any boundary conditions for speciated Hg levels in the atmosphere, and the budget and time-frame of the modeling project, made the choice of a Lagrangian model the only one practical. Yes it is true that models have been written that explicitly include background inputs but again the values used would have been complete guesses.

7. There is no justification for why the Davie site was used as the trajectory endpoints. Since it is inappropriate to attempt model performance evaluation with existing data, then it appears that a site at WCA3 should have been used. This may not be critical, however, depending on the geographical scale of the analysis, which is not clearly defined. That is, the relevant geographical scale of the analysis may be so coarse that WCA3 and Davie may be essentially the same site. However, if this is so, it is questionable whether one can reliably discern the clusters as derived. The choice of the Davie site was explained in the report. It was chosen so the available measurements could be used in the analysis. Since the trajectories used relatively coarse meteorology as input the two locations do have the same trajectories and result in the same clusters. This is not at all important as the RAMS Meteorology was used for the deposition calculations and not the trajectories.

8. While the selection of 2000 GMT for the start of the back-trajectories may be appropriate for the summer-time wet deposition events, there is no discussion of what would be reasonable for non-summer wet deposition and any of the dry deposition days. Untested in this analysis is whether different results would be obtained if cluster analysis was conducted for trajectories calculated more robustly (e.g., four times per day for all days). Sources for non-summer wet deposition, and even more so, for dry deposition situations, are likely to be different. Therefore, the assessment is biased to one, albeit possibly the major, deposition situation. And furthermore, since it only assesses one, unique to South Florida, mechanism, the "pilot" study, is not readily transferable to other locations where wet vs. dry situations and the types of wet situations are more variable.
While the 20Z endpoint was indeed used for all trajectories, trajectories were run for every day of a one-year period. As a result, we would have still characterized flow from a large number of transport patterns, not only flow associated with summertime convection. The statistical clustering performed using all of the trajectories calculated every four hours for each day would not have changed the clusters derived. Since we also verified the cluster assignment using surface and upper air meteorological maps this was not an issue and our results are not biased as suggested. We should have made it more clear in the text. While the cluster categories were derived using the trajectories with a single endpoint (20Z), the deposition estimates from our model runs were based upon 24-hour simulations. Since the actual lifetime of summertime convection in South Florida is typically on the order of a few hours, even for the days on which rainfall occurred, the majority of the day (18 to 21 hours) would have been characterized solely by dry-deposition.

9. It is very difficult to evaluate whether the 12-hour cut-off is valid. First, the location of the NGM grid is not defined. Second, the plots of trajectories in Appendix A do not indicate the time intervals of each trajectory segment nor how many hours total are included. It would also be helpful to see the clusters displayed for 12 vs. 72 hours and to see where the trajectories "fell off the grid." I wonder whether these 60 days may have formed their own cluster or bin? How variable were they as a group in terms of direction and speeds? Finally, there needs to be an illustration of how the 60 days were placed in bins.

The use of 12-hour trajectories for defining the clusters was investigated. The primary reason for not using 72-hour back trajectories was the lack of missing data going back that far over the oceans. We also ran 24 and 48 hour trajectories and also had too much missing data so we used the 12-hour. Again, this was not important as the manual assessment of each day of the year (365) was done to verify that cluster assignment were valid and that the days with missing trajectories were accurately assigned.

10. There is no explanation or illustration of what the authors mean by "represented extremes in the spatial nature of the atmospheric transport and deposition for the given cluster." What is the conceptual model used to make the selection? What were the specific criteria used to make the selection? For example, at a minimum, one has direction and speed (length of trajectory every 2-hours) as possible criteria. Even with just two criteria and assuming one used the extremes (i.e., direction defined to encompass the maximum compass direction bounds and shortest and longest trajectory length at 12 hours), that would require 4 choices per cluster. Even so, on what basis do the authors "hope" this will minimize potential biases? It also appears that some sort of analysis on the variability within clusters should be conducted in order to assess whether 2 or more samples can adequately represent the cluster. Bottom line, much more work is needed here to ensure that the results are robust and relevant to sources that contribute to mercury deposition in WCA3.

This set of questions is answered above. The choice of the days in each cluster were not significant to the annual deposition estimates. The range in the values for wind speed and direction for each cluster is not as great as the reviewer suggests and thus choosing the trajectories that have the greatest difference in direction was not difficult.

11. While the decision to use RAMS is admirable, there is no discussion of how the modeling was conducted or evaluated. There were 30 individual days modeled, very few "near" each other. Applications of models like RAMS (or MM5 or SAIMM, etc.) require multiple days for spin-up and multiple decisions on what parameters to turn-on or -off. How many ramp-up days were used? Were clouds turned on or not? Was four-dimensional data assimilation used and, if so, for what parameters, why, and where did the data come from? What model
evaluation parameters and criteria were used? What were the model performance statistics? What RAMS model outputs were passed on to HYSPLIT? The overall credibility of this part of the effort cannot be assessed without a much deeper discussion.

This is discussed in the Report provided to EPA on the Aggregation Project for S. Florida. Briefly, We performed several tests for the RAMS spin-up time. We performed 48, 24 and 12 hours spin-up and didn’t observe any significant change. So, we chose to go with the 12-hours of spin-up for our RAMS simulated events. The Cloud physics were turned on for grid 3 (5km resolution) and the convective parameterization was used for grids one and two (60 and 20km respectively). The four-dimensional data assimilation (4DDA) by Newtonian relaxation (nudging) was used in all the RAMS runs. The 4DDA is performed using the data in the initialization files that include time series of gridded horizontal wind, potential temperature and total water mixing ratios, which are analyzed from surface and rawinsonde observations, or sometimes the NGM (first-guess fields).

The RAMS model outputs passed on to HYSPLIT on an hourly basis included the following variables at each grid:

At the surface, terrain height, mean sea-level pressure, total precipitation, pressure, temperature, friction velocity, and micrometeorological scaling variables TSTAR and QSTAR. At the vertical levels, the U and V wind components, vertical velocity, specific humidity, temperature, pressure and turbulent kinetic energy.

We have compared the surface pressure systems and wind flow from RAMS simulations to actual observations, and found good agreement.

12. There is no justification given for why the 20 km RAMS outputs were used in HYSPLIT and not the 5 km outputs. Given the focus on local sources (a bias in this reader's opinion) and the separation distances of the sources and WCA3, one would have expected the finer resolution to be used.

The model results using the 20 km grid vs. the 5 km grid were scrutinized and found to give essentially the same values. The computational time needed to run all of the days in a 5 km grid was beyond the budget of this project.

13. There is also no discussion of how long HYSPLIT was run. Were there any ramp-up days? If only run for 24 hours, multi-day effects cannot have been assessed (e.g., land-sea breeze and other recirculation issues).

We performed 24-hr simulations for HYSPLIT. We did not perform spin-up days for HYSPLIT. We did however, perform 48-hr simulations for HYSPLIT for cluster 2, and compared the output to the 24-hr ones. The results showed that the regional sources had little impact. However, the local sources almost doubled the dry and wet deposition.

14. The modeling excludes area sources, any consideration of atmospheric chemistry, initial and boundary ambient air concentrations, and transported/background sources. Area sources might be larger than in EPA's inventory and thus be more important than alluded to here given evasion results from Lindberg. To ignore chemistry without explanation, especially given the recent hypothesis being tested at the University of North Dakota of rapid mercury reduction in plumes, is inappropriate. Transported or background sources cannot be ignored if one wants to allocate responsibility for mercury deposition to any source or source group. These omissions leave major holes in the analysis and makes achievement of allocation of deposition responsibility among emission sources impossible.

The importance of area sources is still unknown. As was stated clearly in the report (page 18) “The US EPA mercury emissions database considered area source emissions to be only in the

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elemental form, Hg(0), and accounted for only 2 percent of the total emissions. As a result, area sources were not considered in this work. The uncertainty in the magnitude, and form, of the mercury emitted from point sources in S. Florida was much greater than the impact of omitting the area sources in this modeling effort. Future evaluations should consider all sources and their differential impacts on the deposition to sensitive ecosystems.”

Chemistry was not included and the reason was discussed earlier. The plume chemistry and reduction reactions have since been showed to be slower than what Seigner et al. previously used in their modeling studies. We agree with the need for better Hg emissions information from point and area sources. Evasion from the surface is likely not as important as other area sources like motor vehicles.

15. There is little, if any, discussion of what RAMS outputs are used by HYSPLIT. In particular, where does HYSPLIT get the cloud location and features as well as precipitation? This detail was thought to be unnecessary. The passing of gridded meteorological fields is common in the modeling community at this time. As mentioned earlier in our answer to question 11, HYSPLIT uses the following hourly RAMS output variables: At the surface, terrain height, mean sea-level pressure, total precipitation, pressure, temperature, friction velocity, and micrometeorological scaling variables TSTAR and QSTAR. At the vertical levels, the U and V wind components, vertical velocity, specific humidity, temperature, pressure and turbulent kinetic energy. There is no direct cloud information that is passed on from RAMS to HYSPLIT, except for the total precipitation, which is one of the surface variables.

16. Again, it is by no means clear how the choice of "spatial extremes" was conducted or how it can "result in a more robust average deposition and conservative standard deviation for a given cluster."

This was discussed above.

17. The fact that clusters 5 and 7 show little dry deposition in WCA3 is no great revelation since the assessment models only local sources and does not appear to model them long enough to consider any recirculation processes, if any. Again, the clusters were only used to define the frequency that the meteorological cluster occurred and RAMS meteorological data was used to perform the deposition calculations and we included spin-up time and up to 48 hours for the model to run.

18. The very fact that clusters 2, 3, and 4 show large modeled day to day variability for dry deposition exposes the concern that the clustering and selection from within the clusters is weakly justified and is highly uncertain. It has not at all been demonstrated that "a significant effort was expended in defining the local wind flows using RAMS." First, as has been commented on above, the representativeness of the selected days has not been clearly explained or justified. Second, the model performance of RAMS for individual days has not been discussed. This was discussed above. RAMS performance for the days modeled was not included in the report but was performed.

19. The justification for using a standard deviation on 2 data points is problematic given lack of assessment of whether these days really represent the cluster. As addressed earlier the uncertainty estimate obtained from the standard deviation on the two days modeled actually over-estimates the uncertainty (See discussion above).
20. Unfortunately, a great deal of effort has gone into a system that is under-specified and under-constrained. It simply models and adds up local contributions when they hit WCA3. If one reduces this contribution, which is defined as linear, one gets the commensurate reduction. The analysis cannot assess the allocated responsibility of the local sources to the whole. In my understanding, that is what a TMDL should do, and this methodology cannot do so.

This is a statement not a question so nothing to respond to here.

21. The discussion of the relative contribution of gaseous and particulate Hg(II) to wet deposition, and the resultant speciation of Hg in wet deposition is simplistic. Clearly, in the aqueous phase, Hg will also partition between the dissolved and gaseous phase such that Hg scavenged from the gas phase could easily partition to particles in wet deposition and vice versa.

This is a statement as well. While the statement is largely correct there is nothing to comment on other than we used a simple atmospheric model due to monetary and time constraints.

GLOBAL BACKGROUND

22. Even if poorly known, RGM from the global background should be included because of its high deposition velocity. There can be no apportionment among sources included in the model without knowledge of background.

This has been discussed earlier as well. We do not agree with guessing at the background levels and then seeing what we get. We stated that we would only model anthropogenic pt sources and we understand that this is not good enough. We still do not know the importance of global sources and the production of RGM.

23. In the conclusions, the authors state, "until measurements or models allow us to constrain the uncertainties in the long-distance transport phenomenon there is no objective basis for addressing this question [of the role of non-local sources]." I want to challenge the assertion of no objective basis. Just a page before, in the third paragraph of the conclusions, the authors give an estimate of background concentrations in rainfall (about 5 ng/L), and clearly lay out the implications (i.e., background deposition of 6.5 ug/m2-yr and the increased difficulty of reaching target fish concentrations). While that estimate might be uncertain, is it not better than the estimate of 0?

No, as this is just one person’s estimate of the background and the background contribution to the dry deposition is not included in this argument! We disagree with the statement presented here.

24. Indeed, the model's failure to predict all of the observed deposition when using the most recent emissions data might logically imply that non-local sources make up the difference. Perhaps the difference in predicted and observed wet deposition fluxes constitutes an objective estimate of non-local sources, or at least provides a basis for estimating non-local contributions. I understand that parameterizing by difference is risky in an uncertain world. Yet, calibrating alternate parameters such as wet-removal coefficients, emissions rates, and emissions speciation also constitutes parameterizing by difference (or to make up a
difference). To me, allocating the difference to non-local deposition is more objective than sticking with the original assumption of 0 non-local deposition and allocating the difference to an altered model parameter set (i.e., what is used as the base case here).

Discussed above.

25. It is noted that while the wet deposition with Scenario #1 more or less matches the observed wet deposition, that with scenario #3 is substantially less. If scenario #3 is more representative of the “actual” emissions, then, this would suggest that approximately 2/3 of the mercury deposition is not coming from identified local sources. This difference – i.e., all the deposition can be accounted for by local sources vs. only 1/3 of the deposition can be accounted for by local sources – is very significant. Clearly, much attention must be paid to improving the accuracy of the mercury emissions inventory. These points are brought out in the Conclusions section of the report.

See discussion above. The confusion with the 3 scenarios has been removed in the most recent version of the report.

26. There is no mention of the atmospheric oxidation of Hg(0) as a source of Hg(II) to the system. Some rational should be provided for the lack of inclusion of atmospheric oxidation of elemental Hg in the model formulation. Clearly, the model only considers local point source emissions and not the “background signal”. The rationale for this appears to be the preformed notion of the research group that local sources are dominant to deposition to the Everglades. This supposition needs to be discussed. I do not agree that one can definitely conclude that all the deposition is local even though this is the hypothesis of the research group that produced the model. Other researchers have presented an opposing view and I feel that the model should be set up to include the possibility of significant input from sources outside of the Florida domain.

Again, statement of bias on the part of the reviewer. We modeled both local and regional sources to the deposition in S. Florida and found that local deposition was >90% of the total so we then proceeded to model the various scenarios using only the local sources. The Hg chemistry was thought to be too slow to be important on the time scales of the emission to deposition observed in this study.

27. The lack of inclusion of any background inputs, or signal except for the local emissions, results in the large discrepancies in both deposition flux per day and deposition flux per cluster in Figs 2 and 3. I do not think this is realistic. The flux values are much lower, for example, for wet deposition for these model efforts compared to the fluxes in Fig. 1. What amount of rainfall was used in the estimations of wet deposition in these simulations?

28. Sensitivity analysis could also be used to assess the impact of different scenarios relative to the Base Case if a significant background signal was present. Clearly, based on deposition velocities, the dry deposition of Hg(II) gaseous species in the global background should be included in the model, even if the value of this term is poorly constrained. While data on reactive gaseous Hg in the atmosphere is limited, there is enough information available to suppose that the global background value is non-zero.

The argument that the global background RGM is non-zero and that based upon its deposition velocities should be included is actually backward. The rate of production of RGM in the atmosphere that then makes its way into the boundary layer would have to be greater than the
rate of deposition for the global background to significantly contribute. The presence of RGM in the atmosphere, especially the free troposphere is not, in and of itself sufficient to show that this global production is important to S. Florida. The importance of the global background will continued to grow in importance as point sources are regulated.

29. The analysis provided here is constrained within the way the question is formulated: “To what extent could abatement of South Florida mercury emissions reduce deposition on the Everglades and subsequent bioaccumulation in Everglades biota?” Ignoring the “background” signal, and modeling only local emissions, is only reasonable if all effects are truly a linear response to input concentration, and are independent of input form. For example, the assumption must be made that particle size distribution and Hg gas species composition (which is thought to be HgCl2) is the same for local and more remote sources. This is probably not true. However, given that it appears that the water model considers all atmospheric inputs to be equal and does not explicitly treat gas and particle deposition differently, this concern is mute unless the MCM model is designed to consider the input type as an important parameter. Overall, I see the major difficulty of any attempt to do a TMDL-type analysis of atmospheric Hg sources is the lack of sufficient knowledge and data on atmospheric concentrations, speciation and reactions. This is improving with on-going research. However, as stated above, point source input functions are also probably changing because of the influence of legislation, in-place or pending. Thus, while it appears that the atmospheric modeling effort has to a large degree captured the meteorology (or perhaps I am just displaying my ignorance here) I am not convinced that the current attempt has succeeded in the goal of modeling accurately Hg fate and transport in the atmosphere for the reason discussed above.

30. Relative importance of local versus intermediate versus global mercury inputs is not known. The report states that new methods have been developed that will be use over the next 2 years to “answer this question with confidence.” The added work needs to ensure that relative contributions from these 3 categories of sources can be made. Note that page 2 defines local as “within a few tens of kilometers.”

ATMOSPHERIC TRANSFORMATIONS

31. No discussion of gas/particle interaction. Apparently, it is not clear that atmospheric transformations are not included. The discussion of the effects on deposition rate of excluding atmospheric transformations is inadequate. Gas and particle have quite different deposition velocities. Also, differences in atmospheric transformations during wet and dry deposition should be discussed. A “sources of error” section is needed for the atmospheric model.

32. The atmospheric modeling analysis did not include any atmospheric chemical transformations of emitted mercury. This may be a reasonable first-order analysis methodology if one is considering only the effect of local sources – as this analysis is doing – but is unlikely to be valid if one were considering regional and longer-range effects. Thus, while this assumption would appear to be somewhat reasonable for this initial analysis, a more comprehensive atmospheric modeling scheme may be desirable in future analyses. This uncertainty is noted in section 4.1.1.

33. While much detail is given on the back trajectory and clustering analysis, it is not explicitly stated anywhere what atmospheric chemistry, if any, is included in the model. At the most
basic, the lack of any gas to particle interconversion is a serious flaw of any atmospheric Hg model as these two phases have such dramatically different deposition velocities. This has been a flaw of previous modeling efforts as well, such as the Bullock et al. (1997) RELMAP model. If chemistry is included, details should be given. In the Bullock model, atmospheric reactions were only possible during cloud formation and wet deposition. Again, this is a simplification of reality that shows up the limitation of the model. Was a similar approach taken here? More details are required.

34. It is well known that Hg(II) is “very sticky” and it is likely that even though the Hg(II) may be emitted from a point source in the gaseous phase, it has the potential to interact with particulate matter during transport. There is likely a steady state between adsorption and desorption from particles that is a function of the particulate concentration. The model should either include gas/particle interactions, or acknowledge and discuss the weakness of not including basic atmospheric interactions in the model.

35. Although there are some difficulties, deficiencies, and unknowns in the atmospheric modeling, particularly the need to include the background sources, I felt that it was a good first attempt. I do not agree that this is the only useful approach to modeling in south Florida. Bullock, in the USEPA Report to Congress, gave credence to global background by incorporating oxidation of a background air concentration. Further, the models do not utilize any chemical transformations. Chemical transformation may be key to understanding atmospheric mercury. Given that their modeling approach does not allow for the inclusion of the global background, other approaches might have given a better assessment.

HENRY’S LAW COEFFICIENT

36. Why not use a Henry’s Law coefficient for HgCl, which is known, instead of simply adjusting the value down. Is this just parameterization of the model to fit the data? Adjustment need may be a consequence of lack of transformation in the atmosphere.

37. In light of this built-in bias, the calibration of this local source atmospheric model to total observed fluxes is a bit troubling. Not much detail or justification is given to the alteration of the wet deposition removal parameter (nominally, Henry's Law constant) in order to match observed total deposition. At a minimum, the authors should show the observed and predicted deposition fluxes at the FAMS stations for the original model parameters and the calibrated model parameters. In addition, the authors should provide at least a short discussion on the physical or chemical implications behind the parameter change (i.e., partitioning of Hg0 and HgII to rainfall is kinetically limited, perhaps).

38. The adjustment of Henry's Law constants is flawed. The choice is based on some unspecified comparisons with observations at the Davie site. Without consideration of initial and boundary conditions and all sources, one cannot justify the adjustment. To do so has to make the unjustified assumption that all of the mercury at the site comes from the modeled sources, clearly an erroneous assumption. I take no comfort in the statement that the change did not affect total deposition downwind. The fact that it didn't change anything downwind leads me to wonder what other compensating effects are occurring in the assessment that we can't assess?

39. It is acknowledged that to make the wet deposition data match, the Henry’s Law coefficient for gaseous Hg(II) had to be reduced in value. Why not use the value for a species such as
HgCl$_2$. These values are known. No explanation or justification is given for the use of a lower value. What is the chemical basis of this? or is this just parameterization to make the model fit the data. Again, this shows up the weakness of the model in that it likely inadequately simulates the fate and interaction of Hg between phases in the atmosphere, and thus it is necessary to arbitrarily modify the “constants” to make the model fit. This does not inspire confidence in the model’s ability to predict reality.

**SOURCE INVENTORY**

40. Source speciation needs more discussion. How would utility information about speciation affect results.

41. Discrepancies in speciation and amount between EPA and Stevens source measurements need to be discussed along with caveat on p37.

42. Not enough emphasis on effects of source inventory on deposition rate.

43. More troubling is the use of older emissions data for the base case. As the authors point out, emissions scenarios 2 and 3 make use of more recently-collected data on the local emissions. Unfortunately, these scenarios produce lower deposition fluxes over the Everglades, indicating the possible importance of long-range sources to make up the difference. There is no indication in the report that the newer data are flawed or biased in any way. I believe that a modeling study should use the latest and best data possible, even (or especially) if it tends to contradict the original assumptions. A case study that minimizes the use of recent, site-specific data for no stated reason is providing a bad example that should not be encouraged by EPA. The base case should use the best, most recent, most local data possible. Alternate cases can be set up to explore uncertainties, of course.

44. Also, in the discussion of the scenarios later in the document (p. 45), there is a statement that “If this latter rate derived from regional sources was more correct.” Why wouldn’t we believe that the scenario with actual speciation data (Scenario) is more realistic than the base case?

45. Also, I believe that there should be some discussion of how the scenarios might truly relate to the current situation. The main document should to explicitly state that the base case is based on 1990 emissions (not just that it was from the Mercury Report to Congress). In addition, we should add some language regarding what reductions in emissions may have occurred since 1990, e.g., have there been any reductions yet as a result of Florida’s standards for medical and municipal waste incinerators.

46. There is little discussion regarding the atmospheric emissions inventory used in this analysis. As this forms one of the fundamental building blocks of the analysis, it would be very useful to have a detailed description of the following: (a) how the inventory was derived, if necessary, on a source-by-source basis; (b) whether emissions estimates were based on stack tests or emissions factors or some other approach; (c) the throughputs and emissions factors used, if applicable; (d) a discussion of sources that are not included in the inventory, e.g., mobile sources, etc. The inventory plays a crucial role in the analysis, and the reader is not given any information to judge its relative accuracy. Such information may be beyond the scope of the Pilot TMDL, as it is currently envisioned, but, would be very important to be
included in future TMDL analyses. The large uncertainty in emissions is noted in Section 4.1.1 and highlighted in the Conclusions (Section 4.3).

47. The sensitivity analysis with regard to emission levels shows how crucial good knowledge of source inventories is. Depending on the choice of how emission inventories are calculated, the deposition estimates vary by a factor of 3-4. Practically, given the fact that most incinerator sources are likely modifying their emissions of Hg by various methods, as a result of voluntary or mandatory regulation, it will be extremely difficult to obtain an accurate account of local source inventories. These are likely to be changing constantly in the short-term. The model results demonstrate that if the input is reduced, the fish concentration goes down. However, given that the inventories are poorly known and likely variable, it will be extremely difficult to apportion the Hg in the true sense of the TMDL approach. Given the difficulty of the model estimations, and the need for more detailed information of many of the processes involved, it will not be possible to accurately assess the importance of each source to the degree required. Also, given that the “background” signal is essentially ignored in the analysis presented here, it is not possible to apportion Hg between the local and the “global” sources with the required accuracy. This is acknowledged in the overall TMDL report.

48. Overall, I think this is an excellent pilot study of the concept of linking air and water models in developing a TMDL for an atmospherically driven contaminant like Hg. But the operative word here is “pilot”. A TMDL for an atmospheric pollutant must be able to fractionate the atmospheric deposition into background (global or regional) sources and local (presumably controllable) sources. The current framework is run with atmospheric loads that, although they are quite uncertain, are admitted to be computed without estimating background contribution. Yet as shown in figure 4, the computed wet deposition (without background estimate) compares reasonably well (some months are a problem) with the FAMS observed wet deposition. So is the local source modeled deposition an over-estimate or is the background wet deposition in reality negligible? I recognize that this is a very difficult question, but in this case even the estimate of background wet deposition (based on an assumed 5 ng/L) is significant relative to the modeled local deposition. And the dry deposition is even more uncertain. How much of the dry deposition could be background?

POLICY RELATED COMMENTS

Some reviewers made comments that seemed to be more related to policy than to technical matters. As discussed above, Florida DEP regards this work as an essential step along the way towards producing a TMDL, but does not regard it as having produced a TMDL. We have included comments on the margin of safety as a subsection of this section.

The differing points of view between those who wished to view this as a TMDL and those who wished to make certain it was not viewed as a TMDL is illustrated by the following statements:

- Keep technical – leave out value or policy statements
- Treat this as a real TMDL and do not simply say the uncertainties are too great.

This conflict resulted in many of the comments that follow. The following comments are included in the belief that they may be useful to others. We have not provided specific responses here but all of these issues have been addressed.
1. This is not a true stakeholder process – does not follow Florida Statutes.

2. The report implies more completeness than justified – almost ready for use. Implies that reducing local emissions by 75% is necessary and will achieve fish target levels in 10 – 20 years.

3. If local sources are solely responsible, all that is necessary is to reduce local sources by the target, percentage reduction – don’t need models for this.

4. Inappropriate policy statement to the effect that background sources cannot be controlled. May be confusing global background and more distant regional sources. It is not conservative to assume that global and regional sources cannot be controlled.

5. Summary of TMDL process should reference specific guidance from EPA. The eight elements do not completely describe the process. In particular, there is no discussion of baseline conditions.

6. The 303(d) process description is oversimplified. This section should discuss the settlement agreement.

7. Site-specific bioaccumulation factors under baseline conditions include all of the complexity and could be used to calculate a target concentration.

8. There is no plan to resolve local, regional, global question.

9. As the fraction contributed by non-included sources, i.e., global background and regional, increases, the extent of abatement by local sources necessary to meet the target increases. This is a policy consideration.

10. No plans are given to improve data for key variables that the models are sensitive to?

11. While this study represents a considerable amount of effort at an initial assessment, it falls short of being an example for anyone to use in an actual TMDL process. In fact, it misses the mark assuming the goal of a TMDL is allocation since it explicitly ignores major pieces of the puzzle. While the report focuses solely on local point sources, their role cannot be properly assessed without addressing all sources. Despite such labels as a "pilot study," I am also greatly concerned that it implies more completeness than is justified. The tools, data, and overall methodology are also not transferable beyond the Everglades, given its unique climate and deposition patterns. Furthermore, the methodology may not survive the test of time as the tools necessary to deal with the other pieces are integrated into a more complete methodology.

12. At best the analysis illustrates where much additional work is needed, at worst, it potentially misleads the reader in that it implies the tools and databases, as cobbled together in this report, are almost ready for use. Furthermore, it leaves the impression that reducing local emissions by > 75% are necessary for and will indeed achieve fish with the target levels of mercury within 10 to 20 years.

13. At a minimum, major disclaimers and caveats are needed right up front. Better still, the effort should be shelved until after the additional worked planned, as claimed in the report, is competed and the tools and data to properly assess the problem are in place for use. All of
this puts aside the considerable issues associated with the legal uncertainties of the TMDL process, especially as it relates to atmospherically derived pollutants. For example, I am not at all confident that we even know what the policy relevant questions are and, therefore, cannot yet design the technical assessment methodology to address them.

14. The most disturbing policy assumption in this work is that only local point sources can (and must?) be controlled to achieve the selected numerical target value.

15. The report makes two critical statements right up front that illustrate my fundamental problem. First, "The pilot study asks: To what extent could abatement of South Florida mercury emissions reduce deposition on the Everglades and subsequent bioaccumulation in Everglades biota?" Second, it states "It gives no information about the significance of global sources, which could limit the efficacy of local controls." The goal as stated cannot be achieved without addressing the very thing the report says it won't do. The phrase "to what extent" requires some knowledge about the whole and some confidence that the portion assessed can be done reliably relative to the whole. The only other way to attempt to achieve the goal would be to demonstrate the veracity of the local source assessment tool, the data for which does not exist. A more minor point is there is neither a definition nor justification for the claim that the important scales for the Everglades are only local and global.

16. There is an encouraging statement here that should be the major disclaimer of the study and up-front in bold type. My edits on this statement are indicated in italic. "Until the apportionment between local, regional, and global emissions and global natural background has been resolved, and the tools and methods to account for this split are developed, tested, verified, and ready for application, Elements 1, 3, 4 and 7 cannot be completed." This and similar statements are prevalent throughout the report saying there is no basis for dealing with one piece or another. Therefore, it should be made clear that this study only attempts to tackle certain pieces of a potential technical process. Unfortunately, at least for the atmospheric piece, the methods used may turn out to be substantially modified in the end when all the relevant pieces come together.

17. The policy assumption made here, "we cannot control background sources" is inappropriate. This assumption drives the "non-conservative" conclusion stated on the previous page. The analysis presented here, intended to show the conclusions of local source control amount could be worse, are one sided. What if one assumed regional and global sources could be controlled, then one should investigate the cost-effectiveness of controlling each source category. Furthermore, what if the hypothesis that mercury reduction is a rapid, in-plume mechanism proves true, might that remove the local source contribution to the regional and global pool?

18. The analysis of inter-annual variability is interesting. However, it is not clear what was done with it. Perhaps, this somehow formed the basis for the conclusion on page 51 that the target level could be reached in 95% of the years with an emission reduction of 79%. If so, then the analysis and assumptions should be more fully discussed in the discussion session, not in the conclusion section. Furthermore, this is also a policy assumption on how such data would be used. Again, I suggest the report stay away from policy assumptions.

19. The title of Section 1.5 (Identification of Violated Water Quality Standards and Impaired Designated Uses), would be more accurate if it was changed to “Identification of Water Quality Criteria that are Exceeded and Impaired Designated Uses.”
20. In the last paragraph on page 12, text incorrectly refers to the Class III water quality standard for methylmercury. The number listed is actually the water quality criteria for mercury, which is for Total Recoverable mercury.

21. In this same paragraph, the last sentence states that DEP recognizes that health advisories for mercury indicate that the current criterion, which is met, is inadequate. We recommend that this statement be qualified in some way, at least to limit it “to this system.”

22. In the first paragraph in section 1.6, the last sentence states that “Methylmercury concentrations in excess of 0.5 mg/kg in fish tissue are considered toxic to mammals, including humans.” However, this is an overly simplistic description of the levels used for fish consumption advisories, and more detail should be provided. We are concerned that this sentence could be misinterpreted to mean that consumption of fish with these levels would cause mortality (“instantaneously” as if someone ingested a toxicant like arsenic) when, in fact, this is the limited consumption advisory level (hopefully, this is not even true at the “No consumption” level of 1.5 mg/kg).

23. Overall, the current pilot study suggests that it is possible to do a TMDL-type Hg study which includes a large atmospheric component. However, if a modeling approach as used here is applied, then the complexity of the approach and the resultant system that is modeled indicates that this will not be successful unless there is detailed knowledge about the system being investigated. The Florida Everglades has been one of the most intensively studied regions in terms of Hg cycling but there are still large gaps in the data or information required to sufficiently model the system with enough certainty. Clearly, it would not be possible to extend the same amount of effort in each particular environment where there is a Hg problem. The sensitivity of the results to the source inventory, and the demonstration here that the actual source signals differ from those assumed (i.e. in the Report to Congress), it is apparent that to accurately model Hg deposition to an environment that is likely to have local sources as major input, then source inventories and speciation will have to be derived for those particular sources. This will likely require substantial research effort in each case. Furthermore, these inventories are likely to be changing in the short-term. Thus, while this study has demonstrated that a detailed analysis of an ecosystem using a coupled atmospheric-aquatic cycling model can provide information that is sufficient, when highlighted uncertainties and missing data have been addressed, to allow allocation of sources, including the atmosphere, in a TMDL approach, it is not likely possible to use the same approach on the numerous water bodies in the USA where Hg fish consumption advisories are currently issued, or will be in the future.

24. The TMDL (total maximum daily load) concept remains the most logical way to preserve water quality. In its wisdom, Congress in the 1970 Water Pollution Control Act defined the integrity of natural waters as fishable, swimmable and drinkable. Such a definition allows for the many uses and the myriad chemical, biological, and physical conditions that exist in natural waters and relate to integrity without controlling it. In this document, the TMDL is defined in many places on pp. 4-6, and should be defined simply at the first notation (p. 4, l. 3) and more completely as shown at the bottom of p. 5. Part of the problem is trying to shoehorn into the TMDL process, the concepts of water quality criteria. USEPA has defined water quality criteria as an easily measured parameter of chemical concentration that controls drinking water quality and surface water integrity. In many cases these criteria work well. In other cases like mercury, load probably controls integrity and not concentration. Thus, it is possible to use loads from any source to calculate the relationships between loads and response. That is why TMDL is such a useful and logical concept.
25. The confidence in a given relationship is key to whether or not a reasonable TMDL can be performed. Arbitrary TMDL’s result from high uncertainty relationships and can lead to non-productive controls. The Foreword to the Florida Everglades TMDL for mercury (FETMDLHg) states “The purpose of this project is to establish the technical basis for more definitive efforts in the future.” It goes on to say “At this time significant uncertainties remain in the basic understanding of the atmospheric mercury cycle and modeling of its transport and fate, and likewise our understanding of the aquatic cycling transformation processes of mercury and its bioaccumulation in aquatic food webs remains incomplete.” I agree with these statements, but have identified inconsistencies in later statements that seem to conflict. Further, several very important parts of the assessment require expansion to complete the TMDL process. I will discuss these in the section on general comments. Specific comments follow the General Comments section.

26. Another issue on this section (4.4.4, Margin of Safety) concerns the supposition that the local sources must bear all the burden of meeting the standard. Furthermore, the last little bit costs the most to remove; it is easiest to remove the large concentration sources. I do not think one should discount global efforts. Global pollutants require international efforts, and this applies to mercury as well as CO₂, CFCs, and DDT. NAFTA and the EEC provide a step in this direction (Pilgrim et al. In Press; STOTEN). Furthermore, if the relationships in the above table hold and global background provides 70 percent of the annual loading (Guentzel et al. In review), then it is unlikely that meeting the standard is achievable without international efforts. One of the reasons why I object to this detailed discussion is because the report is for a pilot study. This kind of discussion suggests that it is real, and that policy decisions can be drawn.

27. With regard to the conclusions (section 5.0); I have a question. Have fish responded to changes in load? Presumably, as incinerators have come into use and later, their emissions have increasingly been controlled; the load to the Everglades must have changed, at least according to the model in App. I. Has time elapsed adequate to observe such changes, or is the assumed linear relationship incorrect? These questions are key to whether you think this is a pilot TMDL. If you agree with the way I read the conclusions, this is no longer a pilot TMDL. No one will be that naive. I think the discussion in the last pp. of section 4.3 (sic) Conclusions, are more accurate. The section 5 conclusions are saying the TMDL is accurate!

28. This document takes a very straightforward approach to describing the current status of what is known and what remains to be determined for mercury cycling (atmospheric and aquatic) in the Everglades. The report was certainly a worthwhile effort in that it brings many new issues to light and updates several others, but the constraints placed on the study make it difficult to see how our current knowledge of mercury in SE Florida can be readily transformed into a defensible TMDL.

29. The maximum safe daily dose for wading birds is not known for any species, but is inferred from mallard duck feeding studies. “Safe daily dose must be determined for the species of interest and compared with actual exposure.” “Without this information, there is no basis for establishing a margin of safety.” The report should note there are other ways to establish a margin of safety as part of the TMDL process. It may not be necessary to determine individual margins of safety for each aspect.

30. Perhaps a summary of those areas needing further investigation that could significantly alter the findings of this report could be presented in the Conclusion and Recommendations.
section. While the report clearly identifies the strength and weaknesses of our existing knowledge when it comes to mercury in the Everglades, I believe the authors were overly optimistic when they conclude that, “There is every reason to believe that, with modest additional effort, these remaining uncertainties can be reduced to levels that will allow reliable, confident allocation of mercury emissions…."

31. The report is generally well-written, succinct, and technically sound. However, it is not a TMDL, as the report specifically states in several places. It is a modeling study that coupled atmospheric and aquatic models to address mercury cycling through the food chain in one location in the Everglades ecosystem. The elements of a TMDL are listed in Section 1.1, and the last paragraph of Section 1.1 states which elements were not addressed in the document. Unfortunately, a cursory review of the document can easily overlook this paragraph. I recommend a new section be added to the Report, titled, Purpose; that it be the first section in the report, preceding the Background Section; and that the general and specific objectives from Appendix II (cited above) be explicitly stated in this Purpose Section. This does not detract from the considerable effort made to address the objectives and sub-objectives listed in Appendix II (2. Aquatic Modeling Objectives, page 1), but this is not a TMDL Study.

32. The TMDL issue is heavily driven by litigation and there should be no misunderstandings about what is contained in this document. The expectations among a significant number of states, environmental advocates, and other stakeholders are that these two prototypes – WI and FL - will establish the process for conducting mercury TMDLs throughout the U.S that satisfy the court-established deadlines. In addition, those stakeholders under court orders will use these results almost verbatim in their TMDLs, in some instances, without the caveats. This includes the relationships between wet and dry deposition, the empirical relationships between Hg(II) deposition and fish Hg concentrations, and the exponential decrease in fish Hg concentrations over time following deposition reductions. It is critical the reader understand that these relationships and the results are NOT transferable to other areas without extensive review and evaluation. I strongly urge you to change the name of the report to state this is a modeling exercise to project the magnitude and timing of changes in atmospheric Hg (II) deposition and subsequent changes in fish mercury concentrations, and not a guidance manual on how to conduct a mercury TMDL Study. This is not a semantics issue.

33. Is there adequate discussion of the conclusions? Are they justified and consistent with current state of knowledge? The first paragraph in the Conclusions Section states that the primary objective of this pilot study was to explore how a TMDL or critical loading analysis can be conducted when the pollutant of interest enters aquatic ecosystems largely through atmospheric deposition. The second paragraph of the conclusions states that there is a linear relationship between fish mercury concentrations and atmospheric Hg(II) deposition. To reach a target of age-3 largemouth bass average concentrations not exceeding 0.5 mg/kg wet muscle for an average year requires an approximate reduction of 75% in atmospheric Hg(II) deposition. The third paragraph states the mercury concentrations in age-3 largemouth bass are predicted to achieve 50% of the ultimate response within 6-7 years and 90% within 20-25 years following sustained load reductions. I am concerned that the messages in the first three paragraphs of the conclusions are: 1) This is how you conduct a mercury TMDL study or critical loading study; 2) Based on this study, a 75% reduction in local emissions will achieve the Action Level needed to eliminate fish consumption advisories in the Everglades; 3) 50% of the fish will be below the fish consumption target level in 6-7 years and 90% will be below the target level in 20-25 years. If the reader proceeded no further, the management strategy would be clear. It is not until the second page that there is any indication that there might be uncertainty in these estimates or that some processes might not be well understood.
Throughout the document, there are caveats, assumptions, sensitivity analyses, and estimates of uncertainty because much of the information needed to support these specific statements is not available. These uncertainties, however, are not reflected in the first page of the Conclusions Section.

34. I would strongly urge you to consider re-writing the first page of the Conclusions Section. This study was an exercise to couple atmospheric transport and transformation models for atmospheric mercury with an aquatic model that would predict the cycling of mercury through a wetland food chain to largemouth bass. With substantially more information, it might be possible to conduct a mercury TMDL using this approach, but this information is currently unavailable. IF ALL THE MERCURY IS ASSUMED TO BE DERIVED FROM LOCAL SOURCES, the coupled model system predicts that significantly reducing atmospheric mercury loading (i.e., >75% reduction) might result in fish tissue mercury concentrations in a 3-year old largemouth bass that were below the target level for issuing fish consumption advisories. Mercury concentrations in older fish (i.e., > 3 years), however, still would likely exceed the fish consumption advisory target level. In addition, this reduction would not be instantaneous. It would require up to several decades to achieve the target levels. This also assumes an instantaneous reduction in atmospheric mercury loadings with no phase-in period for emission reductions. More importantly, it ASSUMES THERE ARE NO OR VERY LIMITED GLOBAL CONTRIBUTIONS OF MERCURY to the site. As the relative proportion of global mercury in deposition increases, the probability of reducing fish mercury concentrations through local emission controls correspondingly decreases. There are substantial uncertainties underlying the available data to perform this mercury modeling study.

35. This draft report is being reviewed from the perspective that it is not an actual Hg TMDL analysis, but rather, as the authors state, a “demonstration project to explore the utility of using the atmospheric and mercury cycling models with the TMDL framework and to provide the stakeholders with technical information that may be used to develop a water quality plan to address mercury issues in the Everglades.” The operative concept is that this is a pilot study that is intended to investigate the feasibility and utility of this approach for a more rigorous and in-depth analysis of Hg in the Everglades as a whole. We should constantly be reminded that this modeling work has been conducted on a relatively small plot and the aquatic model is being calibrated on a site-specific basis; therefore, extrapolation to the Everglades as a whole or worse to other sites around the nation should not be considered. Having said this, I will try to focus on the science and modeling theory in this review, although some comments below will refer to the potential application of this approach as a TMDL framework.

36. In most cases, however, the problem is that our current state of knowledge on a number of Hg cycling processes (as mentioned in the reports) is what is limiting the modeling accuracy and utility. While the report mentions most of the data/knowledge gaps, I do not feel that the model was used to determine a priority listing of process experimentation or data acquisition (see below).

37. I recognize that this study was, by necessity, conducted using only available data. At least for the water model, this has necessitated a strategy that one would call more of a screening model application rather than a management application of a fully calibrated and confirmed model. I really think this point should have received more emphasis in the report, and the “calibration” (see question 6 below) should really be referred to as a “screening-level” or “preliminary” calibration.
38. With regard to setting a “margin of safety” for a Hg TMDL in Florida, there appears to be a wide discrepancy between the current water quality standard of total mercury = 12 ng/L and the level of ambient total Hg (2 ng/L) that is yielding considerable exceedance of the 0.5 ppm guideline for fish levels. I would recommend focusing this modeling effort on determining if there is something unique about the Everglades that leads to this high BAF in fish, and, if so, what condition or combination of conditions is it that leads to this observation. Only in accomplishing this understanding can a decision be made to either alter the WQ standard for the whole state or to issue a resource specific water quality based limit for the Everglades as has been done in the Great Lakes for phosphorus and bioaccumulative chemicals of concern.

39. Another key word here in this overall approach is that the models are “linked”. “Linking” is not “coupling”; there is no feedback between models. The most correct way to do this problem, especially I would think in a system as spread out and diverse as the Everglades, would be to truly couple the air and water models. In this way feedbacks (exchanges) across the air-water and air-land (plant) interfaces can be incorporated in a correct dynamic way. I would definitely recommend considering this in the next generation of this approach; perhaps some relatively simple sensitivity work can be done with the air model to get a feel for the importance of feedback in this system. I realize that there are important scaling issues in truly coupling these two models, but we eventually have to get away from using water/land boundary conditions for our air models and vice versa for our water models.

40. This study is a major step forward in demonstrating the feasibility and utility of conducting a TMDL analysis for a pollutant that has an atmospheric source component. The contributors to this work should be congratulated, and they should be encouraged and funded to continue this path of investigation. However, I am concerned because of some of the initial statements in the Conclusions section that a reader might get the impression that this is a finished product. In particular, I am concerned that this report might be used for decision-making regarding Hg problems in the Everglades on the basis of some of the statements about load reduction requirements and system response times. In spite of the progress demonstrated here, there are still major unknowns that must be addressed prior to a valid TMDL implementation. The following issues – this is a minimum list, there may be others – still need to be addressed before a TMDL can be implemented for Hg in the Everglades:

- local versus global/regional sources of atmospheric deposition;
- the relative contribution and lag time of atmospheric deposition on surface water inflow loads;
- the problem of extrapolating the site-specific WCA-3A model application to the entire Everglades;
- better quantification and characterization of Hg emissions in south Florida; and
- quantification of uncertainty in the development of a load-response curve and confirmation of the response time of the system to changes in loading.

41. Margin of safety needs to account for other water quality effects – sulfate, eutrophication, etc.

42. Questions about 0.5 mg/Kg target have been answered by EPA’s new value of 0.3.

43. Ways of establishing a margin of safety should be discussed instead of pleading ignorance about wading birds.
44. In the discussion of Section 2.3, Identification of Target Levels to be Protective of Beneficial Uses, it would be useful to include additional health endpoint information. For example, how does the 0.5 mg/kg mercury level – specified as being safe for unrestricted consumption – compare with other national and international guidelines? How does this level compare with information from the literature regarding health effects? Since these target levels are the fundamental numbers in the whole analysis, it would be useful to see them in some sort of overall context. While there is a brief discussion of this guideline in Section 4.2.2, more information would be helpful.

45. Consideration of the required margin of safety is difficult. As stated, there is a margin of safety in the fish advisory. For the models, some margin of safety must be included to take care of short-term variability in climatic and other conditions and the managerial desire to have a result in within a few years. For example, implementation of some strategy could be followed by a number of wet or dry years, which could lead to a large difference in input relative to prediction. The models assume a random fluctuation in climatic conditions while it is becoming increasingly evident that climatic changes are more cyclic in nature. Some margin of safety needs to be included to account for the non-random nature of seasonal cycles in the short-term (1-10 years). I’m not sure how to do this.

46. Also, there needs to be a margin of safety to account for other factors changing that impact Hg methylation/bioaccumulation that have nothing to do with emissions. For example, changes in sulfur or carbon loadings to the system could change methylation rate substantially. Changes in eutrophication could influence food web dynamics which would impact overall bioaccumulation. Some attempt needs to be made to add a safety margin to account for such changes in related parameters.

47. I was not comfortable assuming the margin of safety was automatically incorporated through the fish consumption advisory target level. There is a margin of safety in the toxicological endpoint, but there is also an on-going debate about the suitability of this reference dose and what margin of safety is achieved. In addition, a 3-year old bass is being used as the endpoint, but older fish will have higher mercury concentrations, which will result in a greater mercury dose per unit of fish tissue consumed. The other two factors are appropriately addressed. The Appendices nicely discuss the concerns about uncertainty and how these were integrated into the modeling exercise.