Chapter 2B: Mercury Monitoring, Research and Environmental Assessment

Tom Atkeson and Paul Parks[1]

SUMMARY

When the problem of mercury in the Everglades was first discovered in the late 1980s virtually nothing was known of its causes or effects, nor of potential solutions. In response, the Florida Department of Environmental Protection (Department) and the South Florida Water Management District (District) organized a multi-agency group to understand the root causes of the mercury problem in Florida. Operating as the South Florida Mercury Science Program, these agencies have improved our predictive understanding of the sources, transformations and fate of mercury in the Everglades. The program has also been effective at linking local information to that at regional and global levels to better support decision making in South Florida and improve the estimation of risks to fish-eating Everglades wildlife.

Important updated findings from this collaborative effort on mercury include:

- Atmospheric deposition accounts for greater than 95 percent of the external load of mercury to the Everglades. Once deposited, the effect of newly deposited mercury is quickly felt through a burst of methylmercury production occurring over a period of hours to days. The relative proportions of local and long-range transport of mercury to the Everglades remain an open question.
- Methylmercury, the most toxic form, which bioaccumulates in the aquatic food chain, is primarily produced in sediments and its production is strongly influenced by the rate of supply of atmospherically derived mercury.

[1] This chapter continues the previous year's approach in that it is intended to be accessible to a nontechnical audience. However, **Appendices 2B-1** through **2B-3** provide additional detail to meet the EFA requirement that the District and the Department shall annually issue a peer-reviewed report regarding the research and monitoring program that summarizes all data and findings. **Appendices 2B-1** and **2B-2** were written by District scientists; the Department is responsible for **Appendix 2B-3**. **Appendix 2B-1** meets the reporting requirements of the Everglades Forever Act and 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 Chapter 7, and appendices to previous years' Everglades Consolidated Reports (SFWMD, 1999; SFWMD, 2000; and SFWMD, 2001).

- Methylmercury production and bioaccumulation are strongly influenced by many factors associated with water quality, such as nutrients, sulfate, temperature and light levels.
- The Central and Southern Everglades both exhibit strong methylmercury production and bioaccumulation and, therefore, high mercury levels in fish and wildlife. These levels are high enough to pose a risk of chronic toxicity.
- The primary emissions sources of mercury in Southern Florida ca. 1990 were incineration (both municipal solid waste and medical waste) and power generation. Mercury emissions from incinerators of all types have declined by approximately 99 percent since the late 1980s. Principal causes of this welcome decline were reduced mercury in wastes and emissions controls.
- Monitoring of fish and wading birds has indicated a significant decline in mercury in largemouth bass and wading birds, both by about 75 percent at some locations.
- Environmental mercury models have been developed for the Everglades that incorporate the latest findings from atmospheric and aquatic research. Results substantiate a strong relationship between atmospheric mercury load to the Everglades and mercury in top predator fish.
- Modeling analyses also indicate that response times of the Everglades to changes in atmospheric load are short. Significant benefits could be expected within a decade of load reductions, with ultimate benefits occurring within about 30 years.

INTRODUCTION

The accumulation of mercury in fish is a problem in the Everglades. Since 1989, the Florida Department of Health has recommended that fishermen consume only limited amounts of several species of sport fish because of a risk of mercury toxicity to consumers. The high levels found in fish also pose the risk of toxicity to fish-eating wildlife. The pathways of mercury accumulation in fish and wildlife are complex. Although inorganic forms of mercury dominate the environmental cycle of mercury, a small percentage can be transformed into methylmercury. Methylmercury is primarily produced by sulfate-reducing bacteria naturally present in the sediment, where oxygen is absent and a sulfur compound (sulfate) is present. These bacteria take up inorganic mercury and manufacture methylmercury as a byproduct of normal life processes. Microorganisms living in the sediments or overlying water readily absorb methylmercury much faster than they excrete it. As other organisms feed on these microorganisms, methylmercury becomes progressively more concentrated at each higher level of the aquatic food web, a process known as bioaccumulation. This results in a concentrated buildup of methylmercury in larger fish to levels as much as several million times higher than the surrounding water. In sufficient doses, methylmercury is toxic to the brain, liver, kidney and immune system of animals and humans and can have adverse effects on egg and fetus development in exposed mothers.

Many soil, water quality and biotic factors directly or indirectly influence methylmercury production. For example, while sulfate is required for methylmercury production, high sulfur levels tend to inhibit production. Drought and fire can increase the production of methylmercury by changing the proportions of forms of sulfur in the soil, which can worsen the mercury problem, at least locally over the short term. A better understanding of sulfur's role 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 (**Appendix 2B-1**).

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 (ng/L) of mercury in water is of limited use, since fish consumption advisories have proven necessary for waters meeting the state criterion. The U.S. Environmental Protection Agency (USEPA) has recognized the limited utility of its recommended water quality criterion for mercury. In December 2000, the USEPA published in the Federal Register notice of a new water quality criterion for the protection of public health. This new criterion being recommended to the delegated states and tribes is expressed not as a water column concentration of mercury, but as a concentration of 0.3 mg/kg methylmercury in fish tissue. It is expected that the new criterion will be incorporated by states and tribes during the next "triennial review" of water quality standards required by the Clean Water Act, and that all delegated entities will have established revised water quality standards for mercury based on this criterion within five years of its publication.

Resolving other complexities of mercury science and providing management-relevant information on the mercury problem are the objectives of a private-public consortium of state and federal agencies, electric utilities and others known as the South Florida Mercury Science Program (SFMSP). Within the last eight years this program has sponsored a broad array of studies to develop a sound scientific understanding and provide information needed to evaluate potential solutions for mercury-related issues. The past five years of mercury compliance monitoring, in and downstream of the Stormwater Treatment Areas (STAs), showed a positive impact on the downstream mercury problem. Based on these data, the elevated concentrations of methylmercury observed in water and fish during STA startup tend to be 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 (WCAs) were recorded in 2000, but additional information is needed to interpret these changes in an appropriate ecological context. Mercury monitoring of the Advanced Treatment Technologies (ATTs) 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 both environmental monitoring and computer models suggest control of atmospheric sources of mercury can have positive benefits for the Everglades Protection Area. Elimination of mercury from commercial and industrial uses since the late 1980s has reduced mercury emissions from municipal waste incinerators and other sources in South Florida. Monitoring over the last decade suggests these lower emissions are producing a corresponding reduction in mercury burdens of Everglades fish and wading birds. Environmental models developed under the Mercury Science Program relate fish mercury levels to the amount impinging on the Everglades. These models show that control of mercury emissions should significantly alleviate the overall Everglades mercury problem within a decade or two. If control of local emissions is not sufficient, it might 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 2002 Everglades Consolidated Report is designed to support general terminology in all 8 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 portion of Chapter 2.

- **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**: A computer model of mercury cycling being refined under the auspices of FDEP, USEPA and SFWMD to predict changes in Everglades mercury in response to changing loads or water quality.
- **FAMS**, **Florida Atmospheric Mercury Study**: An early study to quantify deposition of mercury from the atmosphere to the Everglades and other parts of Florida.
- **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 readily deposited by rainfall and dry deposition.
- **SFMSP**, **South Florida Mercury Science Program**: A state-federal-private partnership to determine the causes and solution to the mercury problem in Florida.
- **SRB**, **sulfate-reducing bacteria**: Microbes, commonly found in sediments that transform inorganic mercury into methylmercury.
- **TMDL**, **Total Maximum Daily Load**: Load determinations for a water body not meeting its designated use as required under the Clean Water Act.
- **UMAQL**, **University of Michigan Air Quality Laboratory**.

RESEARCH PROGRESS

The following research needs were identified in the 2000 and 2001 Everglades Consolidated Report (ECR). A brief update on this research progress on each need is presented below:

1. Quantify wading bird diet-egg relationship to support a revised numerical Class III water quality standard for total mercury based on methylmercury levels (2000 ECR) Ecological Risks of Mercury (2001 ECR).

The U.S. Department of Interior (DOI), Fish and Wildlife Service, Patuxent Wildlife Research Center, initiated a study of the in-ovo effects of methylmercury during the past year. Dr Gary Heinz, principal author of the much-cited study of the multigenerational effects of mercury on domestic ducks, has obtained extensive collections of fertile eggs of several wading bird species and has begun detailed studies of egg viability and hatchability. The District provided extensive in-kind support for Dr. Heinz' research by collecting and providing eggs gathered from South Florida nests for this work.

The Florida Department of Environmental Protection is presently seeking collaboration with other agencies engaged in similar work of relevance to the Everglades to resume progress with this element of work.

2. Quantify global versus local and new versus old sources of mercury (2000 ECR) Local Source – Receptor Relationships of Mercury (2001 ECR).

The Department and USEPA continue to support atmospheric mercury research specifically aimed at answering questions relevant to mercury control policy in coastal regions of the Southeast. The agencies presently sponsor studies that directly measure transport of mercury species into Florida, describe and quantify the atmospheric reactions of mercury that lead to deposition, and develop models to organize the atmospheric-processes research into decision-making tools. Since the last report, the Department and the Broward County Department of Planning and Environmental Protection, Air Quality Division, have established and operated two intensive air-monitoring sites in Broward County. This project, the Speciated Atmospheric Mercury Study (SAMS), recognizes the paramount importance speciation of mercury in the atmosphere plays in controlling its transport and fate. SAMS makes highly time-resolved measurements of all known forms of atmospheric mercury and associated tracer species.

This measurement and modeling project will continue through Fiscal Years 2002 and 2003 and will provide improved data, tools and understanding to resolve the question of the importance of long-distance transport of mercury into Florida.

3. Revise the Everglades Mercury Cycling Model (E-MCM) to include food web uptake dynamics and relationships between phosphorus and sulfur concentrations and mercury dynamics (2001 ECR).

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 three 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. The data and insight from field studies will feed directly into model formulation and testing. The results of this work will be a calibrated and tested aquatic mercury cycling model that can simulate the effects of various hydrology, water quality or restoration activities.

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

In December 2000, the Environmental Protection Agency (EPA) promulgated a new recommended Class III criterion for mercury. This criterion is expressed not as the typical water column concentration, but as the concentration of mercury in fish flesh. In the course of periodic updates to its water quality standards, the Department will use this new criterion in revising the mercury standard in Florida. The EPA expects states to incorporate this new criterion in their standards within five years.

1. Geochemical controls on mercury methylation (2001 ECR).

The Department has funded companion two-year contracts with D. Krabbenhoft of the U.S. Geological Survey and C. Gilmour of the Academy of Natural Sciences. As detailed in Appendix 7-4 of the 2001 ECR, these studies will use field mesocosm experiments, with stable-isotope and other tracer techniques, to examine the interactions between mercury, sulfur, nutrients and other water quality variables. Fieldwork began with deployment of mesocosms in spring 2001; field experiments are scheduled through June 2003.

The investigations outlined above are continuing efforts. As resources allow, the SFMSP will pursue these topics to their conclusion.

KEY FINDINGS ON THE EFFECT OF WATER QUANTITY AND QUALITY ON METHYLMERCURY PRODUCTION IN REPORTING YEAR 2001

From a management perspective, no subject in mercury cycling is more important than factors involved in transforming inorganic mercury into methylmercury. A major emphasis has been placed on careful examination of methylmercury production. Research in this area is summarized in **Appendix 2B-2** and key findings are provided below.

- At sites immediately downstream of South Florida Water Management District (District) structures, the loading per unit area (flux) of inorganic mercury and methylmercury from Lake Okeechobee releases and Everglades Agricultural Area (EAA) runoff is greater than that from wet and dry atmospheric deposition. This suggests that removal of these species by the STAs could have a beneficial impact on the Northern Everglades.
- Methylmercury is synthesized primarily from new inorganic mercury being supplied by runoff and wet and dry atmospheric deposition, not from soil release, even following a dryout event.
- Methylmercury production is much more temperature sensitive than methylmercury decomposition; this temperature sensitivity changes with location, suggesting that different microbial communities are involved in methylation in these locations.
- Once methylmercury is synthesized in surficial peat soils, enhanced transport from soil to water occurs, which is probably mediated by daily movements of microorganisms and macroorganisms living on and in the soil.
- Once methylmercury is present in the water column, decomposition by sunlight (photodegradation) competes with sorption to settling organic particles as the most significant removal pathway from the water column.
- The concentrations of sulfide in pore water and soil appear to influence methylmercury production by increasing the bioavailability of inorganic mercury to methylating bacteria. Whether the uptake of the inorganic mercury-sulfide complex occurs through passive (diffusion) or active (facilitated) transport remains open to debate.
- The addition of sodium sulfate, sodium sulfide and a slurry of ferrous sulfide (pyrite) inhibited net methylmercury production in laboratory microcosms.
- Iron appears to play a role in mediating sulfur and mercury speciation, and stimulation of methylmercury production at WCA-3A-15 was observed when ferrous chloride was added to a soil slurry. The mechanism(s) by which this occur(s) have yet to be elucidated.
- New biosensors are being developed that can detect bioavailable inorganic mercury in soil and water.

Research supporting these highlights is summarized in **Appendix 2B-2**.

MERCURY IN THE FLORIDA EVERGLADES

THE MERCURY CONCERN

Mercury is a contaminant of concern in the Florida Everglades, as well as in most of the United States 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, yearly mercury emissions to the environment have increased nearly five-fold because of increasing industrial and economic activity. This 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 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 by establishing Florida water quality standards and, to achieve them, implementing regulations for limiting pollution sources. Mercury is an atmospheric pollutant that enters the Everglades Protection Area (EPA) marsh primarily from the air. Therefore, Everglades waters might best be protected by controlling the rate of deposition of mercury from the atmosphere. In South Florida, waste incinerators have been a major source of mercury. Both state and federal regulations implemented since the beginning of this program have greatly reduced incinerator mercury emissions. Mercury use and emissions have been further diminished by a variety of pollution-prevention and waste-minimization efforts. There is evidence that reductions in emissions and other releases in South Florida are beginning to result in a decline in mercury concentrations of Everglades wildlife, but this evidence is preliminary.

The 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 Florida atmospheric 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 multiagency South Florida Mercury Science Program (SFMSP)[2] This group of 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 individually by the Department or District. 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 District with information to make mercury-related decisions about the Everglades Construction Project, as well as other restoration efforts, on the schedule required by the Everglades Forever Act (EFA). 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.

The work of the SFMSP is nearing completion of the plan of study that has guided its activities. The Department has funded a group of atmospheric and aquatic cycling studies that should resolve a significant portion of the remaining uncertainties about the relationships between atmospheric sources of mercury and the controls on its aquatic cycling once it is deposited into the Everglades. These studies will determine whether Everglades waters require additional reductions in atmospheric mercury sources and, if so, what the benefits of additional reductions would be. These final projects are planned for completion in fiscal year 2003 and 2004. An integrated assessment final report will be delivered in late 2004.

Mercury as a Contaminant

The primary forms of mercury that cycle through the environment are inorganic, but they can be transformed to the more toxic organic form, methylmercury (MeHg), by natural processes within aquatic environments, such as the Everglades. Sulfate-reducing bacteria, ubiquitous inhabitants of sediments, mediate this transformation. Given sufficient exposure, MeHg poses a 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. Methylmercury 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.

Methylmercury associated with plant detritus and algae enters the Everglades food web at its base. Once incorporated into the aquatic food web, MeHg is strongly biomagnified by as much as 10-million fold in the Everglades’ top predators, 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 forms not bioavailable. MeHg accumulates in predator organisms when it is taken in faster than it is eliminated. Because of biomagnification, Everglades

[2] This unique partnership of federal, state and local interests includes the Department, the District, the U.S. Environmental Protection Agency (USEPA), the Office of Research and Development and Region 4, the Florida Fish and Wildlife Conservation Commiss
the SFMSP are 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, the University of Miami, the University of Michigan, Texas A &
and Light, Florida Electric Power Coordinating Group, the Wisconsin Department of Natural Resources, the Electric Power Research Institute and the National Oceanic and Atmospheric Administration (NOAA).

predators susceptible to 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 be potentially 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, but rather that Everglades wildlife may be at risk for chronic, sublethal effects. These could adversely affect the health of adult and juvenile organisms, reduce their longevity and ability to reproduce and cause an overall reduction in wildlife populations. The threshold at which such chronic effects occur varies among species and within species, depending on the age, health, nutritional status, exposure to other contaminants and other stressors on the organism involved.

The USEPA, in its 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. Current advisories recommend not eating certain fish from the Everglades and limiting consumption of others.

MERCURY CYCLING IN THE EVERGLADES PROTECTION AREA

MERCURY SOURCES

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 the mercury load from atmospheric deposition is 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 approximately 30 percent to wet deposition for 1996, the year of record for that analysis. This means that more than 95 percent of the annual budget of mercury to the Everglades Protection Area is derived from the atmosphere.

ATMOSPHERIC MERCURY CYCLING

As a naturally occurring element with several appreciably volatile forms, there has always been a natural cycle of mercury in the environment. The global mercury cycle is typified by passive emission (evasion) from the oceans and earth's crust, transport through the atmosphere, deposition and perhaps multiple cycles of re-emission and redeposition before being bound up again in geological sinks. However, it is estimated that approximately 80 percent of today's 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 the mining, smelting, and the use and disposal of mercury. 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 reactive gaseous mercury (RGM), which comprises only a few percent of total gaseous mercury in the atmosphere. 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.

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 (~ 1.6 ng/m^3) and shallow gradients near centers of population or industry.
- RGM, whether from primary emissions or secondarily formed by atmospheric reactions, exhibits a primarily localized effect. Ambient RGM concentrations range from 5 to 200 picograms/m^3 (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. 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. The transport properties of particulate matter are inversely proportional to particle size, with atmospheric half-lives of minutes to days.

The question of the importance of the global background source of mercury coming into Florida remains one of significant debate. Beginning with the observations of the Florida Atmospheric Mercury Study from 1992 to 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; Guentzel et al., 2001). The advection of large amounts of total mercury by trade winds over the Florida peninsula is not in dispute, but it is not known how much RGM is thereby made available to contribute to deposition.

Air-surface interactions of mercury are bidirectional. 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 with a high mercury content). Unless global controls are instituted, the global background of atmospheric mercury can be expected to rise in coming years.

MODELING THE ATMOSPHERIC MERCURY CYCLE

Understanding the relationships between various emissions sources of mercury and the changes that occur during atmospheric transport and deposition requires the use of computer-based models. Adequate models must represent in detail the physical and chemical processes that influence the fate of atmospheric mercury. The Department and USEPA have sponsored a series of model development and evaluation projects to promote the development and testing of state-of-the-art mercury chemistry models. These agencies also have 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.

These studies have progressed from studies in the early 1990s that sought only to determine the extent and magnitude of mercury species in the atmosphere and deposition (Florida Atmospheric Mercury Study, FAMS, 1993-97). They have progressed through intermediate steps to more intensive efforts, such as a pilot study to begin to elucidate detailed source-receptor relationships within South Florida (South Florida Atmospheric Mercury Monitoring Pilot Study, SoFAMMS, 1995 to 98), and a series of detailed process studies designed to elucidate air-surface exchange of mercury in the Everglades.

The final steps are to develop tools for assessing the relationship between sources of mercury emissions and deposition to watersheds and waterbodies within the region. Under joint contract to the Department and USEPA, UMAQL has completed development of a detailed atmospheric chemistry module for the Community Multi-scale Air Quality (CMAQ) processor. This model functions within the Models-3 atmospheric modeling system developed by NOAA and the USEPA. Running atop one of the meteorological models, Models-3 offers the capability of simulating the emissions, transport, conversion and removal processes that govern mercury deposition. CMAQ is a state-of-the art atmospheric chemistry model containing all postulated chemical reactions of mercury with other chemical and physical constituents of the atmosphere.

However, much testing remains to be done before the CMAQ model can be considered validated and ready for application. Laboratory studies are needed to verify which of the potential pathways of mercury reactions are important, how fast the reactions are and the resulting products. In the current Fiscal Year, the Department and USEPA are sponsoring a variety of investigations to complete the parameterization and testing of this atmospheric mercury model. When validated, Models3/CMAQ will allow the agencies to give robust answers and estimates of the major remaining questions about atmospheric mercury, i.e., what are the source-receptor relationships of mercury within the South Florida airshed and how much of the mercury entering the Everglades from the atmosphere is derived from long-distance transport into Florida.

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 factor influencing 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 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 do little to attenuate sulfate concentrations; 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 might inhibit mercury methylation. High sulfide levels might 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 might be limited by insufficient sulfate. The importance of sulfate in governing the rate of MeHg production remains to be determined. **Appendix 2B-2** gives a detailed treatment of the current state of knowledge of the influence of sulfur species on mercury biogeochemistry. New research on this subject was detailed in a research synopsis included as Appendix 7-4 of the 2001 ECR.

MODELING THE AQUATIC MERCURY CYCLE

Development of a geochemical model of mercury cycling in aquatic systems (i.e., 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 in the Midwest. Tetra Tech Inc. developed the model in collaboration with EPRI and the project research team. Because of the sophistication and state of development of the MCM, the SFMSP chose it as the tool to integrate the aquatic cycling process research conducted by the ACME team, USEPA and others. In the mid-1990s, EPRI and the Florida Electric Power Coordinating Group sponsored modification of the MCM to encompass Florida climatic and water quality conditions in the Florida Aquatic Ecosystem Mercury Cycling Project at Lake Barco, a seepage lake similar to those studied in the Mercury in Temperate Lakes Project. Subsequent development of the MCM was supported by USEPA ORD 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 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.

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 FFWCC 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 resource potentially at 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. Consequently, the SFMSP began sponsoring a series of field and laboratory studies and experiments to define the potential risk of mercury to wading birds.

The work is ongoing, and as stated in the Background section there is as yet no clear evidence 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, refer to Chapter 7 of the documents cited above.

Though no new, formal ecological risk assessment is presented in this document, field monitoring and research continue to refine knowledge of mercury biogeochemistry, bioavailability and food web biomagnification. The information is key to developing improved understanding of the food web relationships among mercury in prey and predator and also to supporting further refinements in estimation of ecological risk.

RESPONSE OF NATURAL SYSTEM TO SOURCE REDUCTIONS

Small numbers of largemouth bass collected at three Everglades locations (L-38A, L-35B and L-67A) in 1988 and reported in early 1989 averaged approximately 2.5 mg/kg (ppm) 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 Florida waters. From that time, to determine whether the trend of mercury in fish is increasing or decreasing the Florida Fish and Wildlife Conservation Commission, the 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 monitoring of mercury in fish and wildlife in the Everglades and elsewhere in Florida has yielded annual information on mercury body burdens in nestlings that can be similarly examined for time trends. **Figure 2B-1** is an update of the corresponding figure from the 2001 ECR, showing a continuing, if small decline in mercury in largemouth bass. **Figure 2B-2** shows a similar time course of mercury levels in the feathers of great egret nestlings.

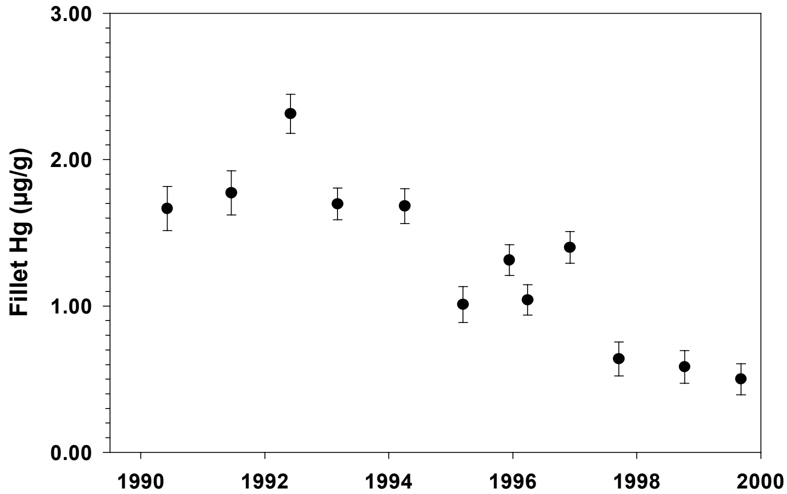

Figure 2B-1. Mercury in fillets of age-standardized largemouth bass in Everglades Canal L-67 (Lange et al., 2000). Adjusted least square means.

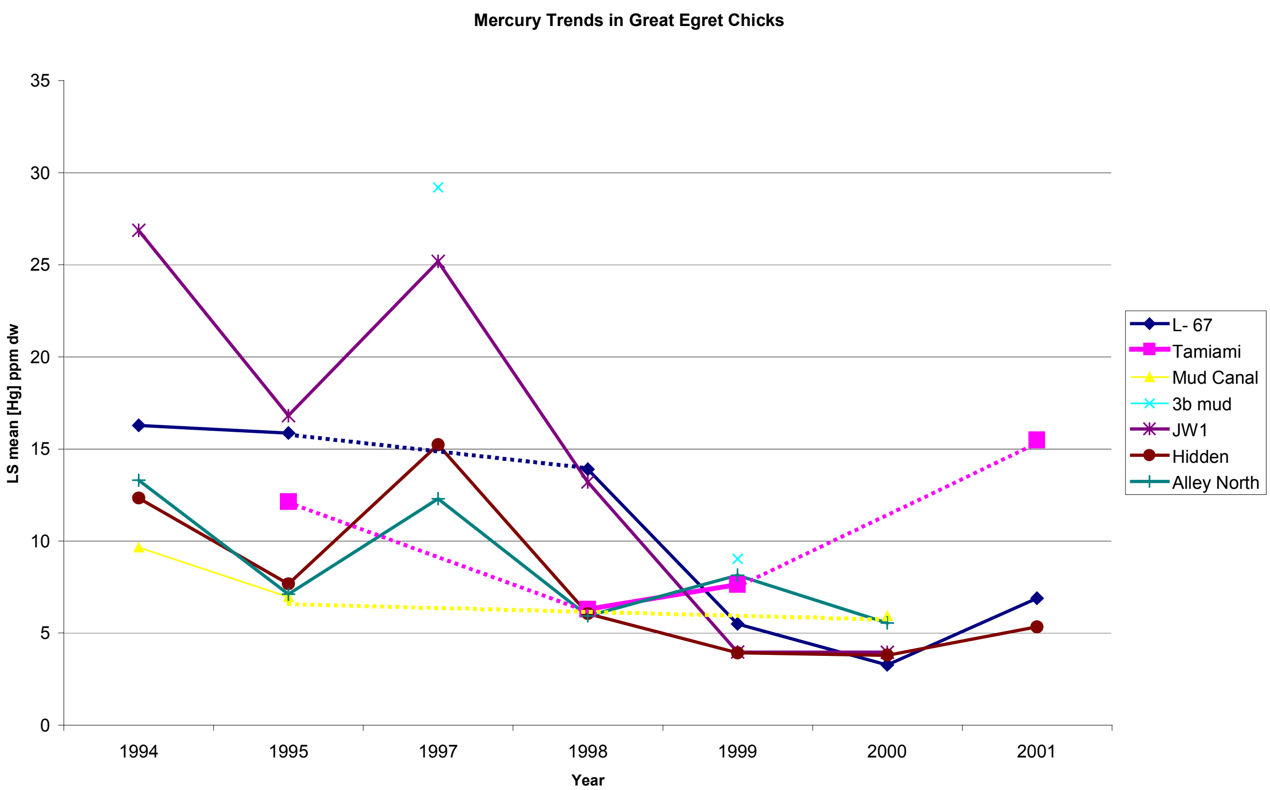

Figure 2B-2. Mercury concentration in the feathers of great egret nestlings standardized to 8 cm bill length (Frederick and Spalding, 2000).

How these trends in mercury in biota compare to trends in mercury load to the Everglades or to emissions trends in the United States or Florida are unknown. **Figure 2B-3** illustrates national estimates of mercury in municipal solid waste from 1970 to 1990, as well as projected trends to 2000. For comparison purposes, presented on a separate scale is the annual trend of Municipal Waste Combustor (MWC) (i.e., incinerator) emissions concentration of all facilities in Florida, from Tampa south.

Atmospheric deposition 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 and continuing 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, collocated with the FAMS site there. The sites, operated by their respective groups side-by-side for 15 months, established that comparability was excellent. After completion of the FAMS project, the District 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, 2001, in prep). It is likely that emissions reductions occurred before the monitoring began in 1994, and data variability will hamper trend detection in deposition data.

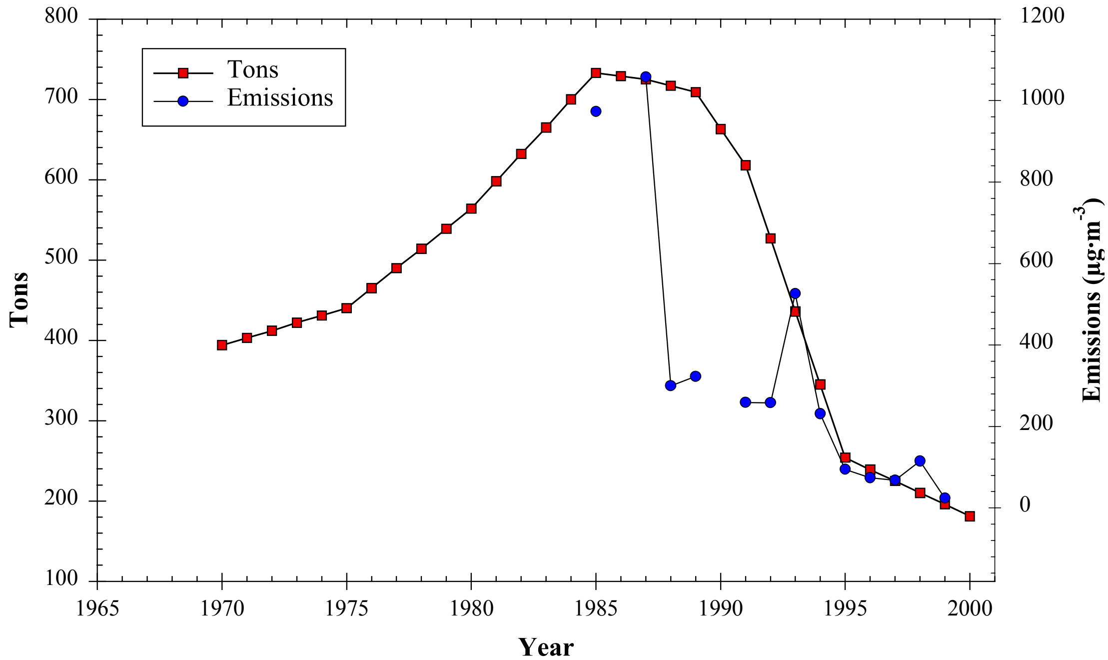

Figure 2B-3. Estimated trends of mercury in U.S. municipal solid waste from 1970 to 2000, and South Florida Municipal Waste Combustor emission concentrations from mid-1980s to 2000. Note: MWC emissions data are few prior to 1994.

Data from about 1994 to the present suggest mercury levels are declining 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 United States. While this evidence is 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 are possible and could 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 the data are limited, this continuing trend remains a working hypothesis that will be subject to data evaluation from other sites within the Everglades and Florida and to rigorous statistical analysis. Monitoring of mercury trends in atmospheric deposition, 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 mercury monitoring 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, consisting of hind-casting emissions and examination of new sediment cores, is underway to test this hypothesis.

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), which has been meeting to discuss technical issues associated with the establishment of such criteria. It is anticipated the Department will initiate this rulemaking in 2002. 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 that would require the Department to deem waters 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.

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 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.

ESTABLISHMENT OF TOTAL MAXIMUM DAILY LOADS FOR MERCURY

If the Everglades are 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 part of that effort and was 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 2011 if the Department fails to act.

ADDITIONAL EMISSIONS CONTROLS

Mercury affecting the Everglades is deposited from the atmosphere directly onto the Everglades and on the watershed of tributary inflows, which passes 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 man-made and may be defined as local (i.e., sources within 100 km of the Everglades), regional (i.e., within 1000 km) and global. These three spatial scales roughly correspond to sources 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 by the Department of the first mercury-limiting standard for municipal waste combustors in 1994, mercury emissions have continued to decline. In addition, USEPA regulation of medical waste incinerators since the early 1990s made such small incinerators uneconomic, and virtually all have ceased operation; mercury emissions from this sector have declined from 8,815 pounds (14 percent) in 1990 to 467 pounds (3 percent) in 1996. Combined mercury emissions from both sources have declined approximately 95 percent over the same 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, is evaded or is otherwise rendered less bioavailable.

Before undertaking further steps to control mercury emissions from local sources, it is essential to know the benefits, expressed as the decline in total mercury deposition. Computing 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. 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 the response will be nearly linear, i.e., a 25-percent reduction in deposition will result in almost a 25-percent reduction in accumulation of methylmercury in top predators. The initial decrease in predator mercury levels will be rapid, i.e., within a decade or so and the response to reduced mercury load will be essentially complete within two-to-three decades (**Figure 2B-3**). Recent data on Everglades responses are considered later in this chapter under "Response of Natural Systems to Source Reductions."

IMPLICATIONS OF STORMWATER TREATMENT AREAS

The STAs are being constructed under the Everglades Forever Act primarily to remove phosphorus from stormwater (Chapter 4). Monitoring confirms 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; 2001 ECR). 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. 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

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 current Class III criterion for mercury is 12 ng/L. The opportunity to fish and to eat one's catch is protected under this use. The fact that many water bodies in Florida and elsewhere comply with the numeric criterion, yet contain unsafe levels of mercury in fish, has led to the conclusion that this criterion is inadequate.

The USEPA has recognized the limited utility of its recommended water quality criterion for mercury, and in December 2000 published in the *Federal Register* notice of a new water quality criterion for the protection of public health. This new criterion being recommended to the delegated states and tribes is expressed not as a waster-column concentration of mercury, but as a concentration of 0.3 mg/kg methylmercury in fish flesh. It is expected that states and tribes will incorporate the new criterion during the next "triennial review" of water quality standards required by the Clean Water Act, and that all delegated entities will establish revised water quality standards for mercury based on this criterion within five years of its publication.

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 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.

The USEPA has departed from its usual practice of promulgating criteria as water-column concentrations because research and monitoring of mercury has shown that in some instances, such as in the Everglades, there is a weak relationship between methylmercury in water and mercury in fish flesh. Most pertinent is that 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).

RELATIONSHIPS TO OTHER WATER QUALITY VARIABLES

The rate of production of MeHg by sulfate-reducing bacteria (SRB) 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. Methylmercury is also destroyed by both aerobic and anaerobic processes in Everglades marshes. The net result of this multiplicity of factors is 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 SRB as a byproduct of their normal metabolism. The 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 largely derived from atmospheric deposition, plus *in situ* mineralization of mercury tied up in Everglades sediments and organic matter and surface water inflows. 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 or by photosynthetic activity. 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.

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-}, 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 in the Everglades, groundwater that could be admixed with ancient seawater containing sulfate and with water containing sulfate from EAA drainage rises to the surface. 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 (**Figure 2B-4**). This is true of areas that appear unlikely to be influenced by sulfate in EAA runoff. Further analysis of REMAP data by USEPA Region 4 may show whether sulfate from EAA runoff increases mercury bioaccumulation in *Gambusia* by comparing 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 nonabatable 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.

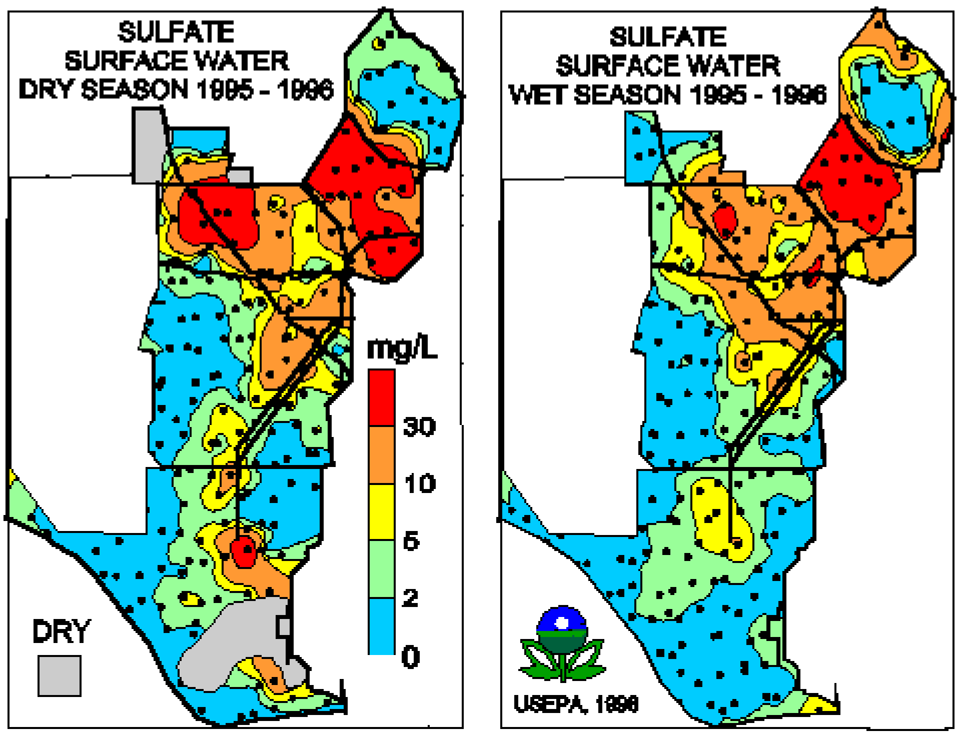

Figure 2B-4. Spatial gradients in surface water sulfate concentrations in the Everglades protection area, and changes from 1995/96 samplings to 1999. Data and graphics from USEPA Region 4 SESD.

The effect of phosphorus on methylmercury production by SRB is indirect through its effect on the rate of organic carbon production, which provides food for the SRB and helps define the dissolved oxygen regime. In addition, dissolved oxygen affects sulfide concentration in other ways, including through the iron cycle. At extremely 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 sequesters methylmercury and inhibits its entry into the food web and may dilute its concentration at the base of the food web.

At the other extreme – 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. Because it strongly influences water quality and the physical qualities of the habitat, eutrophication has profound effects on food-web dynamics and might 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, the E-MCM studies to-date clearly show that reducing the atmospheric deposition rate will reduce fish bioaccumulation in nearly direct proportion.

The theory has been posed that reducing phosphorus to the low levels characteristic of typical Everglades habitats might 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.

REGULATORY COMPLIANCE

The Everglades Forever Act (EFA) 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.

Permits issued by the Department 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" of the 2001 ECR, Appendix 7-7, and details routine permit compliance-related activities conducted by the District during the reporting year ending April 30, 2000. The reported information and analyses are professional and thorough, are an informative summary of the mercury status of ECP-related works and structures and complies with all terms of the relevant permits. The EFA 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.

Because mercury emissions to the atmosphere are 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 be forced to devise management steps to limit methylmercury production. Presently, there is no evidence that this is possible, but there is some evidence that suggests it might be. In the event emissions controls are insufficient, control of sulfate in EAA runoff is a potential candidate for further investigation. It is not presently known 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.

CONCLUSIONS

ADEQUACY OF EXISTING MANAGEMENT STRATEGIES

The public and private agencies comprising the SFMSP have worked effectively to:

1. Describe and define the mercury problem in the Florida Everglades
2. Identify and quantify the sources and causes of the problem
3. 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 an understanding of the sources and causes of the mercury problem. The results have been incorporated into sophisticated environmental models that predict the Everglades will respond to decreases in atmospheric mercury deposited into the marshes in a direct, nearly one-to-one relationship. More encouragingly, the model suggests 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 the beginnings of positive results of 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 additional tools needed to answer questions about the effects of Everglades management and restoration activities on this important water quality problem.

The multiagency 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, multimedia 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 combustors, medical waste incinerators and electric utility boilers. The Department adopted the first U.S. 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.

LITERATURE CITED

Branfireun, B.A., A.Heyes and N.T. Roulet. 1996. The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. *Water Resour. Res.*, 32:1785- 1794.

Bullock, Jr., O.R., W.G. Benjey and M.H. Keating. 1997. Modeling of regional scale atmospheric mercury transport and deposition using RELMAP. *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters.* Joel E. Baker, Ed. Pp. 323-347. SETAC Press. Pensacola, FL.

Cleckner, L.B., P.J. Garrison, J.P. Hurley, M.L. Olson and D.P. Krabbenhoft. 1998. Trophic transfer of methyl mercury in the northern Everglades. *Biogeochemistry*, 40:347-361.

Cleckner, L., C.C. Gilmour, D. Krabbenhoft, P. Garrison and J. Hurley. 1999. Methylmercury production by periphyton in the Florida Everglades. *Limnol. Oceanogr.*, 44:1815-1825.

Cleckner, L.B., C.C. Gilmour, J.P. Hurley and D.P. Krabbenhoft. 1999. Mercury methylation in periphyton of the Florida Everglades. *Limnol. Oceanogr.*, 44(7):1815- 1825.

Colborn, T., D. Dumanoski and J.P. Myers. 1996. *Our Stolen Future.* Penguin Books. New York, NY. 306 pp.

Croot, P.L., B. Karlson, J.T. van Elteren and J.J. Kroon. Uptake of $_{64}$Cu-Oxine by Marine Phytoplankton. *Environ. Sci. Technol.*, 1999. 33:3615-3621.

Expert Panel on Mercury Atmospheric Processes. 1994. *Mercury Atmospheric Processes: A Synthesis Report.* Electric Power Research Institute, Report No. TR-104214. EPRI. Palo Alto, CA.

Frederick, P.C. In Press. Mercury contamination and its effects in the Everglades ecosystem. *Reviews in Toxicology*.

Frederick, P. and M. Spalding. 2000. Temporal and geographic influences in mercury exposure in wading bird colonies across Florida. Ann. Meeting South Florida Mercury Science Program, Tarpon Springs FL. May 8-11. Abstract.

Gilmour, C.C. and E. A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.*, 71:131-169.

Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40:327-345.

Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, G.A. Gill and M.C. Stordall. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40:327-345.

2001 Everglades Consolidated Report, Chapter 7: Everglades Mercury Problem. 7-39.

Guentzel, J.L. 1997. *The atmospheric sources, transport and deposition of mercury in Florida*. Ph.D. Dissertation, Dept. of Oceanography, Florida State University, Tallahassee, FL. 177 pp.

Guentzel, J.L., W.M. Landing, G.A. Gill and C.D. Pollman. 2001. Processes influencing rainfall deposition of mercury in Florida: the FAMS project (1992-1996). *Envir. Sci. and Technol.*

Hudson, R.J., S.A.Gherini, C.J. Watras and D.B. Porcella. Modeling the biogeochemical cycle of mercury in lakes: The Mercury Cycling Model (MCM) and its application to the MCL Study lakes. In Watras, C.J. and J.W. Huckabee, Eds. *Mercury pollution: Integration and synthesis.* Lewis Publishers, Boca Raton, FL. 1994. pp. 473-523.

Hurley, J.P., L.B. Cleckner and P. Gorski. 1999. Everglades Nutrient Removal Project Small Fish Bioaccumulation Study. University of Wisconsin, Madison, WI. Submitted to SFWMD, West Palm Beach FL.

Keeler, G.J., J.T. Dvonch, J.A. Barres, M.S. Landis and R.K. Stevens. 2000. Real-world emissions of mercury from automobiles: The 1998 Fort McHenry traffic tunnel study. Heavy Metals Meeting, Ann Arbor, MI. August 7-11, 2000. Abstract.

Krabbenhoft, D.L. and L.E. Fink. 2000. The effect of dry down and natural fires on mercury methylation in the Florida Everglades. Project report to SFWMD, 12 pp. typescript.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley and A.W. Andren. 1995. Mercury cycling in the Allequash Creek Watershed, Northern WI. *Wat. Air Soil Poll*, 80:425-433.

Lange, T., D. Richard and H. Royals. 2000. Long-term trends of mercury bioaccumulation in Florida's largemouth bass. Ann. Meeting South Florida Mercury Science Program, Tarpon Springs, FL. May 8-11. Abstract.

Lawson, N.M. and R.P. Mason. In Review. The influence of organic complexation on inorganic mercury and methylmercury accumulation by an estuarine diatom. Submitted to *Marine Chemistry.*

McComick, P.V., P.S. Rawlik, K. Lurding, E.P. Smith and F.H. Sklar. 1996. Periphytonwater quality relationships along a trophic gradient in the northern Florida Everglades. *J. N. Am. Benthol. Soc.*, 15(4):433-449.

Mason, R.P., J.R. Reinfelder and F.M.M. Morel. 1995. Bioaccumulation of mercury and methylmercury. *Water Air Soil Poll.* 1995, 80:915-921. NAS, 2000. *Toxicological Effects of Methylmercury.* National Academies, National Academy of Science. July 11, 2000. Washington, D.C.

http://www4.nationalacademies.org/news.nsf/isbn/0309071402?OpenDocument

Paatero, P. and U. Tapper. 1993. Positive Matrix Factorization: A non-negative Factor Model and Optimal Utilization of Error Estimates of Data Values. *Environmetrics* 5:111-126.

Pollman, C.D. and T.D. Atkeson. 2000. Long-term trends in mercury atmospheric inputs and deposition in South Florida. Ann. Meeting South Florida Mercury Science Program, Tarpon Springs, FL. May 8-11. Abstract.

Sepulveda, M.S., G.E. Williams, Jr., P.C. Frederick and M.G. Spalding. 1999. Effects of mercury on health and first-year survival of free-ranging great egrets (*Ardea albus*) from southern Florida. *Archives of Environmental Contamination and Toxicology.*

SFWMD. 1999. *Everglades Interim Report.* South Florida Water Management District, West Palm Beach, FL. January 1, 1999.

SFWMD. 2000. *Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach Florida. January 1, 2000.

Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton and L.R. McDowell. 2000a. Methylmercury accumulation in tissues and its effects on growth and appetite in captive great egrets. *Journal of Wildlife Diseases*, 36, No. 3.

Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton, L.J. Richey, I.M. Schumacher, S.G.M. Blackmore and J. Harrison. 2000b. Histologic, neurologic, and immunologic effects of methylmercury in captive great egrets. *Journal of Wildlife Diseases*, 36.

USEPA. 2000. UMIX and PMF as applied to $PM_{2.5}$. Workshop Proceedings. February 14-16, 2000. EPA/600/A100/048, USEPA. RTP, NC.

USEPA. 1998. *South Florida Ecosystem Assessment Vol. I. Final Technical Report. Phase 1 Monitoring for adaptive management*: Implications for ecosystem restoration. Region 4 and Office of Research and Development. Athens, GA. December. EPA-904-R-98-002.

USEPA. 1997a. *Mercury Study Report to Congress. Volume 1: Executive Summary Report*. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. EPA-42/R- 97-003. December.

USEPA. 1997b. *Mercury Study Report to Congress. Volume 3: Fate and Transport of Mercury in the Environment*. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. EPA-42/R-97-003. December.

USEPA. 1997c. *Mercury Study Report to Congress. Volume V: Health Effects of Mercury and Mercury Compounds*. Office of Air Quality Planning and Standards and Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. EPA-42/R-97-003. December.

USEPA. 1996. South Florida Ecosystem Assessment Interim Report. Monitoring for Adaptive Management: Implications for ecosystem restoration. Region 4 SESD and ORD. EPA-904-96-008. December 1996.

USEPA. 1992. *Characterization of Products Containing Mercury in Municipal Solid Waste in the United States, 1970 to 2000*. Office of Solid Waste.

Virta, M., J. Lampine and M. Karp. 1995. A luminescence-based mercury biosensor. *Analytical Chemistry*, 67:667-669.

Xie,Y.L., P.K. Hopke, L.A. Barrie and S.M. Li. 1996. Identification of Source Nature and Seasonal Variations of Arctic Aerosol by Positive Matrix Factorization. *J. Atmos. Sci.*, 56:249-260.