Chapter 2B: Mercury Monitoring, Research and Environmental Assessment

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SUMMARY

Mercury remains one of the major water quality concerns for the Everglades restoration program. Efforts by the South Florida Water Management District (SFWMD or District) and the Florida Department of Environmental Protection (FDEP) in leading the South Florida Mercury Science Program (SFMSP)[1] continue to improve the understanding of the sources, transformations, toxicity, and fate of mercury in the Everglades. The SFMSP seeks to provide scientific information on environmental cycling of mercury at local, regional, and global levels to better support decision making in South Florida. General information on the nature of the environmental mercury cycle has been presented in previous Everglades Consolidated Reports. This chapter serves to update the findings previously reported, with supporting data and other technical information on mercury being provided in the appendices to this chapter[2].

The updated findings from this collaborative effort on mercury include the following:

- Although the precise proportions of locally-derived versus global mercury remain uncertain, the data indicates that a significant proportion of mercury deposition to the Everglades originates from sources within southern Florida. Newly deposited mercury is converted to methylmercury over a period of hours to days.
- Methylmercury, a highly toxic form of mercury, is primarily produced in sediments by naturally occurring, sulfate-reducing bacteria. Methylmercury strongly

[1] This partnership of federal, state, and local interests includes the FDEP, the District, the U.S. Environmental Protection Agency Office of Research and Development and Region 4, the Florida Fish and Wildlife Conservation Commission, and the U.S. Geological Survey. Other collaborators associated with 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 & M University, Oak Ridge National Laboratory, the Academy of Natural Sciences of Philadelphia, Florida Power 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.

[2] Appendices 2B-1 through 2B-7 of the *2004 Everglades Consolidated Report* provide additional detail to meet the Everglades Forever Act (EFA) requirement that the District and the FDEP shall annually issue a peer-reviewed report regarding the mercury research and monitoring program that summarizes all data and findings. Appendix 2B-5 of this report meets the reporting requirements of the EFA, as well as specific permits issued by the FDEP to the District. Readers who desire additional, detailed scientific information should consult the specific chapters on mercury monitoring and assessment presented in the *1999 Everglades Interim Report* and previous Everglades Consolidated Reports.

bioaccumulates in the aquatic food chain, and its production is highly influenced by the rate of supply of atmospherically derived mercury and by sulfate concentrations.

- Methylmercury production and bioaccumulation are influenced by many factors associated with water quality, including sulfate, sulfide, nutrients, temperature, and light levels.
- The central and southern Everglades exhibit strong methylmercury production and bioaccumulation and, therefore, high mercury levels are found in fish and wildlife. At the apparent peak of mercury in Everglades biota in the mid 1990s, these levels were high enough to pose a risk of chronic toxicity to wildlife. Subsequent declines in body burdens have eased this concern, but mercury risk to humans and wildlife continues to be a water quality concern.
- The primary emissions sources of mercury in southern Florida circa 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 reasons for this decline were pollution prevention activities and emissions controls that resulted in reductions of mercury wastes.
- Monitoring of Everglades fish and wading birds indicates a significant decline in mercury over the period from 1994 to 2003 in both largemouth bass and great egrets by at least 60 percent. Largemouth bass from Central Florida lakes have declined by approximately 40 percent. Largemouth bass mercury levels have not declined in the Everglades National Park, for reasons that remain obscure.
- Mercury levels in largemouth bass, despite substantial declines in recent years, remain well above the proposed 0.3 milligrams per kilogram (mg/kg) fish tissue criterion proposed by the U.S. Environmental Protection Agency.
- Environmental mercury models for the Everglades have been developed and incorporate the latest findings from atmospheric and aquatic research. Results substantiate a strong relationship between atmospheric mercury load to the Everglades and mercury levels in top predator fish.
- Aquatic system modeling analyses indicate that the response times of the Everglades to changes in atmospheric load are short. Modeling analyses suggest that significant benefits can be expected within a decade of sustained load reductions, with the ultimate benefits occurring within about 30 years. Monitoring data suggests that the Everglades has responded to decreased mercury emissions from South Florida. Trend monitoring confirms these reductions, which appear to take effect more rapidly than model predictions.

The monitoring, research, modeling, and assessment studies described in this chapter and its appendices were coordinated among the collaborators in the SFMSP. This group of agencies, academic and private research institutions, and the electric power industry has advanced the understanding of the Everglades mercury problem more effectively and faster than what could have been accomplished individually by either the FDEP or the District. The SFMSP has operated under a coordinated plan; however, each agency operates within its own management and budgeting framework. The goal of the SFMSP is to provide the FDEP and the District with information to help the two agencies make mercury-related decisions about the Everglades Construction Project, as well as other restoration efforts, on the schedule required by the

Everglades Forever Act. Consequently, SFMSP studies are now providing a better understanding of why the Everglades is an "at-risk" system for mercury contamination.

GLOSSARY OF MERCURY-RELATED ACRONYMS AND TERMS

The general glossary in the *2004 Everglades Consolidated Report* includes terminology from all the report's chapters. However, because mercury is a complex environmental contaminant, the following mercury-specific glossary is provided to further assist readers in understanding the material presented in Chapter 2B of this report.

- **ACME Project:** The Aquatic Cycling of Mercury in the Everglades Project. A process-oriented mercury research program organized by the U.S. Geological Survey.
- **E-MCM:** Everglades Mercury Cycling Model. A computer model of mercury cycling. The model is being refined under the auspices of South Florida Water Management District, the Florida Department of Environmental Protection, and the U.S. Environmental Protection Agency to predict changes for mercury in the Everglades in response to changing loads or water quality.
- **EPA:** Everglades Protection Area. The EPA is comprised of Water Conservation Areas 1, 2A, 2B, 3A, and 3B, the Arthur R. Marshall Loxahatchee National Wildlife Refuge, and the Everglades National Park.
- **FAMS:** Florida Atmospheric Mercury Study. An early study to quantify deposition of mercury from the atmosphere to the Everglades and other parts of Florida.
- **Hg:** The standard chemical abbreviation for the element mercury.
- **MeHg:** The standard chemical abbreviation for the compound methylmercury. A particularly toxic organic form of mercury that concentrates in aquatic food webs.
- **REMAP:** Regional Environmental Monitoring and Assessment Program. The U.S. Environmental Protection Agency Region 4 and Office of Research and Development 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 established to determine the causes and possible solutions to the mercury problem in Florida.
- **STA:** Stormwater Treatment Area. A constructed wetland designed to remove phosphorus from inflowing waters prior to discharge into the Everglades.
- **SRB:** Sulfate-reducing bacteria. Microbes, commonly found in sediments, which transform inorganic mercury into methylmercury.
- **TMDL:** Total maximum daily load. Pollutant load determinations for a water body not meeting its designated use as required under the federal Clean Water Act.

RESEARCH PROGRESS

The following research needs were identified in previous Everglades Consolidated Reports (ECRs) from the South Florida Water Management District (SFWMD or District). An update on the progress made with respect to each of the research needs is presented below.

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

   The U.S. Geological Survey Biological Resources Division's (USGS-BRD) Patuxent Wildlife Research Center initiated a study of the *in-ovo* effects of methylmercury. Dr. Gary Heinz, principal author of the much-cited study of the multigenerational effects of mercury on domestic mallard ducks, has subsequently obtained extensive collections of fertile eggs from several wading bird species and has conducted detailed studies of egg viability and hatchability.

   Heinz (2002) found that the embryos of various species of birds differ in their sensitivity to methylmercury. His results indicate that the former, presumably protective, "reference dose" for estimating mercury risk to fish-eating birds was, in fact, not protective. The presumption had been that domesticated ducks used in earlier studies were the most sensitive species, as these largely herbivorous birds have low exposure to methylmercury. However, subsequent study involving several species of fish-eating birds, including species found in the Everglades such as white ibis *(Eudocimus albus)*, great egret *(Casmerodius albus)*, and tricolored heron *(Egretta tricolor)*, indicated that these species were as much as seven times more sensitive to methylmercury toxicity.

   The Florida Department of Environmental Protection (FDEP), with potential support from the USGS-BRD and the U.S. Fish and Wildlife Service (USFWS), plans to complement the laboratory studies being done at Patuxent Wildlife Research Center with a multigenerational feeding study of mercury effects on fish-eating birds. A captive colony of white ibis will be established in Gainesville, FL for controlled experimental studies. It is planned that the aviary will be constructed in time for the 2004 spring breeding season and that the studies will continue for four years.

2. Quantify "global versus local" and "new versus old" sources of mercury (2001 ECR). Local source: Receptor Relationships of Mercury (2002 ECR).

   The FDEP and the U.S. Environmental Protection Agency (USEPA) continue to support atmospheric mercury studies relevant to the mercury control policy in U.S. southeast coastal regions, sponsor studies that directly measure transport of mercury species into Florida, describe and quantify the atmospheric reactions of mercury that facilitate deposition, and employ photochemical grid models to organize the atmospheric processes research into decision making. The operation of two sites in the Speciated Atmospheric Mercury Study (SAMS) project by the Broward County Air Quality Division is continuing. This project focuses on the paramount importance of the speciation of mercury in the atmosphere in controlling the transport and fate of mercury. SAMS makes highly time-resolved measurements of all known forms of atmospheric mercury and associated tracer species. It is expected that this measurement and modeling project will continue through 2003 and will provide improved data, tools, and understanding in the effort to resolve the question of the importance of long-distance transport of mercury into Florida.

Earlier analytical bottlenecks at the USEPA Office of Research and Development (ORD) National Exposure Research Laboratory's x-ray fluorescence laboratory have been resolved, and the substantial backlog of elemental tracer samples has been analyzed. Several reports and publications relating to the measurement and modeling of mercury deposition have been completed or are currently in press (e.g., Malcolm et al., 2003; Marsik, in prep.).

Results from the Pompano Beach site during the Florida Everglades Dry Deposition Study (FEDDS) in summer 2000 indicated that reactive gaseous mercury (RGM) concentrations below onshore wind flow regimes were quite low (typically less than 10 picograms per cubic meter (pg/m^3)), contributing a negligible input of mercury over southern peninsular Florida. Other measurement and meteorological data will be useful in the further modeling of long-distance transport phenomena that potentially influence 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).

Research aimed at defining both the details of the mercury methylation process and its quantitative relationships with factors that influence this process is important to learning what it is that controls the effective net production of methylmercury in the aquatic system. The SFMSP has devoted significant effort to this topic from 2001 through 2003. A specific focus has been to organize the work around the requirements of the E-MCM while incorporating qualitative and quantitative information as it becomes available into the evolving E-MCM to make it a more robust tool for evaluating management options. The data and insight from field studies are being fed directly into model formulation and testing. The results are then used to calibrate and test the E-MCM in order to simulate the effects of various hydrology, water quality, or restoration activities.

The E-MCM development and application is detailed in Appendix 2B-2. It remains an SFMSP goal to continue to develop the E-MCM as a tool to assess systemwide responses to mercury sources, water quality, and management scenarios being evaluated by the Comprehensive Everglades Restoration Plan (CERP).

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

The FDEP continues to support a series of studies with the USGS and the Academy of Natural Sciences of Philadelphia, Estuarine Research Laboratory. Field mesocosm experiments using stable-isotope and other tracer techniques have been used to examine the interactions between mercury, sulfur, nutrients, dissolved organic carbon, and other water quality variables. The results of these mesocosm studies are presented in Appendix 2B-3. Fieldwork began with deployment of mesocosms in spring 2001; field experiments are presently scheduled through June 2005. The further influence of the effects of wetting and drying cycles on methylmercury production is presented in Appendix 2B-1.

5. Trends of mercury in Florida (2002 ECR).

One of the most illuminating uses of monitoring data has been evaluating mercury trends over time. For example, the sediment coring studies of the early 1990s by Rood et al. (1995) revealed that mercury accumulation in Everglades soils was more than five times greater than in 1900, confirming the viewpoint that anthropogenic influences have dominated mercury cycling. However, following that study is a hiatus of 10 critical years in the record to describe the direction and magnitude of mercury impinging on South Florida. To close this data gap, the FDEP is sponsoring a revisit of that work by selecting several water bodies (e.g., lakes and borrow pits) with sedimentary profiles more ideal than those in the Everglades. The prime contractor is the Science Museum of Minnesota, with assistance from the University of Florida, the University of Connecticut, and Tetra Tech, Inc.

Additional fieldwork for sediment coring studies was completed in 2002. However, some cores could not be analyzed from the three water bodies that were initially sampled (Gator Lake, 9-Mile Pond, and West Lake) due to problems encountered with these cores. During a follow-up field trip in 2003, multiple cores also were collected from three lakes in South Florida (Lake Annie, Gator Lake, and Gary Lake [old borrow pits]). Preliminary analyses of the cores indicate that sediment profiles for these lakes are suitable, and the lead-210 dating is currently underway. Project completion is currently on schedule for November 2003. This project should yield high-resolution information on the trend of mercury accumulation (i.e., mercury deposition) in South Florida. It is anticipated that this data, in conjunction with other trend information developed by the FDEP and its collaborators, will allow evaluation of the outcomes and effectiveness of controls on mercury use and emissions. It is expected that this work will be reported in the *2005 Everglades Consolidated Report*.

Analyses of long-term trends of mercury in Everglades wading birds are presented in Appendix 2B-4. Information obtained recently on the relationship between the stability of methylmercury in animal hair and feathers and the potential confounding effects of inorganic mercury formerly used as preservatives in museums has been used by researchers from the University of Florida to construct a historical record of mercury in biota from South Florida. This reconstruction indicates an increasing trend from the late 1800s to approximately 1990. Direct measurements of mercury in animal hair and feathers collected by the District and the FDEP show a decline that began in the mid 1990s.

THE MULTIMEDIA CYCLE OF MERCURY

The accumulation of mercury in fish is one of the water quality problems in the Everglades being addressed by the South Florida Water Management District and the Florida Department of Environmental Protection in their activities under the Everglades Forever Act and the Comprehensive Everglades Restoration Plan. This problem first became apparent in 1989, when the Florida Department of Health issued mercury-related health advisories to fishermen. These recommendations, the first ever in Florida, urged fishermen not to eat largemouth bass (a popular sport fish) from most of the Everglades and to consume only limited amounts of several other species of sport fish because of a risk of mercury toxicity to consumers. The high levels of mercury found in fish also pose a risk of toxicity to fish-eating wildlife.

The mercury problem in the Everglades, as in many other waters, is a multimedia problem, meaning that more than one aspect of the environment is involved. To understand the individual components of the problem, the disciplines of air quality, water quality, and ecological risk must be combined to encompass the disparate facets of the mercury problem. A conceptual model of the mercury problem is presented in **Figure 2B-1**.

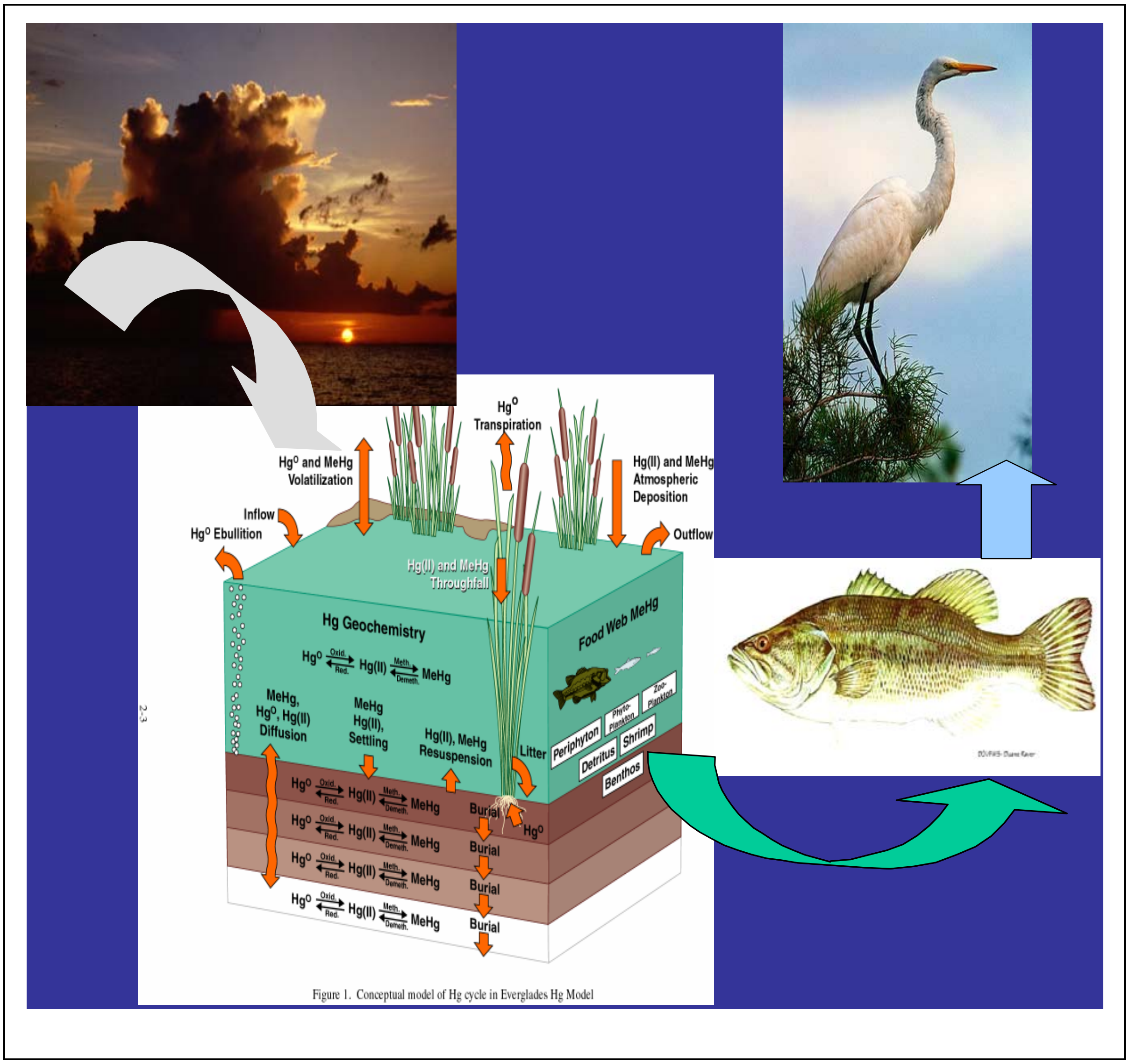

Figure 2B-1. Illustration of the multimedia cycle of mercury for atmospheric transport and fate, aquatic biogeochemical cycling, bioaccumulation, and ecological risk.

The most important concepts to keep in mind regarding the environmental mercury cycle are as follows:

- **The Atmospheric Mercury Cycle.** Human mining, industrial activities, air pollution, and deposition since the Industrial Revolution have increased, by about fivefold, the amount of mercury (Hg) that naturally cycles through the atmosphere. Mercury pollution in the air comes from the mining and smelting of mineral ores (which contain small amounts of mercury), the burning of fossil fuels (e.g., coal and oil), the use and disposal of mercury, and the incineration of waste, principally municipal and medical wastes. The predominant source of mercury to the Everglades is atmospheric deposition. Mercury deposited from the atmosphere is approximately 95 to 98 percent of the total mercury input to the Everglades Protection Area (EPA) (the 1994 and 1995 mean is approximately 220 kilograms per year [kg/yr]); mercury input from discharges of surface water to the EPA is relatively minor (the 1994 and 1995 mean is approximately 3 kg/yr). Dry deposition of gaseous and fine particulate mercury is about one-third of rainfall deposition.

- **The Aquatic Cycle of Mercury – Biotransformation and Bioaccumulation.** Once deposited into the Everglades, mercury is quickly distributed through the shallow water column and into sediments, where a fraction of the mercury is transformed by naturally occurring bacteria to methylmercury (MeHg). Methylmercury is very toxic and bioaccumulates efficiently from the water up through aquatic food webs.

- **Assessment of Methylmercury Risk to Everglades Wildlife – Ecological Risk.** Methylmercury in top predator fish (e.g., largemouth bass) in the Everglades has been measured to be as much as ten-millionfold higher than that of the surface water associated with these fish. This phenomenal bioaccumulation of mercury results in a risk of mercury toxicity to humans and wildlife, such as wading birds, that feed on fish.

THE ATMOSPHERIC MERCURY CYCLE – AIR POLLUTION AND DEPOSITION

When mercury was first discovered to be in Everglades fish in the late 1980s, little was known about the causes of the mercury problem. Answers to even the most basic questions regarding mercury were unknown, such as whether the presence of mercury was simply a natural condition in the Everglades, whether the area had always been that way, what were the sources of mercury, what levels were safe or harmful, and, most importantly, what could be done to reduce or alleviate mercury levels.

These questions were considered by the Mercury in Fish and Wildlife Task Force, which was appointed by the governor of Florida in late 1989. The task force ultimately approved a report calling for a broad range of environmental studies that would attempt to find answers to mercury-related questions. At that time, there were few precedents for the concept that air quality could exert a significant influence on surface water quality. In 1992, however, the District, the FDEP, and the USEPA prepared a comprehensive study plan that called for the evaluation of both air and watershed sources of mercury to the Everglades.

A complementary study of the accumulation of mercury in dated sediment cores from the Water Conservation Areas (WCAs) and the Everglades National Park (ENP or Park) revealed that the rate of mercury accumulation in Everglades soils at the top of the cores, i.e., circa 1992, was approximately six times higher than the core strata representing 1900 (Rood et al., 1995) (**Figure 2B-2**). This study demonstrated that the Everglades was contaminated by mercury. At that time, neither the sources of mercury nor the transport systems delivering it were evident.

Despite the remaining uncertainties regarding the sources and routes of mercury contamination in the Everglades, the two studies illustrated above confirmed that, in terms of its mercury budget, the Everglades is a system contaminated by anthropogenic activities principally mediated by atmospheric transport and deposition.

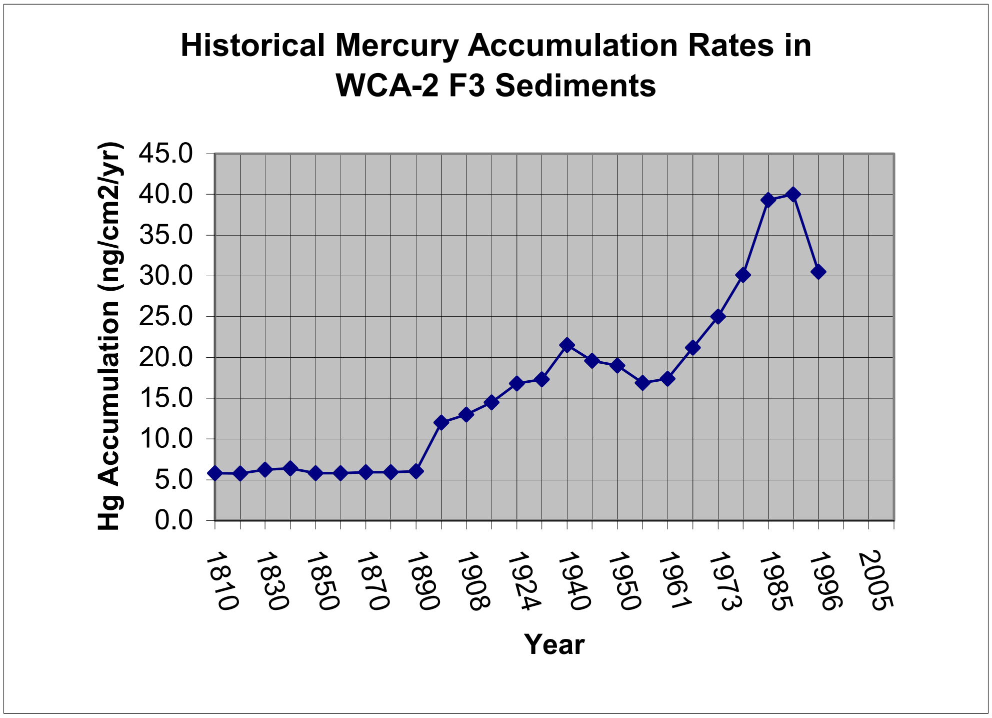

Figure 2B-2. Historical trends of mercury accumulation in Everglades soils. New event analyses are under way to confirm downward trends in recent years.

Because atmospheric deposition of mercury is the dominant source of mercury to the Everglades (**Figure 2B-3**), the FDEP has pursued pollution prevention and emissions controls as having the greatest likelihood for controlling the mercury problem. Major reductions in mercury use and emissions in southern Florida have been achieved, thereby hopefully decreasing the delivery of atmospheric mercury to the Everglades. Findings from both environmental monitoring and computer models suggest that the control of atmospheric sources of mercury can have positive benefits for the EPA. The elimination of mercury from commercial and industrial products and processes since the late 1980s has reduced mercury emissions from municipal waste incinerators and other sources in South Florida.

Monitoring over the last decade suggests that these lower emissions have produced a corresponding reduction in mercury burdens of Everglades fish and wading birds. Environmental models developed by the South Florida Mercury Science Program (SFMSP) relate fish mercury levels to the amount impinging on the Everglades. These models show that the control of mercury emissions should significantly alleviate the overall Everglades mercury problem within one or two decades.

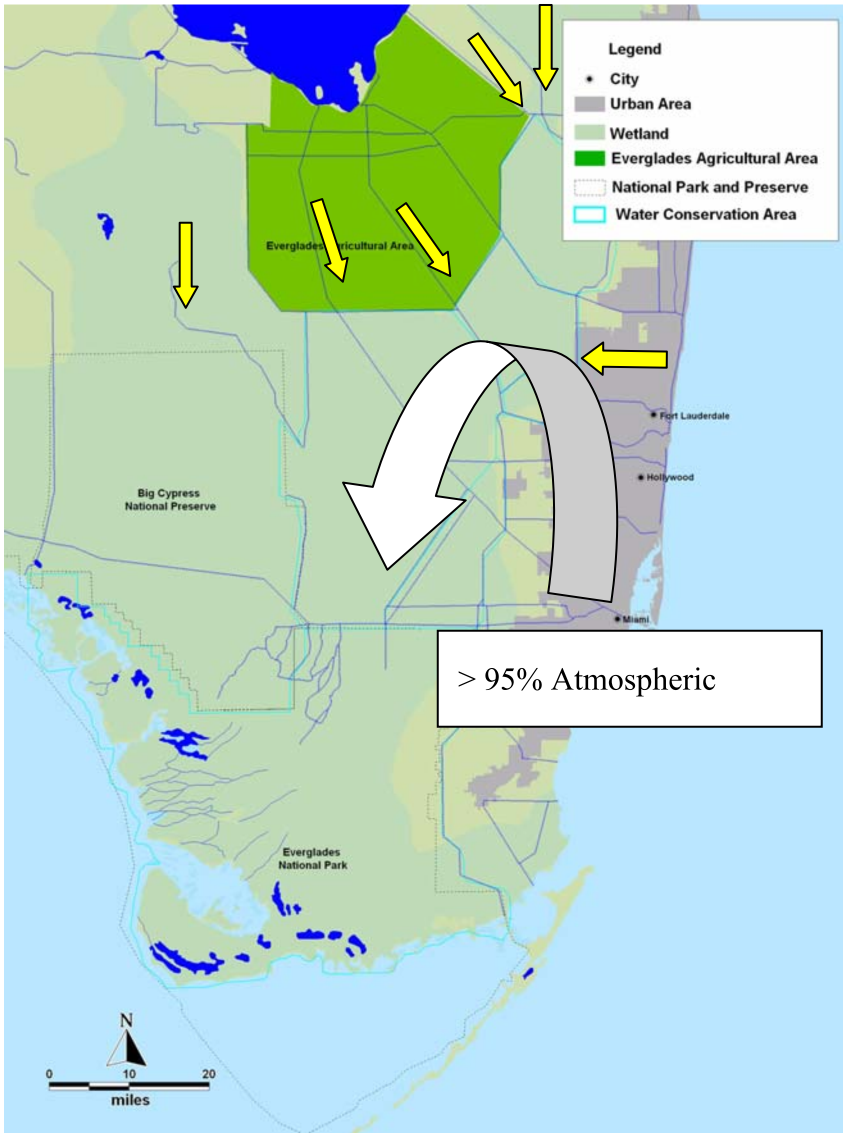

Figure 2B-3. Comparison of mercury inputs via surface water inflows versus atmospheric deposition to the Everglades Protection Area (EPA).

Another important question about atmospheric mercury is that of the nature its sources. The primary transport regimes relevant to South Florida are local scale (i.e., transport times of approximately one day, or about 100 kilometers [km]), regional scale (i.e., transport times of approximately one week or about 1,000 km), and global scale (i.e., transport times of weeks, dispersing over much of the globe) (Expert Panel, 1994). Florida is largely disjunctive from the regional background of emissions that dominates the U.S. mainland, and data suggest a contribution to the Everglades from regional sources within the southeastern U.S. of between 5 percent (Atkeson et al., 2002) to 29 percent of total deposition (Guentzel et al., 2001). Analysis suggests that local scale sources represent at least half of the total atmospheric mercury contribution to the Everglades (Atkeson et al., 2002).

COMPREHENSIVE SOURCE REDUCTION

Finding remedies to address 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. That is, mercury emissions to the environment should be limited to the extent allowable by available information and technology. The FDEP has vigorously pursued the following approaches to address this issue:

- **Pollution Prevention.** The 1993 Florida Solid Waste Management Act required elimination of mercury from some commercial products to reduce the mercury content of wastes. The act 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 seek further reductions in mercury use.
- **Waste Disposal.** Hazardous waste regulations have been tightened to require stricter control of mercury-containing wastes. Proper disposal minimizes 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 FDEP 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 Medical Waste Incineration (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.

THE AQUATIC CYCLE OF MERCURY – BIOTRANSFORMATION AND BIOACCUMULATION

The pathways of mercury accumulation in fish and wildlife are complex. Although inorganic forms of mercury dominate its environmental cycle, a proportion can be transformed into methylmercury in the sediments of water bodies. Methylmercury is primarily produced by sulfate-reducing bacteria (SRB), naturally present in the sediment where oxygen is absent but sulfate is present. These bacteria take up inorganic mercury and convert it to methylmercury as an incidental byproduct of their normal life processes. Other 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. This process is known as bioaccumulation and results in a buildup of methylmercury at each level of the aquatic food chain. In larger fish, levels of methylmercury may bioaccumulate as much as several million times higher than in the surrounding water. In sufficient doses, methylmercury is toxic to the brain, liver, kidney, and immune system of wildlife and humans and can have adverse effects on egg and fetus development.

Many soil, water quality, and biotic factors directly or indirectly influence methylmercury production. For example, while sulfate is required for microbial methylmercury production, high sulfate levels tend to inhibit production. Drought and fire can increase the production of methylmercury by changing the proportions of sulfur forms 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.

If control of local emissions of atmospheric mercury is not sufficient to manage the Everglades mercury problem, then it might be possible to reduce the mercury problem through management of water quality and quantity. This approach would make environmental conditions less favorable for the production of methylmercury. Management of marsh fire frequency, hydrologic patterns, and water constituents, most importantly sulfate, may provide a means for such mitigation. With either approach, less methylmercury would be available, making the accumulation of toxic amounts in fish and wildlife less likely.

More detailed treatments of the general features of the environmental mercury cycle are presented in the 2000, 2001, and 2002 ECR and in Appendices 2B-2 and 2B-5 of the 2003 ECR.

ROLE OF CARBON CYCLING IN METHYLMERCURY PRODUCTION AND BIOACCUMULATION

The hypothesis has been proposed that a reduction in carbon dioxide fixation (productivity) by Everglades plants will exacerbate the Everglades mercury problem. A reduction in Everglades plant productivity could be a consequence of reducing and restoring Everglades phosphorus (P) concentrations to more natural levels – for example, to the proposed 10 micrograms per liter (µg/L) total phosphorus (TP) concentration standard – resulting in less plant growth and plant biomass.

In some aquatic ecosystems, there is an inverse relationship between aquatic plant biomass and mercury in animals in the aquatic food chain. "Biodilution" is the term used to describe the phenomenon where an increase in plant biomass due to a sustained increase in the limiting factor to plant production (i.e., phosphorus in the Everglades) has the effect of reducing the buildup of methylmercury in the aquatic food chain.

Through the mechanism of biodilution, when methylmercury is present in the water column, an increase in plant production results in uptake and sorption of this methylmercury by an increased biomass of plants. This leads to a decrease in the methylmercury concentration per unit of plant biomass. This, in turn, leads to a decrease in methylmercury exposure to organisms that feed on the plants, a decrease in methylmercury concentrations in plant grazers, a decrease in methylmercury concentrations in their predators, and so on up the aquatic food chain.

Biodilution of methylmercury has been demonstrated for a few deep, temperate lakes where the mechanism is relatively simple – increased phosphorus concentrations produce increased phytoplankton biomass. In these deep lakes, there is no significant means of methylmercury production in the water column, or significant methylmercury contribution to the water column from sediments. In contrast, the Everglades algal community is present primarily as periphyton rather than a planktonic community. Specifically for the Everglades, it has been hypothesized that the Everglades periphyton response to nutrient enrichment is analogous to the lake phytoplankton response; that is, periphyton biomass increases with increasing TP concentrations in the range of 10 to 30 μg/L, thereby causing a biodilution effect. If this hypothesis was accurate, then a reduction in TP concentrations to 10 μg/L, causing a reduction in periphyton biomass, could increase mercury levels in the Everglades food chain. However, it has been shown that periphyton biomass actually dramatically decreases with TP enrichment in that range in sawgrass, wet prairie, and slough environments (**Figures 2B-4** and **2B-5**). Thus, the hypothesized mechanism of biodilution for the Everglades is not evident and does not appear to reflect ecological reality.

Additional evidence that the periphyton biodilution hypothesis is not valid for the Everglades is provided by Simon et al. (1999). These data indicate that there is an increase in the methylmercury concentrations in Everglades periphyton with increasing phosphorus concentrations, and not the decrease that would be expected if periphyton were biodiluting methylmercury.

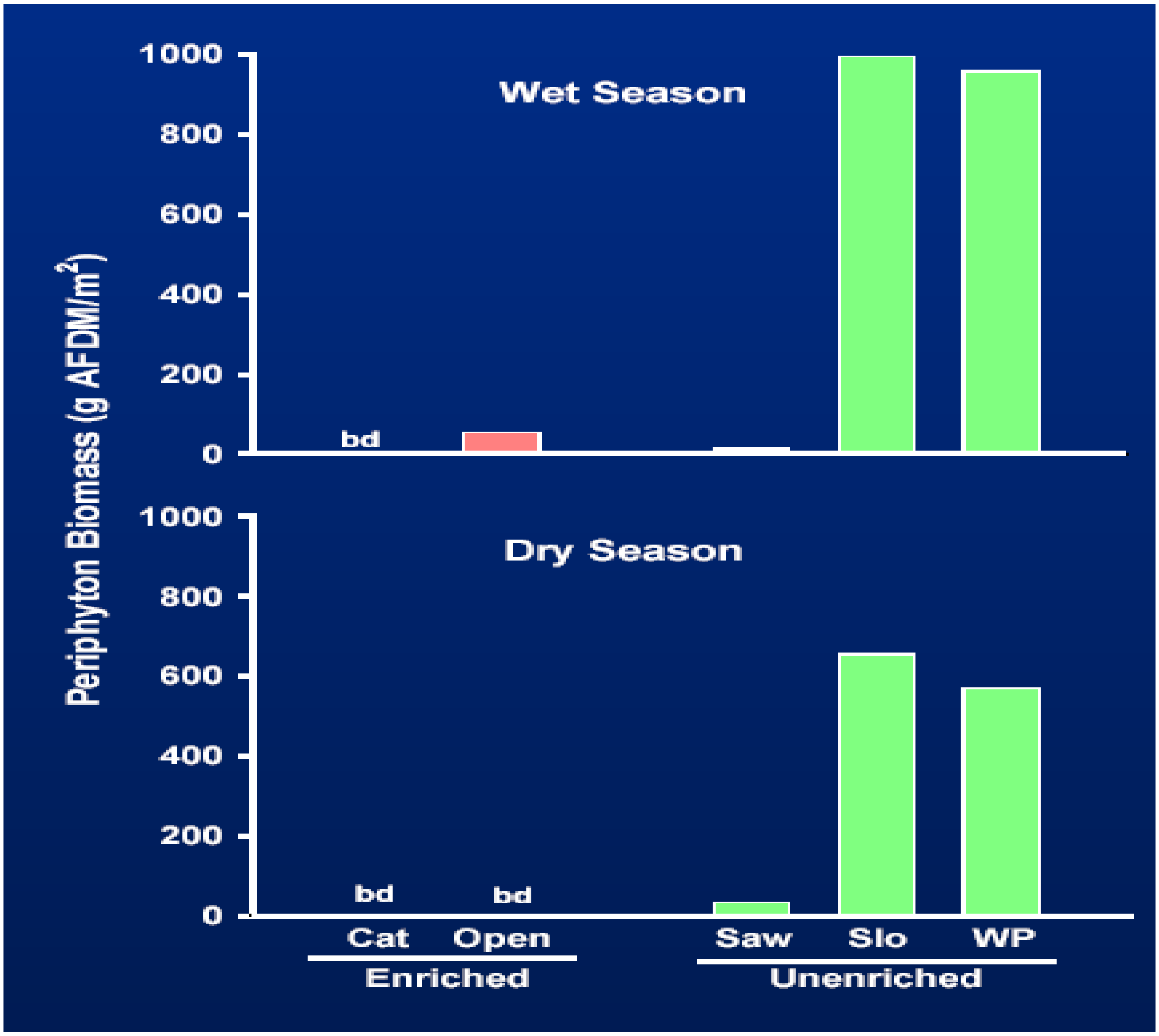

Figure 2B-4. Spatial coverage of benthic and floating periphyton as a function of water column total phosphorus (TP) concentrations (µg/L). This figure was derived from (1) remote sensing data of surface reflectance used to produce areal coverages of different types of plant assemblages, and (2) TP concentrations from monitoring data provided by the District.

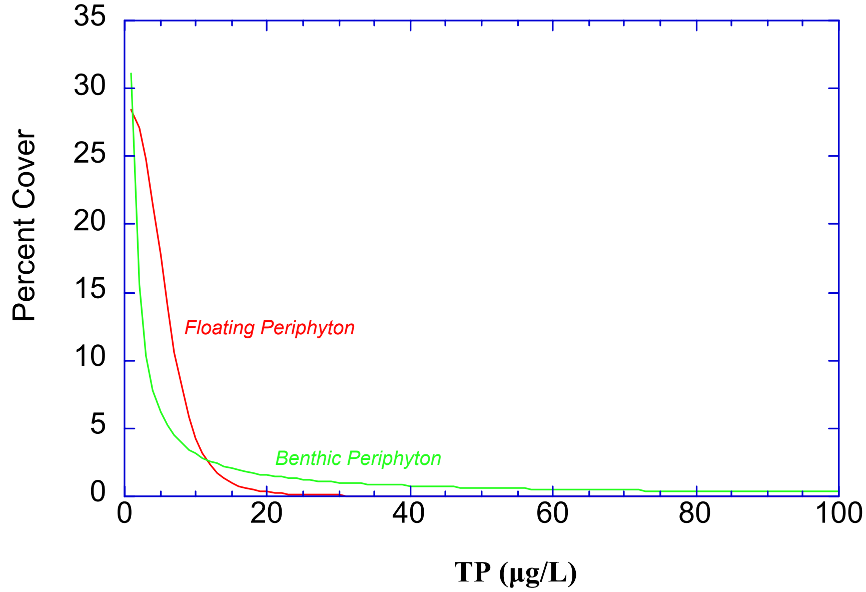

Figure 2B-5. Spatial coverage of benthic and floating periphyton as a function of water column total phosphorus (TP) concentrations (µg/L). This figure was derived from (1) remote sensing data of surface reflectance used to produce areal coverages of different types of plant assemblages, and (2) TP concentrations from monitoring data provided by the District.

ROLE OF SULFUR CYCLING IN METHYLMERCURY PRODUCTION AND BIOACCUMULATION

In surface waters, sulfur exists mostly as sulfate (SO_4^{2-}). Sulfate is not an especially reactive chemical species and it would be relatively innocuous in the Everglades, except for the fact that sulfate is essential for bacterial sulfate reduction (Orem et al., 2003). Bacterial sulfate reduction is the main microbial process responsible for the conversion of inorganic mercury to methylmercury. Conversion of inorganic mercury to methylmercury is the proximate cause of the Everglades mercury problem because methylmercury is much more toxic and biomagnifies much more strongly than inorganic mercury, with fish bioaccumulation factors ranging up to 10 million. Elevated methylmercury concentrations are responsible for about 1 million acres of the Everglades/Big Cypress being under an advisory for fish consumption.

Sulfate entering the Everglades in canal discharge, in combination with the “new” mercury entering the ecosystem predominantly from atmospheric deposition, controls the magnitude and distribution of methylmercury production in the Everglades sediments; sediments are the principal site of methylmercury production by SRB.

The production of methylmercury in Everglades sediments shows distinct geographic patterns. Methylmercury concentrations and methylation rates in sediments are maximal in the central Everglades (WCA-3A) and minimal in the northern, eutrophic areas. The distribution of methylmercury production in the Everglades is not explained by differences in atmospheric deposition of mercury, as deposition is relatively constant (though high) over the entire Everglades. Instead, the distribution of methylmercury is explained by complex biogeochemical interactions between sulfur and mercury. Increasing sulfate concentrations stimulate sulfate reduction and methylmercury production. However, when these sulfate concentrations get too high, buildup of sulfide inhibits methylmercury production. Sulfide is an end product of bacterial sulfate reduction (**Figure 2B-6**).

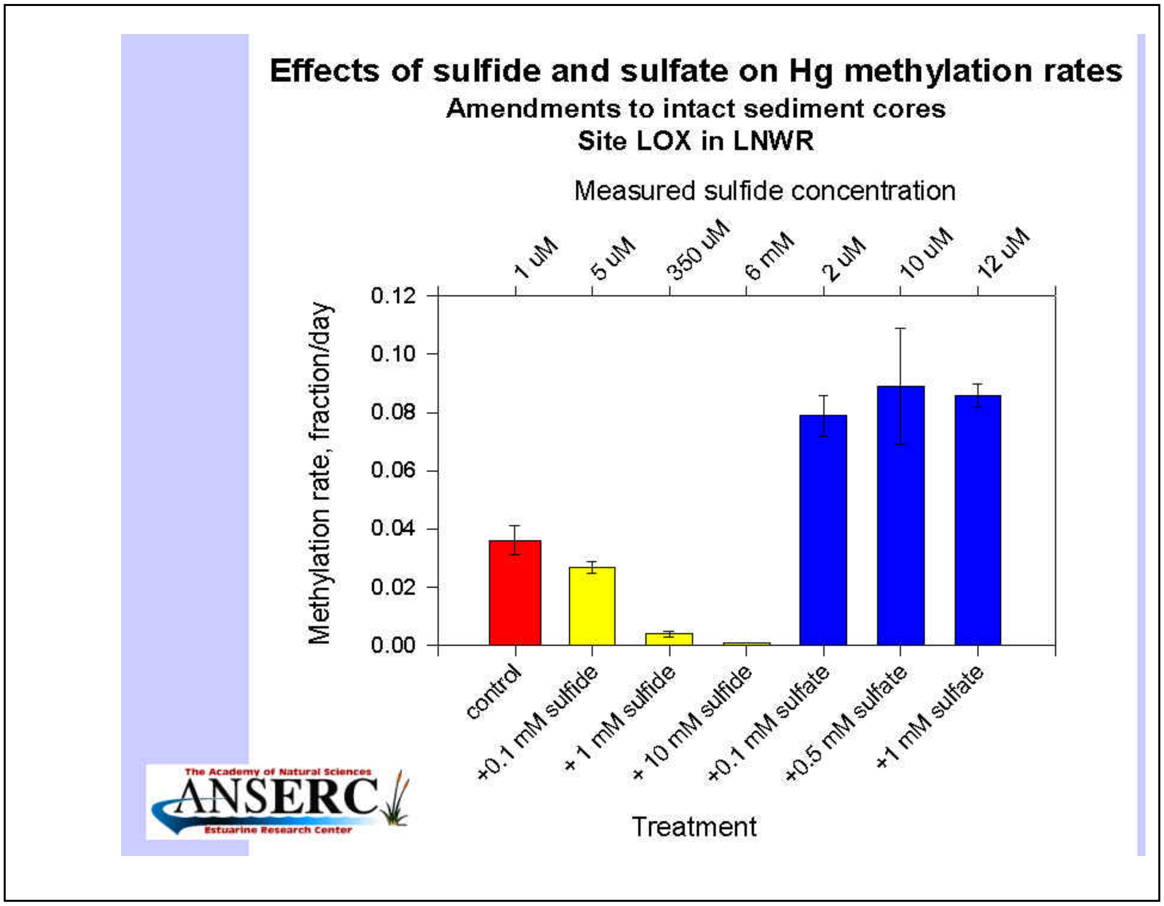

Figure 2B-6. Effects of sulfide and sulfate on Hg methylation rates (C. Gilmour, ANSERC, personal communication).

The distribution of methylmercury in the Everglades is consistent, with the production of methylmercury being highest in areas where bacterial sulfate reduction is stimulated by moderate increases in sulfate concentration from canal runoff, so that sulfide levels in sediment porewater remain relatively low (i.e., where sulfate and sulfide levels are optimal).

Sulfate concentration distributions and sulfur isotope data suggest that the major source of sulfate contamination to the Everglades ecosystem presently is canals draining the Everglades Agricultural Area (EAA); sulfur isotope data are consistent with agricultural sulfur used in the EAA being a major source to the EPA (Bates et al., 2002).

The northern Everglades is heavily contaminated with sulfate with concentrations up to sixty times greater than background levels. The highest concentrations of sulfate are in canal waters in the EAA and in marsh areas near canal discharge sites. The resulting excess in sulfide concentrations suppresses methylmercury production. While in the northern Everglades high sulfur concentrations co-occur with high phosphorus concentrations, mechanistically, sulfur is significantly more important with regard to methylmercury production and to accumulation in fish. Generally, porewater sulfide concentrations are the best predictors of mercury methylation rate and methylmercury concentration in Everglades sediments. Sulfide and methylmercury concentrations are inversely correlated across the northern Everglades (**Figure 2B-7**).

While porewater sulfide concentrations are the best predictors of methylmercury production rates and concentrations in Everglades sediments, methylmercury concentration in Everglades sediments correlate very well with methylmercury concentrations in mosquitofish (*Gambusia spp.*). In turn, USEPA Regional Environmental Monitoring and Assessment Program (REMAP) data show that elevated levels of methylmercury in mosquitofish correspond with high methylmercury concentrations in Everglades wading birds.

Methylmercury concentrations in Everglades fish and wading birds have declined by at least 60 percent in recent years, most probably because of the mercury source reductions and decreased mercury emissions to the atmosphere from municipal solid waste and medical waste incinerators. Atmospheric deposition estimates for mercury (as $\mu g/m^2/yr$) obtained from sediment cores at several Everglades sites from about 1990 to 2001 are presented in **Table 2B-1**.

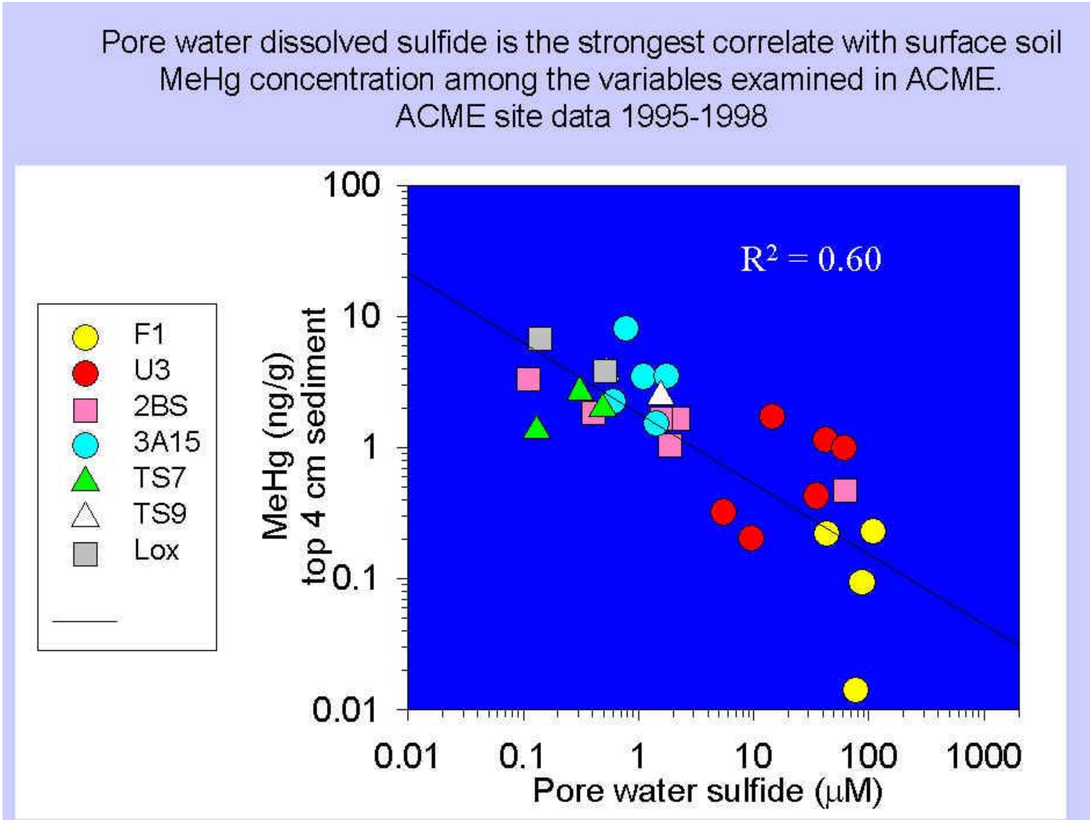

Figure 2B-7. Correlation between porewater dissolved sulfide and surface soil MeHg concentrations from ACME site data from 1995 to 1998 (C. Gilmour, ANSERC, personal communication).

Table 2B-1. The average rate of mercury (Hg) accumulation in Everglades sediments was 54 $\mu g/m^2/yr$ ca. 1990 versus 21 $\mu g/m^2/yr$ in 2001. These data suggest an overall decline in deposition of approximately 60 percent since about 1990, corresponding with an Everglades largemouth bass (fillet) and great egret (feather) mercury concentration decline of approximately 60 percent* from the mid 1990s to 2001.

Sampling Location	Hg Accumulation Rate ca. 1990 ($\mu g/m^2/yr$)	Sampling Location	Hg Accumulation Rate in 2001 ($\mu g/m^2/yr$)
WCA-1	79	ENR Project	21
WCA-2	59	NA	--
WCA-3	39	Andytown	24
ENP	40	ENP	18

Source: Rood et al., 1995; NADP MDN, 2002 (Online at http://nadp.sws.uiuc.edu/mdn).

Note: *This estimate was based on the geometric mean of Hg concentrations in great egret feathers for all active colonies for each year. Because of the high Hg variability among colonies, and to conform to protocols used for many other Everglades analyses, a geometric mean is preferred, resulting in an estimated decline of 60 percent.

Despite these mercury declines in Everglades biota, there is no reason for complacency, and reason to be concerned about future sulfate inputs to the Everglades from agricultural operations, stormwater, and groundwater including Aquifer Storage and Recovery (ASR) sources. Largely in response to sulfide and sulfate concentrations, methylmercury production rates vary by almost two orders of magnitude across the Everglades. This variation is far greater than that due to variation in atmospheric deposition of mercury across the Everglades. As such, the management of sulfur may be an important mechanism for controlling the mercury problem in the future.

Presently, the sulfate contamination plume from the EAA reaches as far south as the middle of WCA-3 as well as into Shark River Slough, where sulfate concentrations may now be optimal for methylmercury production. Given the effect of the EAA sulfate plume on the Everglades, there is reason to be concerned about future sulfate inputs to the Everglades. As such, there is reason to begin to predict (model) the effects of CERP hydrological restoration alternatives as well as other sulfur sources on future sulfur distribution, methylmercury production rates, and methylmercury bioaccumulation across the ecosystem.

Based on the information presented above, the following can be concluded:

1. Biogeochemical interactions between sulfur and mercury explain the variation in methylmercury production rate in sediments across the Everglades, and methylmercury concentrations in fish and wading birds.
2. Sulfate contamination originating from the EAA plays a key role in regulating the concentration and distribution of methylmercury in Everglades sediments and fish.

3. Reduction of mercury sources to the Everglades has successfully reduced mercury levels in fish and wildlife and this remains a viable management option, with sulfur input reduction also being an important management option; phosphorus is not an effective or ecologically responsible control agent for the Everglades mercury problem.

RESPONSE OF THE NATURAL SYSTEM TO SOURCE REDUCTIONS

According to data reported in early 1989, small numbers of largemouth bass collected at three Everglades locations (L-38A, L-35B, and L-67A) averaged nearly 2.5 milligrams per kilogram (mg/kg) of total mercury in the edible fillet. These findings were promptly confirmed and led to the Florida Department of Health issuing an unprecedented health advisory to fishermen to cease consumption of largemouth bass from those areas. Subsequent sampling showed that mercury problems extended to many other Florida waters. Since that time, the Department of Health, the Florida Fish and Wildlife Conservation Commission (FWC), and the FDEP began collaborating on annual collection and testing of fish from five sites in Florida (including the L-67 site) to determine whether the trend of mercury concentrations in fish is increasing or decreasing.

Subsequent monitoring of mercury in fish and wildlife in the Everglades and other areas in Florida has yielded annual information on mercury body burdens in nestlings. This information can be similarly examined for temporal trends in an update of the corresponding figure (Figure 2B-14) from the *2003 Everglades Consolidated Report*, which shows an overall decline in mercury concentrations in largemouth bass, with year-to-year variability (**Figure 2B-8**). **Figure 2B-9** shows a similar trend with the mercury concentrations in the feathers of great egret nestlings decreasing over time. However, it has been difficult to determine how these trends in mercury levels in biota compare to trends in the mercury load to the Everglades or to emissions trends in the United States or in Florida. This difficulty is caused by the limitations of available data, models, and other tools to model the local, regional, and global scales of air-pollutant cycling.

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 FDEP sponsored the installation of one of the first Mercury Deposition Network (MDN, a sub-network of the National Atmospheric Deposition Program [NADP]) sites at the Park's Beard Research Center, co-located with the FAMS site. The sites, operated side-by-side by their respective groups for 15 months, established that comparability was excellent. After completion of the FAMS project, the District assumed responsibility for the Park's MDN site and established two others (Andytown and Everglades Nutrient Removal [ENR] Project) 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 temporal trend. However, it is likely that emissions reductions occurred before the monitoring began in 1994. It is also likely that data variability will hamper attempts to detect trends in deposition data.

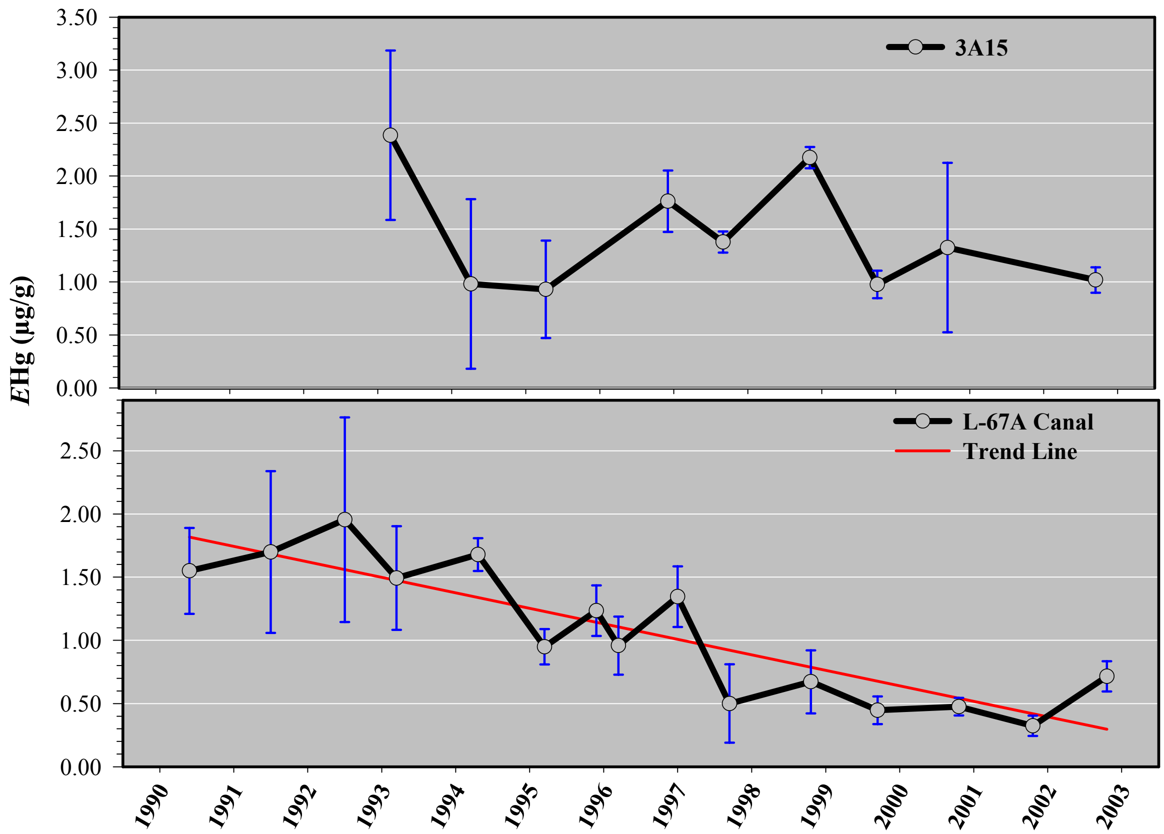

Figure 2B-8. Mercury concentrations (µg/g, with adjusted least square means) in fillets of age-standardized largemouth bass in the Everglades L-67 canal and at WCA-3A-15, the mercury "hot spot" (Lange et al., 2003).

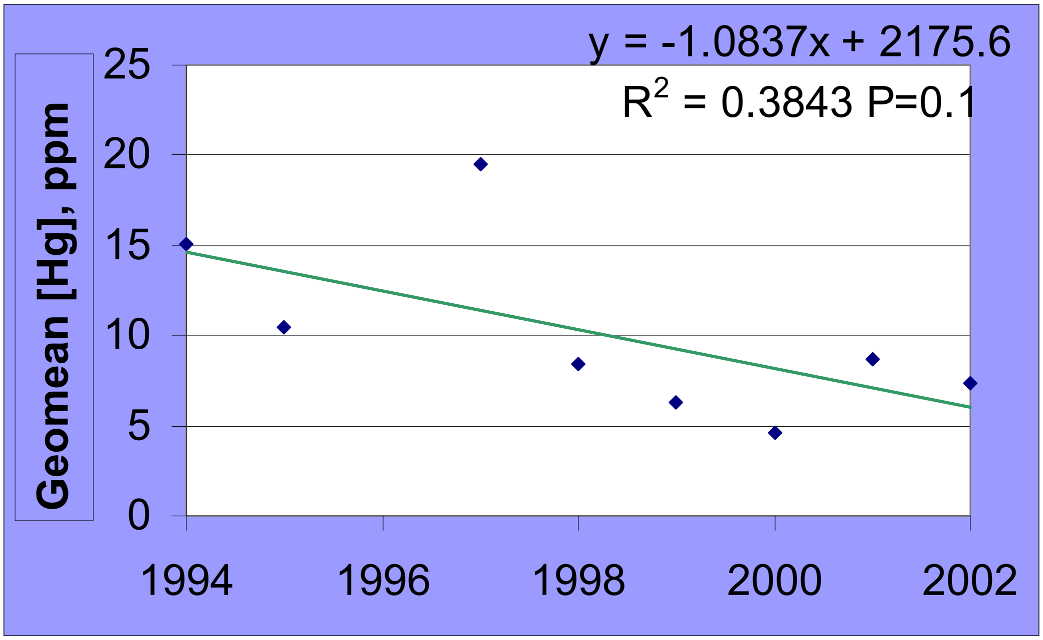

Figure 2B-9. Geometric mean concentrations of mercury in great egret chick feathers collected from active Everglades colonies each year from 1994 through 2002. Mercury exposure to great egret chicks has declined approximately 60 percent over this period.

Data from about 1994 to the present suggests that 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 waste 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 also possible and could produce a greater 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.

As presented in Appendix 2B-4, a new historical analysis of the long-term trends of mercury in wading birds was completed in 2003 (**Figure 2B-10**). This illustrates a trend concordant with the trend of mercury accumulation shown in **Figure 2B-2**.

It is anticipated that the 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. Further work, consisting of hind-casting emissions and examination of new sediment cores, is underway to test this hypothesis.

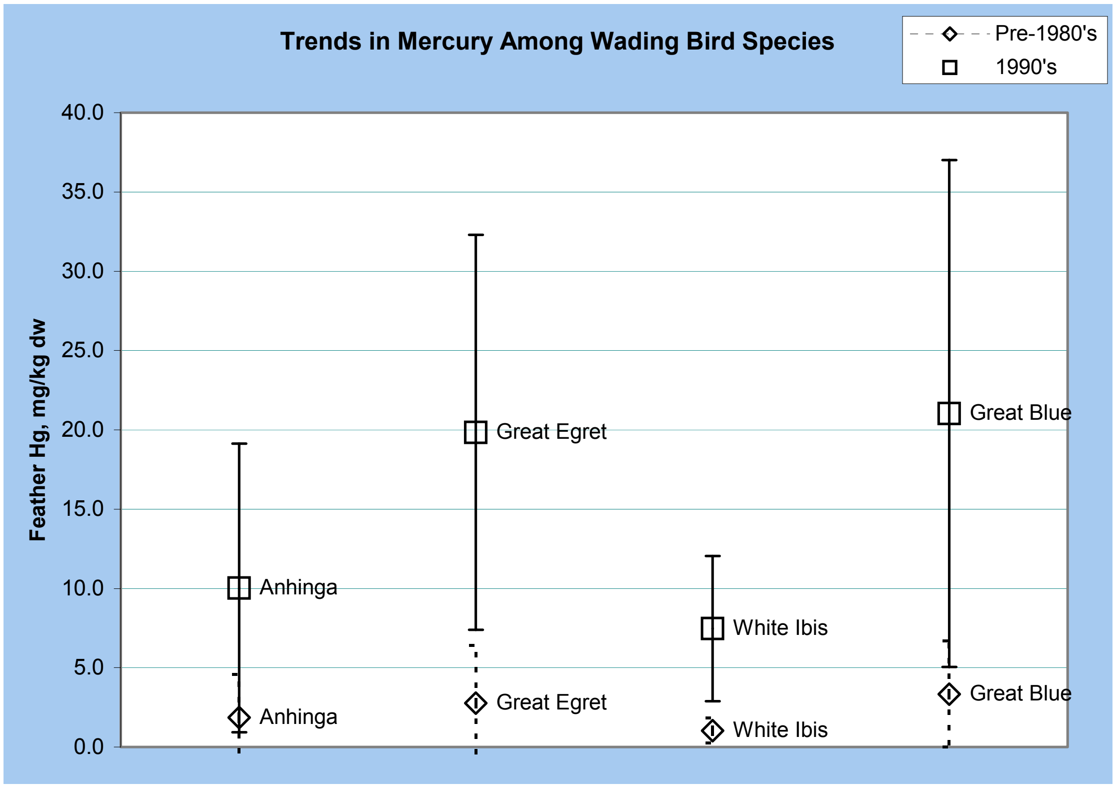

Figure 2B-10. Historical comparisons among wading bird species in mercury content of feathers through time. Samples collected from North American museums for specimens tagged with a South Florida origin.

CONCLUSIONS

ADEQUACY OF EXISTING MANAGEMENT STRATEGIES

The public and private agencies comprising the South Florida Mercury Science Program have worked effectively to achieve the following:

1. Describe and define the mercury problem in the Everglades
2. Identify and quantify the sources and causes of the mercury problem
3. Develop and implement appropriate environmental controls to abate the mercury problem and monitor the effectiveness of the abatement measures

A comprehensive program of monitoring, modeling, and research 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 models suggest that significant benefits from decreased mercury loading should be seen in less than a decade, with full benefits within a generation. Current monitoring trends for mercury within the Everglades system indicate the beginning of positive results of pollution prevention and control efforts that were initiated in the mid 1990s.

As a result of a series of international, North American, and Florida initiatives, mercury usage in North America has declined by approximately 90 percent since 1990. In addition, environmental controls have been developed and implemented for Medical Waste Incineration (MWI) and Municipal Solid Waste Incineration (MSWI), both of which have resulted in emissions declines in excess of 95 percent for each source sector. At the time of publication of the *2003 Everglades Consolidated Report*, there was a pending decision with regard to control policy by the USEPA. The USEPA had made its decision under the Clean Air Act Amendments of 1990 to regulate mercury emissions from coal- and oil-fired utility boilers, and was to develop regulatory specifics by the end of 2003. The proposed Clean Skies Initiative has since superceded promulgation of the Maximum Achievable Control Technology (MACT) standards for mercury from utilities under the Clean Air Act Amendments of 1990. At this time, it is not known what direction will be taken on national mercury emissions control policy with regard to the limits of mercury emissions from this industrial sector.

The atmospheric mercury studies conducted by the FDEP and its collaborators in the SFMSP have been completed in close collaboration with the USEPA to ensure rapid transfer of new technologies and information into the national program. The FDEP is pleased to have provided useful information to the USEPA and other federal agencies and has thereby assisted and promoted a sound scientific basis for policy decisions.

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.

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