Chapter 7: The Everglades Mercury Problem

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This chapter diverges from the approach of previous years; it is intended to be more accessible to a nontechnical audience. However, **Appendices 7-1** through **7-16** provide additional detail to meet the Everglades Forever Act (Act) requirement that the South Florida Water Management District (District) and Florida Department of Environmental Protection (Department) shall annually issue a peer-reviewed report regarding the research and monitoring program that summarizes all data and findings. **Appendices 7-8** through **7-16** were written by District scientists; the Department is responsible for the others. **Appendix 7-9** meets the reporting requirements of the Act and non-Act permits issued by the Department to the District. Readers who desire more detailed, scientific information are urged to consult the appendices to this chapter and previous versions of Chapter 7 and their appendices (SFWMD, 1999; SFWMD, 2000).

SUMMARY

The accumulation of mercury in fish is a problem in the Everglades. Since 1989, the Florida Department of Health has recommended limited consumption of several species of sport fish because of risk to consumers. The high levels found in fish could also be toxic to fish-eating wildlife species.

The pathways leading to mercury accumulation in fish and wildlife are complex. The form of mercury found in fish and fish-eating animals, methylmercury, is not like the elemental form found in thermometers or the inorganic mercury salts in seed treatments. Methylmercury is primarily produced by bacteria naturally present in the sediment where oxygen is absent and a sulfur compound, sulfate, is present.

The sulfate-reducing bacteria take up inorganic mercury and manufacture methylmercury as a byproduct of the normal life processes. Methylmercury in water or food is readily absorbed into living tissue, by the process of bioaccumulation, much faster than it is released. This results in the buildup of concentrations in larger fish to levels millions of times higher than the surrounding water. Methylmercury in animals and humans can be toxic to the brain, liver, kidney and immune system, and can have adverse effects on egg and fetus development in exposed mothers.

Marsh fires and dry periods increase the production of methylmercury and can worsen the mercury problem, at least locally over the short term. Also, lower sulfur concentrations tend to promote methylmercury production, while higher sulfur levels

tend to inhibit production. A better understanding of the role played by sulfur, in mercury accumulation at sites with different levels of nutrient enrichment, will permit agencies to evaluate the potential for minimizing the mercury problem through the management of water and its constituents.

The fact that methylmercury bioaccumulation is influenced by many factors questions the utility of a mercury water quality criterion expressed as a single surface water concentration. The current Florida water quality criterion of 12 nanograms per liter for mercury in water is of limited utility since fish consumption advisories have proven to be necessary for waters meeting the state criterion.

Resolving other complexities of mercury science and to provide management-relevant information on the mercury problem are the objectives of a private-public consortium of state and federal agencies, utility interests and others known as the South Florida Mercury Science Program. Within the last eight years, this program has sponsored a broad array of studies to develop a sound scientific understanding and to provide information needed to evaluate potential solutions. The past five years of mercury compliance monitoring of the Stormwater Treatment Areas showed a positive impact on the downstream mercury problem. Based on these data, the elevated concentrations of methylmercury observed in water and fish during Stormwater Treatment Area startup tend to be relatively short-lived and are not expected to represent an immediate threat to the fish-eating wildlife attracted to them. Some increases in fish mercury levels in the Water Conservation Areas were recorded in 1999, but additional monitoring data are needed to interpret these changes in an appropriate ecological context. Mercury monitoring of the Advanced Treatment Technologies has not revealed substantially elevated levels of inorganic mercury or methylmercury in outflow water or solid residues.

Source controls have the greatest likelihood for reducing the mercury problem by decreasing the delivery of atmospheric mercury to the Everglades. Findings from computer models and environmental monitoring both suggest that control of air sources of mercury can have positive benefits for the Everglades Protection Area. Elimination of mercury from commercial and industrial uses has already reduced mercury emissions from municipal waste incinerators and other sources in South Florida. Monitoring over the last decade suggests that these lower emissions are producing a corresponding reduction in Everglades' fish and wading birds. A mathematical model, developed under the Mercury Science Program, relates fish mercury levels to the amount impinging on the Everglades. The model shows that control of mercury emissions could significantly alleviate the overall Everglades mercury problem within a decade or two. If control of local emissions is not sufficient, it may be possible to reduce the mercury problem through management of water quality and quantity. This second approach is to make environmental conditions less favorable for the production of methylmercury. Management of marsh fire frequency, hydrologic patterns and water constituents, such as sulfur, may provide means for such mitigation. With either approach, less methylmercury would be available, making the accumulation of toxic amounts in fish and wildlife less likely.

GLOSSARY OF MERCURY-RELATED ACRONYMS AND TERMS

The general glossary in the 2001 Everglades Consolidated Report is designed to support general terminology in all 14 chapters. Mercury is a complex environmental contaminant involving several specialized scientific disciplines. The following terms should assist the reader in understanding the material presented in this chapter.

- **ACME Project, The Aquatic Cycling of Mercury in the Everglades Projects**: Process oriented mercury research program organized by the U.S. Geological Survey
- **E-MCM, Everglades Mercury Cycling Model**: An integrated model of mercury cycling being refined under the auspices of DEP, USEPA and SFWMD.
- **FAMS, Florida Atmospheric Mercury Study**: A study to quantify deposition of mercury from the atmosphere
- **MeHg, methylmercury**: A particularly toxic organic form of mercury that concentrates in aquatic food webs
- **REMAP, Regional Environmental Monitoring and Assessment Program**: The USEPA Region 4 and ORD have used the REMAP approach to conduct an Everglades-wide ecosystem assessment for mercury and water quality.
- **RGM, reactive gaseous mercury**: A form of gaseous mercury in the atmosphere that is deposited readily in rainfall
- **SFMSP, South Florida Mercury Science Program:** A multi-organizational partnership to advance the science involved with mercury
- **SRB, sulfate-reducing bacteria:** Microbes found commonly in sediments that transform inorganic mercury into organic methylmercury
- **TMDL, Total Maximum Daily Load:** Load determinations for a water body not meeting its designated use required under the Clean Water Act.
- **UMAQL, University of Michigan Air Quality Laboratory**

BACKGROUND

THE MERCURY CONCERN

Mercury is a contaminant of concern in the Florida Everglades as well as in most states of the U.S. and in other parts of the world. Mercury is a concern because it is a toxic element that accumulates to high levels in top predator fish in many aquatic ecosystems. Since the Industrial Revolution, mercury emissions to the environment have increased approximately five-fold because of increasing industrial and economic activity, which is thought to have resulted in similarly increased levels of mercury in fish and other aquatic organisms. Mercury levels seen today in North America and several other parts of the world have prompted health authorities to issue warnings to limit consumption of wild caught fish, an otherwise valuable source of protein and beneficial nutrients. Mercury may pose a risk to wildlife resources that live or feed in aquatic systems as well.

Solutions to the Everglades mercury problem are being pursued through Florida water quality standards and the regulations for limiting pollution sources to achieve them. Mercury is an atmospheric pollutant that is deposited on the Everglades Protection Area (EPA) marsh by wind and rain. Therefore, Everglades waters will be better protected through control of the rate of deposition of mercury from the atmosphere. In South Florida, waste incinerators have been a major source of mercury. Steps already taken have greatly reduced their mercury emissions. Mercury use has been further diminished by a variety of pollution prevention and waste minimization efforts. There is suggestive evidence that reductions in emissions and other releases within South Florida are beginning to result in a decline in the mercury concentrations of Everglades wildlife, but this evidence ispreliminary. The Florida Department of Environmental Protection (Department) is working to learn if further benefits would result from additional reductions of mercury from local atmospheric sources near the Everglades. While control of atmospheric emissions of mercury is the primary strategy, it may not be feasible to abate atmospheric Florida mercury sources to the extent necessary to achieve water quality standards. The Department is also assessing whether the effects of atmospheric mercury deposition into the Everglades can be minimized through management of water quality and quantity.

The mercury monitoring, research, modeling and assessment studies described in this chapter and its appendices are coordinated through the multi-agency South Florida Mercury Science Program (SFMSP)[1]. This unique partnership of federal, state and local

[1] In addition to the Department, the District, the U.S. Environmental Protection Agency (USEPA) Office of Research and Development and Region 4, Florida Fish and Wildlife Conservation Commission and the U.S. Geological Survey, other collaborators associated with the SFMSP are the, the U.S. Fish and Wildlife Service, the U.S. Park Service, the U.S. Army Corps of Engineers, the University of Florida, Florida State University, Florida International University, University of Miami, University of Michigan, Texas A & M University, Oak Ridge National Laboratory, Academy of Natural Sciences of Philadelphia, Florida Power and Light, Florida Electric Power Coordinating Group, Wisconsin DNR, and the Electric Power Research Institute.

agencies; academic and private research institutions; and the electric power industry has advanced our understanding of the Everglades mercury problem faster and more effectively than could be accomplished by the Department or South Florida Water Management District (District) alone. The SFMSP has operated under a coordinated plan; however, each agency has operated within its own management and budgeting framework. The goal of the SFMSP studies is to provide the Department and the District with the information to make mercury-related decisions about Everglades Construction Project, as well as other restoration efforts, on the schedule required by the Everglades Forever Act (Act).

When this work began, all that was known was that Everglades fish had unusually high levels of mercury. Now, SFMSP studies are providing a better understanding of why the Everglades is an "at risk" system for mercury contamination and a pathway for determining whether Everglades waters require additional reductions in atmospheric mercury sources and, if so, what benefits would result from such additional reductions.

MERCURY AS A CONTAMINANT

The primary forms of mercury that cycle through the environment are inorganic but can be transformed to the more toxic organic form, methylmercury (MeHg), by natural processes within aquatic environments such as the Everglades. This transformation is mediated by sulfate-reducing bacteria, ubiquitous inhabitants of sediments. Given sufficient exposure, MeHg poses the risk of toxicity to the central and peripheral nervous systems, can be toxic to the developing fetus or egg, and can cause a number of other adverse physiological effects to humans and animals. Upon production and release into pore waters or surface water itself, MeHg exhibits a strong affinity for the surface of decaying plant material or it can become incorporated into the cells of living algae. MeHg becomes concentrated in higher organisms by the process of biomagnification or bioaccumulation, a process by which contaminants are concentrated toward the apex of food webs.

MeHg associated with plant detritus and algae enters the Everglades food web at its base. Once incorporated in the aquatic food web, MeHg is strongly biomagnified, by as much as 10 million fold, in top predators of the Everglades, posing potential risks to humans and wildlife. While dietary exposure is the dominant uptake pathway, fish and other aquatic animals may also absorb MeHg through their gills or skin. MeHg is continuously lost by animals through excretion or by its biochemical conversion to non-bioavailable forms. MeHg accumulates in predator organisms when it is taken in faster than it is eliminated. Because of biomagnification, Everglades predators that may be accumulating toxic doses of MeHg are the highest-level predators that feed on fish and other aquatic organisms.

At this time, it has not been established that mercury has had an adverse effect on Everglades wading birds. The studies necessary to evaluate this risk are ongoing but have not yet been completed. Everglades organisms thought to potentially be at risk include wading birds, otter, mink, raccoons, panthers, alligators, snakes, turtles, frogs and largemouth bass. The concern is not for acute toxicity and death, rather that Everglades wildlife may be at risk for chronic, sublethal effects. These could adversely affect the health of adult and juvenile organisms, reducing their longevity and ability to reproduce, thus causing an overall reduction in wildlife populations. The threshold at which such chronic affects occur varies among species and within species depending upon the age, health, nutritional status, exposure to other contaminants, and other stressors on the organism involved.

U.S. Environmental Protection Agency (USEPA) scientists in the 1997 National Mercury Study Report to Congress developed recommendations for the safe threshold for human exposure to MeHg. Congress subsequently directed the USEPA to have this mercury risk assessment objectively reviewed by the National Research Council, the operating arm of the National Academy of Sciences. This review, completed in July 2000, affirmed the USEPA risk analysis, and supported strict human exposure guidelines. The U.S. Food and Drug Administration is responsible for setting and enforcing limits on MeHg in fish that are for sale for human consumption. In Florida, human health is protected from MeHg in recreationally caught fish by Florida Department of Health fish consumption advisories. There are currently advisories issued that recommend not eating certain fish from the Everglades and limiting consumption of others.

MERCURY SOURCES IN THE EVERGLADES PROTECTION AREA

Mercury enters the Everglades both from runoff from the watershed and from atmospheric deposition. Comparison of mercury loads from surface water inflows versus rainfall deposition indicates that the mercury load from atmospheric deposition is from 20 to 40 times greater than mercury loads from surface water inflows (USEPA, 1996). Recent modeling of point-source emissions of mercury in the Southeast estimated that gas and particulate dry deposition added an additional approximately 30 percent to wet deposition for 1996, the year of record for that analysis (**Appendix 7-6**). Thus, over 95 percent of the annual budget of mercury to the Everglades Protection Area is derived from the atmosphere, in some years approaching 99 percent.

ATMOSPHERIC MERCURY CYCLING

As a naturally occurring element with several significantly volatile forms, there always has been a natural cycle of mercury in the environment, typified by passive emission (evasion) from the oceans and crust, transport through the atmosphere, deposition, and perhaps multiple cycles of reemission and re-deposition before being again bound up in geological sinks. Present estimates are that approximately 80 percent of the present global mercury budget is ultimately derived from anthropogenic sources, primarily the result of mining and smelting of mineral ores, burning of fossil fuels (principally coal), and mining, smelting, use and disposal of mercury itself.

The proximate sources of mercury contributing to atmospheric deposition are water-soluble gases and fine particulate matter, which are transported to Everglades marshes by wind and rain. In terms of its influence on deposition, the most important chemical form of mercury in the atmosphere is termed "reactive gaseous mercury" (RGM), which comprises only a few percent of total gaseous mercury in the atmosphere. The existence of RGM in the ambient atmosphere was considered unlikely as recently as the early 1990s and its importance not appreciated until the mid 1990s. Although exceedingly low in concentration and therefore very difficult to measure, it is understood that RGM is the chemical form of mercury that controls deposition. Therefore, understanding the sources, atmospheric chemistry and environmental fate of RGM are essential to developing an adequate understanding of the effective sources of mercury to the Everglades.

Mercury in the atmosphere exerts its effects on three spatial scales, governed by the chemical and physical properties of the various forms:

- Elemental mercury vapor (Hg^0) is the dominant form of mercury in the atmosphere and exhibits an atmospheric half-life of one to two years. Elemental mercury is relatively inert and interacts only weakly with the earth's surface, resulting in even background concentrations (ca. 1.6 ng/m^3) and shallow gradients near centers of population or industry. Hg^0 is slowly oxidized to the reactive forms by as yet poorly understood chemical processes. Most natural emissions of mercury and large fractions of anthropogenic emissions are in the elemental form, thus exerting a relatively uniform global effect.
- RGM, whether from primary emissions or secondarily formed by atmospheric reactions, exhibits a primarily localized effect. Ambient RGM concentrations range from 5 - 200 pg/m^3. Because of its high solubility and high dry deposition velocity from the gas phase, RGM emitted into or produced within the planetary boundary layer has a half-life measured in hours to days. Emissions of RGM from all but the tallest emission stacks are likely deposited by wet or dry processes within ca. 100 km of its origin.
- Particulate Associated Mercury (Hg_p) consists of primary emissions or secondary interactions between RGM and particulate matter. RGM has a high "sticking coefficient" indicating that it readily adsorbs to any surfaces that it may encounter, including airborne particulates. Coarse particulate matter (>2.5 microns), and any mercury associated with it, settles out within a very few miles of the source. Conversely, mercury associated with fine particulate matter ($PM_{2.5}$), which has low gravitational settling, can have an atmospheric residence time of days to weeks, thus exerting a regional effect out to nominally 1000 km.

Local mercury sources near the Everglades are primarily in the heavily developed southeastern coast of Florida and include medical waste incinerators, municipal solid waste combustors, cement kilns and power plants. Automobiles, ships, trucks and other engines powered by fossil fuels also contribute to mercury emissions; the magnitude of mercury emissions from the petroleum side of the energy economy is a matter of emerging debate. Other sources not important within Florida but significant in some other areas include metal extraction, smelting and chlorine production.

The question of the importance of the global background "source" of mercury coming into Florida has emerged as one of significant debate. Beginning with the observations of the Florida Atmospheric Mercury Study from 1992–1997 and supplemented by additional measurements in South Florida and elsewhere, deposition has been shown to be strongly seasonal. Approximately 85 percent of rainfall mercury deposition to the Everglades occurs during the summer months when the easterly trade winds come from the Atlantic Ocean (Guentzel, 1997). That the trade winds advect large amounts of total mercury over the Florida peninsula is not in dispute, but it is not known how much RGM is thereby made available to contribute to deposition. A recent experiment to estimate the magnitude of RGM transport into Florida from the Atlantic Ocean is described in the New Research section on Page 7-17.

Air-surface interactions of mercury operate in two directions. Whatever its ultimate source, mercury in water bodies, wetlands or upland soils may be chemically reduced to the volatile, elemental form and emitted to the atmosphere. With its long residence time in the atmosphere, elemental mercury emitted or re-emitted from the earth's surface enters the global atmospheric mercury cycle, becoming a source of atmospheric mercury even in regions remote from human activities. Much of the increasing energy consumption predicted for developing nations will come from the combustion of coal, a fuel high in mercury. Unless global controls are instituted, the global background of atmospheric mercury can be expected to rise in coming years.

Three regulatory classes of atmospheric mercury sources exist: (1) local sources that are within in the Department's jurisdiction; (2) regional sources in the United States and potentially controllable by the USEPA and other local agencies; and (3) global sources elsewhere in the world that can only be controlled by international agreement.

Additional background information of the atmospheric mercury cycling, SFMSP planning for the atmospheric phase of the work, and more detail on dry deposition studies are included in **Appendix 7-5**.

MODELING THE ATMOSPHERIC MERCURY CYCLE

Understanding the relationships between various emissions sources of mercury, and the physical and chemical changes that may occur in the atmospheric transport and deposition requires the of a physical and chemical, computer-based model. The University of Michigan Air Quality Laboratory (UMAQL), with support from USEPA and the Department has conducted a series of field and modeling studies in South Florida to determine the source emissions strengths and speciation within the South Florida region and to model the transport and fate of those emissions. The most intensive study to date was the South Florida Atmospheric Monitoring and Modeling Pilot Study (SoFAMMS) with fieldwork conducted from August 6 through September 6, 1995. SoFAMMS collected event rainfall as well as ambient gaseous and particulate mercury samples at a frequency of at least twice daily at 17 sites throughout the study domain. A host of ancillary chemical and meteorological data was also collected.

The University of Michigan Air Quality Laboratory uses a hybrid approach to model the fate of pollutants emitted within a modeling domain. This approach employs meteorological, dispersion and chemical models.

The basic element of atmospheric transport analysis is a meteorological model that assimilates diverse sources of weather data and simulates wind transport vectors across the study domain. For modeling mercury emissions sources within South Florida during the SoFAMMS project, UMAQL chose the Regional Atmospheric Modeling System (RAMS). RAMS was developed for modeling Florida's meteorology and has superior capability for simulating the complex land/sea breeze regimes of coastal areas. RAMS calculates meteorological flows and energy and mass conservation among a multi-layer gridded framework covering the model domain. Grid models are typically applied as a series of nested grids of progressively finer resolution. For the SoFAMMS project, a 1000 x 1000 km coarse grid was used to capture the very large-scale, synoptic weather patterns. An intermediate grid of 40 km resolution -- covering all of Florida, portions of adjoining states and adjacent waters -- simulated the wind flows within the Southeast region. The finest-scale grid of 4 x 4 km spacing was centered over the South Florida study area to resolve the details of local flows such as the land-sea breeze. The quality of the RAMS meteorological data was excellent as UMAQL used "4-dimensional dynamic data assimilation" to constrain the error propagation by periodic forcing with real-time meteorological data.

To simulate pollutant transport, chemistry and deposition from mercury emissions sources within South Florida, the hourly RAMS wind fields (simulations) were used as inputs to the NOAA HYSPLIT_4, a general purpose dispersion model that incorporates sophisticated chemistry and physics routines to estimate transformations and deposition. UMAQL customized HYSPLIT for SoFAMMS by incorporating basic mercury physical parameters and chemical processes, and adding the ability to simulate the fate of the various mercury forms (gaseous elemental and reactive, particulate) to the basic model. UMAQL employed this RAMS/HYSPLIT tool to model every day of the SoFAMMS 30-day intensive (August 6 – September 6, 1995), and used a meteorological clustering or aggregation approach to estimate annual source-receptor patterns for the entire 1995-96 period of record.

For application of the Florida Everglades Dry Deposition Study conducted from 1998 through 2000, UMAQL further modified the model to allow speciated Hg emissions data from the SoFAMMS field study to be used together with the high-resolution meteorological data to estimate the wet and dry deposition of the Hg species to the Florida Everglades.

Application of this modeling approach in the context of the ongoing TMDL Pilot Study is detailed in **Appendix 7-6**. Work to develop improved models is described in the section on ongoing research.

MERCURY CYCLING WITHIN EVERGLADES MARSHES

Mercury entering Everglades marshes is subject to transformation through a variety of complex biogeochemical processes. End points of these processes can result in mercury sequestration in sediments, reduction and emission back to the atmosphere, or, of greatest concern in this context, production of MeHg. The factors that govern the net production of MeHg are key, as only this chemical form bioaccumulates strongly in aquatic food webs and poses the greatest risk to humans and wildlife. MeHg is produced from inorganic mercury in anaerobic environments by sulfate-reducing bacteria in a process analogous to the use of oxygen by most organisms.

In the past two years, increasing attention has been devoted to the role of sulfate as a potential control on MeHg production. Information developed by the USEPA Region 4 Regional Environmental Monitoring and Assessment Program (REMAP) and USGS Aquatic Cycling of Mercury in the Everglades (ACME) projects indicates that agricultural practices in the Everglades Agricultural Area result in significant export of sulfate into the Everglades Protection Area. The Stormwater Treatment Areas (STAs) and Everglades marshes only attenuate sulfate weakly; therefore, a sulfate gradient extends south through the Water Conservation Areas to Everglades National Park. It is postulated that sulfate may act to either promote or inhibit MeHg production, either by controlling mercury bioavailability or by modulating activity of sulfate-reducing bacteria. At high sulfate concentrations, production of sulfide may inhibit mercury methylation. High sulfide levels may limit mercury bioavailability by influencing the electrical charge of mercury-sulfide complexes, or by binding mercury into insoluble compounds. At intermediate concentrations sulfate may stimulate mercury methylation by enhancing the activity of sulfate-reducing bacteria. At very low sulfate concentrations, the growth and respiration of these bacteria may be limited by insufficient sulfate. How important sulfate may be in actually governing the rate of MeHg production remains to be determined. Therefore, it would be premature at this time to speculate on whether there may be any opportunity to affect MeHg in the Everglades Protection Area through management of sulfate.

Additional information on the role of sulfate in mercury cycling is given in **Appendices 7-4** and **7-8**. Planned research on this question is discussed in the section on New Research beginning on Page 7-17.

MODELING THE AQUATIC MERCURY CYCLE

Development of a geochemical model of mercury cycling in aquatic systems, the Mercury Cycling Model (MCM), was initiated by the Electric Power Research Institute (EPRI) in the late 1980s as an integrative tool for the investigations of the Mercury in Temperate Lakes Project (MTL) in the Midwest. Tetra Tech Inc. developed the model in collaboration with EPRI and MTL researchers. Because of the sophistication and state of development of the MCM, the South Florida Mercury Science Program chose it as the tool to integrate the aquatic cycling process research conducted by the USGS ACME team, USEPA and others. In collaboration with Florida Electric Power Coordinating Group in the mid-1990s the MCM was modified to encompass Florida climatic and water quality conditions in the Florida Aquatic Ecosystem Mercury Cycling of Mercury Project (FAEMCMP) at Lake Barco, a seepage lake similar to those studied in the MTL project. Subsequent development of the MCM was supported by USEPA ORD ERL-Athens to adapt the lake model to wetland conditions, now denoted the Everglades Mercury Cycling Model (E-MCM). Continuing refinement of the E-MCM is supported by the Department and the District. The E-MCM will be used to better understand the effect of these biogeochemical processes on MeHg production and predict fish mercury concentrations at given atmospheric deposition rates and under various water quality and hydrologic conditions.

A preliminary application of the E-MCM in its present form is provided in **Appendix 7-3**. Continued development of the E-MCM is discussed in the Continued Research section, which begins on Page 7-10. Research to improve the E-MCM simulation of Everglades conditions is treated in **Appendices 7-4** and **7-8**.

ECOLOGICAL RISK TO EVERGLADES WILDLIFE

The concern for potential mercury risks to wildlife began shortly after the first findings of high levels of mercury in largemouth bass in 1989 and the issuance of health advisories to fishermen. In late Spring 1989, three Florida panthers died in eastern Everglades National Park. These were necropsied by FWC and USFWS scientists. Tissue samples from each were analyzed and found to contain very high concentrations of mercury. These findings stimulated concern that many forms of Everglades wildlife might be at risk for mercury toxicity.

In early planning sessions, the SFMSP identified wading birds in the Everglades as one of the resources at potentially greatest risk for mercury toxicity. Not only had wading bird populations declined sharply in the Everglades during preceding decades, but studies of contaminant problems elsewhere often found birds to be at greatest risk of harm. Therefore, the SFMSP began sponsoring a series of studies to define the potential risk of mercury to wading birds, involving both field and laboratory studies and experiments. The work is ongoing, and as stated in the Background section, there is as yet no clear evidence to date that wading bird populations are harmed or limited by mercury.

Because wading birds have been identified as one of the key success indicators of the Comprehensive Everglades Restoration Plan (CERP, Chapter 10), interest in wading bird ecology and population health has continued unabated. In previous years, District scientists and scientists working on behalf of the Sugar Cane Growers Cooperative of Florida have performed in-depth and progressively more sophisticated, formal toxicological risk assessments of mercury risks to wading birds of the Everglades. These studies were treated extensively in the initial report of this series (*Everglades Interim Report*, Chapter 7 pp. 40-46, SFWMD, 1999) and in the previous year's *Everglades Consolidated Report* (pp. 21-29, SFWMD, 2000).

These analyses are not repeated here. For a thorough treatment of ecological risk assessment analyses, please refer to Chapter 7 of the two documents cited above.

Although no new, formal ecological risk assessment is presented in this document, field monitoring and research continue to refine our knowledge of mercury biogeochemistry, bioavailability and food web biomagnification. The information produced is key to developing improved understanding of the food web relationships among mercury in prey and predator, and to supporting further refinements in estimation of ecological risk. **Appendix 7-11** contains extensive new information on the seasonal dynamics of mercury in Everglades food webs and on relationships with water quality.

One new element of work relating to ecological risk concerns is a one-year screening study of mercury in Florida Bay performed by the District. Stimulated by the recognition that improved water supply and hydroperiod management were crucial to revitalization of Florida Bay. The scoping study was intended to establish baseline data on seasonal loading of mercury and of MeHg bioaccumulation in eastern Florida Bay. This work is included as **Appendix 7-12**.

RESEARCH NEEDS IDENTIFIED IN ECR 2000

The following research needs were identified in the *2000 Everglades Consolidated Report*. A brief update on this research progress on each need is presented below:

- Quantify wading bird diet-egg relationship to support a revised numerical Class III water quality standard for total mercury based on methylmercury levels.

  Due to resource limitations, studies to address this research need are being conducted through a variety of projects by different agencies/organizations. Studies of the potential risks posed by present concentrations of mercury in the Everglades food web continue. The Department supports University of Florida researchers in field and laboratory studies of the effects of mercury on wading birds and their populations. The USGS Biological Resources Division is presently conducting controlled studies of the effects of dietary mercury on the reproduction of birds. The District and the Florida Sugar Cane Growers Cooperative have performed in-depth risk assessments to synthesize information relevant to present policy options. SFMSP agencies also collaborate or sponsor field and laboratory studies being conducted around North America.

- Quantify global versus local and new versus old sources of mercury.

  The Department and USEPA support atmospheric mercury research aimed specifically at answering the questions relevant to control policy in coastal regions of the Southeast. The agencies are sponsoring studies to directly measure transport of mercury species into Florida, to describe and quantify the atmospheric reactions of mercury that lead to deposition, and to develop models to organize the atmospheric processes research into decision-making tools.

- Revise the E-MCM to include food web uptake dynamics and relationships between phosphorus and sulfur concentrations and mercury dynamics.

  The key to learning what controls the production of MeHg in the aquatic system is research to define the details of the methylation process and the quantitative relationships with the factors that influence it. The major effort of the SFMSP will be devoted to this purpose over the next two years. As this work progresses, the information gained will be incorporated into the evolving E-MCM to make it a more robust tool for evaluating management options.

- Use the new Class III mercury standard and the E-MCM to develop total maximum daily loads (TMDLs) for mercury and sulfur control.

  The current Class III criterion for mercury is 12 ng/L. This criterion appears inadequate since fish consumption advisories are necessary in waters meeting the criterion; therefore, a revision to the criterion seems appropriate. However, existing data show only a weak relationship between water column total mercury or MeHg concentrations and fish tissue mercury concentrations. The Department is presently evaluating alternative approaches to determine whether designated uses are attained. A TMDL Pilot Study is under way to determine the technical requirements of such an analysis, and the Department is obligated to complete TMDLs for atmospherically derived pollutants to 2010.

RECENT RESEARCH FINDINGS

CONTINUED RESEARCH

The following section highlights recent research findings from a suite of important projects. For a complete listing of publications and reports of SFMSP collaborators, please see **Appendix 7-1**.

Florida Everglades Dry Deposition Study (FEDDS)

Gerald Keeler, UMAQL; Steven Lindberg, ORNL; Frank Marsik, UMAQL; Hong Zhang, ORNL; Matthew Landis, USEPA ORD NERL-RTP; Elizabeth Malcom, UMAQL; Robert K. Stevens, Florida Department of Environmental Protection

Initial studies of the atmospheric sources of mercury focused on rainfall deposition and measurements of particulate-associated mercury in the atmosphere. With the appreciation of the importance of RGM as the controlling factor in mercury deposition, the potential importance of dry deposition of gaseous forms of mercury emerged as a critical unknown. The Florida Everglades Dry Deposition Study (FEDDS) was conceived by its principal investigators at the Oak Ridge National Laboratory (Dr. Steven Lindberg) and UMAQL (Dr. Gerald Keeler) as an intensive study to improve our understanding of the processes of mercury dry deposition. Its objectives were to provide information to improve the representation and parameterization of dry deposition in atmospheric models, and to make deposition estimates to serve as validation check on the models applied. FEDDS was funded by EPA Region 4 and the Department, with invaluable in-kind support from the District. FEDDS field intensives were conducted in February and March 1998 and June 2000.

Appendix 7-5 gives further details of the FEDDS project.

Mercury Emissions from Mobile Sources

Matthew Landis, USEPA ORD NERL-RTP; Gerald Keeler, UMAQL, John Ondov, University of Maryland; Peter Milne, University of Miami; and Robert K. Stevens, Florida Department of Environmental Protection

Obtaining source emissions information is a critical need in all types of atmospheric pollution investigations. One potential source of emissions of RGM not previously examined is the potential for emissions by mobile sources – gasoline or diesel powered vehicles. Vehicular emissions of RGM result from oxidation of both mercury in the fuel and oil, and oxidation of Hg^0 in ambient air used in combustion. The objectives of this project were to develop mobile source signatures for automobiles and heavy diesels, and to estimate the magnitude of mercury emissions rates from the two classes of vehicles.

During September 1998, the Department and USEPA ORD-NERL sponsored a collaboration between agencies and the Universities of Miami, Maryland and Michigan to collect and analyze samples of tunnel air during the peak rush hour periods. Samples were collected for volatile, semi-volatile and particulate organic matter; elemental and volatilizable carbon; elemental, particulate and reactive mercury; and fine and coarse particle mass and trace elements. The study was conducted at the Interstate 95 Fort McHenry Tunnel complex near Baltimore, Md. Samples were collected for one week at three locations: an ambient reference site above the tunnels, in one tunnel carrying primarily automobiles, and in a second tunnel carrying primarily heavy diesel trucks.

Data analysis is presently proceeding (Keeler, 2000) in the participating laboratories and final project reports are due in early 2001.

Development of improved atmospheric mercury model

Khalid Al Wali, UMAQL; Gerald Keeler, UMAQL; Sandy Sellman, University of Michigan; and Russell Bullock, USEPA ORD NERL-RTP

The first serious attempt to model the national pattern of mercury emissions and deposition was conducted by USEPA for the Mercury Study Report to Congress (Bullock, et al., 1997, USEPA 1997b) using the RELMAP model. At that time, the understanding of mercury speciation, and its importance on the fate of emissions and deposition, was just emerging. There were few speciated emissions data available, little or no ambient RGM data, thus simplifying assumptions had to be made for the modeling to proceed. As described above in the section on Atmospheric Mercury Models, the limited scope of the SoFAMMS study allowed the application of finer resolution for southern Florida but still relied on general-purpose models with limited detail in the representation of chemical and physical phenomena that influence mercury transport and fate.

In 1997, the Department and USEPA Region 4 and ORD agreed to jointly sponsor development of a more fully featured mercury chemistry model. This mercury model was to conform to the modular interface specifications of the modeling family being developed by USEPA, Models-3. The Atmospheric Chemistry Processor within Models-3 is the Community Multi-Scale Air Quality Model, or CMAQ. Models-3 and CMAQ allow specialized sub-models to be developed for application within the modeling framework. CMAQ embodies detailed representations of the full atmospheric oxidant chemistry that has emerged from many years' research on acid rain, ozone and fine particulate matter by the atmospheric chemistry community at large. Given proper parameterization of processes and rates, the net of these reactions should describe the chemical transformations of mercury on local and regional scales.

The University of Michigan Air Quality Lab was chosen to lead development of this CMAQ mercury sub-model, in concert with atmospheric scientists elsewhere within the university. Delays in the delivery of operable versions of CMAQ and its documentation have slowed progress on this project. Functional versions of the model are operating at UMAQL and students from various departments are working on aspects of model development. Anticipated completion of this task is mid to late 2002.

Determination of key atmospheric mercury reactions

Anthony Hynes, University of Miami

The Department has sponsored the University of Miami, Rosenstiel School of Marine and Atmospheric Sciences, Marine and Atmospheric Chemistry Program to make quantitative determinations of potentially important atmospheric reactions that may convert Hg0 into RGM at a rate sufficient to contribute to observed rates of deposition. Two candidate homogeneous gas-phase reactions, the Hydroxyl Radical (OH-) and Chlorine gas (Cl_2) were studied by Laser Induced Fluorescence at the University of Miami and determined to be too slow to be significant removal mechanisms.

USEPA Region 4, the USEPA Persistent Bioaccumulative Toxics Program and the Department will co-fund further reaction rate studies in the coming year. Candidate reactions include aqueous phase reactions of OH- and halogens that may proceed in cloud droplets. Information gained on oxidation processes and rates will be incorporated into the mercury sub-module being developed for the CMAQ model.

Developing a bacterial biosensor for aquatic mercury (II) speciation and bioavailability

William M. Landing, Lita M. Proctor and Paulo Barrocas, FSU

In order for mercury to be methylated to form its most toxic and bioaccumulative form, MeHg, it must be initially in a chemical form that can move through the cell membrane of the sulfate-reducing bacteria responsible for methylating mercury.

In aquatic systems, the uptake of trace metals, including Hg(II), by microorganisms is governed by the redox and solution speciation of the metals. The chemical forms of the metals that can be classified as “bioavailable” are determined by the nature of the transport mechanism used by a particular organism for a specific metal. For dissolved copper, it is the free cupric ion (Cu^{2+}) that becomes toxic to microorganisms at only moderately elevated levels (low micromolar). For iron, it is the free Fe^{3+} ion, and labile complexes with inorganic ligands such as chloride and hydroxide that have proven to be bioavailable to phytoplankton. For both of these metals (and many other trace metals), complexation with natural dissolved organic ligands reduces the free metal concentrations to extremely low levels (picomolar), and protects microorganisms from the toxic effects of the metals.

For mercury, recent research suggests that phytoplankton and bacteria take in neutral inorganic complexes such as $HgCl_2^0$ and HgS^o in addition to neutral Hg(II) complexes with low molecular weight organic ligands (Lawson and Mason, 1998; Benoit et al., 1998). The rate of production of MeHg by sulfate-reducing bacteria appears to be controlled to a large extent by the concentrations of these neutral Hg(II) complexes and their rates of passive diffusion into cells. As a result, the movement of Hg(II) into an ecosystem, and its bioaccumulation as MeHg in higher trophic levels, is strongly influenced by the very first step in the sequence; the uptake of bioavailable forms of Hg(II) by bacteria. Understanding of this first critical step is limited by the lack of analytical methods that can accurately and rapidly detect the concentrations of bioavailable Hg(II) in natural waters. The ideal technique would be highly sensitive, work with small sample volumes, and have a response that is proportional to the concentration (or activity) of a particular Hg(II) solution species.

A very sensitive and stable biosensor was reported by Virta et al. (1995), who coupled the *mer operon* with firefly luciferase enzyme expression in a common E. coli bacterium. This biosensor is easy to culture and the light production in response to bioavailable Hg is far less impacted by the metabolic state of the bacterium. In their research, they found a linear response between Hg(II) exposure and light production from levels as low as 0.1 femtomolar (0.02 pg/L) to as high as 100 ng/L In their experiments, detectable light emission was quantified using as little as 100 µL of Hg(II) solution, thus the technique, as published, should prove useful for analyzing Hg bioavailability on small volume samples such as those obtained from pore water sampling.

Initial experiments will center on the calibration of the biosensor bacteria vs. Hg(II) solutions of known (modeled) speciation. During the second and third years of the project, Hg(II) bioavailability will be tested in natural water samples collected from Florida lakes and rivers, as well as from the Everglades, in conjunction with ongoing research projects. Samples from the Florida Everglades will be collected in collaboration with the ACME research group including Cindy Gilmour and Dave Krabbenhoft.

The benefits of this research include improvement of the Everglades Mercury Cycling Model so that better predictions can be made of the response of the ecosystem to altered mercury loads and management practices. To date this research has concentrated on developing the methodology for quantifying mercury species bioavailability. This research will be finalized at the end of 2002.

Evaluation of advanced treatment technologies for mercury effects

Peter Rawlik and Larry E. Fink, South Florida Water Management District

The Department and District are evaluating the potential of treatment technologies being studied to remove phosphorus from runoff from the Everglades Agricultural Area to also affect the concentration of MeHg in discharge waters.

Eutrophication from excess phosphorus supplied by the runoff from the Everglades Agricultural Area has been acknowledged as a serious problem in the Everglades (SFWMD, 1999, Chapter 3). The Everglades Forever Act requires optimization of the operations of STAs - constructed treatment wetlands -- for the removal of phosphorus and other pollutants, including mercury, to protect the Everglades ecosystem.

The Everglades Forever Act requires the Department to initiate rule making to establish a numeric phosphorus criterion for the Everglades Protection Area and establishes a default criterion of 10 parts per billion (ppb) if such rule making has not been initiated by December 31, 2001. In the interim, the District is constructing STAs to lower phosphorus concentrations in agricultural runoff. STAs have been shown to effectively reduce phosphorus concentrations to less than 50 ppb.

A variety of research projects is being conducted to determine the most effective combination of STAs and additional treatment (termed Advanced Treatment Technologies (ATTs)) to further lower phosphorus concentrations past the 50 ppb level (see Chapters 1, 3, 6 and 8). The 10 ppb default has been set as the working goal of these research projects.

Potential effects of the STAs and ATTs on the formation of MeHg are being evaluated as a component of the STA and ATT research. Particular consideration is being given regarding potential effects of periphyton-based STAs and chemical addition of compounds that may promote mercury methylation or exacerbate bioaccumulation.

The transformation of mercury into MeHg appears to be carried out by anaerobic sulfate-reducing bacteria (SRB) (Gilmour and Henry, 1991). In the Everglades and associated ecosystems, there are three microhabitats that appear to be capable of supporting SRB: the sediment/water interface (Gilmour et al., 1998), the extensive periphyton mats (Cleckner et al., 1999), and the root zones of floating macrophytes such as water hyacinth and water lettuce (Hurley et al., 1999). Consequently, any ATT that uses sediments, periphyton or floating macrophytes may potentially provide areas for increased mercury methylation. Additionally, any ATT that affects the concentration of sulfur and/or impacts the sulfate-sulfide ratio may also provide opportunities for increased mercury methylation.

Several ATTs are being evaluated as to their effectiveness in removing phosphorus and their effect on MeHg concentrations. One such ATT being evaluated is Chemical Treatment and Solid Separation, a technology that uses iron or aluminum salts, in combination with a variety of mixing and solids separation devices, to remove phosphorus. This technology was tested at two pilot plants: one upstream of STA-1 West near the inflow and one downstream of the project located at the outflow. The upstream sites used iron sulfate, while the downstream site used aluminum sulfate. Samples were collected on a weekly basis from the inflow, discharge and sludge following District protocols for the collection of ultra-trace total mercury (THg) and MeHg. The filtered and unfiltered inflow and discharge samples were analyzed for THg and MeHg.

Results indicate that the CTSS technology did not appear to elevate MeHg concentrations in the discharge. Additionally, based on the crude mass balance, the technology did not appear to transform THg into MeHg in the residuals. Therefore, this technology does not appear to increase mercury methylation rates. Additional ATTs are scheduled for testing (**Appendix 7-10** has further detail).

Uptake of methylmercury by algae

Anson Moye, Carl Miles[1] and Ed Phlips, University of Florida

It is important to understand uptake of MeHg by algae because this is the first mercury bioconcentration step in most aquatic food webs and it is the step with the highest bioaccumulation factor. The amount of MeHg in the algae cytoplasm is also important because it has been shown that the cytoplasm is the portion that is transferred up the trophic chain (Mason et al., 1995). Mercury models, such as Everglades Mercury Cycling Model (E-MCM) (Hudson et al., 1994), require quantification of the amount of MeHg that is transferred from water to phytoplankton and the mechanism of uptake. The goal in Phase 1 of this research, which has been completed, was to provide this information. The goal in Phase 2 is to describe the mechanism, determine uptake rates, and investigate the effects of sulfide and dissolved organic carbon (DOC) on uptake rates.

In Phase 1, phytoplankton-water partition constants (K_{pl}) for MeHg were determined in the laboratory for two green algae *Selanastrum capricornutum* and *Cosmarium botrytis*, and the blue-green algae *Schizothrix calcicola*. Three methods were used to determine K_{pl}; the Freundlich isotherm, flow-through/dialysis bag, and the diluted-algae method. The Freundlich isotherm, and flow-through/dialysis bag methods yielded K_{pl} of $10^{6.6}$, while K_{pl} was $10^{7.3}$ for the diluted-algae method. The K_{pl} for MeHg and *S. capricornutum* (exponential growth) was not significantly different in systems with predominantly MeHgOH or MeHgCl species. Partitioning constants, determined with exponential, stationary and phosphorous-limited, stationary phase cells at the same conditions, were not significantly different. This is consistent with other studies that show metal speciation controls uptake kinetics, but the reactivity with cellular components controls steady-state concentrations. Apparently, these cellular components were not affected by the different experimental parameters chosen here. The K_{pl} for *Cosmarium botrytis* ($10^{6.7}$) was similar to *S. capricornutum* while the K_{pl} for *Schizothrix calcicola* was significantly lower ($10^{6.3}$). If partition constants are determined as volume-to-volume concentration factors (VCF), then VCF increases as the cell size decreases. This agrees with theoretical models that small phytoplankton cells accumulate more MeHg than larger cells.

The second component of our Phase 1 goals, a description the mechanism of uptake, has provided preliminary information for Phase 2 work. Our kinetics data from Phase 1 used the disappearance rate of MeHg in water to infer algae concentrations. This introduced error that can be eliminated by using short-duration uptake of ^{14}C MeHg directly into algae (used now). Phase 1 kinetics experiments showed a weak correlation of MeHg uptake rate into algae with changing D_{ow}, suggesting passive mechanism not the dominant mechanism, but experimental reproducibility was questionable.

Results from this research and experience of others (Croot et al., 1999) show that determination of surface areas and culturing viable and bacteria-free algae is not a trivial

[1] As a token of our respect, we would like to express our sadness at the passing of Carl Miles on October 1, 2000. Carl was a fine scientist, a valued colleague and a good friend to all of those who worked on mercury issues in the Everglades. Carl's enthusiasm for his work and collegial nature will be remembered by those with whom he worked at the District and Department.

task. This has slowed exploration of uptake into other species and testing the uptake mechanisms over a wide range of species. Preliminary work with *Cosmarium* and *Shizothrix* is near completion and will answer the question if the partitioning and kinetic processes observed so far, are general or specific for the type of algae.

Hypotheses to be tested in Phase 2 include:

- 1-MeHg uptake by algae occurs primarily via passive diffusion.
- 2-Sulfide and DOC inhibit the bioavailability of MeHg to phytoplankton.
- 3-Active uptake of MeHg by algae is small or insignificant.

Everglades mercury cycling model modification and application

Curtis D. Pollman and Reed Harris, Tetra Tech Inc.

The Everglades Mercury Cycling Model (E-MCM) was developed under a subcontract from USEPA ORD, Environmental Research Laboratory, Athens, Ga. In its form as prepared for the USEPA, it was a spatially simple, but conceptually complex model of mercury biogeochemistry adapted to a wetland environment. In that form, the water chemistry for other than mercury species was defined by the user for each physical compartment. This was not adequate for management-relevant applications to the Everglades mercury problem in the context of the Everglades Construction Project (ECP; phosphorus removal from EAA waters) or the reconfiguration of the South Florida water management system under the Federal Restudy (hydropattern restoration).

This E-MCM will be used to predict changes in localized and downstream water quality associated with the various restoration alternatives, both with and without reductions in loadings from local and regional mercury atmospheric sources.

To allow the E-MCM to predict the consequences of various restoration alternatives on Everglades mercury concentration and bioaccumulation, modifications must be made to the model. The required modifications to the time-dependent E-MCM model are occurring in phases. Phase 1 modifications incorporated changes to the E-MCM input format structure to facilitate the linkage of the E-MCM to other models to make the E-MCM more readily applicable to problems involving changes in total phosphorus loads to filter marshes and downstream receiving waters. Phase 1 was completed in 1999. Phase 2 modifications will incorporate directly into E-MCM the ability to simulate sulfur dynamics using a coupled mass balance - thermodynamic approach. In addition, E-MCM will be modified during Phase 2 to change its representation of bioenergetics and trophic level interactions to accommodate a “bottom-up” approach.

Another pending enhancement of the E-MCM is incorporation of a Monte Carlo simulation routine to allow for more rigorous analysis of uncertainties in the model outputs. One goal of the present TMDL Pilot Study for Atmospheric Mercury is to fully evaluate the uncertainties inherent in concatenating models of atmospheric cycling, aquatic cycling and food web dynamics. Uncertainty and sensitivity analyses of model performance should identify information or understanding gaps in the present model formalism, and guide future research to improve model representation of sensitive processes.

Coupled with the Phase I modifications, the changes resulting from Phase 2 will make E-MCM more readily applicable to problems involving changes in phosphorus and sulfur loadings and to water quality standards development.

RELEVANT COMPLETED RESEARCH

The effect of dry down and natural fires on mercury methylation in the Everglades

David P. Krabbenhoft, U.S. Geological Survey, Larry E. Fink, South Florida Water Management District, and Mark Olson, U.S. Geological Survey,

Extensive fires occurred in the impounded Everglades in May and June 1999 following a La Nina-driven dry period. In some locations, the fire burned through exposed peat soil to the underlying rock. In response, the U.S. Geological Survey and the South Florida Water Management District conducted a collaborative study on the effect of sediment drying and fires on Hg speciation and bioaccumulation in wetlands.

Results indicate a 10x increase in net methylation efficiency at burned sites. Given that HgT and DOC quantity and quality were constant for burned sites, while sulfate showed demonstrably higher levels (about 2.4x) in response to the drying and burning, infers that sulfate was a primary driving factor for excess methylmercury production in burned/dried areas. Regardless of the precise geochemical mechanism, data collected from this study suggest that geochemical changes induced by prolonged drying or burning of Everglades peat can favor Hg methylation through increased availability of important substrates such as sulfate. This subject is treated more fully in **Appendix 7-8** and later in this chapter under "Relationships to other water quality variables."

NEW RESEARCH

Speciated atmospheric mercury profiling experiment (SAMPEX)

Matthew Landis, USEPA ORD NERL-RTP, Robert K. Stevens, Florida Department of Environmental Protection, and Gerald Keeler, UMAQL

One of the policy-relevant questions that has been difficult to assess is the potential for long-range transport of mercury from sources around the globe to contribute to mercury deposition in southern Florida. To the extent that the "reactive" forms of mercury are brought over Florida by the easterly trades during the summer when ~85 percent of rainfall mercury deposition occurs, this would lessen the effectiveness of any controls applied to emissions within the region. For example, if 50 percent of the RGM passing over the Everglades were to be from the global background and 50 percent from local sources, the benefit realized of a 50 percent cut in local emissions would be no more than a 25 percent reduction in deposition. The point of diminishing returns on emissions controls within the region would be reached quickly.

There are several hypotheses that have been put forward to suggest that long-range transport may be significant. The first was proposed by investigators of the Florida Atmospheric Mercury Study conducted in Florida from 1993 through 1996. Drs. Guentzel and Landing measured wet and bulk deposition of mercury at nine sites in

Florida, seven of which were in southern Florida and four adjacent to the Everglades. Rainfall samples were also analyzed for trace element constituents. Using multivariate statistical techniques, the investigators found little correlation between rainfall mercury and trace elements indicative of sources such as municipal waste incineration, and concluded that in the absence of such associations, local source contributions must necessarily be small (Guentzel, 1997). It is the view of some observers, however, that this lack of correlation was not conclusive because the protocol for FAMS was to collect monthly-integrated rain samples, which often resulted in the mixing of a number of rainfall events, thereby obscuring trace element relationships.

The second hypothesis put forward to suggests a potentially significant contribution of RGM from marine air masses is the recent interest in the potential role of marine aerosol-derived reactive halogen species in the marine boundary layer. The existence and potential importance of marine halogen species was proposed by Keen et al. (1990) and remains a subject of active investigation. Determination of the rates of this type of reaction and its potential significance in contributing a source of non-anthropogenic mercury to the U.S. is one of the key questions raised by staff and reviewers at the recent peer review workshop on the EPA Mercury Research Strategy.

Recent papers by Dickerson et al. (1999) and Knipping, et al. (2000) suggest that the presence of free halogen oxidant species in the temperate marine boundary layer can be significant. The recent finding that the sulfide mercury reduction pathway (Van Loon, et al., 2000) is effectively several hundred-fold slower than heretofore assumed, which was an important constraint in atmospheric chemistry models, and heightens the importance of the question of chlorine and bromine oxidation reactions in the marine air.

Arguing against the potential importance of this hypothesized halogen oxidation, with respect to Florida, is the estimated atmospheric half-life of elemental mercury of 1 to 2 years. The upper bound of any major reaction pathway is constrained by the inverse of this half-life, i.e. a global average total oxidation rate of ~0.1 – 0.3 percent per day. Given, as discussed in the Background section of this document that the half life of a soluble reactive species in the marine boundary layer would be on the order of one day, only that mercury oxidized in a short transit time would have the potential to impinge on Florida; mercury oxidized farther away would be deposited before reaching Florida.

Given the paucity of knowledge about the atmospheric reaction pathways of mercury and their rates, present global models are too crude to constrain the potential impacts of marine air masses on coastal areas.

In an effort to provide information that would aid in constraining this question, the SAMPEX project was conceived to make direct measurements of mercury species at various altitudes over the Atlantic east of Florida during the period when easterly trade winds advect large amounts of marine air across Florida. A collaborative project between the USEPA Office of Research and Development and Region 4, NOAA Air Resources Laboratory, the Department, Broward County Department of Planning and Environmental Protection, Air Quality Division (DPEP) and the University of Michigan Air Quality Laboratory was developed to plan and conduct an airborne measurement campaign. The NOAA ARL Twin Otter aircraft was equipped with its atmospheric research package consisting of sophisticated equipment and data systems for measuring pollutant gases and particles. This equipment was augmented by the Department and EPA designed mercury speciation equipment to measure elemental, reactive and particulate-associated forms of mercury.

Twenty flights of this aircraft were conducted during January and June 2000 and excellent operational results were obtained. Equipment reliability and data capture were excellent. Two high temporal frequency ground-based monitoring sites were operated during the summer intensive in 2000, a beach site and a site near the eastern boundary of the Everglades. Data analysis is presently underway; a preliminary report is anticipated in fall 2000. Final reports and manuscripts for publication should follow in the first half of 2001.

Atmospheric mercury 'super site'

Matthew Landis, USEPA ORD NERL-RTP; Robert K. Stevens, Florida Department of Environmental Protection; and Ken Larson, Broward DPEP

As a continuation of the program of atmospheric mercury research conducted by the Department, USEPA and other collaborators, in the Spring of 2000 the Department, USEPA ORD-NERL, and the Broward County Department of Planning and Environmental Protection, Air Quality Division established an atmospheric monitoring station in western edge Coral Springs, Fla. The site was chosen because of the availability of an existing Broward DPEP site at a location as near the Everglades as practicable. The purpose of this station is to collect highly time-resolved measurements of mercury species, ancillary atmospheric tracer species and mercury deposition to address questions about the sources of mercury to the eastern boundary of the Everglades. The suite of measurements to be taken at the site are given below:

Coral Springs 'Super Site' Measurements

Measurement	**Instrument**	**Frequency**	**Analytical Method**
Elemental Mercury	Tekran 2537A	5 min	Gold Amalgamation CVAFS
Reactive Gaseous Mercury	Tekran 1130	2 hr	Gold Amalgamation CVAFS
Particulate Mercury	Tekran 1135[1]	2 hr	Gold Amalgamation CVAFS
Particulate Mercury, manual	Denuder/Filter Packs	[2]	EPA Method 1631
Fine & Coarse Particulate Carbon	R& P Dichotomous Sampler	24-hour	Combustion, Flame Ionization
Wet Deposition	Automated MIC-B	Daily	CVAFS
Fine & Coarse Particulate Mass & Trace Metals	R& P Dichotomous Sampler	Daily	EDXRF, Al to Pb
SO_2	TECO-42C	1 min	Fluorescence
NO, NO_2, NOx	TECO-NOx	1 min	Chemiluminescence
CO	TECO	1 min	Gas-Cell Correl. Spectrometry
Meteorological	Various		WS, WD, Temp, RH, SI, Wetness

[1] Pending method validation
[2] Intensives only

This site is planned to operate for 3 years and is expected to yield a long-term record of high temporal resolution data on elemental relationships with observed atmospheric mercury species. The data will be used in receptor models such as the EPA-approved Chemical Mass Balance 8 model (USEPA, 2000), and newer statistical receptor models such as PMF models (Paatero and Tapper, 1993; Xie, et al., 1996). The information gained from this measurement program should be very useful in determining the sources contributing mercury to deposition by RGM and Hg_p at this site.

Effects of mercury on wading birds in the Everglades

The Department will continue to support research to develop information on effects of mercury on wading birds. Three endpoints seem relevant for assessing the effects of mercury contamination on wading birds:

First, many contaminants have their most severe effects at embryonic stages, and developmental abnormalities at the gross and histologic level seems to be a first endpoint to examine.

Second, many contaminants may work to reduce fecundity and reproductive success. There are many possible pathways for this, including endocrine disruption in adults (Colburn et al., 1996), altered motor control leading to poor foraging, courtship, and parental skills (Spalding et al., 2000a, 2000b; Frederick, In Press), and differential effects on the sexes leading to altered breeding sex ratio.

Third, mortality is often high during the first year of survival in wading birds, and it is likely that contaminants may affect the ability of a juvenile bird to forage, escape predators, meet the other demands of their life history. Wading bird nestlings are largely protected from the effects of mercury during the period of rapid feather growth. The effects of mercury are most likely to manifest themselves when feathers stop growing and the nestlings fledge. Demographic models of wading birds indicate that population change is extremely sensitive to even small changes in the post-fledging survival rates (Sepulveda et al., 1999).

Regarding the first endpoint, embryonic effects are being addressed by a team working at the Patuxent Environmental Sciences Center (Gary Heinz and Dave Hoffman), working explicitly on effects of mercury on eggs. As such, these effects will not be assessed in the work proposed here.

For the second endpoint, effects of mercury on adult reproductive success will be addressed by monitoring endocrine function and reproductive success of wading birds raised in captivity, on diets with ecologically relevant mercury doses. It is planned to use White Ibises (*Eudocimus albus*) and Snowy Egrets (*Egretta thula*) for this work. Reproductive success of these birds will be monitored in several ways, including quantification of courtship behavior, onset of reproductive activities, success of nesting, number of young fledged, parental behavior, and survival of offspring.

To address the third endpoint, it is planned to experimentally dose wild Great Egret (*Ardea albus*) nestlings with methylmercury at a “clean” site in Tampa Bay; this allows the inclusion of a true control group, something that would be difficult to achieve in the Everglades. The nestlings will be dosed at levels that would be commonly experienced in the South Florida environment, by supplemental feeding of the chicks during the nestling period. These nestlings will be dosed through the first three months of life, and their post-fledging survival monitored using a combination of satellite and conventional telemetry; controls and dosed birds will be compared. Post-fledging dosing may be accomplished either through implantable capsules or by training young egrets to regularly forage from baited stations. This work will allow measurement of any effects of mercury on survival. Using existing demographic models, estimates will be made of the possible effects of mercury on juvenile survival and on population change.

Mesocosm studies to quantify how methylmercury in the Everglades responds to changes in mercury, sulfur, and nutrient loading

Cynthia C. Gilmour, Academy of Natural Sciences, and
David P. Krabbenhoft, US Geological Survey

In 1994, a consortium of agencies began a study of the factors contributing to the high levels of Hg in Everglades biota, the Aquatic Cycling of Mercury in the Everglades (ACME) project. The overall objective has been to understand Hg cycling well enough to create management strategies that will minimize MeHg bioaccumulation in the Everglades, while fulfilling other management objectives such as nutrient reduction and hydropattern restoration.

Methylmercury production appears to be favored in wetlands and impounded wetlands, which can produce MeHg (e.g. Krabbenhoft et al. 1995; Branfireun et al. 1996, Gilmour et al. 1998; Heyes et al. in prep.) in quantities that may ultimately lead to elevated fish MeHg concentrations (Cleckner et al. 1998; Krabbenhoft et al. in prep). High rates of microbial MeHg production, driven by high organic matter inputs and flows of nutrient bearing water, are the probable cause. The ACME project has focused on the processes that lead to from atmospheric deposition of Hg to MeHg formation and bioaccumulation.

Key findings of the ACME Project to date include:

1) The spatial MeHg pattern is not driven primarily by total Hg concentration;

2) Sulfur has a large impact on MeHg production;

3) Methylation is rapid in certain types of periphyton (Cleckner et al. 1999), however, methylation in surface sediments appears to be the dominant source of new MeHg.

To model the potential effects of Everglades restoration efforts on Hg cycling, the relationships between sulfur, nutrient and Hg loading and MeHg production and bioaccumulation need to be better, and separately, quantified. The next phase of this research will quantify these individual relationships, and the interactions among these three key parameters through amendments of Hg, S and nutrients, individually and in combination, to *in situ* mesocosms.

Stable Hg isotope amendments are proposed to examine the relationship between Hg loading and MeHg production and bioaccumulation. This new approach will track the fate of newly deposited Hg separately from the larger existing pools, and track the bioavailability of new Hg over time. The use of individual stable Hg isotopes allows the research follow the cycle of new Hg added to the system, from initial partitioning, accumulation in vegetation, MeHg production and accumulation in sediments, fluxes and accumulation in the food web. The investigation will also be able to trace burial, post-depositional reworking of Hg through sediments and plants, and Hg^0 formation. Stable isotopes will allow the study to address are the changes in phase speciation of newly-deposited Hg over time, the relative availability of new Hg for methylation as phase speciation changes, bioavailability from decaying plant material relative to sediments for methylation, and the recycling of buried Hg to the sediment surface through plant growth and decay.

Using stable Hg isotope amendments and Hg, sulfur and nutrient amendments to mesocosms, the following questions will be addressed:

- How will changes in Hg loading affect the magnitude and spatial distribution MeHg production and bioaccumulation in the Everglades?
- How will changes in sulfur loading affect MeHg production and bioaccumulation in the Everglades?
- How will changes in nutrient loading affect MeHg production and bioaccumulation in the Everglades?
- How do these stressors interact to affect MeHg production and bioaccumulation?
- How do the effects of these stressors change across the trophic gradient of the Everglades?

REGULATORY IMPLICATIONS

MERCURY IMPAIRMENT

Section 403.067, Florida Statutes (F.S.), requires the Department to adopt by rule the criteria by which impairment of the State's waters will be determined. The Department has formed a Technical Advisory Committee (TAC) that has been meeting to discuss technical issues associated with the establishment of such criteria. It is anticipated that the Department will initiate this rulemaking in 2000. At this time, based on the TAC's discussions, it appears likely that existence of a fish consumption advisory such as the one that has been issued for the Everglades will be one of the criteria, which would require the Department to deem waters as impaired. However, it cannot be formally stated that the Everglades is impaired by mercury prior to conclusion of the TAC's deliberations and adoption of the rule.

It should be noted that the 1998 list prepared by the Department and approved by the USEPA under section 303(d) of the Clean Water Act contains two water segments in the Everglades that have been identified as being impaired for mercury based on the fish consumption advisory. However, Section 403.067(2)(a), F.S., expressly states that this list cannot be used in the administration or implementation of any of the Department's regulatory programs. Only after a water body has been determined to be impaired using the criteria adopted by rule will a water be truly "impaired" for purposes of state law.

A synopsis of the relevant requirements of the Everglades Forever Act is given in **Appendix 7-7.**

ESTABLISHMENT OF TOTAL MAXIMUM DAILY LOADS FOR MERCURY

If the Everglades is determined to be impaired by mercury under the rule established in accordance with Section 403.067, F.S., then a total maximum daily load (TMDL) will be established. The Department is conducting a TMDL Pilot Study for Mercury to determine the technical feasibility and information needs of such a TMDL in recognition that such a requirement is likely. A March 2000 peer-review draft pilot study document was prepared as a part of that effort and submitted to an independent panel for review. Development of a revised TMDL report is in progress at the time of this writing.

As mentioned previously, the Department's 1998 USEPA-approved 303(d) list contains two water segments in the Everglades that have been identified as being impaired for mercury based on the fish consumption advisory. If these water segments remain on the 303(d) list, under the Consent Decree in Florida Wildlife Federation Inc., et al. V. Browner and U.S. Environmental Protection Agency, the USEPA will adopt mercury TMDLs for these two water segments by the year 2011 if the Department fails to act.

ADDITIONAL EMISSIONS CONTROLS

Controlling mercury sources

Mercury affecting the Everglades is deposited from the atmosphere directly on the Everglades and on the watershed of tributary inflows, which pass some mercury into the Everglades. By reducing atmospheric deposition rates through control of emission sources, mercury impacts can be reduced. Sources of atmospheric mercury emissions are both natural and manmade and may be defined as local (i.e., sources within 100 km of the Everglades), regional (i.e., within 1000 km) and global. These 3 spatial scales correspond roughly to sources that are under Florida's regulatory control, those that may be regulated by the USEPA, and those that can be addressed only by international agreement.

Mercury emissions in southern Florida have declined significantly in the past 10 years. Mercury in municipal solid waste began declining in the late 1980s because of removal of mercury from consumer and industrial products (USEPA, 1992). Following the implementation of first mercury-limiting standard for municipal waste combustors in 1994 by the Department, mercury emissions have continued to decline. In addition, USEPA regulations of medical waste have discouraged this practice and emissions from medical waste incinerators have declined as well. Combined mercury emissions from both sources have declined approximately 95 percent over this period. The Department has vigorously pursued other mercury reduction strategies, from mandating the recycling of mercury-containing lamps and devices, to pollution prevention initiatives, and working with the health care industry to reduce mercury in the chronically high hospital waste stream. The effect of these emissions reduction measures will not be fully realized for years, as previously deposited mercury is slowly bound up in sediments, evaded or otherwise rendered less bioavailable.

Before undertaking further steps to control mercury emissions from local sources, it is essential to know the benefits, which are expressed as the decline in total deposition. To compute the decline in total mercury deposition that could result from Department regulation of local sources requires numerical values for the total mercury deposited on the Everglades from both local and background sources, the fraction contributed by local sources, and the efficacy of control technologies as applied to local sources. These can be estimated by application of the data and models described above and in **Appendix 7-6**.

Reduction in the rate of atmospheric deposition of mercury would reduce levels of toxic methylmercury in top predators. Studies performed with the Everglades Mercury Cycling Model show that the response will be nearly linear, i.e., a 25 percent reduction in deposition will result in about a 25 percent reduction in accumulation of methylmercury in top predators. The initial decrease in predator mercury levels will be fairly rapid, i.e. within a decade or so, and the response to reduced mercury load will be essentially complete within 2–3 decades (**Appendix 7-3**). Recent data on Everglades responses are considered later in this chapter under "Response of Natural Systems to Source Reductions."

IMPLICATIONS FOR BEST MANAGEMENT PRACTICES, STORMWATER TREATMENT AREAS

The STAs are being constructed under the Everglades Forever Act primarily to remove phosphorus from stormwater. Monitoring confirms that the STAs also sequester incoming mercury rather than enhance its release to the downstream Everglades. Recent work showed that where the Everglades marsh dried and was then reflooded, MeHg in fish tissue increased significantly (Krabbenhoft, 2000; **Appendix 7-8**). This suggests that if the STAs are allowed to dry, a significant increase in mercury methylation may result when they are reflooded. This result also indicates that hydroperiod is an important variable in Everglades mercury cycling and that this may be an important consideration in water management aspects of Everglades restoration and STA operation. Further work is in progress on this question (**Appendix 7-16**). The E-MCM model, when completed, will help predict these effects and provide guidance on water management for the Everglades and STAs.

MANAGEMENT IMPLICATIONS

ADEQUACY OF THE EXISTING CLASS III MERCURY CRITERION AND CORRELATIONS BETWEEN WATER QUALITY AND FISH TISSUE CONCENTRATIONS

As part of Florida’s water quality standards, narrative and numeric criteria are established to protect the designated uses. The designated use (Class III) of Everglades waters is "recreation, propagation and maintenance of a healthy, well-balanced population of fish and wildlife." The opportunity to fish and eat one’s catch is protected under this use. The current Class III criterion for mercury is 12 nanograms per liter (ng/L). This criterion appears inadequate, since fish consumption advisories are necessary in waters meeting the criterion; therefore, a revision to the criterion seems appropriate.

Research and monitoring of mercury and MeHg in Everglades sediments, sediment pore waters, surface waters (filtered or unfiltered) and fish have revealed a weak correlation between surface water concentrations of total or methylmercury and fish tissue MeHg concentrations. Analysis of data collected in the USEPA Region 4 REMAP studies shows variable relationships between surface water total mercury and fish tissue MeHg along a north to south gradient in the Everglades, and surface water MeHg concentrations and fish tissue MeHg concentrations tend to be inversely related (USEPA, 1998).

The reasons for the weak relationship between surface water mercury and fish tissue MeHg are inherent in the complex interrelationships among the sequence of biogeochemical processes of mercury in natural waters. Fish tissue MeHg concentration is a function of the source strength of the inorganic mercury substrate, the rate of MeHg production and the efficiency of food chain biomagnification, each of which is controlled by a host of somewhat independent factors.

This calls into question the utility of developing a conventional water quality criterion expressed as a surface water concentration. Pore water methylmercury correlates more strongly, but this is an operationally difficult and expensive measurement to make and would be prohibitive for routine ambient water quality or compliance monitoring.

There has been discussion between the USEPA and the states about defining a human health criterion as the sport fish action level. In its 1997 Mercury Study Report to Congress (USEPA, 1997c), the USEPA proposed a reference dose for mercury of 0.1 mg/kg/day. Congress subsequently directed the USEPA to have this mercury risk assessment independently reviewed by the National Research Council, the operating arm of the National Academy of Sciences. The NAS review was completed in July of his year, affirmed the USEPA’s choices of data and procedure and supported the USEPA’s proposed reference dose (NAS, 2000).

It is likely that this information will be used in revision of the USEPA’s recommended mercury water quality criterion to the states for the next triennial review cycle. What form this guidance may take is unknown. Therefore, until the technical basis for a revised standard is established, or some appropriate alternative or surrogate is developed, the Department does not have a sufficient technical basis for the establishment of a revised criterion for mercury.

RELATIONSHIPS TO OTHER WATER QUALITY VARIABLES

The rate of production of MeHg by sulfate-reducing bacteria varies in a complex way with many physical and chemical water quality factors. Mercury cycling is tied to the carbon, sulfur and iron cycles of the Everglades. Important variables include mercury load, nutrients (phosphorus and nitrogen), pH, chloride, sulfate, dissolved oxygen, water depth and flow, hydropattern and fire. MeHg is also destroyed by both aerobic and anaerobic processes in Everglades marshes. It is the net of the multiplicity of factors that results in bioavailable MeHg.

Methylmercury is a particularly toxic and highly bioaccumulative form of mercury that is the proximate cause of the Everglades mercury problem. It is produced by sulfate reducing bacteria (SRB) as byproduct of their normal metabolism. SRB are ubiquitous in the Everglades marsh, where, in sediments or other anoxic microhabitats, they use organic carbon from decaying plant material as a source of energy for growth and reproduction. To form methylmercury, the SRB must have the typical nutrients, organic carbon, very low dissolved oxygen and sulfate in the presence of available inorganic mercury. Inorganic mercury is derived from atmospheric deposition and *in situ* mineralization of mercury tied up in Everglades sediments and organic matter. Organic carbon comes from plant senescence and decay. Oxygen is absent when productivity is so high that the rate of aerobic decay of plant material consumes oxygen faster than it can be replenished from the atmosphere. Where phosphorus is sufficient to produce eutrophic conditions, dissolved oxygen concentration falls and organic carbon builds up.

Sulfide is produced by the action of SRB on organic carbon and sulfate, and much has been learned about the role of sulfide as an influence on mercury chemistry. For SRB to convert inorganic mercury to methylmercury, inorganic mercury must first gain entry into the bacterial cell. As discussed in Appendix 7-4, present thinking holds that mercury enters the SRB primarily as a soluble, neutral HgS complex. As sulfide concentration increases, negatively charged complexes of mercury and sulfide such as HgS_2^{-2} predominate. These charged complexes do not enter the SRB. Because it controls the charge of mercury-sulfide complexes, excess sulfide inhibits mercury methylation. Sulfide concentration is intimately related to eutrophication, which is a function of phosphorus availability. Because eutrophication results in rapid production of organic carbon, it promotes low dissolved oxygen and a high rate of SRB metabolism with a concomitant production of sulfide.

SRB require sulfate as a substrate for their metabolism. Sulfate in Everglades waters is derived from a variety of natural and human sources. Sulfate of both natural and anthropogenic origin is deposited from the atmosphere. EAA stormwater runoff contains high concentrations of sulfate that arise from the use of elemental sulfur to control soil acidity. In some conditions, groundwater rises to the surface in the Everglades, which may be admixed with ancient seawater that contains sulfate and with water containing sulfate from EAA drainage. Judging from measured sulfate levels in water and mercury levels in *Gambusia* observed in the USEPA REMAP studies, there is no part of the Everglades without sulfate or conditions that allow mercury methylation. This is true of areas that appear unlikely to be influenced by sulfate in EAA runoff. Further analysis of REMAP data by USEPA Region IV may show whether sulfate from EAA runoff increases mercury bioaccumulation in *Gambusia* by comparison of Everglades locations where EAA runoff is and is not present. It is not known whether any management action could abate sulfate to levels that would reduce the rate of methylmercury production by SRB. It may be that the non-abatable background of sulfate in the Everglades is more than sufficient to produce maximum production, in which case reduction of the abatable fraction of sulfate would have no effect.

The effect of phosphorus on methylmercury production by SRB is indirect through its effect on the rate of organic carbon production, which provides the food for SRB and also helps define the dissolved oxygen regime for the SRB. In addition, dissolved oxygen affects sulfide concentration in other ways, including through the iron cycle. At the extreme of high phosphorus concentration, and where sulfate concentration is sufficient, mercury methylation is inhibited by excess sulfide. Eutrophication also affects the amount and qualities of dissolved and particulate organic material, which can inhibit methylmercury from entering the food web and may dilute its concentration at the base of the food web. At the other extreme of low phosphorus concentration, production of organic carbon may proceed so slowly that aerobic processes consume it, leaving the SRB with little substrate and higher than optimum dissolved oxygen. In this case, little methylmercury would be produced. This situation has been postulated for the very oligotrophic southern Everglades, but evidence has not been published. Because it radically alters water quality and the physical qualities of the habitat, eutrophication has profound effects on food web dynamics and may result in the exclusion of some species such as largemouth bass and wading birds. While there is no direct effect of phosphorus on the Everglades mercury problem, its concentration affects both the rate of production of methylmercury and its bioaccumulation at higher trophic levels.

With so many variables interacting in air, water, sediment, plants and other organisms, it is unlikely that effects of changing water quality on mercury speciation and chemistry can be understood and predicted without further field work and its application to the E-MCM. However, one thing is clear from the E-MCM studies to-date; reducing the atmospheric deposition rate will reduce fish bioaccumulation in nearly direct proportion.

The question has arisen whether reducing phosphorus to the low levels characteristic of typical Everglades habitat would interfere with restoration by increasing mercury levels in the prey of wading birds. Restoration of the presently impacted eutrophic areas to a state resembling more pristine Everglades habitat is likely to result in mercury levels typical of such areas as well, i.e. some increase in prey fish mercury levels . Concomitant with restoration will come hydrological and habitat changes that influence prey density, availability and other factors governing exposure, but it may be that there will be some increase wading bird exposure as well. The Department agrees that SFWMD has presented evidence its probabilistic risk assessment comparing an impacted and a reference site (i.e. one that resembles the expected condition of the impacted areas after restoration) that the increased exposure of wading birds will not rise to the level of harm. As discussed in the next section, trend-monitoring data for Everglades fish and birds suggest declining mercury contamination. While this evidence is somewhat preliminary, it is consistent with the time lag predicted by modeling for a decline in atmospheric deposition resulting from decreasing amounts of mercury emitted by air sources within south Florida. Further declines in wildlife mercury exposure from these control measures are possible. Additional controls may be possible and may produce more reduction in exposure. With existing evidence, it is premature to rule out the possibility that emissions controls can further reduce exposures in the entire Everglades including the impacted areas.

Because mercury emissions to the atmosphere were the first step in creating the mercury problem, the Department's primary strategy for control is emissions reduction. If it becomes apparent that emissions controls are not sufficient to reduce Everglades mercury to acceptable levels, the Department will necessarily turn to the second step, devising management steps to limit the production of methylmercury. At present, there is no evidence that this is possible, but there is suggestive evidence that it may be. In the event that emissions controls are insufficient, a candidate for further investigation is control of sulfate in EAA runoff. It is not known at present how strongly the present-day range in concentration of Everglades sulfate may contribute to mercury methylation nor whether sulfate control is a feasible technique for alleviating the Everglades mercury problem. At present, the Department has no clear evidence that control of sulfate in EAA runoff has the potential to alleviate methylmercury bioaccumulation in Everglades biota. If evidence comes to light that control of EAA sulfate is both necessary and efficacious, the Department would begin to work toward that end in cooperation with EAA growers. In the meantime, the Department has no plan or intention to institute such controls.

REGULATORY COMPLIANCE

The Everglades Forever Act requires the District to apply for and receive permits from the Department for many of the construction and operational aspects of the Everglades Construction Program. Under federal statutes, the District is also required to obtain additional permits from the U.S. Army Corps of Engineers. To the greatest extent possible, the permitting agencies have sought to coordinate permit requirements for monitoring, research and reporting, which are being consolidated via this chapter to prevent undue duplication of effort and cost.

The Everglades Forever Act (Act) permits for operation of STAs contain consistent monitoring requirements for all of the ECP. The monitoring program is described in the "Mercury Monitoring and Reporting Plan for ECP, The Central and Southern Florida Project, and the Everglades Protection Area."

Appendix 7-9 describes permit routine compliance-related activities conducted by the District during the reporting year ending April 30, 2000. The reported information and analyses are professional and thorough and the result is an informative summary of the mercury status of ECP-related works and structures, and complies with all terms of the relevant permits.

The Act permits also require a "Quality Assurance Project Plan for the Mercury Monitoring and Reporting Program," which contains additional contingent requirements for responses to excursions from anticipated operational performance or evidence of potentially important problems with the operation or effects of any facility.

Appendices 7-13 and **7-16** summarize such mercury-related follow-up studies at STA-6 initiated as a result of repeated occurrences of outflow mercury concentrations being higher than the inflow, an indicator of potentially adverse influences on the downstream receiving waters. The Department concurs with the District monitoring and analysis that, while the findings at STA-6 represented initial cause for concern, monitoring of the longer-term performance of this system suggests that this was a transient start-up phenomenon and that recent data indicate that STA-6 performance is converging with those of the other STAs (i.e., both total mercury and MeHg in outflows are lower than in inflows). Therefore, it does not appear that STA-6 discharges will either cause or contribute to mercury-related water quality problems in the receiving waters.

During the year covered by this report the enlargement of the pilot-scale STA (the Everglades Nutrient Removal Project), Cell 5 of what is now known as STA-1 West, became operational. Various permits required pre- and post-startup monitoring, which is detailed in **Appendix 7-14**.

Appendix 7-10 is an analysis of a related question of the potential mercury-related impacts of implementation of ATTs being considered for improvement of STA phosphorus removal efficiency. The concern addressed was whether the implementation of ATT adjuncts to the STAs would have negative consequences for transformation or bioaccumulation either within STA or in the downstream receiving waters. The ATT evaluated in this report was Chemical Treatment and Solids Separation. Although limited to a pilot-scale scooping study, there was no evidence that the CTSS technology would have direct or indirect deleterious effects.

The Department has reviewed the information supplied in these documents and accepted the activities and the information submitted as being in compliance with all relevant permit requirements.

RESPONSE OF NATURAL SYSTEM TO SOURCE REDUCTIONS

Small numbers of largemouth bass collected at three locations in the Everglades (L-38A, L-35B and L-67A) in 1988 and reported in early 1989 averaged approximately 2.5 parts per million total mercury in the edible fillet. These findings were promptly confirmed and led to the unprecedented issuance of health advisories to fishermen by the Florida Department of Health to cease consumption of largemouth bass from that area. Subsequent sampling showed that mercury problems extended to many other waters of Florida. From that time, in order to determine whether the trend of mercury in fish is increasing or decreasing, the Florida Fish and Wildlife Conservation Commission, Department of Health and the Florida Department of Environmental Protection began collaborating on annual collection and testing of fish from five sites in Florida, including the L-67 site.

Subsequent investigations of mercury in wading birds have yielded annual information on mercury body burdens in nestlings that can similarly be examined for time trends. **Figure 7-1** shows the data on trend monitoring of mercury in largemouth bass at the L-67A canal in the Everglades. **Figure 7-2** shows a similar time course of mercury levels in the feathers of great egret nestlings.

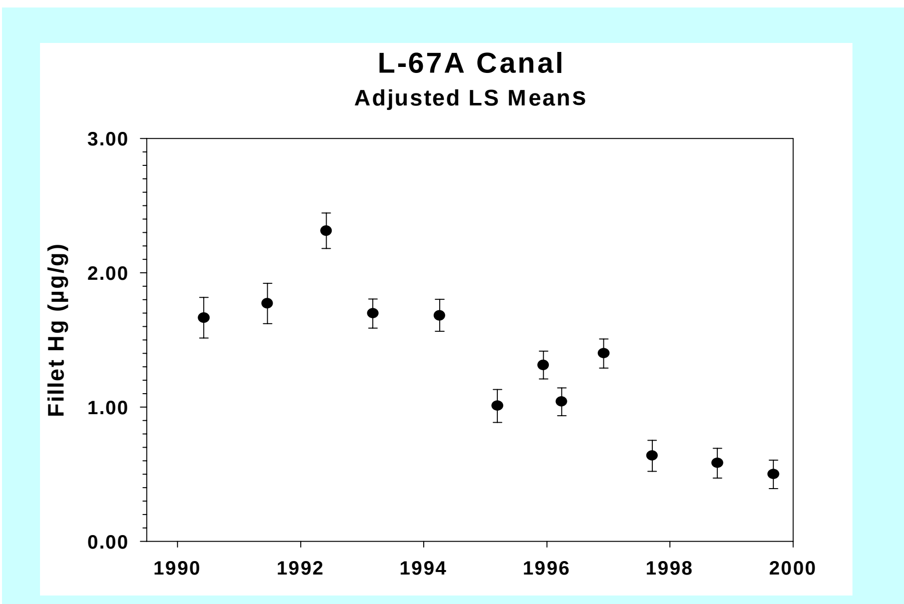

Figure 7-1. Mercury in fillets of age-standardized largemouth bass in Everglades Canal L-67 (Lange et al., 2000). Adjusted least square means.

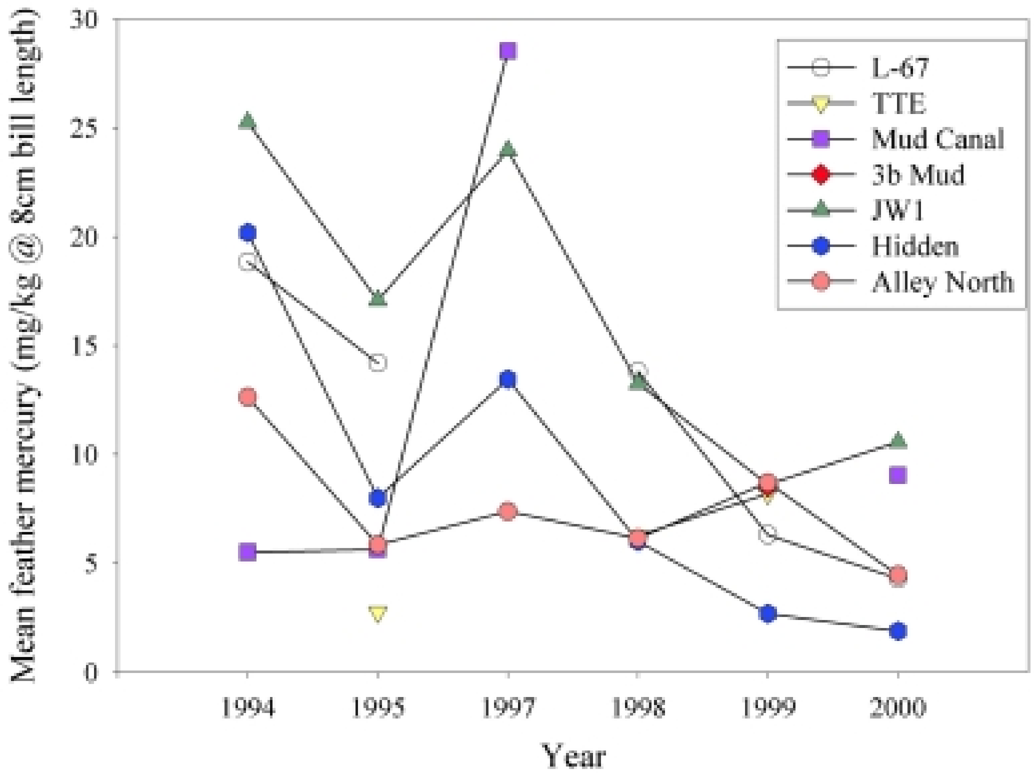

Figure 7-2. Mercury concentration in the feathers of great egret nestlings standardized to 8 cm bill length (Frederick and Spalding, 2000)

Trend monitoring of rainfall mercury deposition began in South Florida with the establishment of four monitoring sites of the Florida Atmospheric Mercury Study (FAMS) adjacent to the Everglades in 1994 and 1995, which continued through 1996. In 1995, the Department sponsored the installation of one of the first Mercury Deposition Network (MDN, a sub-network of the National Atmospheric Deposition Program) sites at the ENP Beard Center, which operated collocated with the FAMS site for approximately 15 months. After completion of the FAMS project, SFWMD assumed responsibility for the ENP MDN site and established two others (Andytown and ENRP) to ensure continuity of long-term trend monitoring of atmospheric mercury wet deposition to the Everglades. Recent meta-analysis of mercury wet deposition from both FAMS and MDN does not indicate any significant trend (Pollman and Atkeson, 2000). However, it is likely that emissions reductions occurred before the monitoring began in 1994 and data variability will hamper trend detection in deposition data.

Data from about 1994 to present *suggest* that mercury levels are falling in Everglades fish and birds. This apparent trend is consistent with the timing and extent of a national trend in the mercury content of incinerated trash in the U.S. and with the time lag predicted by the E-MCM for changes in mercury deposition to be realized in fish (**Appendix 7-3-38, Figure A7-3-25**).

It is important to note that because the data are limited, this declining trend is a working hypothesis that will be subjected to data evaluation from other sites within the Everglades and Florida and to rigorous statistical analysis. Monitoring of mercury trends in atmospheric deposition and in fish and wading birds will continue indefinitely. It is likely that much of the emissions reduction responsible for this apparent trend occurred prior to the initiation of monitoring of mercury in wet deposition in south Florida. The time lag between emissions reduction and fish and bird reduction is consistent with the lag predicted by E-MCM modeling. Further work is underway to test this hypothesis. This consists of hindcasting emissions and examination of new sediment cores.

CONCLUSIONS

ADEQUACY OF EXISTING MANAGEMENT STRATEGIES

The public and private agencies comprising the SFMSP have worked effectively to describe and define the mercury problem in the Florida Everglades, identify and quantify the sources and causes of the problem, and to develop and implement appropriate environmental controls to abate the problem and monitor the effectiveness of the abatement measures.

A comprehensive program of research and monitoring has broadened our understanding of the sources and causes of the mercury problem. The results have been incorporated in a sophisticated environmental model that predicts that the Everglades will respond to decreases in atmospheric mercury deposited into the marshes in a direct, nearly 1 to 1, relationship. Even more encouragingly, the model suggests that significant benefits from decreased mercury loading should be seen in less than a decade, and full benefit within a generation. Current monitoring trends in mercury within the Everglades system indicate that we may be beginning to see the positive results of the pollution prevention and control efforts that began in the mid-1990s.

The proposed research laid out below will build upon the work described herein and will provide the additional tools needed to answer questions about the effects of Everglades management and restoration activities on this important water quality problem**.**

The combined agencies' approach to the mercury problem in south Florida has been a notable example of the successful marriage of science and policy. This comprehensive, long-term approach has enabled Florida to become the model for addressing a complex, multi-media environmental problem.

COMPREHENSIVE SOURCE REDUCTION

Finding remedies for the problem of excessive mercury in fish has been limited by predictive knowledge of its causes. However, one general aspect of the solution is clear; mercury emissions to the environment should be limited where available information and technology allow. The Department has vigorously pursued the following approaches:

- Pollution Prevention - The 1993 Florida Solid Waste Management Act required elimination of mercury from some commercial products and will reduce the mercury content of wastes. It bans the use of mercury in packaging materials, prohibits incineration of mercury-containing devices, promotes recycling of such products, and phases out the use of mercury-containing batteries. Presently, international treaties within North America and between North America and Europe are seeking further reductions in the use of mercury.
- Waste Disposal - Hazardous waste regulations have been tightened to require stricter control of mercury containing wastes. Proper disposal minimizes the long-term releases of mercury into the environment. A side effect of stricter regulation of mercury discharges has been to encourage elimination of mercury from commercial products and industrial processes.
- Emissions Control - A Florida emissions inventory found that the major sources of atmospheric mercury were municipal solid waste combustor, medical waste incinerators and electric utility boilers. The Department adopted the first US regulations limiting emissions of mercury from waste combustors and has adopted USEPA regulations for medical waste incinerators. Solid waste combustor emissions controls are in place on most facilities in Florida and MWI emissions have dropped sharply as the industry has moved away from incineration in response to emissions regulations. Emissions in Florida from each of these sectors have dropped more than 90 percent since 1990.

ADDITIONAL RESEARCH NEEDS

The SFMSP research plan envisioned a phased approach toward resolving key management questions relating to mercury. Phase I investigations focused on scoping studies and system characterization to describe major features of the Everglades mercury problem. Phase II studies focused on system linkages and process delineation, characterizing key sources, pathways and processes affecting mercury exposure and effects. These phases are complete.

Phase III studies focus on quantifying key processes and rates, confirming the predictive tools (i.e. models) that have been developed, reducing remaining uncertainties that have management implications, and evaluating potential management alternatives for remediating mercury impacts. Two years of additional field work and a further year for analysis and preparation of an integrated assessment will complete the work of the SFMSP.

The Phase III investigations envisioned will focus on two areas:

- <u>Geochemical Controls on Mercury Methylation</u>: Led by David Krabbenhoft of the USGS and Cynthia Gilmour of the Academy of Natural Sciences, the ACME project will employ dosing of multiple stable isotopes of mercury and radiotracers of sulfur and phosphorus into replicated mesocosms at several locations within the Everglades

Protection Area. The experimental control and analytical precision gained by these methods will allow for direct examination of the individual and combined effects of important water quality variables governing the methylation process. The experiments to be performed and analysis of the results will be coordinated with the developers of the E-MCM to ensure that the field research is closely tied to the needs of the model. Details on this project can be found under "New Research" earlier in this chapter.

- Local Source-Receptor Relationships of Mercury: Determination of the relative contributions of local atmospheric sources of mercury vs. that transported into Florida from sources beyond U.S. control is a key management question. Specific plans are to continue to monitor magnitude and trends in mercury deposition in south Florida, maintain intensive operations at the ‘Super Site’ in Broward County, and complete development of regional mercury transport and fate model. Details on this project can be found under "New Research" earlier in this chapter.

- Ecological Risks of Mercury: In addition to the human health concern for mercury in sport fish, the SFMSP has also taken cognizance of the special concern for the health of wading bird populations in southern Florida. As stated in the Background section, there has been no clear determination that mercury in the Everglades food web has deleteriously affected wading bird populations in the Everglades Protection Area. Nevertheless, wading bird recovery is a key restoration success criterion for the Comprehensive Everglades Restoration Plan, and it is incumbent upon the Department and District. we have felt it incumbent upon us to closely examine the potential effects of mercury on these birds. The Department is presently collaborating with wading bird researchers, both within Florida and elsewhere, to define key parameters in toxicological assessments of risks to wading birds. In collaboration with the USGS South Florida Office and university-based researchers, the Department plans to develop and support proposals for studies to answer key questions about wading bird risks.

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