Chapter 7: The Everglades Mercury Problem

Larry Fink, Darren Rumbold and Peter Rawlik

Summary

The Problem: Everglades sport fish have the highest average concentrations of mercury in Florida. Human health advisories remain in effect for a number of sport fish species throughout the Everglades, Big Cypress, and eastern Florida Bay. Federal and Florida water laws protect public health, wildlife populations, and the designated uses of a water body, including sport fishing. Until the advisories are lifted, sport fishers will not be able to freely consume the fish they catch. This denies them full enjoyment of the resource. The use of the sport fishery has thus been impaired. Studies are being conducted to determine whether the high concentration of mercury in Everglades fish are toxic to Everglades wildlife like wading birds.

Adequacy of Standards: Data collected by the U.S. Environmental Protection Agency (USEPA) in the period 1993-1997 indicate that the Florida Class III numerical Water Quality Criterion for total mercury of 12 parts per trillion is not being exceeded anywhere in the Everglades canals and marshes. South Florida Water Management District (District, SFWMD) canal monitoring in 1997-1998 confirms this finding. These results have prompted DEP to reevaluate the mercury Water Quality Criterion. The DEP has determined that it is inadequate to protect recreational use and is funding studies to determine what criterion will protect human health and wildlife.

Historical Inputs: A 1991-1992 study co-funded by the District, the DEP, and U.S. Geological Survey (USGS) found that the rate of mercury deposition from the atmosphere to the Everglades had increased about five-fold since the late 1800s. This leads to the conclusion that the Everglades has been contaminated by mercury emissions from modern human activity. Some of the previously deposited mercury in Everglades peat can be recycled back into the ecosystem by natural processes, while the rest is buried. Mercury is being supplied to the Everglades in stormwater runoff, groundwater discharge, and atmospheric deposition (rain, dust, and gaseous dry deposition). The relative contributions of previously deposited and recently deposited mercury to the Everglades mercury problem are under investigation. A recent modeling study conducted by USEPA suggests that the recovery time of the Everglades following the reduction in new mercury inputs would be on the order of decades, not centuries.

Present Day Water Inputs: The low total mercury concentrations in samples collected biweekly by the District at eight canal sites in 1994-1997 demonstrated that runoff from the Everglades Agricultural Area (EAA) is not a significant source of new mercury to the Everglades. Data from a joint District-USGS study conducted in 1995-1997 suggest that groundwater discharge is not a significant source overall.

Present-Day Air Inputs: The 1992-1996 Florida Atmospheric Mercury Study (FAMS) demonstrated that atmospheric deposition to the Everglades is roughly double the rate in rural Wisconsin. Together with the canal data discussed above, one can calculate that atmospheric deposition accounts for more than 95% of the new mercury reaching the Everglades each year. However, the relative contributions

of local and background or global mercury sources to this new input can only be quantified with further study.

Positive and Negative Impacts of the Everglades Construction Project: Four years of District data from the Everglades Nutrient Removal (ENR) Project support the conclusion that the Stormwater Treatment Areas (STAs) are unlikely to cause or contribute to a new mercury problem within their borders. A new baseline analysis of the mercury risks to wading birds feeding in a relatively unimpacted area of WCA-2A supports the conclusion that restoring phosphorus-impacted areas to the no-imbalance condition will not result in a significant risk to wading birds that feed exclusively in the restored areas. Based on ENR Project studies, the STAs are likely to remove between 50% and 75% of the mercury load in EAA runoff. Modeling investigations are underway to determine if this will have a significant positive impact on mercury concentrations in the phosphorus-impacted areas immediately downstream of the District's structures in the northern Everglades. However, because more than 95% of the mercury entering the Everglades each year is deposited from the air, this is unlikely to have a significant beneficial effect on the Everglades as a whole. Overall, the weight of evidence continues to support the conclusion that the benefits of phosphorus reduction will outweigh any negative effects from mercury. Continued mercury monitoring of the STAs, the District structures, the interior marshes, and atmospheric deposition will provide ongoing corroboration that this overall conclusion remains valid.

The Everglades Restoration Strategy: Mercury is of concern in both the Everglades Construction Project (ECP), which was authorized by the Everglades Forever Act, and in the U.S. Army Corps of Engineers Central and Southern Florida Comprehensive Review Study (Restudy). The ECP deals principally with alleviation of eutrophication of the Everglades caused by stormwater runoff from the EAA. The Restudy deals principally with creation of patterns of flows and depths that are more favorable to Everglades fish and wildlife. There is a concern that projects of the ECP and Restudy might exacerbate mercury bioaccumulation. There is also a concern about the cause and remedy for widespread mercury impacts in the Everglades that arise from atmospheric depositions and are independent of these projects. Mercury would be of concern without the ECP or the Restudy. This report directly addresses the question of whether ECP projects will exacerbate mercury bioaccumulation. It deals less directly with the same question for Restudy projects (since those are not yet defined) and it deals with the more general problem of mercury contamination in the Everglades and elsewhere.

The DEP has the regulatory responsibility for protecting human health and the environment from the toxic effects of mercury. For the short term, DEP has issued permits to the ECP structures and the so-called non-ECP structures to ensure the protection of downstream water quality relative to the existing mercury Water Quality Standard. The Department is also funding studies of mercury exposure and toxicity to support the evaluation of a more protective mercury Water Quality Criterion. The District, the DEP, USEPA, and USGS are funding studies of the underlying processes that govern the production and bioaccumulation of methylmercury. The District, the DEP, and USEPA are funding the development of a mathematical model that will integrate all of the information on sources, transport, biogeochemistry, and bioaccumulation into a self-consistent quantitative predictive framework to guide management decision-making. Together with information on air sources and wind transport, the Everglades Mercury Cycling Model will aid in predicting the response of the Everglades to additional control of local emissions sources. The model will also be used to evaluate the response of the Everglades to changes in the quality and quantity of District discharges into the EPA. In addition, the model will be used to evaluate the mercury impacts of the changes in water management proposed as the result of the Restudy.

Multi-Agency Program: The mercury monitoring, research, modeling and assessment studies described in this chapter are being coordinated through the multi-agency South Florida Mercury Science Program (SFMSP)[1]. This unique partnership of federal, state, and local agencies, academic and private research institutions, and the electric power industry has advanced the understanding of the Everglades mercury problem with greater breadth, depth, and speed than could be accomplished by the DEP and the District alone. The goal of these phased studies is to provide the DEP and the District with the information to make mercury-related decisions about ECP projects on the schedule required by the Everglades Forever Act (EFA).

Introduction

Sport fish in the Everglades have the highest average concentrations of mercury of any area in Florida. Human health advisories recommending no consumption or limited consumption of several sport fish species remain in effect for the Everglades, Big Cypress, and eastern Florida Bay. In some locations, the high concentrations of mercury in the aquatic ecosystem may also threaten top predators like alligators, otters, and the endangered Wood Stork. The District and the DEP are cooperating with other state and federal agencies, academic institutions, and private entities to understand and solve the Everglades mercury problem.

Organization of this Chapter

This chapter describes the progress being made in carrying out the mercury studies to understand and solve the Everglades mercury problem. This Chapter is organized around five key mercury management questions:

1. What is the significance of the Everglades mercury problem?
2. Can the sources of Everglades mercury be adequately controlled?
3. Can management of water quality and quantity reduce Everglades mercury risks to acceptable levels?
4. How will the Everglades Construction Project affect mercury risks?
5. What is the status of District and DEP efforts to understand and solve the Everglades mercury problem?

A section titled **The Mercury Cycle** provides background information on the physical, chemical, and biological (biogeochemical) processes that transport, store, and transform mercury in the natural environment. This section also discusses the influences of water quantity and quality on the production and

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

bioaccumulation of methylmercury in aquatic ecosystems in general and the Everglades in particular. In the five sections that follow it, each of the key management questions is answered in order. For questions 1-4, the answers are developed to the extent permitted by the present understanding of various aspects of the Everglades mercury problem. Where the question calls for predictions about the mercury-related effects of activities that have not yet occurred, best professional judgment has been used to estimate what is likely to happen. In some cases, the results of mathematical models are used to guide best professional judgment. Following the answer to the last of the five questions, a summary of conclusions and recommendations is presented.

Introduction to the Mercury Problem

The element mercury (Hg) is naturally present in the earth’s crust. Pure elemental mercury, which is a silver-colored liquid metal at room temperature, is obtained by smelting its most abundant ore, mercuric sulfide or cinnabar (Sidgwick, 1950). Pre-industrial human uses of mercury were surprisingly significant, with the ancient Romans reported to have used more than two tons per year (Clarkson, 1994; Nriagu, 1996). Modern human uses of mercury include gold mining, chlor-alkali production, batteries, turf and seed treatments, contact explosives, silent and pressure switches, thermometers and manometers, fluorescent lights, house paints, and fillings for dental cavities (USEPA, 1997). During the cold war, a significant fraction of the world's supply of mercury was diverted to military use, primarily as a solvent for the separation of lithium isotopes for hydrogen bomb production (Clarkson, 1994). In more primitive cultures mercury use is limited primarily to folk medicinal and magico-religious applications.

The toxicity of mercury salts and elemental mercury to humans has been known since the dawn of history. Toxicity to humans increases with the form of mercury in the order inorganic mercury salts, elemental mercury vapor, and methylmercury salts (WHO, 1976; USEPA, 1980; WHO, 1990; Clarkson, 1994; USEPA, 1997). Inorganic mercury and methylmercury are also highly toxic to wildlife species (Eisler, 1987). Use of inorganic mercury or methylmercury salts as a seed treatment is now prohibited in the U.S., and the use of mercury compounds as a turf treatment in the U.S. is highly restricted (USEPA, 1980). Mercury as a fungicide in house paints has been curtailed, and mercury in batteries is being voluntarily phased out (USEPA, 1997).

Methylmercury is also produced naturally from inorganic mercury in the aquatic environment by bacteria in sediments under conditions devoid of dissolved oxygen (Jensen and Jernelov, 1969). Once produced, methylmercury is readily taken up but only slowly eliminated by fish (Norstrom et al., 1976). This results in a phenomenon referred to as **bioaccumulation**. The ratio of the methylmercury concentration in a fish to the concentration in the surrounding water is its **bioaccumulation factor (BAF)**. Although fish can take up environmental contaminants via the gill and gut, in the case of methylmercury, uptake is primarily via the gut (Norstrom et al., 1976). Fish will bioaccumulate higher concentrations of methylmercury than what they feed on. This results in a phenomenon referred to as **biomagnification**, which occurs at each successive step in the aquatic food chain (Wood, 1974). In general, small, short-lived fish at the lowest trophic level exhibit BAFs in the range of 10,000-100,000, their larger, longer-lived predators exhibit BAFs in the range 100,000-1,000,000, and for top-predtor fish like largemouth bass, BAFs in the range 1,000,000-10,000,000 are not uncommon (Watras, 1993). For example, in the most contaminated portion of the Everglades in Water Conservation Area 3A, the BAF for a 3-year old largemouth bass can approach 10,000,000 (Lange et al., 1998). Without such high BAFs, methylmercury would not be a problem in the Everglades and elsewhere.

Understanding the Everglades Mercury Problem

To put the Everglades mercury problem in context and perspective, nationally, the U.S. has a mercury problem, with at least 40 states having issued fish consumption health advisories for mercury-contaminated waters (USEPA, 1997). Statewide, Florida has a mercury problem, with more than 50% of its inland waters now under Health Department advisories for limited or no fish consumption because of mercury. Sport fish from the Everglades canals and marshes have the highest mercury concentrations in the State (Lange et al., 1998). Human health advisories remain in effect for a number of sport fish species throughout the Everglades, Big Cypress, and eastern Florida Bay. The area covered by the Florida advisories may be the largest in the U.S.

Federal and Florida water laws protect public health, wildlife populations, and the designated uses of a water body, including sport fishing. Until the advisories are lifted, sport fishers will not be able to freely consume the fish they catch. This denies them full enjoyment of the resource. The use of the sport fishery has thus been impaired. Studies are underway to determine whether the high concentration of mercury in Everglades fish are toxic to Everglades wildlife that eat them, such as wading birds, otters, and Florida panthers.

The Everglades appears to be especially susceptible to a methylmercury problem. Is this because the Everglades is receiving a higher atmospheric deposition rate than elsewhere? Is the Everglades more efficient at converting inorganic mercury to methylmercury than elsewhere? Is the Everglades food web more efficient at bioaccumulating methylmercury at each level of the food chain? How much of the methylmercury in fish comes from previously deposited mercury that has been recycled from peat soil and how much comes from present-day mercury falling on the Everglades as atmospheric deposition? Of the present-day mercury depositing on the Everglades from the air, how much originates with local sources how much with the global background? The answers to these questions are very important, because they will determine how the Everglades would respond to the reduction of local air emissions sources or to manipulation of water quantity and quality to reduce methylmercury production and bioaccumulation.

A more complete set of hypotheses has been put forward to account for the apparent susceptibility of the Everglades to a mercury problem (SFMSP, 1996), including:

- a high historical accumulation of inorganic mercury in the downstream sediment attributable to the historical oxidation of peat in the EAA.
- a high mobilization rate of inorganic mercury from the sediment associated with the dry-wet cycles in the EAA and some locations in the WCAs.
- a high atmospheric deposition flux of inorganic mercury from local or global sources.
- a high rate of net methylation of inorganic mercury associated with high concentrations of conducive factors in water and sediment pore water.
- a high fraction of methylmercury available to be bioaccumulated and biomagnified.
- the absence of a freeze-thaw cycle and high average annual temperatures that accelerate mercury methylation and bioaccumulation processes.
- high bioaccumulation and biomagnification factors resulting from the complex aquatic and terrestrial food webs.
- any combinations of the above.

The South Florida Mercury Science Program

Efforts to understand and solve the Everglades mercury problem began in 1989 when the Florida Departments of Health[1] and Environmental Protection[2] and the Game and Fresh Water Fish Commission discovered the Everglades mercury problem and initiated a long-term monitoring program to define its nature, magnitude, extent, and trends. The initiative was further focused by the Governors' Mercury in Fish and Wildlife Task Force, which was formed to assess the seriousness of the Florida mercury problem and outline the steps to take to understand and solve it. Due to its special status, great emphasis was given to the serious mercury contamination problem evident in the Everglades. The Task Force Report to the Governor was delivered in December 1991. The recommendations in the Report have guided efforts to understand and solve the Everglades mercury problem ever since.

As the significance of the Everglades mercury problem became known, the District and a number of federal agencies joined this initiative. Since 1992, the DEP and the District have participated in the **South Florida Mercury Science Program (SFMSP)**, a consortium of federal, state, and local agencies, academic and private research institutions, and the electric power industry[3]. This unique partnership has made it possible to advance the understanding of the Everglades mercury problem with greater breadth, depth, and speed than could be accomplished by the DEP and District alone. The results of these studies will make it possible to meet the mercury-related requirements of the Act and guide timely ECP decision-making.

The Florida Game and Fresh Water Fish Commission has continued its studies of mercury bioaccumulation in largemouth bass to monitor mercury status and trends in the Everglades and elsewhere (Lange et al., 1998). USEPA Region 4 has taken the lead in defining the nature, magnitude, and extent of the Everglades mercury contamination on the spatial scale of the Everglades (USEPA, 1993a), and the two years of semi-annual monitoring has begun to discriminate the influences of meteorology and hydrology from water chemistry and ecology on the seasonal and spatial patterns of mercury bioaccumulation in the Everglades (USEPA, 1998). The USEPA sampling sites are depicted in **Figure 7-1a** and **b** and the results of these studies are summarized in the sections that answer the questions: *What Is the Significance of the Everglades Mercury Problem*? and *Can the Sources of Everglades Mercury be Adequately Controlled*?

Another important element in the SFMSP is the characterization of transport pathways. This has included monitoring of EAA runoff by the District for USEPA Region 4 (USEPA, 1998) and monitoring of atmospheric concentrations of mercury on aerosols and mercury in wet and dry deposition at seven monitoring sites near the Everglades in South Florida (See **Figure 7-2**) within the framework of the **Florida Atmospheric Mercury Study** or **FAMS**, with funding by DEP, the District, and other sources (Landing et al., 1995; Pollman et al., 1995). Focusing on sources, special screening studies of potentially significant local air emissions sources have also been conducted by the University of Michigan (Dvonch et

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[1] At that time, the Department of Health and Rehabilitative Services.

[2] At that time, the Department of Environmental Regulation.

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

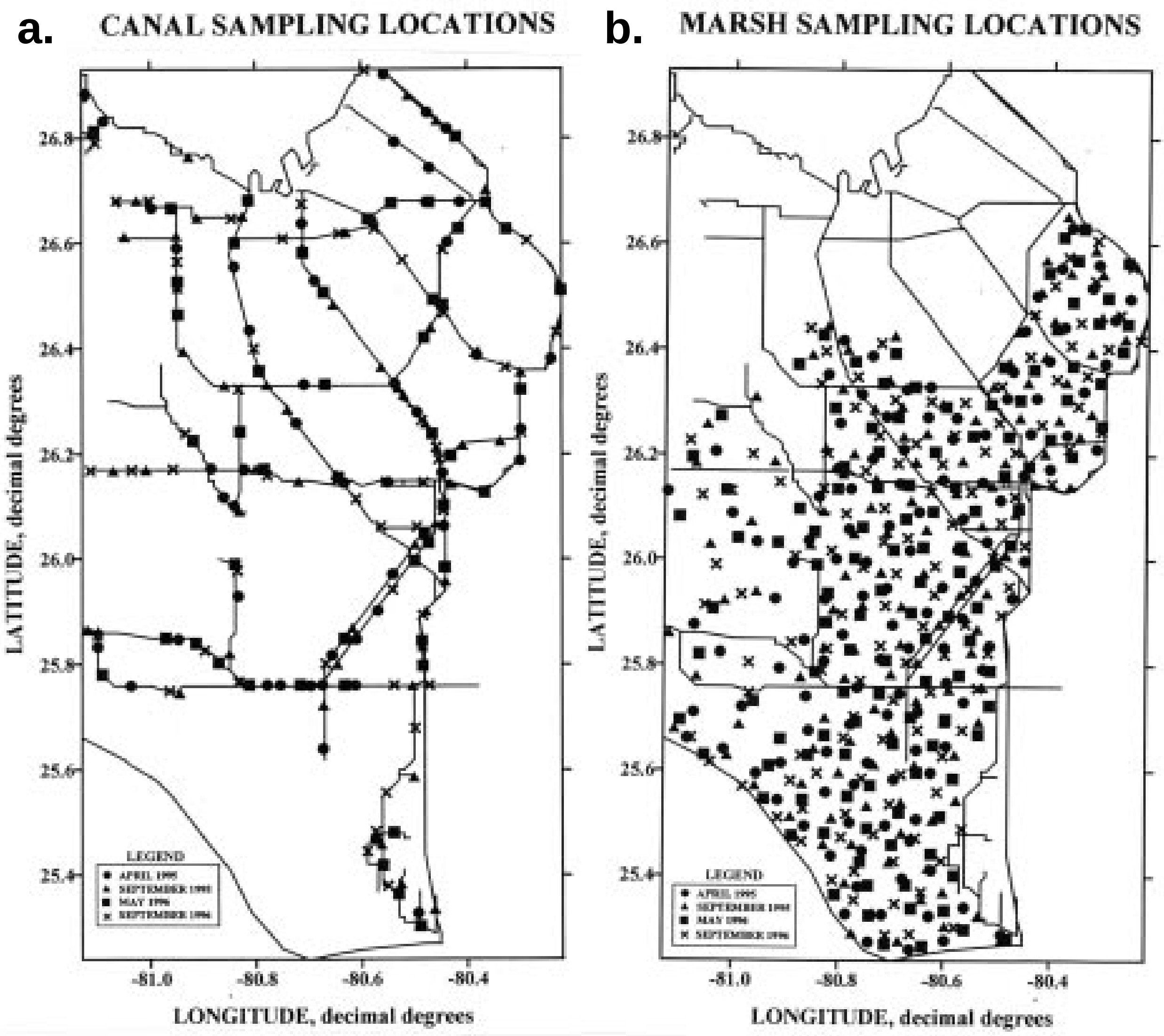


Figure 7-1. Sampling sites in the Everglades **(a)** canals and **(b)** marsh for USEPA (1998) Region IV Regional Environmental Monitoring and Assessment Project (REMAP).

al., 1998). The results of these studies are summarized in the sections that answer the questions, *What is the significance of the Everglades mercury problem?* and *Can the sources of Everglades mercury be adequately controlled?*

Recognizing that the results of source, receptor, and ambient monitoring alone cannot discriminate between hypotheses about Everglades susceptibility to mercury, the SFSMP has placed great emphasis on understanding and quantifying the underlying processes that govern the transport, storage, transformation, and bioaccumulation of mercury in the Everglades. These process studies include:

1. Formation, decomposition, and properties of peat and its decomposition products by William Orem and co-workers at the USGS in Reston, VA (Orem et al., 1998).

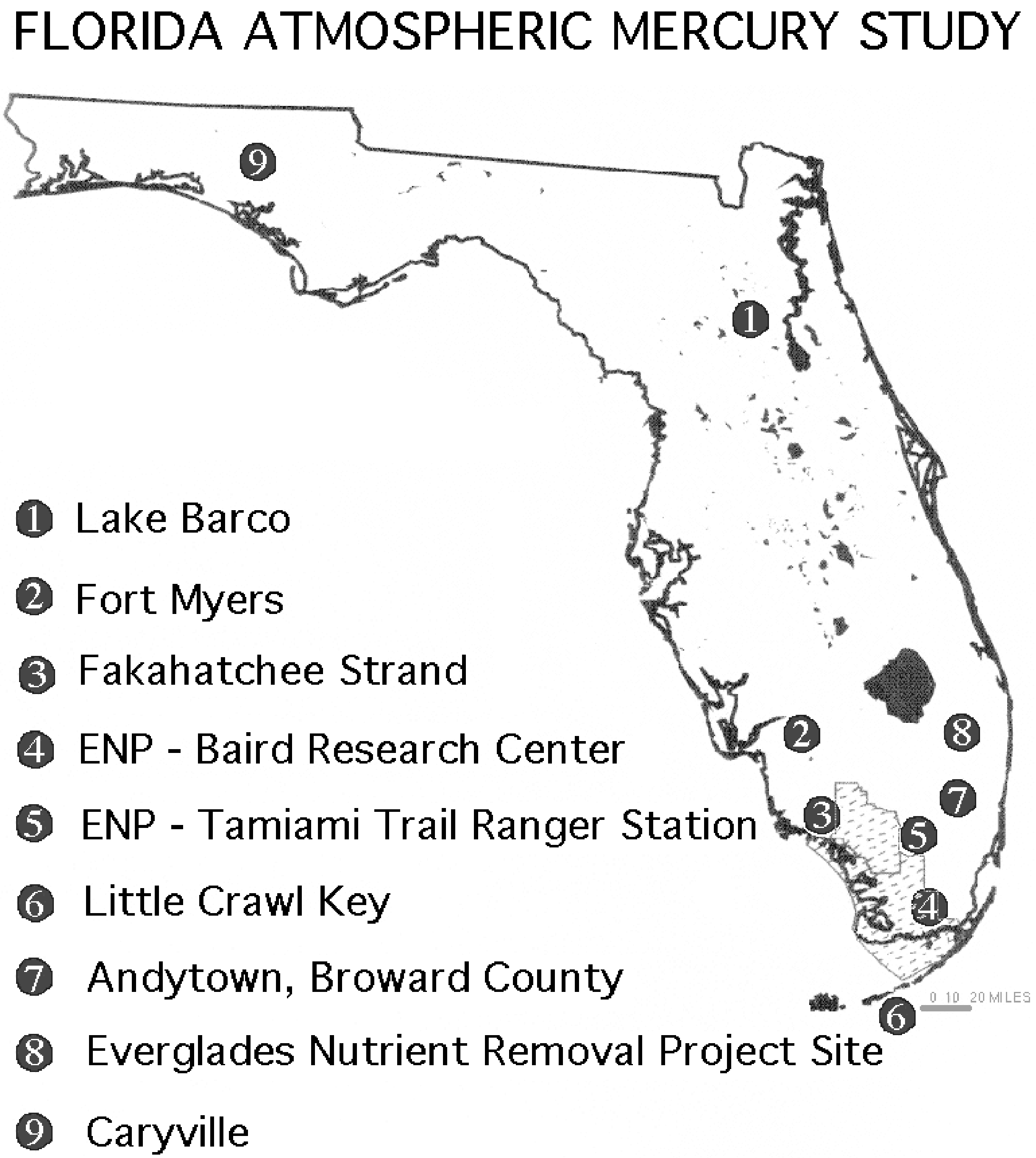


Figure 7-2. Location of sampling towers in the Florida Atmospheric Mercury Study (FAMS) Monitoring Network.

2. Formation, transformations, and properties of dissolved organic carbon, including its affinities for inorganic mercury and methylmercury in surface and pore water by George Aiken and Michael Reddy at the USGS in Boulder, CO (Aiken and Reddy, 1997) and its role in mercury sulfide dissolution (Ravichandran et al., 1998).
3. Photochemistry of elemental mercury production and decomposition and methylmercury decomposition in the presence of DOC by Dave Krabbenhoft and co-workers of the USGS in Madison, WI (Krabenhoft et al., 1998).
4. Production of methylmercury from inorganic mercury in surface and soil pore water by sulfate-reducing bacteria by Cynthia Gilmour and co-workers of the Academy of Natural Sciences and the fluxes of inorganic mercury and methylmercury into and out of the peat soils by Gary Gill and co-workers at Texas A&M University at Galveston (Gilmour et al., 1998a, b).
5. Decomposition of methylmercury by aerobic and anaerobic bacteria in peat soil by Mark Marvin-Di Pasquale, Ron Oremland, and co-workers of the USGS at Menlo Park, CA (Marvin-DiPasquale and Oremland, 1998).
6. Dissolution, sorption, complexation, and precipitation of mercury in the presence of sulfate/ sulfide, iron(III)/iron(II), calcium, carbonate, chloride, and DOC using WHAM, a thermochemical speciation model, by Mike Reddy of USGS at Boulder, CO (Reddy and Aiken, 1998).
7. Feeding habits, food web linkages and bioaccumulation and biomagnification factors for the northern and central Everglades aquatic food web by Ted Lange and co-workers at FGFWFC and Paul Garrison and co-workers at the WDNR in Madison, WI and the southern Everglades by William Loftus and co-workers at the USGS National Biological Service offices in Miami, FL (Loftus, 1997; Lange et al., 1998).
8. Feeding habits, food web linkages, residues, and toxic effects of mercury in dosed chicks and adults for the Great Egret by Peter Frederick, Marilyn Spalding and co-workers at the University of Florida in Gainesville (Fredrick et al., 1997).
9. Feeding habits, food web linkages, residues, general health and mercury toxic effects for the Florida panther by Tom Logan, Sharon Taylor, DVM, and co-workers of the Florida Game and Fresh Water Fish Commission (T. Logan, FGFWFC, pers. comm., 1998).
10. Transport, biogeochemistry, and bioaccumulation of mercury species within a self-consistent, mechanistic, quantitative predictive modeling framework by Robert Ambrose, Rochelle Araujo, and Craig Barber of USEPA's Office of Research and Development in Athens, GA and Reed Harris and Curt Pollman of TetraTech, Inc. (Ambrose and Araujo, 1998; Harris and Pollman, 1998).

The locations of these process study sites are depicted in **Figure 7-3** and the results of these studies are summarized in the section, ***The Mercury Cycle***, and the section that answers the question, ***Can Management of Water Quantity and Quality Reduce Mercury Risks?***

The required monitoring, research, modeling, and assessment studies conducted by each of the participating agencies has been designed, carried out, and documented under the internal scientific peer review protocols of each agency. The studies have been organized and coordinated within the framework

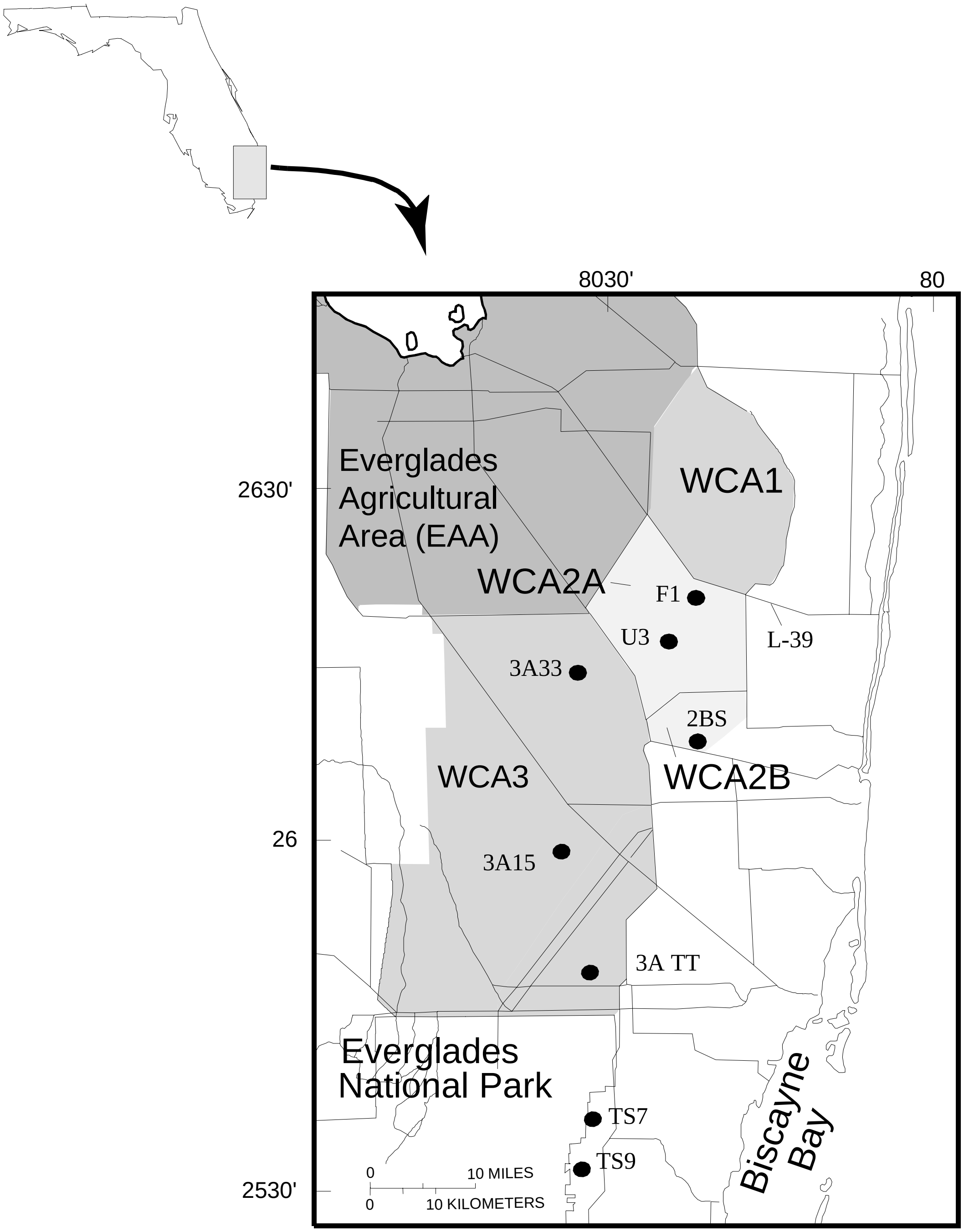


Figure 7-3. Mercury research sites for the Aquatic Cycling of Mercury in the Everglades (ACME) Project (USGS, Wisconsin DNR et al.).

of the Plan of Study of the SFMSP (SFMSP, 1996). The studies have been implemented in phases, with results from earlier phases guiding study design in later phases. The data from the Phase 1 or scoping studies are now being analyzed, synthesized, and integrated within a mass balance framework according to a logical, systematic process to yield a coherent, quantitative understanding of the Everglades mercury problem. From this understanding, predictive models can be developed with which to determine if mercury in Everglades biota can be reduced to acceptable levels and to select the best option for doing so.

Solving the Everglades Mercury Problem

The solution to the Everglades mercury problem has several steps. The first step is to learn what level of mercury in fish is safe for both humans and wildlife. The second step is to learn what human actions are causing or contributing to the Everglades mercury problem. Potential causes include present-day atmospheric deposition, mercury in stormwater runoff and reentry into the ecosystem of mercury that was previously buried in Everglades peat soil. Potential contributing factors include changes in water quantity and quality that might liberate buried mercury for recycling in the Everglades or facilitate its accumulation in fish and wildlife. The third step is to understand how the Everglades processes inorganic mercury from atmospheric deposition, runoff, and peat soil into methylmercury, the most toxic form of mercury in the aquatic environment. The fourth step is to understand how to relate the quantities of inorganic mercury added to the Everglades ecosystem each year to the concentration of methylmercury in fish. This is to be done with mathematical models that represent all of the key processes governing methylmercury production and bioaccumulation. The fifth step is to determine the best way to reduce the levels of methylmercury in fish to safe levels by managing mercury sources and water quantity and quality using the model. Potential candidates for management are emissions from local air pollution sources, chemical constituents in stormwater runoff from the Everglades Agricultural Area, and water depth and flow.

Table 7-1 is the District-DEP work plan for the implementation of the Research and Monitoring (RAM) project for Mercury (RAM-11). **Table 7-2** contains a timetable for carrying out the required elements of the South Florida Mercury Science Program to implement this strategy.

Key Conclusions

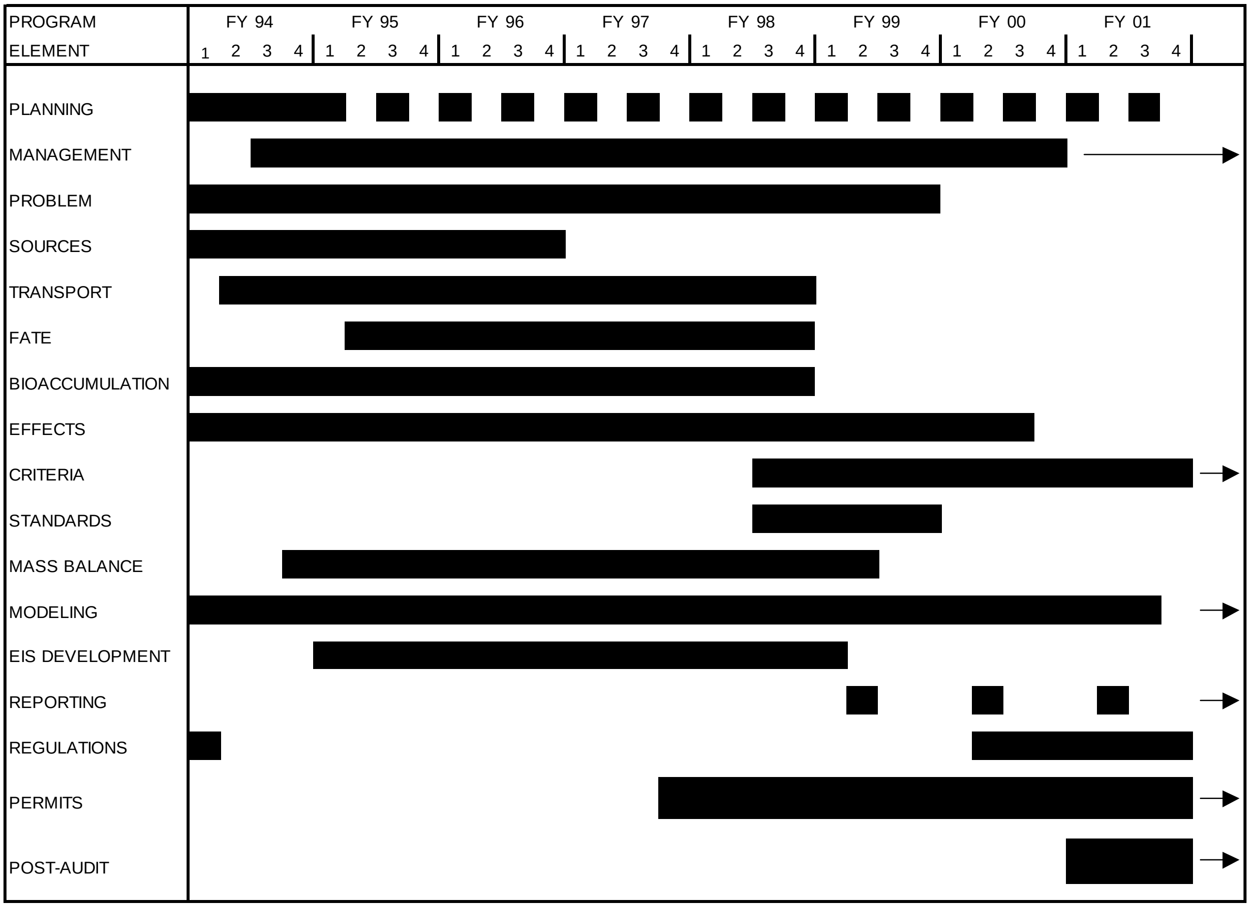
Based on a thorough review of the literature, the results of the USEPA Everglades Mercury Study and the USGS ACME project, four years of intensive mercury monitoring of a prototype Stormwater Treatment Area, and a new analysis of the mercury risks to wading birds feeding in the impacted areas in WCA-2A, there is no reason to believe that there will be any substantial adverse mercury impacts to the Everglades as a consequence of the ECP. Atmospheric deposition of mercury constitutes more than 95% of the new mercury entering the Everglades each year. The analysis of the sources, biogeochemistry, bioaccumulation, and toxic effects of mercury in the Everglades before and after the ECP suggests that the solution to the Everglades mercury problem will most likely come through control of the mercury present in atmospheric deposition, but control of the quality and quantity of discharges to the Everglades may also provide opportunities for reducing the bioaccumulation of mercury in fish and wildlife.

Finally, no single water quality constituent can be used to predict the changes in the downstream mercury concentrations and risks to wildlife from the changes in water quality and quantity to be brought about by the ECP. This can only be done with a mechanistic model of mercury transport, biogeochmistry,

Table 7-1. The District-DEP work plan for the implementation of the Research and Monitoring (RAM) project for mercury (RAM-11).

PROJECT MANAGEMENT PLAN	
PROJECT NAME: RAM-11: Mercury Monitoring and Research	
EFA Reference: Section 2.(4).(d).1. **1991 Settlement Agreement Reference: Not Included.**	
Lead Agencies: Department of Environmental Protection and the South Florida Water Management District	
Lead Groups: Division of Technical Services / Water Resources Evaluation Department	
SFWMD Project Manager: Larry Fink **DEP Project Manager: Tom Atkeson**	
Objective:	By January 1996, the Department and the District will review and evaluate available mercury data for the EPA and tributary waters and identify any additional information necessary to adequately describe mercury in the EPA and tributary waters. If necessary, by January 1996, the Department and the District shall initiate a research and monitoring program to generate any such information. The Department and the District shall employ all means practicable to complete this research by December 31, 1998. This research shall be completed no later than December 31, 2001.
End Products:	Integrated mercury and water quality models by 12/99; evaluation of mercury water quality standard.
Activities, Milestones and Target Completion Dates:	1. Complete District/DEP ENR Mercury Research Plan Complete 5/10/95 2. Complete District/DEP detailed Everglades Research Plan Complete 9/30/95 3. Analyze existing mercury data Complete 8/1/94 4. Develop research planning framework: Interagency Scope of Study of Mercury Contamination in the Everglades Ecosystem Complete 8/1/94 5. Initiate ENR project mass-balance monitoring 8/18/94 6. Complete Everglades mercury monitoring and research by 12/31/98 if practicable (date specified in Act) 12/31/01 7. Complete integration of mercury and water quality models 12/31/99 8. Early evaluation of Class III mercury water quality standard 12/31/00 9. Evaluate Class III mercury WQ standard (date specified in Act) 12/31/01
Associated Projects	1. RAM-1: Description of WQ in the EPA & Tributary Waters will provide information to this project. 2. RAM-2: Evaluation of BMP Effectiveness will provide information to this project. 3. RAM-3: Evaluation of Existing WQ Standards for the EPA. 4. RAM-4: Evaluation of WQ Standards and Classifications of EAA Canals will exchange information with this project. 5. RAM-5: Optimize STA Operation will receive information from this project. 6. RAM-7: Peer-Reviewed Interim Report will receive information. 7. RAM-8: Annual Peer-Reviewed Report will receive information. 8. RAM-13: BMP Strategies for Additional WQ Parameters will provide information to this project. 9. REG-1: Establish Discharge Limits for the EPA & EAA Canals will receive information. 10. REG-8: Permits for Long-Term Compliance with state WQ Standards will receive information. 11. REG-10: Long-Term Compliance with District WQ Rules will receive information from this project.
Support From Other Agencies and Departments	1. Environmental Monitoring and Assessment Program study of extent, magnitude &correlates ENP, USEPA 2. Construction and operation of “clean lab” and overflow contract for ultra-trace analysis of mercury species DEP 3. Geochemistry/water quality studies USGS 4. Florida Atmospheric Mercury Study DEP/ENP/EPRI 5. Provide support & coordination to DEP in the Environmental 6. Monitoring Assessment Program study USFWS-ES, USFWS-LOX
Major Uncertainties Associated With Project Activities:	1. Applicability of existing geochemical process and environmental models. 2. Laboratory capacity to analyze relevant levels of mercury species. 3. Source of funding for identified scope.

Table 7-2. Timetable for carrying out the required elements of the South Florida Mercury Science Program to implement this strategy.



and bioaccumulation in wetlands, initialized and calibrated with Everglades data. Such a model is being developed by USEPA and has been used to support the preliminary evaluation of the potential mercury impacts of the ECP and the Restudy. Successive refinements of the model over the next three years will reduce the uncertainties in model output, but these refinements are unlikely to reverse the conclusions presented in this Chapter. Below the technical basis for these conclusions is provided.

The Mercury Cycle

This section presents a review of the key literature on the sources, transport, transformation, and deposition of mercury in the atmosphere and the sources, transport, transformation, and bioaccumulation of mercury in aquatic ecosystems. From this review, a conceptual model of mercury cycling in aquatic ecosystems is developed and applied to the questions of how water quality and quantity influence methylmercury production and bioaccumulation. The focus here is on the influence of phosphorus, carbon, oxygen, sulfur, and iron on mercury methylation in aquatic ecosystems and the influence of phosphorus on the carbon, oxygen, sulfur, and iron cycles in aquatic ecosystems.

Sources and Cycling of Mercury in the Atmosphere

Mercury in the natural environment originates in the soils and sediments deposited with the formation of the earth's crust and the early atmosphere (Clarkson, 1994). A significant source of atmospheric mercury is the natural evasion of elemental mercury from the surface of soil and water. (Fitzgerald, 1989). Deposition from the atmosphere back to the earth's surface completes this cycle and ensures a continuous supply of newly available inorganic mercury for biogeochemical transformation, including formation of elemental mercury and methylmercury.

In addition to its natural background sources, atmospheric mercury is generated by a variety of human activities, including combustion of fossil fuel and waste, mining and smelting of mineral ores, and the use and disposal of mercury itself (USEPA, 1997). Mercury may be removed from the air and deposited on water, soil, or plant surfaces in wet deposition (rain or snow) or dry deposition (particle settling and gas adsorption to the solid or liquid surface). Although the relative proportions may change depending on the source, mercury exists in the atmosphere in three forms, which differ greatly in their air chemistry and in the physical properties that determine their rates of removal from air by wet and dry deposition processes. These forms are elemental mercury, particulate mercury, and reactive gaseous mercury or RGM.

Elemental mercury (Hg^0) [1]gas is relatively inert in air, with a half-life in the lower atmosphere of approximately one year (Slemr et al., 1985; Schroeder and Munthe, 1998). At remote sites (i.e., away from cities or industrial facilities) more than 95% of total atmospheric mercury is in this form (EPMAP, 1994; Mason et al., 1994). Hg^0 interacts only weakly with rain, vegetation, the ground or water surfaces (Lee et al., 1998; Schroeder and Munthe, 1998). As a result of its low chemical reactivity and low affinities for soil, water, and plant surfaces, it is transported great distances from the point of emission (Pai et al., 1997). The concentration of elemental mercury in air, the temperatures of the air and water surfaces, and the relative affinities for soil, plant, and water surfaces determine its concentrations in these media.

RGM is composed of the gaseous forms of oxidized inorganic mercury (Hg (II)). This form of mercury is thought to be primarily mercuric chloride ($HgCl_2$), but other forms of Hg (II) may exist (Prestbo and Bloom, 1995; Stratton and Lindberg, 1995; E. Prestbo, Frontier Geosciences, pers. comm., 1996). Its sources are postulated to be slow conversion of Hg^0 in the atmosphere by poorly-understood gas-phase photochemical processes, by aqueous-phase (i.e., droplet) reactions with atmospheric oxidants (e.g., Munthe, 1992; Pleijel and Munthe, 1995), or direct emissions from sources such as power plants, incinerators or other human sources (EPMAP, 1994). At remote sites typically less than 5% of total atmospheric mercury is in this form (EPMAP, 1994), but despite its small concentration, RGM controls the rate of mercury deposition to the earth's surface (Petersen et al., 1995; Pai et al., 1997; Lindberg and Stratton, 1998; Stratton and Munthe, 1998). RGM behaves very differently in the atmosphere than elemental mercury: it is readily scrubbed by clouds or rain, adsorbs to atmospheric particulate matter, and,

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1. Elemental mercury is abbreviated as Hg^0; inorganic mercury is abbreviated as Hg(II); methylmercury is the cation CH_3Hg+ and is abbreviated as MeHg.

in the absence of rain, is rapidly deposited on available surfaces (EPMAP, 1994). RGM emissions are likely to be deposited locally, e.g., within 100 km of the source (EPMAP, 1994).

Particulate mercury (Hg_p) is oxidized inorganic mercury adsorbed to fine or coarse atmospheric particulate matter. Particulate mercury may be emitted directly by emission sources, formed by condensation reactions in plumes, or result from atmospheric reactions in the free atmosphere (Schroeder and Munthe, 1998). Fine particulate mercury (i.e., < 2.5 μm) is intermediate in its deposition properties between Hg^0 and RGM. It is less readily scrubbed by rain and can travel hundreds of miles, but deposits more readily than Hg^0 (EPMAP, 1994; Lee et al., 1998). At remote sites typically less than 5% of total atmospheric mercury is in this form, as is the case in central and south Florida (Guentzel, 1997).

To complete this section on interactions of atmospheric mercury with the earth's surface, it should be noted here that recent work has established that significant amounts of mercury in soils, sediments, and surface waters can be reduced to Hg^o. This volatile form of inorganic mercury can then be recycled to the atmosphere by volatilization or evasion from the soil (Carpi and Lindberg, 1998) or water surface (Lindberg et al., 1995; Poissant and Casimir, 1998) or actively transported from soil or sediment pore water along with water transpired by terrestrial or aquatic macrophytes (Lindberg and Meyers, 1998). This phenomenon is treated in greater detail in the following section on aquatic cycling.

Methylmercury is also present in wet deposition, albeit at much lower concentrations than inorganic mercury ion, falling in the range of 0.5% to 5% of total mercury in rainfall in one study of methylmercury deposition to a remote location in northwestern Ontario (St. Louis et al., 1995). Higher concentrations of methylmercury in rainfall are encountered in regions influenced by ocean upwellings (E. Prestbo, Frontier Geosciences, pers. comm., 1997) and industrial air emissions (Hultberg et al., 1994). Methylmercury concentrations in South Florida rain are generally considered environmentally insignificant (E. Prestbo, Frontier Geosciences, pers. comm., 1996; Guentzel, 1997).

Sources and Cycling of Mercury in Aquatic Ecosystems

Figure 7-4 summarizes the general conceptual model of mercury cycling and bioaccumulation in the aquatic ecosystem. Oxidized inorganic mercury(II) and methylmercury enter a body of water via watershed runoff (Mierle, 1990; Johansson et al., 1991; St. Louis et al., 1994), groundwater discharge (Krabbenhoft and Babiarz, 1992; Watras et al., 1994) and direct atmospheric deposition (Fitzgerald et al., 1991, 1994; Hultberg et al., 1994) and leave via overflow and groundwater recharge. Oxidized inorganic mercury or Hg(II) and methylmercury are present in land surface runoff in river and lake watersheds and the percentage of total mercury that is methylmercury present in such runoff tends to increase as the wetlands area of the watershed increases (St. Louis et al., 1994; Krabbenhoft et al., 1995; St. Louis et al., 1996) and the humic content of the runoff water increases (Mierle and Ingram, 1991). It has been observed that the significance of atmospheric deposition of methylmercury as a source of methylmercury to a watershed or water body decreases with distance from areas of ocean upwelling (E. Prestbo, Frontier Geosciences, pers. comm., 1996) and industrial sources (Hultberg et al., 1994). In North America, there appears to be a decreasing gradient of methylmercury atmospheric deposition from west to east (E. Prestbo, Frontier Geosciences, pers. comm., 1996). So, for example, Krabbenhoft et al. (1995) report a methylmercury production rate in the Allequash Creek watershed, Wisconsin, three to six times higher than the measured atmospheric deposition rate, while the contribution of atmospheric deposition to methylmercury loadings to the Everglades is low (Guentzel, 1997).

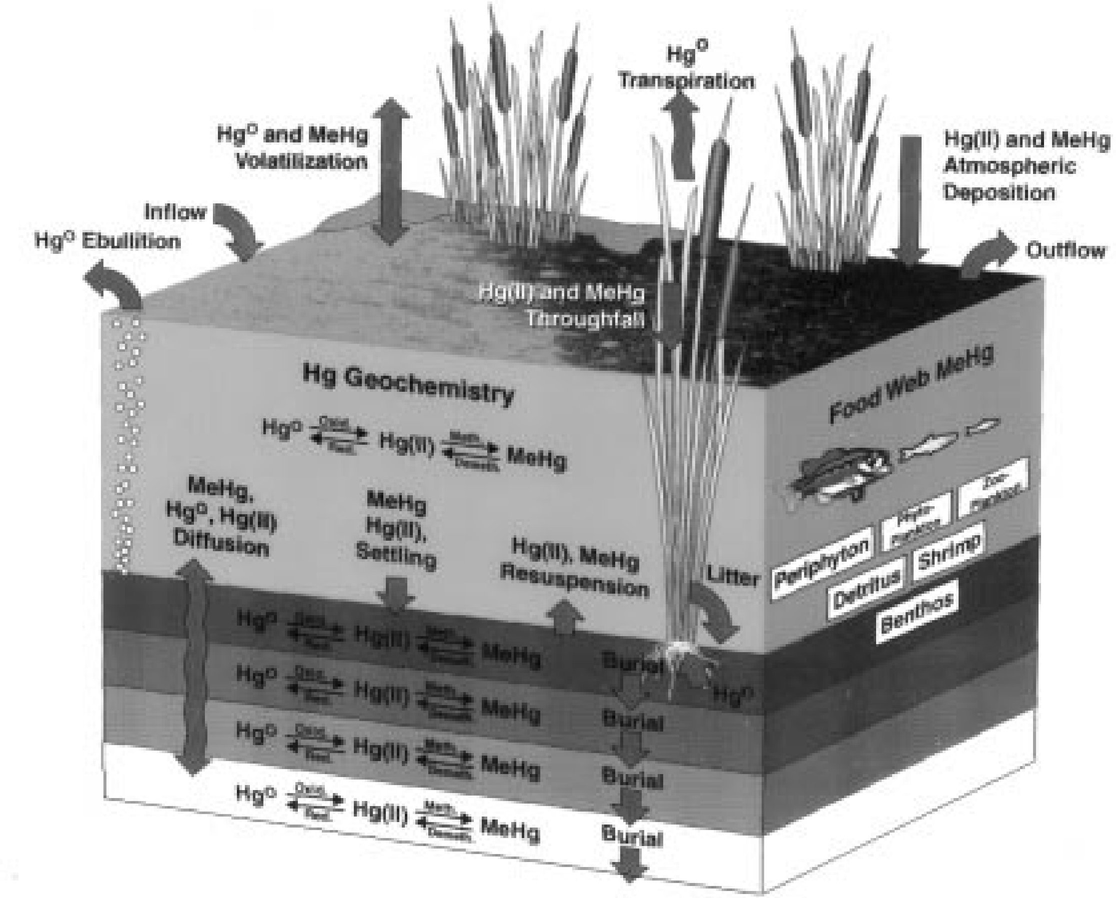

Figure 7-4. Simplified conceptual model of the mercury cycle in the Everglades from the ACME project. The model highlights linked submodels for mercury biogeochemistry and food web bioaccumulation.

Mercury is found in aquatic ecosystems in three forms. In descending order of occurrence they are inorganic mercury, Hg(II), methylmercury, and elemental mercury, Hg^{o}. Once present in an aquatic environment, inorganic mercury can be converted to methylmercury by microbially-mediated processes in the water column under anoxic conditions (Waters et al., 1995) but more often in the sediment (Wood et al., 1968; Campeau and Bartha, 1985; D'Itri, 1990; Gilmour et al, 1992). Although inorganic mercury methylation has been demonstrated to occur by non-living processes (Rodgers, 1977; Nagase et al., 1982, 1984; Berman and Bartha, 1986) and methane-producing bacteria (Wood et al., 1968), the predominant methylation route in natural fresh and salt water aquatic environments is now well-established to be by sulfate-reducing bacteria (*Desulfovibrio* spp.) under conditions in which dissolved oxygen is virtually absent (Jensen and Jernelov, 1969; Beijer and Jernelov, 1979; Campeau and Bartha, 1985; Choi and Bartha, 1993). The rate of inorganic mercury methylation by these bacteria is affected by pH (Winfrey and Rudd, 1990; Gilmour and Henry, 1991; Miskimmin et al., 1992), sulfate (Gilmour et al., 1992), sulfide (Gilmour et al., 1998b) and dissolved organic carbon (Watras et al., 1994). The rate of methylation in

Canadian shield lakes was found to increase and that of demethylation to decrease with increasing water temperature (Bodaly et al., 1993).

Photodemethylation of methylmercury in water under sunlight has also been reported (Sellers et al., 1996). Methylmercury in Everglades water is demethylated by sunlight at the water's surface but not at depth (Krabbenhoft et al., 1998), probably because the high concentrations of dissolved organic matter strongly absorb the photoactive wavelengths of sunlight (D. Krabbenhoft, USGS, pers. comm., 1998). Methylmercury is also demethylated in sediment under anoxic conditions by carbon dioxide-producing or methane-producing bacteria (Marvin-DiPasquale and Oremland, 1998).

Oxidized inorganic mercury is reduced to elemental mercury by sunlight in soil (Carpi and Lindberg, 1998). Some inorganic mercury is reduced to elemental mercury in the water column in the dark (Winfrey and Rudd, 1990) and in sunlight (Amyot et al., 1997), in the water column by eucaryotic phytoplankton (Mason et al., 1995a) and in sediment pore water by an as yet unspecified mechanism believed to be microbial in origin (Lindberg and Myers, 1998). Elemental mercury has significant affinity for organic soil particles (Feng, 1978) and may be absorbed through stomata in plant surfaces (Lindberg et al., 1991) but its affinities for live and dead plant matter, sediment and dissolved organic matter (DOM) in water have not been accurately measured and may be low (D. Krabbenhoft, USGS, pers. comm., 1996). Elemental mercury is readily emitted from ocean (Fitzgerald, 1989), lake (Vandal et al., 1991) and soil (Kim et al., 1995; Lindberg et al., 1995) surfaces by a process sometimes referred to as evasion.

Plants have been shown to take up and emit elemental mercury through stomatal pores in the leaf surfaces, with the possibility of either a net flux from the forest canopy to the air or from air to canopy, depending on the local atmospheric elemental mercury levels (Lindberg et al., 1992). The source of any emitted mercury is believed to be the soil rather than sorption from the air with subsequent reemission during daylight hours. Hanson et al. (1995) demonstrated that tree seedlings in controlled chambers can emit Hg added to soil water in the rooting zone by irrigation. Elemental mercury formed in sediment pore water appears to be transported through stems and leaves of rooted aquatic plants and released to the air at the ENR Project (Lindberg and Myers, 1998). Little is known about the factors controlling the rate of production and transport of elemental mercury to the atmosphere by this pathway. Fluxes exhibit a strong day-night cycle, parallel to that of carbon dioxide and water exchange, which are controlled by the pores (stomata) in leaves.

Inorganic mercury and methylmercury have high affinities for particles of geological and biological origin (Hurley et al., 1991; Watras et al., 1992; Watras and Bloom, 1994) and for dissolved organic matter or DOM (Hintelmann et al., 1995; Hurley et al., 1998). This influences their relative distributions amongst the solid, DOM and truly dissolved phases and their rates of removal from the water column via sorption to settling particles (Hurley et al., 1994). Inorganic mercury and methylmercury are strongly associated with living and dead organic matter (Hurley et al., 1998) and both are rapidly removed from the water column by settling organic matter (Watras et al., 1994; Ambrose and Araujo, 1998). This removal process is counteracted to some extent by the affinities of inorganic mercury and methylmercury for DOM (Hurley et al., 1994; 1998), which is a product of the decomposition of plant matter.

In smaller aquatic organisms that respire via direct uptake of dissolved oxygen across external membranes, the uptake of methylmercury directly from the water via passive diffusion competes with ingestion of contaminated food as the most significant uptake route. So, for example, Huckabee et al. (1975) found that less than 15% of the methylmercury uptake by the exposed water flea (*Daphnia pulex*) was via food. However, for animals that meet their oxygen demand via uptake across gill structures, the most significant route of uptake is via ingestion of contaminated food (Huckabee, et al., 1975), and the relative importance increases rapidly with increasing size (Norstrom et al., 1976; Rodgers, 1994; Post et al., 1996). Methylmercury is absorbed across the gut from food items (McCloskey, et al., 1998). The most significant route of loss of methylmercury from fish is believed to be across the gill membrane (C. Barber, USEPA/ORD-Athens, pers. comm., 1998). As a consequence, methylmercury is only slowly excreted in fish, with half-lives that increase with size (Norstrom et al., 1976; Sharpe et al., 1977; Rodgers, 1994; Trudel and Rasmussen, 1997).

Because the methylmercury depuration (loss) rates decrease and bioaccumulation factors increase with increasing size in fish (Norstrom et al., 1976; Sharp et al., 1977; Rask et al., 1994; Rodgers, 1994; Simonin et al., 1994; Trudel and Rasmussen, 1997) and age in fish (Rask et al., 1994) and average fish size increases with each trophic level (Rask et al., 1994; Rodgers, 1994; Becker and Bigham, 1995), large, top-predator fish will bioaccumulate methylmercury up to several million times the concentration in the water column, as is the case for several species of top-predator fish at some locations in the Everglades (Lange et al., 1998). Where standing crop plant biomass is low and fish bioaccumulation factors are high, the storage of methylmercury in standing crop fish biomass may prove to be a significant reservoir (Fitzgerald and Watras, 1989; Hultberg et al., 1994; Rask and Verta, 1995). This is probably not the case in the ENR Project, however (Jordan, 1997).

In rapidly growing fish, some of the methylmercury bioaccumulated via ingestion of contaminated prey is diluted by the additional mass added by the fish. This phenomenon is often referred to **as growth dilution** (Norstrom et al., 1976). Since the growth rate in fish is affected by water temperature, quality and quantity of habitat, sex and reproductive status, the significance of year-to-year increases or decreases in methylmercury concentrations in fish is not always clear.

A number of environmental factors are believed to influence methylmercury bioaccumulation in fish in aquatic ecosystems. Methylmercury bioaccumulation tends to be higher in fish in waters with high temperature (Bodaly et al., 1993), low pH and alkalinity (Wren and McCrimmon, 1983; Cope et al., 1990; Grieb et al., 1990; Bloom et al., 1991; Simonin et al., 1994; Watras et al., 1994) and high DOM (Winfrey and Rudd, 1990; Rask et al., 1994), but varies inversely with DOC (Watras et al, 1994), high suspended solids (Rudd and Turner, 1983), and degree of eutrophication (Hakanson, 1980). All of these factors are varying along the nutrient gradient in WCA-2A. In an analysis prepared for this report, the District found that DOC and calcium were better predictors of methylmercury in mosquitofish collected along the WCA-2A nutrient gradient than total phosphorus, which is often used as a surrogate for the degree of eutrophication in a P-limited water body (Carlson, 1984). An inverse relationship between fish bioaccumulation of methylmercury and water column selenium has also been observed in lakes by Turner and Rudd (1983) but not by Wren and MacCrimmon (1986). If selenium suppresses methylmercury bioaccumulation, it appears to be effective only in predatory fish, suggesting that it must be taken up via the food chain (Rudd et al., 1983).

There has been a general observation that fish in reservoirs and impoundments tend to bioaccumulate higher concentrations of methylmercury than in nearby natural lakes receiving the same mercury load and that the fish in newer created lakes tend to have higher methylmercury concentrations than fish from older created lakes (Cox et al., 1979; Meister et al., 1979; Bodaly et al., 1984; Verta et al., 1986; Phillips et al., 1987; Verdon et al., 1991). This is the so-called **“reservoir effect”**. With the “classic” reservoir effect, methylmercury production first increases then decreases following permanent inundation.

To explain this general phenomenon, the hypothesis that has gained the widest acceptance is that the initial increase in methylmercury production can be traced to the liberation of inorganic mercury from its storage depots in flooded terrestrial plant material (Morrsion and Therien, 1994) and flooded soils (Cox et al., 1979; Meister et al., 1979; Bodaly et al., 1984) together with nutrients and plant decomposition products that stimulate the growth of aquatic microrganisms. The eventual decrease can be traced to the depletion of these labile pools over time, leaving an increasingly recalcitrant fraction behind which is less bioavailable for methylation. The increase in methylmercury production first manifests itself as an increase in the methylmercury concentrations in water and the one-celled plants and animals that form the base of the food chain. This increase then propagates up the food chain with biomagnification at each link, peaking in top-predator fish in the same age chort (e.g., years 2 or 3) at up to five times typical concentrations in nearby lakes (Verdon et al., 1991) within about two to five years after flooding (Scruton et al., 1994). The concentrations in this reference age cohort then decline gradually back to concentrations more typical of surrounding natural lakes in about 5-10 years in small catchment reservoirs and longer in large catchment reservoirs (Scruton et al., 1994).

However, if one follows the same cohort as it ages, methylmercury residue levels will continue to increase with time until the cohort dies out. It then takes about one top-predator fish lifetime to clear this short-term increase of methylmercury production from aging fish at the top of the food chain (R. Harris, Tetra Tech, pers. comm., 1997). For largemouth bass with a mean life span of about five to seven years, this would mean that a system that reached its peak concentration in two years would begin to show a decline in the oldest fish in about seven to nine years and a system that peaked at five years would begin to show a decline in the oldest fish in 10 to 12 years. For longer-lived species like pike and sturgeon, the clearance time for the population is even longer (Anderson et al., 1995; Morrison and Therien, 1995). This clearance rate may be retarded by the tendency of older, larger fish to feed on older, larger prey species with time.

The above summarizes the essence of the “classic” reservoir effect, but not all reservoirs behave classically. Some fish methylmercury concentrations showed seasonal patterns in California reservoirs, probably associated with turnover and mixing of the hypolimnetic and epilimnetic waters (Slotton et al., 1995). In another reservoir in Labrador, Canada, there is evidence of significant clearance in whitefish, some in trout, but none in pike after more than 20 years since flooding (Anderson et al., 1995). In a study of Ontario reservoirs, some of which were created more than 75 years ago, there was no pattern in the relationship between age of reservoir and concentration of mercury in fish, with the two oldest exhibiting background levels, but a much shallower system created 10 years later exhibiting extremely high methylmercury concentrations (Rodgers et al., 1995). As with the lake studies, the reasons for these differences are probably associated with differences in lake catchment, chemistry and morphology.

Focusing on the role of soil composition in determining the magnitude and duration of a reservoir effect, soils high in sulfide content will precipitate inorganic mercury as mercuric sulfide, which is relatively inert, even under wet, reducing conditions that occur cyclically during river flooding (Barnett et al., 1997). A study of forest soils from a hydroelectric reservoir in Quebec, Canada, before and after flooding demonstrated that soil iron oxy-hydroxide complexes under dry, oxidizing conditions will release the bound inorganic mercury following flooding, when anoxic conditions set in. However, no significant loss of bound inorganic mercury from the organic fraction of the soil was observed (Dmytriw et al., 1995). In the ferralitic soils of a tropical rain forest, about 20% of the inorganic mercury bound to the iron oxy-hydroxide complexes was released upon flooding to create reducing conditions (Roulet and Lucotte, 1995). No significant loss of inorganic mercury from the organic component of well-characterized soils was detected in an exhaustive leaching study (Yin et al., 1997). This effect was attributed either to the long diffusive path through which the inorganic mercury must migrate or the presence of sulfhydryl binding sites with extremely high affinities for mercury that will not respond to a change from dry, oxidizing conditions to wet, reducing conditions.

Peat soils have been used to calculate absolute mercury deposition rates because the mercury in those soils does not readily migrate from the stratum in which it was laid down (Delfino et al., 1993; Benoit et al., 1994). After decades of draining and flooding EAA soils, there is no evidence that inorganic mercury has accumulated through leaching into the underlying soils, suggesting that the inorganic mercury in the soil is strongly bound to the organic fraction of the soil (Patrick et al., 1994) or is lost by some other mechanism, perhaps evasion as elemental mercury (S. Lindberg, ORNL, pers. comm., 1996). No first flush effect has been observed in the ENR Project which is underlain with peat soils, and no reservoir effect has been observed in the ENR Project at any trophic level four years after flooding (SFWMD, 1998).

An excellent summary of the cycling and bioaccumulation of mercury in wetlands is contained in Zillioux et al. (1993). In what follows, the above information is applied to develop a conceptual model of the various influences of water quality and quantity on the mercury cycle.

The Role of Phosphorus in Mercury Cycling in Aquatic Ecosystems

Phosphorus cannot be demonstrated to directly influence methylmercury production in aquatic ecosystems (Gilmour et al., 1998a). However, it can have an indirect influence via the carbon, oxygen, sulfur and iron cycles. Below we develop a conceptual model of P cycling in aquatic ecosystems, focusing on the Everglades experience where relevant information is available. P is expected to influence inorganic mercury methylation rates and methylmercury demethylation rates through its indirect effects on water chemistry. P is expected to influence inorganic mercury and methylmercury concentrations in water and peat primarily through its effects on plant types, standing crop densities, production rates and decomposition rates, which, in turn, govern sorbed mercury species settling, dilution or production in accumulating peat and dissolved organic carbon (DOC) concentrations and properties. DOC, in turn, affects sorption and photochemistry via complexation of inorganic mercury and the absorption of photoactive wavelengths of sunlight. P influences methylmercury bioaccumulation through its effects on water chemistry, plant community types, densities and productivities and the relative importance of the autotrophic and saprotrophic or detrital sources of energy at the base of the food web. The possible mechanisms by which P is expected to exert each of these influences are discussed below.

The Influence of Phosphorus via the Oxygen Cycle

Where total P in the water column is high, plant densities and production rates are high, as are the densities and production rates of dead and decomposing plant matter. This decomposing plant matter takes up dissolved oxygen from the water column. In the interior marsh during the day, plant production of dissolved oxygen often exceeds the biochemical oxygen demand of the microbes involved in plant matter decomposition, but this is not the case at night, when dissolved oxygen concentrations in the water column decline precipitously and are virtually zero for most of the night (Krabbenhoft et al., 1998). Such conditions are referred to as highly anaerobic or anoxic. Sulfate plays a role in anaerobic decomposition of plant matter by acting as an electron acceptor (Reddy et al., 1991).

Anaerobic conditions in the sediment favor the production of elemental mercury from inorganic mercury (J. Qualls, U. Nevada-Las Vegas, pers. com., 1998). Methylation of inorganic mercury by sulfate-reducing bacteria also occurs under anaerobic conditions (Gilmour et al., 1992); however, no measurable methylation is occurring in the water column of the Everglades (Gilmour et al., 1998). Methylation occurs primarily in sediments at 2 cm or more depth (Gilmour et al., 1998). Everglades sediments are generally anaerobic even during the day in areas where P concentrations are low, also referred to as oligotrophic areas (Orem et al., 1998). The only exception observed is in the immediate microzone of influence of the roots of plants capable of transporting oxygen to the roots (e.g., cattail) (Chanton, 1998a, b).

There appears to be no direct influence of P on the rate of demethylation of methylmercury, but the addition of sulfate to Everglades soil cores appears to stimulate demethylation (Marvin-DiPasquale and Oremland, 1998). The spatial trends in demethylation of methylmercury in the Everglades from this study are unclear.

The Influence of Phosphorus via the Carbon Cycle

Inorganic mercury and methylmercury both have a high affinity for aquatic plant matter, whether living, dying, dead, or in the form of peat soil. Algae and mats of algae (periphyton) should therefore absorb inorganic mercury and methylmercury directly from the water column. This phenomenon has been observed both in the laboratory (Mason et al., 1995) and in the field in the Everglades (Krabbenhoft et al., 1998; Hurley et al., 1998). Floating macrophytes like Water Hyacinth (Wolverton and McDonald, 1978) and Water Lettuce (SFWMD, 1998) have also been demonstrated to take up inorganic mercury and methylmercury directly from the water column. All other things being equal, the faster the plants grow, die and settle to the bottom, the faster the settling plant matter should be able to remove inorganic mercury and methylmercury from the water column (H. Hultberg, Swedish Environmental Research Institute, pers. comm., 1996). Because P is the limiting nutrient in the Everglades, an increase in water column total P concentrations is associated with increased plant densities and growth and decay rates and, by inference, with lower inorganic and methylmercury concentrations in the water column.

Based on evidence from the Everglades (Reddy et al., 1991; Delfino et al., 1993; USEPA, 1998), the rate of peat accumulation is higher where water column P concentrations are higher, all other things being equal. If the inorganic mercury loading rate remains unchanged, then the concentration of inorganic mercury in peat from areas where phosphorus concentrations in water are high will be lower than in low phosphorus areas because it is diluted by the increased volume of peat. This relationship has already been observed in the Everglades (Vaithiyanathan et al., 1996; USEPA, 1998). In the ENR Project, the concentration of inorganic mercury in newly accumulating peat soil appears to be declining over the first three years of operation (SFWMD, 1998). However, another process that may be contributing to the decline of the inorganic mercury concentration in these soils is the formation of elemental mercury and its subsequent transport out of the sediment via the roots of transpiring rooted aquatic plants (Lindberg and Meyers, 1998).

The reduction in the concentration of inorganic mercury in peat may have ramifications for methylmercury, as well. One of the factors that determine the rate of methylmercury production is the concentration of inorganic mercury in the fresh peat layer. All other things being equal, one might expect that methylmercury concentrations in sediment pore water, the overlying water column and at each link in the food chain will be lower in enriched relative to unenriched areas of the Everglades.

In addition to enhanced biomass production, with the attendant enhanced removal of inorganic mercury and methylmercury from the water column, phosphorus can also influence inorganic mercury methylation by sulfate-reducing bacteria via the carbon cycle. The affinity of inorganic mercury for DOM in Everglades surface waters and sediment pore waters is very high (M. Reddy, USGS, pers. comm., 1998) and the size and affinity of DOM for inorganic mercury and methylmercury is a function of its origin (G. Aiken, USGS, pers. comm., 1997).

The first indirect effect of P on the carbon cycle in the Everglades is in the change in plant communities (Koch and Reddy, 1992; Grimshaw et al., 1993; Koch and Rawlik, 1993; Browder et al., 1994; **Chapter 3**), which changes the composition of plant tissue to be decomposed and the relative rates of anaerobic versus aerobic decomposition of plant tissue (W. Orem, USGS, pers. comm., 1998), as well as the corresponding rates of aerobic and anaerobic rates of production of DOM species (G. Aiken, USGS, pers. comm., 1997). These changes, in turn, may alter the rates of production of short-chain organic molecules required as a carbon source by sulfate reducing bacteria (R. Oremland, USGS, pers. comm., 1998; J. Chanton, FSU, pers. comm., 1998; C. Gilmour, ANS, pers. comm., 1998). Changes in the chemical composition of these molecules may also change their affinities for inorganic and methylmercury, which in turn could influence the bioavailability of these species to methylating and demethylating bacteria and algae at the base of the food web.

DOM has been demonstrated to “redissolve” mercuric sulfide (cinnabar) due to the complexing power of the sulfur binding sites (sulfhydryl groups) on the DOM (Ravichadran et al., 1998). The extent to which this “redissolved” inorganic mercury is available for other processes such as methylation or reduction to elemental mercury is now under investigation.

Another way in which DOM influences the mercury cycle is by enhancing the transport of inorganic mercury and methylmercury through sediment pore water. Although DOM diffuses through sediment more slowly than free inorganic mercury ion, in fact, the inorganic mercury ion is not free, because it interacts with the solid peat substrate, slowing its migration out of the sediment. This is not the case with DOM-bound inorganic ion, which exchanges only reluctantly with the binding sites on peat soil. The result is that the diffusion rate of inorganic mercury bound to DOM may exceed that which is exchanging with binding sites on the peat soil.

The upward flux of DOM bound mercury may be enhanced or retarded by the direction and magnitude of groundwater seepage through the peat. The interaction of groundwater seepage and pore water complexation processes is under active investigation in the ENR Project (S. King, USGS, pers. comm., 1998). Upwelling increases the flux of DOM-bound inorganic mercury and methylmercury complexes out of the sediment into the overlying water where they can enter into a variety of processes, which, for methylmercury, includes transformation back to inorganic mercury by sunlight or bacterial action or sorption to plant tissue with subsequent bioaccumulation up the food chain.

DOM influences the mercury cycle through its influence on the reactions of inorganic mercury and methylmercury in the dark and in sunlight. As noted above, DOM forms complexes with inorganic mercury and methylmercury ions. When these complexes interact with the appropriate wavelengths of sunlight in water, the inorganic mercury ion, Hg(II), may form elemental mercury, (Xiao et al., 1994, 1995) which is believed to have little affinity for DOM and is liberated from the complex. This reaction may also occur in the dark, but at a slower rate. Because DOM also acts as a sunscreen, absorbing wavelengths of sunlight that might otherwise stimulate a chemical reaction, it may reduce the rate of production of elemental mercury or the demethylation of methylmercury by sunlight (photodemethylation). It is also possible that methylmercury bound to DOM is more resistant to transformation back to inorganic mercury by chemical and biological processes. The sunscreen effect of DOM may also reduce the concentration of photoxidants produced by incident sunlight and thus the reoxidation rate of elemental mercury. Because the intensity of these readily absorbed wavelengths decreases with increasing water depth, DOM provides a direct link between the hydrology and water chemistry of the system.

Ultimately, it is the balance among these competing processes of photosensitive and photoinsensitive processes mediated by DOM that determines the net rate of production of elemental mercury and methylmercury from inorganic mercury during the day and at night. All of these known and potential effects of DOM are under active investigation in the Everglades.

The Influence of Phosphorus via Changes in Ecosystem Quantity and Quality

***Quantity Effect (Biodilution)*:** All other things being equal, if the rate of methylmercury production per unit area is a constant, then the amount of methylmercury available for bioaccumulation in aquatic animals in any given area of an aquatic ecosystem in any given time span is a constant. If an increase in water column P increases plant densities and growth rates and, providing there is sufficient dissolved oxygen, this, in turn, supports greater animal densities at each trophic level of an aquatic ecosystem without affecting the methymercury production rate, then this constant amount of methylmercury will be diluted amongst more plant and animal standing crop mass (biomass), so that the concentration of methylmercury in any particular portion of that biomass at each level in the food chain is lower than it was before the addition of the excess P. Thus, where the biomass production at each trophic level in a lake is high, methylmercury concentrations in organisms at each trophic level are generally low (D'Itri et al., 1971; Hakanson, 1980; Rodgers and Beamish, 1983; Hakanson et al., 1988; Lathrop et al., 1989). This is the so-called **“biodilution effect”** (Hakanson, 1980). The biodilution effect may be operative in Florida lakes, because highly eutrophic lakes like Okeechobee and Apopka do not have a mercury problem in top-predator fish, while more pristine lakes with the similar rates of atmospheric deposition do (Lange et al., 1993). It has also been suggested that the biodilution effect is occurring in the remnant northern Everglades in the zone of P impact immediately downstream of the S-10 structures in WCA-2A, where methylmercury concentrations in mosquitofish are low (PTI, 1994).

However, others have argued that the phenomenon of biodilution is not the explanation for the observed inverse relationship between eutrophic conditions in lakes and methylmercury concentrations in top-predator fish and question the applicability of results from lakes to marsh ecosystems (Watras, 1995). In fact, in Little Rock Lake, WI, methylmercury in top-predator fish increased as production increased (Wiener, 1986), probably as a consequence of the relationship between production, pH and methylmercury dynamics (Watras, 1995). In the Florida lake study, pH, alkalinity and calcium were more strongly inversely correlated with mercury concentrations in largemouth bass than with total P (Lange et al., 1993). In the Everglades along the WCA-2A nutrient gradient, the water is buffered against acidity changes caused by increased production. In addition, due to the effect of cattail shading, the periphyton densities and production rates are not proportional to the water column total P concentrations, thus uncoupling water column total P from the most common index of excess production. Moreover, the observed decrease in methylmercury concentrations in mosquitofish with increasing total P in the water column has been attributed primarily to the presence of excess sulfide in sediment pore water due to the presence of high concentrations of water column sulfate, not a biodilution effect (C. Gilmour, ANS, pers. comm., 1998).

Quality Effect (Change in Trophic Structure): In addition to reducing the quantities of biomass at each trophic level, a decrease in the limiting nutrient can also affect the quality of biomass at each trophic level by fostering community shifts from species that thrive in high nutrient environments to species that thrive in low nutrient environments and vice versa. With this shift to low-nutrient plant communities comes a shift in the organisms that feed on them. In addition, lower total P concentrations are associated with higher dissolved oxygen concentrations, which support a wider variety of species at each trophic level, including the more desirable sport fish species like largemouth bass at the top of the food chain. Where predators at each trophic level can feed on more species at the next lowest trophic level, their methylmercury bioaccumulation factors will increase and this increase will propagate and magnify at each successive link in the food chain. This feeding preference shift to a higher percentage of higher trophic level organisms in the diet has the effect of increasing methylmercury bioaccumulation.

The Role of Sulfur in the Cycling of Mercury in Aquatic Ecosystems

The sulfur cycle in aquatic ecosystems is highly complex (Bauld, 1986), involving chemical and biochemical reactions that consume or produce sulfate, sulfide and sulfur. Under anaerobic conditions in sediment, sulfate-reducing bacteria take up sulfate ion (SO_4) to oxidize organic carbon. In the process, sulfate is reduced to sulfide (Faque et al., 1991). This is analogous to animals breathing in O_2 to oxidize food (organic substrate). In general, in the absence of dissolved oxygen, the activity of these organisms is determined by the concentration of SO_4 and organic substrates in sediment pore water and the ambient temperature. Such conditions are found throughout the Everglades. Sediments are generally anoxic, either throughout the profile or within micro-niches.

Sulfate concentrations in the northern Everglades are more than sufficient for rapid sulfate reduction. Sulfate concentrations in WCA-2A often exceed 30 mg/L, while sulfate reducers thrive even below 1 mg/L (Gilmour et al., 1998a). In central and southern WCA-3A and Everglades National Park (the Park), sulfate concentrations can be extremely low (<0.5 mg/L), but it appears that rapid recycling of sulfur through photosynthetic sulfide oxidation maintains enough sulfate to support rapid microbial sulfate reduction. Organic substrate availability is also high, supplied through the growth and decay of plants. Therefore, at least in the northern Everglades, sulfate reduction is rapid and probably not currently limited by sulfate supply (C. Gilmour, ANS, pers. comm., 1998).

While sulfate-reducing bacteria are important methylators of inorganic mercury, the product of their metabolism, sulfide, can be demonstrated to inhibit the methylation reaction, but the mechanisms, whereby sulfide inhibits Hg methylation are not clear. In the northern and central Everglades, the concentration of sulfide in pore water appears to be a better predictor of Hg methylation rates and MeHg concentrations in sediments than is sulfate (Gilmour et al., 1998b). This may be because sulfate is always present in excess of its limiting concentration or because the inhibition of methylation by sulfide has a stronger effect on methylation than the control of sulfate reduction rates by sulfate. Phosphate has no direct effect on the activity of sulfate reducing bacteria or the rate of Hg methylation. However, as described above, P can indirectly influence the production of methylmercury by influencing the rate of production of plant biomass and hence the supply of organic matter to bacteria. Phosphate-driven eutrophication also enhances anoxia and sulfide production, which limits inorganic mercury methylation (C. Gilmour, ANS, pers. comm., 1998).

The present-day supplies of both phosphate and sulfate to the Everglades exceed natural and historical supplies (Orem et al., 1998; **Chapter 4**). High sulfide concentrations produced under anoxic conditions in sediment inhibit methylmercury production. These conditions are found in WCA-2A in the P-impacted area immediately downstream of the S-10 structures and in the ENR Project. Intermediate sulfate concentrations, or conditions that favor rapid sulfide oxidation, however, favor methylmercury production. These conditions are found in central WCA-2A and WCA-3A.

This is the essence of the sulfide hypothesis and the explanation for the observed spatial distribution of methylmercury production rates and concentrations in sediment pore water, surface water and biota. The District considers the sulfide hypothesis to be the most self-consistent explanation for the observed pattern of methylmercury contamination of the Everglades. The status of the Park and southern WCA-3A with regard to sulfate, sulfide and methylmercury production remains under study. Very low sulfate and phosphate concentrations may or may not limit the activity of sulfate reducing bacteria and hence inorganic mercury methylation in the most pristine Everglades (C. Gilmour, ANS, pers. comm., 1998).

The Role of Iron in Mercury Cycling in Aquatic Ecosystems

Iron with formal oxidation state II or III predominates in waters low and high in dissolved oxygen, respectively. Although free iron species may be present in significant concentrations under highly acidic and anoxic conditions (Stumm and Morgan, 1970), this is not the case near neutral pH under oxic conditions, in which iron forms oxy-hydroxide complexes with a high affinity for positively charged metal species, including inorganic mercury (Dmytriw et al., 1995). When oxic soils are flooded, conditions change from oxic to anoxic, resulting in the dissolution of the iron oxy-hydroxide complexes, which releases the inorganic mercury for chemical and biochemical reactions, including methylation (Dmytriw et al., 1995). Recent studies in Lake Superior have demonstrated the ability of dissolved Fe(III) to significantly increase the photoproduction of elemental mercury in surface water under oxic conditions (Hong and Lindberg, ORNL, pers. comm., 1998).

Iron influences the mercury cycle through the sulfur cycle by forming a Fe_xS_y polysulfide complex or as FeS, which is very stable precipitate under a variety of anoxic ambient freshwater conditions. By sequestering the $S^=$ produced by sulfate reducing bacteria in one of these two ways, the presence of Fe(II) may alter the concentration of the neutral polysulfide complex of inorganic mercury that is believed to determine the rate of inorganic mercury methylation by sulfate-reducing bacteria under anoxic conditions. However, the Everglades peat soils are naturally deficient in Fe (Snyder, 1992), but the importance of this to the Everglades mercury cycle remains to be learned.

In enriched surface waters, the daily cycle of enrichment and then depletion of dissolved oxygen with the photosynthetic cycle of plants can be matched by the shift from a Fe(II) to Fe(III) predominance during the day and Fe(III) to Fe(II) predominance at night. This links the iron cycle to the oxygen, carbon and phosphorus cycles. Photoreduction of Fe (III) to Fe (II) has also been observed in highly humic water (Miles and Brezonik, 1981). This links the iron cycle to the sun cycle.

What is the Significance of the Everglades Mercury Problem?

This section describes the nature, magnitude, and extent of the Everglades mercury problem, and summarizes our current understanding of mercury as an environmental contaminant with health implications for both humans and wildlife.

Full Enjoyment of the Sport Fishery is No Longer Possible

In 1989, the results of a joint monitoring project by the DEP, Game and Fresh Water Fish Commission, and Department of Health indicated that largemouth bass from several locations in the Everglades averaged approximately 2.4 parts per million (mg/Kg) of mercury in the edible portion of the fish (Wave et al., 1990). By comparison, the Department of Health action level for limited human consumption is 0.5 ppm and that for no consumption is 1.5 ppm. This led to the issuance of a series of health advisories by the state Health Officer beginning in March 1989 that eventually encompassed all of the Everglades, Big Cypress National Preserve, and eastern Florida Bay (Strom and Graves, 1995). These advisories recommend no consumption of a number of sport fish species caught from Water Conservation Areas 2 and 3 and limited consumption for several species of fish caught from Water Conservation Area 1 (the Refuge), Big Cypress National Preserve, and eastern Florida Bay.

Human Health Effects from Everglades Mercury Exposures Remain a Concern

What are the known and potential consequences of mercury in the Everglades on human health? Based upon current knowledge of mercury toxicity, there are no direct effects to human beings from drinking or contact with waters containing the levels of inorganic mercury and methylmercury that are found in the Everglades (WHO, 1976; USEPA, 1980; WHO, 1990; Clarkson, 1994; USEPA, 1997). The only quantitatively significant pathway for methylmercury to exert its toxic effects on humans by consumption of predators high in the food chain, which have bioaccumulated high levels of mercury. If humans, particularly pregnant women, were to eat sport fish from the Everglades, they would be at risk from methylmercury toxicity (USEPA, 1997). Signs at some water access points warn of these effects. Literature prepared by the Game and Fresh Water Fish Commission for distribution with fishing licenses also contains these warnings.

No documented adverse human health impacts from environmental methylmercury exposures are known in South Florida. Studies of people eating fish caught in South Florida carried out by the University of Miami (Fleming et al., 1995) and the Centers for Disease Control (CDC, 1994) found that mercury body burdens were proportional to fish consumed, but not sufficiently elevated to cause toxicity. However, these studies had limited representation of subsistence fishermen.

Wildlife Effects from Everglades Mercury Exposures May be Problematic

The high concentrations of methylmercury in largemouth bass could potentially interfere with egg viability (J.Wiener, USGS, pers. comm., 1997), but the studies planned to address such effects have not yet been conducted. Fish-eating top predators like the alligator (Heaton-Jones, et al., 1997), the otter (FPIC, 1991), the raccoon (FPIC, 1991), and the Great Egret (Frederick et al., 1997) are exposed to high mercury concentrations in Everglades fish and all have been shown to bioaccumulate methylmercury to high levels in some locations. However, there is as yet no evidence of adverse effects on reproductive success in any of these species in any location that can be attributed to methylmercury exposure. In some instances, for example for the otter, this is because no such studies have been conducted, and in other instances, for example for wading birds, the evidence is ambiguous.

The Florida panther exhibits a preference for hog and deer (Roelke and Glass, 1992) but under some circumstances will feed on the raccoon (Roelke and Glass, 1992), an animal that is linked by its feeding preferences to the aquatic food web and may bioaccumulate high concentrations in mercury, depending upon diet and feeding location. Thus, panthers that feed on raccoons may bioaccumulate mercury, as well (FPIC, 1989). Mercury contamination of Florida panthers has been documented, with the highest levels observed in animals examined in the southern Everglades in the late 1980s and early 1990s. Elevated mercury levels were documented in three panthers that died in Everglades National Park in the period 1989-1991. Clinical symptoms of mercury toxicosis were not evident, but mercury contamination could not be ruled out as a contributing cause of death. Effects of mercury on the panther population and reproductive success are unknown. Recent data suggest that mercury levels in these populations have declined substantially over the last decade (T. Logan, FGFWFC, pers. comm., 1998). A comprehensive review of Florida panther mercury monitoring data for the last 10 years and an assessment of the risks posed by methylmercury exposure will be conducted during 1999 (T. Logan, FGFWFC, pers. comm., 1998).

Based on studies conducted by Peter Frederick, Marilyn Spalding, and co-workers at the University of Florida, high concentrations of mercury have been found in a variety of organs and tissues from the Great Egret. Methylmercury in the diet of individual birds may be sufficient to produce chronically toxic effects (Zillioux et al, 1993), but there is as yet no definitive evidence of effects at the population level (Frederick et al., 1997). There have been no systematic studies of Florida Bay bird colonies for mercury effects, but in a reconnaissance study, mercury concentrations in cormorant livers ranged from virtually non-detectable to almost 200 mg/kg (Powers, 1994; Sepulveda et al., 1996). There has been an estimated 90% decline in wading bird populations in South Florida since the mid-1930s. While loss in habitat area and quality is believed to be the primary cause (SFWMD, 1992), methylmercury toxicity has not yet been ruled out as a contributing factor. Ongoing studies supported by the DEP continue to examine the effects of methylmercury on the various species of Everglades wading birds. The culmination of this work will be a large, regional, population-based study of the effects of mercury on wading bird reproduction and survival, presuming that a suitable species can be selected and multi-agency funding secured.

Does the Florida Class III Water Quality Standard for Total Mercury Need Revising?

In the early 1990s, Florida adopted as its Class III numerical Water Quality Standard the mercury criterion for surface water recommended by the USEPA, which is 12 parts per trillion (ng/L). USEPA Region 4 collected water, fish, and sediment samples semi-annually in May and September at about 50 sampling sites in the Everglades canal system in 1993-94 (**Figure 7-1a**) and at about 150 sites in the interior marshes (**Figure 7-1b**) in 1995-1996 using new sampling and analytical methods for ultra-trace mercury analysis. From 1994-97, the District also assisted USEPA Region 4 in collecting biweekly water samples for total mercury and methylmercury analysis at eight structures in the Everglades canal system. No samples exceeded 12 ng/L (J. Stober, USEPA Region 4, pers. comm., 1998). In 1997 the District began quarterly monitoring of nine structures in the Everglades canal system (see **Figure 6**). The data obtained by the District to date are consistent with the USEPA results.

These water quality data demonstrate that mercury concentrations in the Everglades Protection Area are consistently below the Florida mercury criterion of 12 ng/L (USEPA, 1998). Despite the fact that the criterion is not being routinely exceeded, it has been necessary to issue public health advisories for human fish consumption. In addition, fish-eating birds (Frederick et al., 1997) and other animals (Fink and Rawlik, 1998) are exposed to potentially harmful levels of methylmercury in their diet. The high concentrations of methylmercury in Everglades preyfish species may be toxic to wildlife like fish-eating birds, including the anhinga, and fish-eating mammals, including the otter (Fink and Rawlik, 1998). Ongoing studies are intended to determine whether such toxic thresholds have been crossed.

There is now widespread belief that the recommended Standard is not adequate to protect human health and wildlife populations where methylmercury concentrations and bioaccumulation factors are high, as is the case in the Everglades. Recognizing this, the USEPA has stated its intent to initiate rule making to develop a more appropriate water quality criterion (J. Perciasepe, Assistant Administrator for Water, USEPA, pers. comm., 1996) to guide the states in promulgating updated Water Quality Standards for mercury. To support to development of a revised Everglades Water Quality Standard for mercury, monitoring and research in the area should be expanded, especially as regards wading bird feeding behaviors and susceptibilities to methylmercury toxicity.

The DEP has determined that Health Department warnings about fish consumption impair the designated beneficial use of recreation that applies to these Class III waters. Because those waters do not exceed the existing Standard, but are use-impaired, the Standard is inadequate and must be revised. Studies are underway to define a criterion for methymercury that is adequate for both human fish consumption and the propagation and maintenance of a healthy, well-balanced population of fish and wildlife.

Can the Sources of Everglades Mercury be Adequately Controlled?

Mercury levels in the Everglades have increased substantially in the 20th Century, most probably as a result of human activity. A comparison of surface water inputs with atmospheric inputs indicates that at present more than 95% of the new mercury entering the Everglades each year is from the atmosphere. Determining how much of this contribution comes from local versus global sources is a difficult scientific problem. Initial studies of atmospheric mercury are nearing completion and others are planned to more completely address this question. Although the District and DEP have limited influence on the availability of previously deposited mercury for recycling back into the Everglades ecosystem, modeling suggests that the natural creation of fresh peat should be able to bury previously-deposited mercury beneath the zone of maximum methylation in a timeframe of decades, not centuries.

To put the potential sources of Everglades mercury contamination into perspective, first a summary of the worldwide trends in mercury accumulation is presented followed by trends in the Everglades. Next, the contributions to the annual Everglades mercury load from EAA stormwater runoff, rainfall, and dry deposition are quantified. Then the evidence regarding the contributions of local versus global sources of atmospheric deposition to the Everglades is considered. Finally, several new studies, which are just underway, are discussed to quantify the relative contributions of the most significant air source categories. Ultimately, the results of these new studies will guide source control decision-making.

Historical Trends of Mercury Worldwide

Since the advent of the Industrial Revolution, atmospheric emissions and deposition back to the earth's surface have increasing substantially. Present-day emissions to the atmosphere are thought to be approximately five times the pre-industrial, background rate (USEPA, 1997). The major sources are combustion of fossil fuel, particularly coal, and municipal and medical waste incinerators. Other sources are mining and smelting of mineral ores, including mercury ore, and the use and disposal of mercury-containing goods (USEPA, 1997). Globally, mercury concentrations in the air over sites remote from local air emissions sources are increasing (Slemr and Langer, 1992; Hultberg et al., 1994) and have increased about three-fold over pre-industrial background levels (Fitzgerald, 1989). Atmospheric deposition to those environments is high (Rada et al., 1989; Swain et al., 1992; Hultberg et al., 1994). Pristine lakes from remote regions exhibit high concentrations of total mercury in top-predator fish and the terrestrial organisms that consume them (Hakanson et al., 1988; Fitzgerald and Watras, 1989; Lathrop et al., 1991). In some heavily populated, industrialized regions, there has been up to a 10-fold increase in mercury deposition (Mercury Atmospheric Processes Expert Panel, 1994). The greatest increases in deposition are in industrialized regions and reflect both increased total emissions and the enhanced local deposition rate caused by particulate and reactive forms of mercury that do not enter the global cycle. However, in a radiodating study of a ombrotrophic peat bog cores in rural Minnesota, Benoit et al. (1994) concluded that mercury deposition has actually declined beginning in the 1960s. A similar pattern may have been observed in Florida Bay sediment cores (T. Atkeson, DEP, pers. comm., 1997).

Historical Trends of Mercury in the Everglades

The DEP, District and USGS sponsored studies of the profiles of mercury in Everglades soils. Dr. Joseph Delfino and his students of the University of Florida collected and sectioned approximately 50 soil cores from the three WCAs and Everglades National Park. Using the activity of an isotope of lead, Pb^{210}, produced in the hydrogen bomb blasts of the early 1960s as a date reference, they developed a relationship between peat depth and time of deposition. Dates were corroborated using an isotope of cesium, ^{137}C, also originating with hydrogen bomb testing. The sections were analyzed for total mercury concentration and, together with the estimated sediment accumulation rates, the scientists were then able to reconstruct the historical profiles of mercury accumulation rates in the Everglades from approximately 1900 to 1990. Although the results between sites were highly variable, on average the mercury accumulation rate in Everglades peat appeared to increase approximately five-fold since the late 1800s (Rood et al., 1996). Thus, the DEP and the District have concluded that the Everglades is a mercury-contaminated system, with mercury concentrations in modern peat well above pre-industrial background.

Surface Water Discharges of Mercury into the Everglades

From February 1994 through February 1997, the District assisted USEPA Region 4 with biweekly collections of water quality samples representative of Lake Okeechobee and EAA discharges at seven of the District's major structures. Samples were collected using clean technique for ultra-trace analysis of total mercury and methylmercury by Florida International University. No significantly elevated concentrations were evident in the District's canals, and the total annual load of total mercury into the northern Everglades from the EAA was in the range of 1 to 4 Kg/yr (USEPA, 1998), which is less than 5% than the amount estimated to be deposited on the Everglades by bulk rainfall (see below). In May 1997, the District expanded the mercury monitoring network to nine structures, but the frequency of collection was reduced to quarterly. This monitoring program is now a requirement in permits issued for each of the STAs and for the so-called “non-ECP” structures. Based on the first full year of monitoring, an apparent seasonal influence of inorganic mercury deposition from rainfall on surface water quality has been observed in Everglades canals, with both inorganic mercury and methymercury concentrations increasing in the summer and fall wet season and decreasing in the winter and spring dry season.

Mercury in Rainfall

From 1992 through 1996, the DEP, the District and others co-funded the Florida Atmospheric Mercury Study (FAMS), conducted by Dr. William Landing of FSU, Dr. Gary Gill of Texas A & M and Dr. Curtis Pollman of Tetra-Tech (Guentzel et al., 1995). The FAMS monitoring sites are depicted in **Figure 7-2**. FAMS monitored mercury concentrations in wet and bulk deposition, mercury on particles, and total gaseous mercury concentrations (mostly elemental mercury) in air at seven, 48-ft. towers in southern Florida through December of 1996. Samples were collected over a month-long period to integrate wet, bulk, and particulate mercury deposition over a relatively long period of time. This study focused on wet deposition and provided little information about dry deposition, which is not likely to be captured efficiently even by the bulk rainfall collector (J. Keeler, UMAQL, pers. comm., 1996). FAMS results demonstrated that there is little mercury on atmospheric particulate matter. It also demonstrated that the mercury concentration in rain was considerably higher during the wet season than during the dry season and had a volume-weighted annual average concentration of about 14 ng/L for the six sites near the Everglades (Guentzel, 1997). This equates to a rainfall deposition rate of about 21 $\mu g/m^2/yr^1$, which is about twice the rate reported for northern Wisconsin (Vandal et al., 1995). Assuming this is a representative value over the entire 3,150 square miles of the remnant Everglades, this is equivalent to an annual atmospheric wet deposition of approximately 140 kg/yr (USEPA, 1998).

Mercury in Dry Deposition

As discussed in the **The Mercury Cycle** section, mercury in air may be deposited on water, soil, or plant surfaces in rainfall, on settling dust, or in one of two gaseous forms: elemental mercury and reactive gaseous mercury or RGM. Due to its volatile nature, elemental mercury tends to adsorb to and be re-emitted from surfaces relatively rapidly, and, due to its relatively low concentrations and low reactivity, it may be of little environmental significance until it is converted to RGM. RGM, on the other hand, has a high affinity for surfaces and readily deposits on them, even without the assistance of settling dust. This dry deposition is in contrast to wet deposition, in which RGM is scavenged from the air by cloud formation or rain. Using the best estimates presently available for RGM air concentrations and deposition rates, together with cattail and sawgrass leaf turnover rates, one can estimate a dry deposition rate for mercury to the Everglades that is up to double the wet deposition rate (W. Landing, FSU, pers. comm., 1996). This may explain the discrepancy between the average mercury deposition rate obtained by Delfino et al., (1993) in the radiodated sediment core study of about 45-50 µg/m2/yr and that obtained in the FAMS study of 21 µg/m2/yr.

Dry deposition has not been extensively studied because of the difficulty of measuring it and the literature and present estimates of its abundance and properties are few and highly uncertain. DEP and

USEPA have developed new methods to measure RGM in air. Direct and rapid measurement of RGM will be essential to understanding the contributions of local emissions sources to Everglades mercury deposition. Field measurements of RGM and its deposition began in August 1998 and will continue through 1999.

Estimation of Mercury from Local Sources

A screening-level inventory of air emissions sources in Florida indicated that there are a number of significant sources in Broward and Dade counties (KBN, 1992). The South Florida Atmospheric Monitoring Pilot Study was conducted to more accurately quantify mercury emissions from representative local air sources in South Florida. This effort was a one-month intensive study of a municipal waste incinerator, a medical waste incinerator, and a cement kiln located in Dade or Broward Counties, coupled with intensive ambient measurements at 17 monitoring sites in the wind sector downwind of the sources. The conclusions that can be drawn from this preliminary study are: (1) local municipal and medical waste incinerator emissions account for between 250 and 500 kilograms per year of mercury air emissions in South Florida; (2) RGM, the predominant species in both rainfall and dry deposition, was present in emissions from these sources in much greater proportions than previously believed; and (3) local sources have the potential for significantly affecting mercury deposition on the Everglades (Dvonch et al., 1995; Dvonch et al., 1998; Dvonch, 1998). A more extensive study is planned.

The Potential Efficacy of Local Source Control

Significant reductions in local air emissions of mercury have occurred as a result of regulation of municipal solid waste incinerators and further reductions are anticipated in response to DEP rules precluding the disposal of the mercury-containing wastes like batteries and fluorescent lights destined for municipal incineration. Similar rules will also reduce the mercury emissions from medical waste incinerators. Additional emissions controls could then be required to reduce emissions still further to meet Everglades water quality restoration objectives. However, if local source emissions are not making a significant contribution to Everglades contamination, with what justification could these additional emissions controls be mandated? Thus, it is first critical to establish the link between local air emissions sources and Everglades mercury contamination. Unfortunately, our current knowledge of mercury sources and the effectiveness of source control are too limited to make the required predictions with the desired confidence at this time. This is now the focus of follow-up studies co-funded by the DEP and USEPA.

Can Management of Water Quantity and Quality Reduce Mercury Risks?

In this section, an attempt is made to identify possible manipulations of Everglades water quantity or quality that might be able to reduce methylmercury production, bioaccumulation, and exposure to acceptable levels. However, based on the present level of understanding and in the absence of a complete mathematical model with the required linkages between Everglades water quantity and quality and the mercury cycle, this analysis must be considered educated speculation at present. As the uncertainties in the basic understanding of the processes that govern mercury methylation and bioaccumulation in the Everglades are reduced over the next several years and the Everglades Mercury Cycling Model is completed, this section will be revised as needed.

Managing Methylmercury Production and Transport through Hydrological Controls

Based on the conceptual model of mercury cycling in aquatic ecosystems developed in the **The Mercury Cycle** section, an increase in hydraulic residence time should result in an increase in methylmercury concentrations in the water column at a constant rate of production of methylmercury per unit area of sediment. However, there is a link between water flow and depth based on the resistance to flow by the bed and vegetation over and through which the water passes. If flow and depth increase or decrease simultaneously, the effect on hydraulic residence time and thus methylmercury concentrations is less clear. Pulsed inflows and outflows or hydrologic short-circuiting further complicate this relationship. In addition to effects on retention time, flow and depth affect the transport of oxygen from the air to the sediments. Dissolved oxygen is involved in the biogeochemistry of mercury methylation in several important ways. Flow and depth also affect water temperature in the marsh. These are complex relationships. Absent the results from a calibrated model of the Everglades that links hydrodynamics to particle transport and water chemistry, the prediction of the effect of depth, flow, or both simultaneously on water column methylmercury concentrations must be considered highly speculative.

Some of the results of the USEPA study of the Everglades mercury problem (USEPA, 1998) indicate that methylmercury concentrations in water and fish in WCA-3A are highest in the dry season, when water depths drop and flow is virtually nonexistent. The extremely long hydraulic residence times arising from these conditions can be considered the equivalent of standing water, in which circulation and mixing are wind-induced, not flow-induced. A similar pattern has emerged in the mass budget studies in the ENR Project, where methylmercury concentrations in the supply canal and the discharge canal appear to increase when the canals are stagnant and decrease when the pumps are running. However, the opposite pattern is observed in the ENR Project in open water areas following the onset of the intense, highly contaminated summer rainfall, with methylmercury concentrations peaking four to eight weeks later and mosquitofish concentrations peaking in the following quarter (SFWMD, 1998).

Water depth may also affect water chemistry by another mechanism. An increase or decrease in water depth may decrease or increase the wind-induced agitation of the sediment and mixing of the water column, resulting in a decrease or increase in the dissolved oxygen concentration in the water column at any depth. Thus, deeper water may result in lower dissolved oxygen concentrations, especially near the sediment-water interface during the day and throughout the water column at night when plants switch from being oxygen producers to oxygen consumers. This may increase the rate of inorganic mercury methylation by sulfate-reducing bacteria that require an oxygen-free environment in the surficial sediments.

Due to the high concentrations of dissolved organic matter (DOM) present in EAA runoff and northern Everglades water (**Chapters 4** and **3**), increased water depth will reduce the penetration of the photoactive wavelengths of light through the water column (G. Aiken, USGS, pers. comm., 1997). Light reduction will have the probable effect of reducing the rate of photodemethylation of methylmercury (D. Krabbenhoft, USGS, pers. comm., 1997) and the photoproduction of elemental mercury (S. Lindberg, ORNL, pers. comm., 1997).

Water depth also affects the interaction of surface water and ground water. At some locations in the northern Everglades where the confining layer never formed or has been breached by human activity (e.g., canal construction), the head difference between adjacent impoundments can cause surface water to seep down into the peat and calcareous rock formations and under levees only to well up at other locations at lower head (Harvey et al., 1998). When the direction of seepage is downward, the concentration of inorganic mercury in the peat pore water may be more strongly determined by the concentration in the overlying water than by equilibrium partitioning amongst pore water phases. In addition, readily exchangeable fraction of inorganic mercury in the peat soil may be leached into the underlying soil and thence the surficial aquifer. Methylmercury produced at the soil-water interface may be transported (advected) into the peat in competition with diffusion into the overlying water. This would have the net effect of reducing the influence of peat methylmercury production on the concentration of methylmercury in the overlying water column.

Where the direction of ground water movement is up through the peat into the overlying water column, methylmercury production may be enhanced by increasing the rate of supply of bioavailable inorganic mercury, carbon substrate, or sulfate oxidizer or suppressed by increasing the concentration of sulfide in pore water. Once produced, the methylmercury will be advected into the water column in the same direction as the diffusion gradient, enhancing the influence of the underlying peat on water column methylmercury concentrations.

The study of groundwater-surface water interactions and their influence on methylmercury production and transport is now the focus of a University of Wisconsin doctoral dissertation by Sue King of the USGS (S. King, USGS, pers. comm., 1997). King is conducting this work in conjunction with groundwater transport studies being carried out in the ENR Project and WCA-2A by Judson Harvey of the USGS (Harvey, 1998).

Managing Methylmercury Exposure through Hydrological Controls

Water depth may affect feeding rates and food web relationships and, in this way, affect the bioaccumulation of mercury by Everglades biota. Water depth is thought to affect the rate of growth of fish in the Everglades, with deeper waters favoring increased growth rates and shallower waters favoring slower growth rates (T. Lange, Game and Fish, pers. comm., 1996; Chapter 4). Shallow waters will have the effect of crowding the fish into deeper pools, and crowding is known to reduce growth rates in fish. In addition, shallow waters limit access of large fish to their prey. This may result in reduced feeding rates or prey switching. Shallow waters will also tend to be warmer, and warmer water results in an increase in fish metabolism, with increased feeding rates, which can increase the bioaccumulation of methylmercury. Higher rates of fish feeding and respiration, coupled with slower growth rates, are likely to result in an increase in methylmercury concentrations in the fish (Norstrom et al., 1976; Rodgers, 1994). This effect could be amplified by an increase in methylmercury concentrations in these shallow, stagnant pools. The opposite effect is expected to occur in deeper water. These natural cycles in the concentrations of methylmercury in fish tissues related to the hydrology of the system complicate the identification and interpretation of long- term trends in overall methylmercury exposures in the Everglades ecosystem.

Where the depth is too great, wading birds will not feed (D. Gawlik, SFWMD, unpublished data, 1997); thus, they will not be exposed to whatever mercury their prey contains in these locations. On the other hand, in areas where vegetation types and densities do not preclude access, shallow water depths favor foraging by wading birds. If shallow pools facilitate methylmercury production as speculated above, wading birds foraging there during low-water conditions might be more exposed. However, the consequences of this may not be serious because of the wide-ranging nature of wading birds and the long half-life of methylmercury in their bodies that integrates and averages exposures over many months. The exception to this might be in consecutive years of extended drought and extended flood over all of South

Florida, when average methylmercury concentrations in the wading birds that did not migrate from the area might be expected to increase and decrease, respectively. If they occur, these natural cycles in the concentrations of methylmercury in wading bird tissues related to the hydrology of the system will complicate the identification and interpretation of long-term trends in overall methylmercury exposures in the Everglades ecosystem.

While the qualitative predictions given above may be helpful in the design of further studies, it is not now possible to quantify the relationship between stage-duration at a particular location and the magnitude of methylmercury increase or decrease in a particular fish species due to these depth-related phenomena. Also, correlation between depth-duration and methylmercury concentrations in fish obtained in the interior marsh would not necessarily apply to wide-ranging fish with access to the canals such as gar and largemouth bass. This is also true of wading birds. Thus, the accurate, quantitative prediction of the effect of stage-duration (hydroperiod) changes on methylmercury bioaccumulation in fish and wading birds is beyond the state of the science at this time.

Managing the Methylmercury Production and Bioaccumulation via Water Quality Controls

Water quality in the discharges from District structures to the Everglades will be affected through upstream treatment in STAs and any additional treatment that may be associated with them. STAs will remove phosphorus and nitrogen and will otherwise alter the quality of runoff discharged into the Everglades Protection Area in many ways that may affect the biogeochemistry of mercury methylation. The relationship between hydrology and chemistry is summarized above. The effect of the reduction of downstream loadings and concentrations of phosphorus will be taken up in the next section on the effects of the STAs on mercury risks within their borders and downstream. The potential effects of changing EAA soil amendment practices with sulfur and iron is taken up here, along with the possibility of chemical addition of sequestrants and detoxicants like selenium to treated EAA runoff prior to discharge to the Everglades.

Sulfate is important because it is an obligatory substrate for the sulfate reducing bacteria that create methylmercury. Sulfide, which is a product of the metablism of sulfate reducing bacteria, may be essential in low concentrations for entry of inorganic mercury into the bacterial cell. In higher concentrations, sulfide may render inorganic mercury unavailable. Thus, sulfide may facilitate or inhibit methylmercury production depending upon concentration (Gilmour, 1997). Sulfide production and its destruction or recycling into sulfate may be related to phosphorus levels and eutrophication.

Studies carried out by Orem et al. (1998) on the isotopes of sulfur in various potential source waters have allowed them to distinguish the relative contributions of rainfall, groundwater, and EAA stormwater runoff to the sulfate concentrations present in the northern and central Everglades. Their results indicate that the EAA stormwater runoff is a significant source of sulfate to the ENR Project and the northern and central Everglades. Orem et al. (1998) have traced some of the sulfate in EAA discharges to the practice of amending EAA soils with a polysulfur compound to lower soil pH and release bound phosphorus for sugar cane plant uptake. This practice may be partly responsible for the high levels of sulfate in WCA-2A and downstream. Based on the work of Harvey (1998) and Orem et al. (1998), the ENR Project removes some sulfate from EAA runoff. STAs are expected to behave in the same way. How changes in agricultural sulfur addition would influence Everglades mercury cycling is unknown. There is little quantitative rate information about how the sulfur cycle and eutrophication interact to affect mercury methylation rate, but this is understood to be fundamental. The continuation of Dr. Cynthia Gilmour’s studies on the role of the sulfur cycle in the Everglades mercury problem is considered essential for determining how the post-ECP rate of discharge of sulfate to the northern and central Everglades will affect the Everglades mercury problem.

Understanding the interaction of the iron and sulfur cycles with the mercury cycle should become a high priority for Phase 2 of the SFSMP. Some of the proposed supplemental technologies (e.g., ferric sulfate precipitation of phosphorus) may inadvertently affect the rates of inorganic mercury methylation or methylmercury bioaccumulation by changing the iron and sulfate content of EAA runoff. The protective effects of selenium on animals bioaccumulating mercury are not well understood. Chemical addition experiments involving the introduction of selenium in Swedish lakes to decrease inorganic mercury availability for methylation and to decrease the toxic effects of the bioaccumulated methylmercury have proven generally unsuccessful (D. Porcella, EPRI ret., pers. comm., 1997).

How Will the Everglades Construction Project Affect Mercury Risks?

Introduction

As is the case for many water bodies in Florida and elsewhere, there is a mercury problem in the Everglades. An important question is whether mercury will bioaccumulate to even higher than present levels in top predators as the result of changes brought about by the ECP. This section addresses the potential for increased bioaccumulation of mercury caused by the changes in water quantity and quality following the construction and operation of the STAs. The following concerns have been addressed:

- Mercury released from newly flooded soil following STA construction will cause harmful amounts to be discharged to the Everglades (“soil release effect”).
- Mercury bioaccumulation in invertebrates and fish living within the STAs will harm wildlife that prey on them (“reservoir effect”).
- Mercury from inflows that is bound to newly formed sediments in the STAs will eventually build up to a hazardous concentration (“hazardous waste site effect”).
- Mercury exposure to wildlife will increase because STA phosphorus removal will reduce the extent of eutrophication in the Everglades marsh downstream of the STAs (“inverse relationship effect”).

Mercury measurements made by the District over a four-year period on the ENR Project, a prototype STA, show that the first three concerns are not supported by the data (See **Appendix 7-1**).

The fourth concern was put forth by the Sugar Cane Growers Cooperative (Coop) in a formal challenge to the permit issued to the District for the ENR Project under Section 402(a) of the Clean Water Act in May 1994. Supporting documentation was supplied by its contractor, PTI (1994). The documentation was submitted during testimony on the draft legislation for the Everglades Forever Act (PTI, 1994), at the time of issuance of the Programmatic Environmental Impact Statement for the ECP in September 1996 (PTI, 1995b), before the Environmental Regulation Commission in January 1997 (PTI,

1997) and at the time of issuance of the Clean Water Act Section 404 Dredge and Fill Permit for the ECP in March 1997. A revised report has been prepared by PTI/Exponent (1998) as a formal submission of data and findings to be considered in this Everglades Interim Report.

Since the Coop first filed its mercury-related challenges to the ENR Project permit in 1994, the documentation supporting this challenge and subsequent comments have not been updated with important new data on wading bird exposures and toxic effects (PTI, 1994, 1995a,b; 1997; Exponent, 1998). The District has now done this and its methods, data, and results of a new methylmercury ecological risk assessment for Everglades wading birds are detailed in **Appendix 7-2**. The updated assessment summarized in this section shows that operation of the STAs is not likely to increase methylmercury risks to downstream wading birds in the phosphorus-impacted areas to unacceptable levels. DEP concurs with this conclusion.

Effects Internal to the STAs

Prior to passage of the Act, the ENR Project was constructed on former farmland as a 3,815-acre demonstration-scale STA. It is located at the northwest corner of the Arthur R. Marshall Loxahatchee National Wildlife Refuge. Extensive studies of the ENR have provided much valuable information about how the STAs will behave. The ENR Project was designed to treat about one-third of the stormwater runoff from the EAA that would otherwise be discharged untreated through the S-5A Pump Station into the Refuge, an Outstanding Florida Water (Guardo et al., 1995). Both state and federal permits were required to construct and operate the ENR Project. The federal permit to discharge was issued under Section 402 of the Clean Water Act in May 1994. Challenges to the permit were filed by the Sugar Cane Growers Cooperative of Florida, the Miccosukee Tribe of Indians of Florida, and the Everglades Coalition. In August 1994, a temporary order was issued by a U.S. Environmental Protection Agency administrative law judge that allows the District to operate the ENR Project until such time as the issues raised in these administrative petitions are resolved.

The key mercury concerns raised by the petitioners were that mercury might be released from newly flooded soils, that it might bioaccumulate in wildlife prey species in the STAs and that mercury would eventually accumulate to hazardous levels in the newly created sediment. These hypotheses are discussed in this subsection. The concern that mercury exposure to wading birds might increase as a result of alleviation of eutrophication was also raised; this is discussed in the following subsection. Subsequently, these same concerns were raised in comments on the Programmatic Environmental Impact Statement for the Everglades Construction Project, in comments on the 404 Dredge and Fill permit issued by the U.S. Army Corps of Engineers for the ECP, in the administrative challenges to the EFA permit for the so-called “non-ECP” structures, and in comments on the EFA STA 6 permit.

In the absence of the results of scientific studies, these concerns were based on analogies to experiences elsewhere with some lakes and wetlands. Since then, four full years of ENR mercury monitoring (Miles and Fink, 1998; SFWMD, 1998) have demonstrated that these concerns were unwarranted (See **Appendix 7-1**). The District’s data show the following:

- The Florida Class III Water Quality Standard for total mercury was never exceeded at the outflow.

- On an annual average, ENR outflow concentrations for total mercury and methylmercury were always less than inflow concentrations. Between 50% and 75% of the total mercury and methylmercury entering through the ENR inflow pump was removed.
- Fish in the ENR have less mercury than those found anywhere else in the Everglades system, with but a few exceptions. Fish from the interior and outflow ENR stations have lower mercury concentrations than at the inflow and L-7 reference site, with but a few exceptions.
- Mercury concentrations in ENR sediments are below the Everglades average of 150 µg/Kg, are less than the 100 ug/kg used by USEPA Region 4 to define hazardous levels, and are declining.

Based on the review of the literature and the conceptual model of mercury transport, fate, and bioaccumulation in the section on **The Mercury Cycle**, and based on the further development and application of that conceptual model in the section that answers the question, *Can the management of water quality and quantity reduce mercury risks to acceptable levels?*, the District and DEP have concluded that there is no reason to believe that the STAs will perform substantially differently than the ENR Project with respect to either phosphorus or mercury removal. Thus, the USACE, USEPA and DEP continue to have reasonable assurance that the STAs will not exhibit soil release, reservoir, or hazardous waste site effects, or experience increased mercury levels in the fish growing within them.

While the above results are highly encouraging, there are two caveats that must be considered. First, the ENR Project has only been operated for four years and its retention efficiencies could change during its working lifespan (see Chapter 6). However, there is no evidence to indicate that this or any other constructed wetland will become any more susceptible to a mercury problem than the portions of the impounded northern Everglades they are designed to emulate. The reasons for this are summarized in the section that answers the question *Can the management of water quality and quantity reduce mercury risks to acceptable levels?* Second, the results of the first two quarterly grab samples in the first three months of operation indicated that STA 6 outflow concentrations were numerically higher than the inflow concentrations, although the differences were not statistically significant. The third quarterly sample results reversed this relationship. Additional sampling should make it possible to determine whether this apparently anomalous behavior is an artifact of the choice of outflow sampling site or a transient phenomenon associated with start-up (see Chapter 6). STA 6 performance will be evaluated further in the next Everglades Peer-Reviewed Report when more data have become available.

Effects Internal to Supplemental Technologies

Supplemental technologies are designed to reduce the total P concentrations in STA effluent from 35-50 ppb to the threshold no imbalance concentration or 10 ppb, whichever is appropriate. Several of the supplemental technologies to be evaluated using the ENR Project mesocosms (test cells) will employ more conventional treatment chemistry and physics (e.g., precipitation, flocculation, and settling, and/or filtration) to achieve this water quality objective, while others will employ conventional (wetland) or unconventional (periphyton-based wetland) biological treatment systems. These proposed supplemental technologies and their testing schemes are described in **Chapter 8** of this report. To ensure that supplemental technologies will not become sources of inorganic mercury or methylmercury in wastewater discharges or solid wastes, a scoping-level monitoring program will be implemented. If the outflow concentrations exceed those in the inflow, or if there is substantial accumulation of either total mercury or methylmercury in the solid residues (or fish), the adaptive management strategy calls for the implementation of a more intensive study. Among other things, this screening study will determine whether periphyton-based systems can methylate inorganic mercury, as has been observed in the Everglades (Cleckner et al., 1998). The mercury data collected in each of the scoping studies will not be considered in the overall evaluation of the performance of the supplemental technology unless a problem is encountered.

Effects External to the STAs and Supplemental Technologies

In the previous section of this chapter, the conceptual model of mercury transport, transformation, and accumulation in the Everglades was applied to determine whether changes in water quantity or quality could aid in reducing the production or bioaccumulation of methylmercury or the exposure of wildlife. Using the same conceptual model, in this subsection, the discussion focuses on the potential positive and negative effects that could be brought about by the operation of the STAs, again through expected changes in water quantity and quality. Particular interest is paid to the potential downstream effects from the reduction in phosphorus loads and concentrations to be brought about by the ECP, with and without the potential positive effects of the anticipated simultaneous reduction in stormwater mercury loads. The current status of development of the USEPA Mercury Cycling Model is also discussed and the results of its preliminary applications are summarized and compared to earlier predictions.

To put this discussion in legal context, Section 373.4592(e)3, F.S. of the Act states:

> The department shall use the best available information to define relationships between waters discharged to, and the resulting water quality in, the Everglades Protection Area. The department or the district shall use these relationships to establish discharge limits in permits for discharges into the EAA canals and the Everglades Protection Area necessary to prevent an imbalance in the natural populations of aquatic flora or fauna in the Everglades Protection Area, and to provide a net improvement in the areas already impacted. …

For purposes of implementing this section of the Act, the best information available to define the relationships between the quality of the water discharged to and the resulting water quality in the downstream Everglades is that which has been generated under the South Florida Mercury Science Program, as summarized in the Introduction to this chapter. Using the best available information and a multiple-lines-of-evidence approach, the District and DEP have concluded that restoring the phosphorus-impacted areas to unimpacted conditions by reducing phosphorus loads and concentrations in EAA runoff is unlikely to cause further imbalance in aquatic flora or fauna due to the toxic effects of inorganic or methylmercury, either through direct exposure or via bioaccumulation in the aquatic food chain. The District and DEP have concluded that an increase in the downstream mercury risks to wading birds from the operation of the STAs to unacceptable levels is highly unlikely. Thus, one need no longer give primary consideration to the potential negative effects of mercury on the downstream environment in evaluating the ECP. It follows, then, that there is no reason to slow or halt the construction of STAs 1W, 2, or 5 or to delay the construction of STA 3/4 on the basis of potential mercury risks to aquatic or terrestrial flora or fauna. This subsection provides the technical support for this conclusion.

Background

Risk is the likelihood or probability of experiencing injury or harm from exposure to an intrinsically hazardous substance or circumstance. In this subsection, the focus is on the risk to Everglades wading birds from exposure to methylmercury, a toxic substance produced by naturally occurring bacteria from inorganic mercury. Because methylmercury bioaccumulates up to 10,000,000 times in top-predator fish in the Everglades ecosystem, the primary route of exposure of wading birds to methylmercury is through ingestion of contaminated prey.

The principal tasks in conducting an ecological risk assessment are exposure characterization, effects characterization, and finally the integration of the two results in a risk characterization. In general, use of a suite of methods (e.g., literature values, bioassays, and field studies) produces a more complete characterization of ecological effects than relying on a single measure or literature value. When selecting ecological effects endpoints, ideally, toxicity data will be available for the most sensitive life stage of the most exposed, most sensitive species tested to date over a period of time sufficient to bring out the full toxic effect in the test organism or population. When available, measured concentrations of the toxic substance are always preferred over estimated or modeled values for exposure characterization. Risk characterization then integrates the results of the preferred exposure and ecological effects data for the evaluation of the likelihood that adverse impacts are occurring or will likely occur.

Following the tiered, iterative approach advocated by USEPA (1998b), early risk assessments often rely on simple models to estimate exposure when site-specific data are limited (for case studies, see USEPA, 1993d). Appropriately, these preliminary risk assessments also use maximum concentrations, worst case assumptions about wildlife behaviors (e.g., prey preferences that favor highly contaminated organisms, 100% time of contact in contaminated area), and uncertainty factors to provide the required margins of safety in extrapolating results between short- and long-term studies, between low and no effect endpoints, between life stages, and between species. However, as recommended by the Presidential/ Congressional Commission on Risk Assessment and Risk Management (1997), subsequent assessments should move away from using the hypothetical “maximally exposed individual” to evaluate whether a risk exists, toward more realistic scenarios as more data become available. This was underscored in the experience of promulgating the new methylmercury water quality criterion for the Great Lakes Initiative (Meyers, 1998).

Due to the inherent differences between individuals in a population, the toxicity threshold value, even for a uniformly exposed population, is not a single value but a range of values, with most members of the population exhibiting a toxicity threshold near the mean, and only a few members exhibiting extremely low or high toxicity thresholds. To ensure the protection of a population of organisms in the wild, one must select a highly protective toxicity threshold value. This can be achieved by dividing the laboratory toxicity threshold value for the species of interest by a safety factor or by using a toxicity threshold value from another species known or reasonably expected to be much more sensitive to the toxic substance than the species of interest. This latter approach is the one used by the District. The toxicity threshold value obtained in this way is often referred to as a Toxic Reference Value or TRV.

Following the recommended USEPA procedure for carrying out an ecological risk assessment, the relative likelihood or risk of a toxic effect occurring in a wildlife population can be expressed as a hazard quotient. The hazard quotient is calculated as the ratio of the daily dose actually taken up by the organism through ingestion of contaminated food to the toxicity threshold value for that species. As defined and applied by USEPA, the hazard quotient is an expression of relative risk and should not be used to calculate the absolute risk of toxic effect to an individual organism or a population. As the hazard quotient increases beyond a value of 1, the likelihood that the exposed population will experience a toxic effect in a significant number of its members increases. The more protective the choice of a TRV, the smaller the likelihood or risk that a toxic effect will occur at hazard quotient values greater than 1. By choosing a very protective TRV, one can generally assume that when the hazard quotient is calculated to be less than 1, there is little likelihood or risk of a toxic effect occurring in a significant number of the members of the exposed population. That is the assumption adopted here by the District.

The approach summarized here and set forth in greater detail in **Appendix 7-2** completes the multiple-lines-of-evidence approach for Everglades wading birds advocated by USEPA. The results of this approach reinforce the results of the field population and laboratory bioassay studies of Great Egret exposures to methylmercury in their food (Frederick et al., 1997). Therefore, there is a relatively high confidence level in the results of the ecological risk assessment for wading birds described below.

Wading Bird Risk Assessment

The Importance of Wading Bird Mercury Risks

One of the Class III designated beneficial uses for Everglades waters is the propagation and maintenance of a healthy, well-balanced population of fish and wildlife. In terms of human values, wading birds are one of the most important wildlife assets of the Everglades. For several years the Sugar Cane Growers Cooperative of Florida (Coop) has actively promoted the hypothesis that the P removal for which the STAs are designed will increase the exposure of wading birds and other Everglades wildlife to mercury by eliminating marsh eutrophication. The area where this effect is predicted to be most pronounced is in the “footprint” of the S-10 structures in WCA-2A, where P has accumulated in soils and dense cattail stands have replaced the normally more abundant sawgrass. The Coop arrived at this concern by analogy to the experience with eutrophic lakes and supported the extension of this analogy to the Everglades with a limited set of data collected along the nutrient gradient downstream of the S-10 structures in WCA-2A (PTI, 1995a,b; Exponent, 1998). Many new and relevant data sets have been gathered since the PTI/ Exponent report was written and deserve careful consideration.

The District and the DEP have carefully examined the data and methodology used in the Exponent (1998) mercury risk analysis regarding the choice of maximum allowable daily mercury dose. District and DEP scientists agree with their choice of a maximum allowable daily mercury dose for wading birds. District and DEP scientists do not agree with Exponent’s procedure for estimating the change in the daily intake of mercury that may result from the ECP.

Using extensive data generated by the South Florida Mercury Science Program, the District has performed an independent evaluation of the daily intake of mercury by wading birds. The District also evaluated the methods used by Exponent (1998) to compute daily intake. From these evaluations, the DEP and the District conclude that Exponent’s procedure substantially overestimates the daily intake of mercury by wading birds and, thereby, greatly overstates the risk. Using the District’s more reliable estimates of daily intake of mercury, the DEP and the District find that the ECP will not cause the daily intake of mercury by wading birds to exceed their threshold reference value significantly in the restored areas in the northern Everglades. This means that there is little likelihood that the STAs will increase the mercury risks of downstream wading birds to unacceptable levels. Thus, one need no longer give primary consideration to the potential negative effects of mercury on the downstream environment in evaluating the environmental impacts of the ECP. Details are given below.

Background

In aquatic ecosystems, an increase in the rate of addition of the limiting nutrient above natural rates is often accompanied by unnatural increases in plant densities and growth rates, and a shift from plants that thrive under low-nutrient conditions to those that are competitive only under higher nutrient conditions. The overproduction of plants results in an overabundance of decaying plant matter, which robs the water of dissolved oxygen. This drives out the more sensitive, pollution-intolerant species and allows the encroachment of less sensitive or rough, pollution-tolerant species. At the same time, the primary source of food energy in the ecosystem shifts from living to dead plant matter, and the rate of formation of organic sediment increases. Given sufficient time, if the addition of excess limiting nutrient is unchecked, this acceleration of the process of sediment accumulation will result in fundamental changes in the structure of the ecosystem. Waters manifesting one or more of these characteristics of overproduction are referred to as eutrophic, and the process of the unnaturally accelerated aging of an aquatic ecosystem through the stimulation of excess production is referred to as eutrophication. In the Everglades, P is the limiting nutrient. The characterization of Everglades eutrophication and its relationship to P concentrations and loads are taken up in detail in **Chapter 3**.

The primary purpose of the ECP is to construct STAs to remove P from EAA farm runoff and improve ecosystem hydrology. In this way, eutrophication now occurring in natural marsh areas, over time, will be shifted upstream into STAs built on land that was formerly cultivated, and the marsh will be restored to its natural community composition and function. For some measures of biological imbalance, P levels in water and peat soil serve as a useful surrogate for the biochemical and biological effects of eutrophication. There is evidence to suggest that many eutrophic lakes do not experience a mercury problem and that this is because the lakes are buffered by their overproduction. If it is assumed that inorganic mercury and methylmercury loading rates and the methylmercury production rate are not influenced by the conditions of eutrophication, the increase in biomass standing crop and turnover stimulated by the presence of excess limiting nutrient will result in a decrease in inorganic mercury and methylmercury concentrations in water and biota. As discussed earlier in this chapter, the dilution of methylmercury in plant biomass at the base of the food chain and each successive link in the food chain is referred to as biodilution (Hakanson, 1980).

However, the assumption that methylmercury production is unaffected by eutrophication is probably not valid, with the more anaerobic conditions associated with eutrophication favoring higher rates of methylmercury production, all other factors being equal (USEPA, 1998). Also, excessive plant production changes other water chemistry constituents, such as pH, alkalinity, and dissolved organic matter, among others. Thus, in actuality, the mechanisms by which this “inverse relationship” occurs are not well established, and there are exceptions to its occurrence (Watras, 1995).

There is a tendency to generalize the lake inverse relationship experience to wetlands, even though wetlands do not behave physically like lakes, have some different plant communities and recycle P by some different mechanisms. Thus, there is little likelihood that the lake inverse relationship effect will translate directly into a wetlands or Everglades inverse relationship without major qualification. The South Florida Mercury Science Program is exploring the nature of the important linkages between enrichment and mercury cycling.

Data collected over the entire Everglades during the USEPA study indicate that both TP in water and mercury in mosquitofish decline from the central to the southern Everglades (USEPA, 1998) in a direct rather than inverse relationship. In addition, no inverse relationship has been detected in mosquitofish by USEPA Region 4 in WCA-1 (PTI, 1994) or largemouth bass in WCA-1 (T. Lange, Game and Fish, pers. comm., 1995) or in mosquitofish or largemouth bass in the ENR Project (Lange et al., 1998; SFWMD, 1998). As described by the PTI (1994, 1995a,b)/Exponent (1998), an inverse relationship is evident between mosquitofish mercury concentrations in WCA-2A and distance downstream of the S-10 structures. More recent District data from the same area also display this trend, albeit at much lower concentrations (SFWMD, unpublished data, 1998).

A number of water constituents are changing with distance downstream of the S-10 structures, of which water column TP is but one example. PTI/Exponent focused on the correlation between water column TP and mercury concentrations in mosquitofish. However, an extensive statistical analysis of the recent available data carried out by the District indicates that water column concentrations of calcium and dissolved organic carbon (DOC) are better predictors of the mosquitofish mercury concentrations than TP, but that neither the Exponent (1998) model nor the District's model (See **Appendix 7-3**) is a good predictor of mosquitofish mercury concentrations in WCA-3A. It is thus difficult to continue to attribute validity to the PTI/Exponent model or reliability to the mercury risk predictions it generates.

As STAs become operational and reduce the discharge of P through the S-10 structures, but not the discharge of DOC or calcium, there is some possibility that mosquitofish mercury levels will rise in the impacted area near the S-10s, primarily due to a loss of plant production. The question is then one of degree. How much of the apparent inverse relationship between water column TP and mosquitofish mercury concentrations along the nutrient gradient in WCA-2A is actually due to a reduction in plant production? The PTI/Exponent model cannot tell, because it cannot make such mechanistic distinctions. There is a model that can make such distinction, however.

As described in **Appendix 7-4**, USEPA's Office of Research and Development has constructed a model with the capability of quantifying the partitioning, accelerated settling, and peat dilution effects on inorganic mercury and methylmercury directly by simulating the effect of plant growth as a function of water column P (Ambrose and Araujo, 1998). In the relevant simulation, the water column TP concentration is decreased from an average of 50 ppb to 10 ppb in a 10-km wide by 7.5-km long box stretching from the S-10 structures to a point between F4 and F5. When existing mercury loads from EAA runoff and atmospheric deposition remain unchanged, the model predicts an increase in mosquitofish mercury levels of only about 55% (R. Ambrose, USEPA/ORD, pers. comm., 1998), not the 660% predicted by PTI/Exponent's one-variable model.

While some have argued that the TP concentrations in the water column have been declining in the zone of impact downstream of the S10 structures in WCA-2A over the last five years (Sugar Cane Growers Cooperative, 1998), the concentration of mercury in largemouth bass standardized to age class 3 years collected in this area have not increased. In fact, over the last four years, mercury concentrations in largemouth bass collected there show a general decline (Lange et al., 1998). The relationship between mosquitofish mercury and P found in WCA-2A does not seem to apply to largemouth bass in WCA-2A or even to mosquitofish in the southern Everglades. For cleanup to increase the mercury risk to wading birds, their rate of mercury ingestion must increase compared to their present rate. The Everglades food web is complex. Mosquitofish mercury levels appear to follow an inverse relationship with P in the impacted area, but not in other places. Even if mosquitofish mercury levels do rise in the impacted area following cleanup, it does not necessarily follow that mercury levels in wading bird prey species will rise to the same extent.

Clearly, there is greater complexity to the apparent inverse relationship than can be accounted for in the PTI/Exponent model. While the USEPA model cannot yet capture all of the required complexity, it points us away from decreased plant production as the primary cause of the observed increase in mosquitofish mercury concentrations along the WCA-2A nutrient gradient. An understanding of the real complexity underlying the apparent simplicity of the WCA-2A inverse relationship can only come through intensive study of the underlying physical, chemical, and biology processes that link the various biogeochemical cycles to methylmercury production, and link ecological structure and function to methylmercury bioaccumulation. This is the ultimate goal of the South Florida Mercury Science Program.

The PTI/Exponent Wading Bird Mercury Risk Assessment

Exponent (1998) uses three models to calculate post-ECP methylmercury risks to wading birds feeding in the northern Everglades. The first model predicts post-ECP water column TP concentrations in various zones of influence in the northern Everglades from estimated post-ECP reductions in P loads from treated EAA runoff. The second model, a one-variable regression equation, uses the modeled water column P concentration to predict the methylmercury concentration in mosquitofish. The third model, a food chain bioaccumulation model, uses the modeled methylmercury concentration in mosquitofish to predict the methylmercury concentrations in fish at the same step in the food chain and one step up in the food chain. Wading bird diet preferences are simplified to favor top-predator fish. Wading bird exposures to methylmercury are then calculated using the model estimates of the concentrations in prey and the simplified diet preferences. Each of these steps introduces uncertainty or error into the calculation of exposure.

The toxicity reference value for each of the wading bird species is derived by dividing the multi-generation mallard duck lowest observed adverse effect level (LOAEL) by a factor of 2. The mean or 95th percentile upper confidence level hazard quotient for the Wood Stork, the Great Egret, or the Great Blue Heron is calculated as the ratio of its mean or 95th percentile upper confidence level exposures to the toxicity reference value (Exponent, 1998). As will be evident from the discussion below, this approach significantly overestimates present-day and post-ECP methylmercury risks to wading birds in the Everglades. In what follows the focus is on the models for predicting methylmercury concentrations in mosquitofish and top-predator fish one step up in the food chain.

The Mosquitofish Model. In WCA-2A the relationship between the extent of eutrophication (as measured by the concentration of P in water) and the extent of mercury bioaccumulation (as measured by the concentration of mercury in mosquitofish) has a decreasing, asymptotic curve in which mercury rises sharply as phosphorus declines (See **Figure 7-5**). This is the so-called **“inverse relationship”**. This equation is a “model” that PTI/Exponent has used to simulate or predict mosquitofish mercury levels at various values of phosphorus concentration. This kind of model is called an empirical relationship. This means that its form and adjustable parameters are derived from an analysis of raw or reduced data to fit a particular statistical model rather than from a knowledge of the underlying physical, chemical, and biological processes that link cause to effect. This also means that the scatter of the data used for the derivation of this equation limit the accuracy and precision of predictions of mosquitofish mercury levels made using this equation.

PTI/Exponent used this equation to predict mosquitofish mercury levels in the impacted area after the STAs have eliminated the eutrophic condition of this area. PTI/Exponent used both the best-fit equation

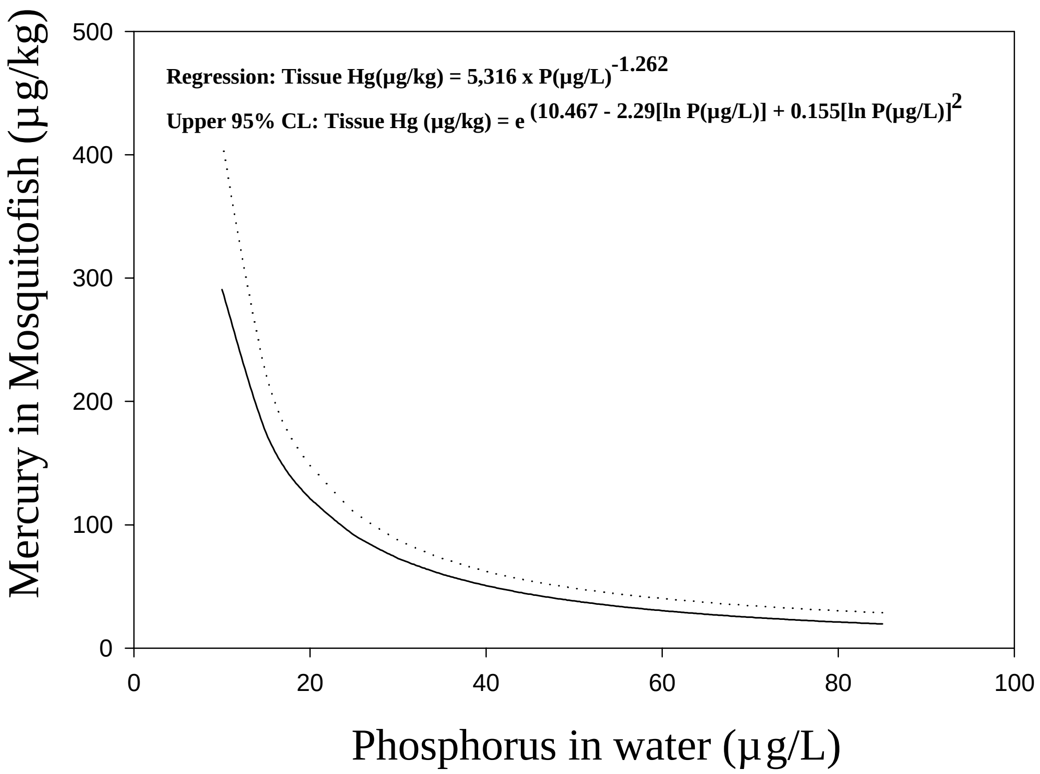

Figure 7-5. Regression analysis for mosquitofish data along water chemistry gradient in WCA-2A. Data not shown, lines redrawn based on equations (Exponent, 1998).

(solid line) and the equation for the 95th percentile upper confidence limit (dashed line above the solid line) to predict mosquitofish mercury levels after cleanup. However, PTI/Exponent has emphasized the high exposure levels predicted by the upper confidence limit. Mercury levels predicted from the 95th percentile upper confidence limit equation are about double those of the best fit equation at 10 ppb TP. It may be argued that this choice is intentionally conservative and protective of the resource. However, these high estimates of mosquitofish concentrations are then used in a second model that predicts the mercury concentrations in other fish at higher trophic levels. The use of this second model is necessary because wading birds do not typically feed on mosquitofish (Ogden et al., 1976; Smith, 1994; Frederick et al., 1997).

The Food Chain Model. In the approach used by PTI/Exponent, the prediction of mercury concentrations in other fish species from mosquitofish mercury concentrations is based on an idealized food chain expected to occur in the Everglades. The concentrations of mercury in fish and shellfish at the same step in the food chain as mosquitofish are assumed to be equal to the concentration in mosquitofish. This includes sunfish species, which are a preferred prey item. The concentrations of mercury in fish at one step up from mosquitofish in the food chain, the top-predator level where bass and gar are found, are calculated in the PTI/Exponent approach using national average predator-prey factors obtained from USEPA (1993a). These predator-prey factors are typical ratios of concentrations of mercury in predator fish to the concentrations in their prey one step down in the food chain. These national average predator-prey factors are more than double those actually observed in the Everglades at the unimpacted reference site evaluated by the District in its ecological risk assessment (Lange et al., 1998; **Appendix 7-3**).

Combining the unrealistically high mosquitofish concentration predicted by the second model with the unrealistically high predator-prey factors in the third model produces greatly exaggerated exposure and risk estimates for the wading birds feeding in the post-ECP Everglades. These very high exposure estimates are then further magnified by using the 95th percentile upper confidence limit estimate of mosquitofish concentrations. It was these greatly exaggerated exposure and risk estimates in the PTI/ Exponent report that formed the basis for the Coop's comments on the ECP PEIS, the CWA Section 404 Dredge and Fill permit for the ECP, and the EFA permits for the STAs. The PTI/Exponent methodology and calculations are compared with those of the District in **Appendix 7-3**.

The District's Wading Bird Mercury Risk Assessment

The District's approach to estimating the post-ECP daily intake of mercury by wading birds is entirely different from that of PTI/Exponent. It is simpler and relies on direct measurement rather than on the predictions of models. PTI/Exponent *simulated* methylmercury concentrations in wading bird prey in the impacted area after recovery using a combination of three models. The District was able to avoid modeling altogether and take advantage of *measured* methylmercury concentrations in the species of fish and shellfish preferred by wading birds. The District was able to do this by using mercury concentration data from specimens collected from an unimpacted area of WCA-2A downstream of the S-10 structures. This site is considered representative of the impacted area after cleanup. This site is U3 in WCA-2A, about 10.5 km southwest of the S-10 structures. Over the last year, this site has averaged about 7.3 ppb TP in the water column (SFWMD, unpublished data, 1998).

The District calculated the daily mercury intake in the wading bird diet using very simple calculations and few assumptions. The District obtained measured values of the mercury content of fish in the size ranges routinely consumed by wading birds from the FGFWFC (Lange et al., 1998). When mercury concentration data were unavailable, data from the same location for a species with similar feeding habits was used. Taking into account the feeding rate of a typical bird, the District then multiplied the mean and maximum concentrations of mercury in each prey species in the appropriate size range by its percentage in the wading bird diet to calculate the observed daily mean and maximum mercury exposure rate. The DEP and the District believe these estimates of the mercury levels in a typical wading bird diet to be much more representative of levels expected in the impacted area after cleanup than corresponding values derived by the sequential application of the three models used by PTI/Exponent.

The District then divided the daily mean and maximum exposure rates by the toxicity reference value to obtain the hazard quotient for each wading bird species at the U3 reference site. The resulting hazard quotients are 0.6, 0.9, and 0.6 for the Wood Stork, Great Blue Heron, and Great Egret, respectively. Corresponding hazard quotient values calculated by PTI/Exponent for similar conditions from the simulation of daily mercury intake were 6, 10, and 2, for the respective species using the best-fit equation to predict post-ECP mosquitofish concentrations (Exponent, 1998). When the District's maximum concentration values of mercury in wading bird prey are used, hazard quotients obtained from the U3 reference site are 1.3, 1.7, and 1.4 for Wood Storks, Great Blue Herons, and Great Egrets, respectively. Using the 95th percentile upper confidence levels for its simulation of mosquitofish mercury concentrations, the PTI/Exponent obtained corresponding hazard quotient values of 8.5, 14, and 3, respectively. Because the District and the PTI/Exponent used the same value for the toxicity reference value, differences in the methods of quantifying exposure are responsible for differences in the values of the hazard quotients calculated for these three species.

Based on the District's analysis of the U3 reference site, the typical daily mercury intake for these three species of wading birds will be less than the toxicity reference value for birds feeding in the impacted area. For the endangered Wood Stork, assuming that it consumes only fish with the maximum mercury concentrations measured at U3, the hazard quotient does not significantly exceed 1. In addition, a review of the methylmercury toxicity literature strongly suggests that the use of the no observable adverse effect level from methylmercury toxicity studies of the Mallard Duck as the toxicity reference value for wading birds is probably overprotective of the wading birds in the same life stage (See **Appendix 7-2**). Finally, site U3 is believed to be a conservative representation of mercury exposures expected in the impacted area after restoration. The reasons for this are discussed later in this section.

Based on the above results, the DEP and the District conclude that after the STAs have restored a more normal balance of aquatic plants and animals and more normal water chemistry in the first 7 or 8 km downstream of the S-10 structures like conditions at U3 now, wading birds feeding exclusively in what was the impacted area will not be exposed to more than the maximum allowable daily dose of mercury. In other words, the ECP is highly unlikely to increase mercury risks to wading birds to unacceptable levels in the downstream areas presently impacted by phosphorus.

A summary of the differences in the wading bird risk assessment approaches of PTI/Exponent and the District is given in **Appendix 7-3**.

The District also has conducted a methylmercury baseline ecological risk assessment for the wading birds feeding exclusively in WCA-3A. WCA-3A is home to two wading bird rookeries (Frederick et al., 1997). Both of these rookeries are near methylmercury "hot spots" in WCA-3A (USEPA, 1998). During nesting, the wading birds tend to stay closer to the nest while foraging for food**.** The District has carried out this calculation using the fish methylmercury data collected at WCA-3A-15, which is in one of the "hot spot" areas. For wading birds foraging exclusively in WCA-3A in the vicinity of these hot spots, the hazard quotient values based on mean methylmercury concentrations in the diet are 2.4, 3.2, and 2.4 for the Wood Stork, Great Blue Heron, and Great Egret, respectively. These hazard quotients are three to four times the corresponding values in WCA-2A at U3. However, the methylmercury "hot spots" in WCA-3A are least likely to be affected by the ECP. More detailed, spatially explicit modeling of the effects of this change in water routing, quantity, and quality to these areas should be a high priority to verify this supposition.

Even though wading birds feeding in WCA-3A may have more exposure to mercury, it is not clear whether these hazard quotient results are of biological significance at the population level. It should be noted that in the Everglades as a whole, the most exposed wading bird populations do not exhibit signs of reduced reproductive success relative to the least exposed populations (P. Frederick, UF, pers. comm., 1998). This supports the contention that the toxicity reference value derived from Mallard Duck feeding studies is protective when applied to wading birds and provides an ample margin of safety in the ecological risk assessment for the Everglades wading birds. The bioassay studies conducted by Frederick et al. (1997) using daily dosing rates equivalent to the highest exposures routinely encountered in WCA-3A also support this observation. Within the framework of a multiple-lines-of-evidence approach to ecological risk assessment, these results are mutually reinforcing, which supports the belief that the results of the ecological risk assessment are valid, especially for the Great Egret.

Changes in Flows and Depths

The construction and operation of the ECP will not only change water quality but the routing, timing, and quantity of EAA stormwater runoff, as well. This is expected to change stage-duration patterns throughout the northern and central Everglades, while increasing the delivery of water to ENP and Florida Bay. The discussion of the possible effects of water flow, depth, and stage-duration on methylmercury production and bioaccumulation are taken up in some detail in the section that answers the question, *Can the management of water quality and quantity reduce mercury risks to acceptable levels?* The modeling effort described in what follows and in Appendix 7-4 will eventually make it possible to quantify the downstream effects of the simultaneous changes in mercury, P, and sulfur loads and depth and flow on methylmercury production and bioaccumulation. Preliminary results in this regard are discussed below.

USEPA Everglades Mercury Cycling Model

Rigorous quantitative modeling studies are required to predict with known confidence how changes in water quality and quantity will affect the biogeochemistry of mercury methylation. A mercury cycling model for the Everglades is being developed by USEPA's Office of Research and Development in Athens, Georgia. In its present state of development, it is of some assistance in considering mercury transformations in the Everglades. The USEPA Everglades Mercury Cycling Model (EMCM) (Ambrose and Araujo, 1998) incorporates the key relationships between TP in water and the plant densities and turnover, settling, and decomposition rates that determine the net peat accretion rate and the net inorganic mercury and methylmercury settling rates. The model also incorporates the methylation and demethylation processes in the sediment and periphyton mats and methylmercury bioaccumulation in mosquitofish. The model has been initialized with various physical, chemical, and biological data collected by various agencies over the last five years. The model structure, initialization and calibration procedures, and sensitivity analysis results are summarized in **Appendix 7-4**, along with a comparison of its key features to those of other mercury cycling models.

By initializing the model to inorganic mercury methylation rates and methylmercury demethylation rates obtained from studies on intact sediment cores and periphyton mats from the impacted area in WCA-2A, the model implicitly incorporates the influence of the P and sulfur cycles on these processes. However, there is no explicit representation of the influence of the sulfur cycle on the mercury cycle. The EMCM has undergone several peer reviews within and outside of USEPA (R. Ambrose, USEPA, pers. comm., 1997; SFMSP peer review, 1997; S. Bartell, SENES, Inc., pers. comm., 1998).

In its present form, the District believes this model has utility as a screening-level model to place the results of other screening-level models in perspective and to guide the design of experiments and data collection. For example, the model was run to simulate effect on methylmercury in water, sediment, and fish when the ECP reduces water column TP concentrations from an average of 50 ppb to 10 ppb in the first 7.5 km stretch of the already impacted area down stream of the S-10 structures. The USEPA model predicts that restoring the entire area to 10 ppb would result in no more than about a 55% increase in mosquitofish methylmercury on average, based on what is known about the relationship between water column TP and plant production, mercury dilution, sorption, settling, and burial, and site-specific methylmercury bioaccumulation factors for mosquitofish (R. Ambrose, USEPA/ORD, pers.comm., 1998). Under these same conditions, the PTI/Exponent one-variable regression model predicts an average increase of 660% (Exponent, 1998). The USEPA model estimate is about 12-fold lower than that of the PTI/Exponent model. When the benefits of at least a 50% reduction in the inorganic mercury load by

Stormwater Treatment Areas is taken into account, that increase decreases to 42% (R. Ambrose, USEPA/ ORD, pers. comm., 1998). This is a 16-fold lower estimate of mercury in mosquitofish than that of the PTI/ Exponent model.

The District's ecological risk assessment does not use the USEPA model results or any other model results as the basis for its risk predictions for wading birds. However, these modeling results do suggest that the mercury concentrations in fish at the most impacted site in WCA-2A at F1 are unlikely to increase to U3-like conditions as a result of the loss of plant production when water column TP concentrations decrease from an average of about 100 ppb to 10 ppb. This should increase the confidence that the actual post-ECP risks to wading birds have not been seriously underestimated by assuming U3-like conditions after restoration.

While the USEPA model can be used for such applications, the confidence one can place in the results at this time must be tempered by an understanding of the process and influences the model cannot yet simulate. The model cannot simulate the effect of a post-ECP reduction in water column P concentrations on dissolved oxygen, with its attendant effects on methylmercury production via the carbon and sulfur cycle, and on food web structure, with its attendant effects on methylmercury bioaccumulation. It can overcome these limitations by using the methylmercury production and decomposition rates and the fish bioaccumulation factors measured at an oligotrophic site like U3, just as the District overcame the limitations of not being able to collect empirical data at a post-ECP site by using measurements of fish concentrations from U3.

Although the use of U3 data is a useful temporary fix, ultimately the USEPA model requires enhancement to allow it to predict the effect of changing P loads and concentrations in EAA runoff on the sulfur cycle and of changing sulfate loads and concentrations in EAA runoff on the mercury cycle. It also requires the ability to link changes in plant production to changes in biomass and bioaccumulation factors of that biomass at each successive link in the food chain. The model is now undergoing the required further development. With these changes the model should be able to quantify the combined effect of a reduction in the phosphorus and mercury loads in EAA runoff with and without a reduction in the sulfate load. However, based on the U3 reference site data, in its present form it is still likely to be a much more reliable tool than the PTI/Exponent model for predicting the effects of changing phosphorus loads and concentrations in EAA runoff on downstream mercury risks.

Conclusions

- The baseline methylmercury risks to wading birds feeding exclusively in the minimally impacted areas of WCA-2A are not unacceptable.
- Restoring the impacted areas in the WCAs to the conditions which now exist in the minimally impacted areas further downstream are unlikely to cause wading birds feeding in those areas to exceed their maximum allowable daily dose.
- The methylmercury risks to wading birds feeding exclusively in the most contaminated areas of WCA-3A, which actually occurs during the nesting season, are of potential concern and warrant further study. These areas are the least affected by EAA discharges at present and are not expected to change as a result of the ECP. The mercury risks at this location reflect an Everglades mercury problem that is not likely to be strongly influenced by present or future stormwater quality.

- The ECP is likely to reduce inorganic mercury loads in EAA runoff delivered to the northern Everglades by between 50% and 75%, but the magnitude of the potential positive impacts on the sites immediately downstream of District structures in the northern Everglades has not yet been systematically quantified using a combined hydrodynamics-phosphorus-mercury model.
- Based on analysis of the time to respond to mercury source reduction, the Everglades mercury Cycling Model (EMCM) predicts that the Everglades is not very efficient at recycling historically deposited inorganic mercury from the sediments, so that the benefits of atmospheric source reduction should be felt within the timeframe of a decade rather than a century.
- The EMCM model cannot as yet account for the influence of the sulfur cycle on the mercury cycle or the influence of the phosphorus cycle on the sulfur cycle.

Recommendations

Modeling

- More detailed and validated modeling of the benefits of the inorganic mercury load reduction to WCA-2A and of increased flow to the interior of WCA-3A should be a high priority.
- A mathematical model of methylmercury bioaccumulation and disposition in wading birds should be developed.
- The EMCM should be upgraded to include additional process complexity to accommodate the influence of the sulfur cycle on the mercury cycle and the phosphorus cycle on the sulfur cycle.

Everglades Program

- The ECP should go forward as planned, because there is reasonable assurance that there will be no significant increased mercury risks associated with the operation of the STAs.
- Further study of the effect of the sulfate in EAA runoff should become a high priority for follow-up or Phase 2 studies by the South Florida Mercury Science Program.
- The District should conduct monitoring to provide ongoing corroboration the ECP will not increase mercury risks within the STAs or downstream.

Research and Monitoring

- Efforts to characterize and control local air emissions sources of mercury should continue.
- The District should monitor experiments on Supplemental Technologies to ensure that they do not exacerbate mercury risks (in progress).
- The foraging preferences of wading birds should be studied with greater rigor, especially the Great Blue Heron.
- To test the hypothesis that wading birds are not as sensitive to methylmercury toxicity as the Mallard Duck, the results of preliminary studies of the toxicity of methylmercury to wading birds should be confirmed, focusing on methylmercury residues in the egg and the development of diet-to-egg ratios.

What is the Status of District and DEP Efforts to Understand and Solve the Mercury Problem?

This section first summarizes the Act requirements and timetables as they relate to the Everglades mercury problem and the efforts being taken by the DEP and District to fulfill them. The section then lists the major accomplishment of the DEP and District in obtaining the information, developing the tools, and supporting the multi-agency efforts to understand and solve the Everglades mercury problem.

Status of Efforts to Meet Requirements of the Everglades Forever Act[1] Related to Mercury

- By January, 1996, initiate a research and monitoring program to generate any additional information identified as necessary to describe water quality in the Everglades and to evaluate the effectiveness of BMPs and STAs.

  Studies were initiated prior to the required date and are still under way to evaluate water quality with respect to mercury in the Everglades. The effects of BMPs and STAs on mercury are being investigated through work in the prototype STA, the ENR Project. To date the ENR Project presents no increased mercury risks and is actually benefiting the down stream environment by removing 50% to 75% of the total mercury and methylmercury load in EAA runoff.

***Figure 7-6** depicts the permit monitoring locations for the collection of fish at downstream marsh sites and water at downstream canal sites to monitor the mercury response of the Everglades to the ECP.*

- The research and monitoring program is also to include research seeking to optimize the design of the STAs and to identify superior technologies.

  Work is under way to determine how the various proposed supplemental technologies may influence mercury transformation and bioaccumulation within and downstream of the STA. The present proposal to implement pilot-scale periphyton-based alternative treatment will be evaluated carefully.

- By January 1, 1999, the District, in cooperation with the DEP, is required to prepare a peer-reviewed, interim report, which is to include a summary of the USEPA Everglades Mercury Study, the results of research and monitoring of water quality and quantity in the Everglades region, and current information on the ecological needs of the Everglades.

  The USEPA Everglades Mercury Study is presently undergoing peer review and no updated summary is available. However, the data have been used by USEPA to assess water quality status, from which they conclude that the Class III Water Quality Standard for total mercury is not being exceeded routinely at any location in the Everglades. There is also evidence of several “hot spots” in WCA-3A where mosquitofish concentrations are especially high, and follow-up studies are underway to determine why this is the case, just as follow up studies are underway to determine why the ENR Project is a “cold spot.”

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[1] Independent of any Everglades restoration efforts, the Department must also protect the beneficial uses of Everglades waters as required by Chapter 403, F.S. The District also has general, environmental water quality and quantity obligations under Chapter 373. F.S.

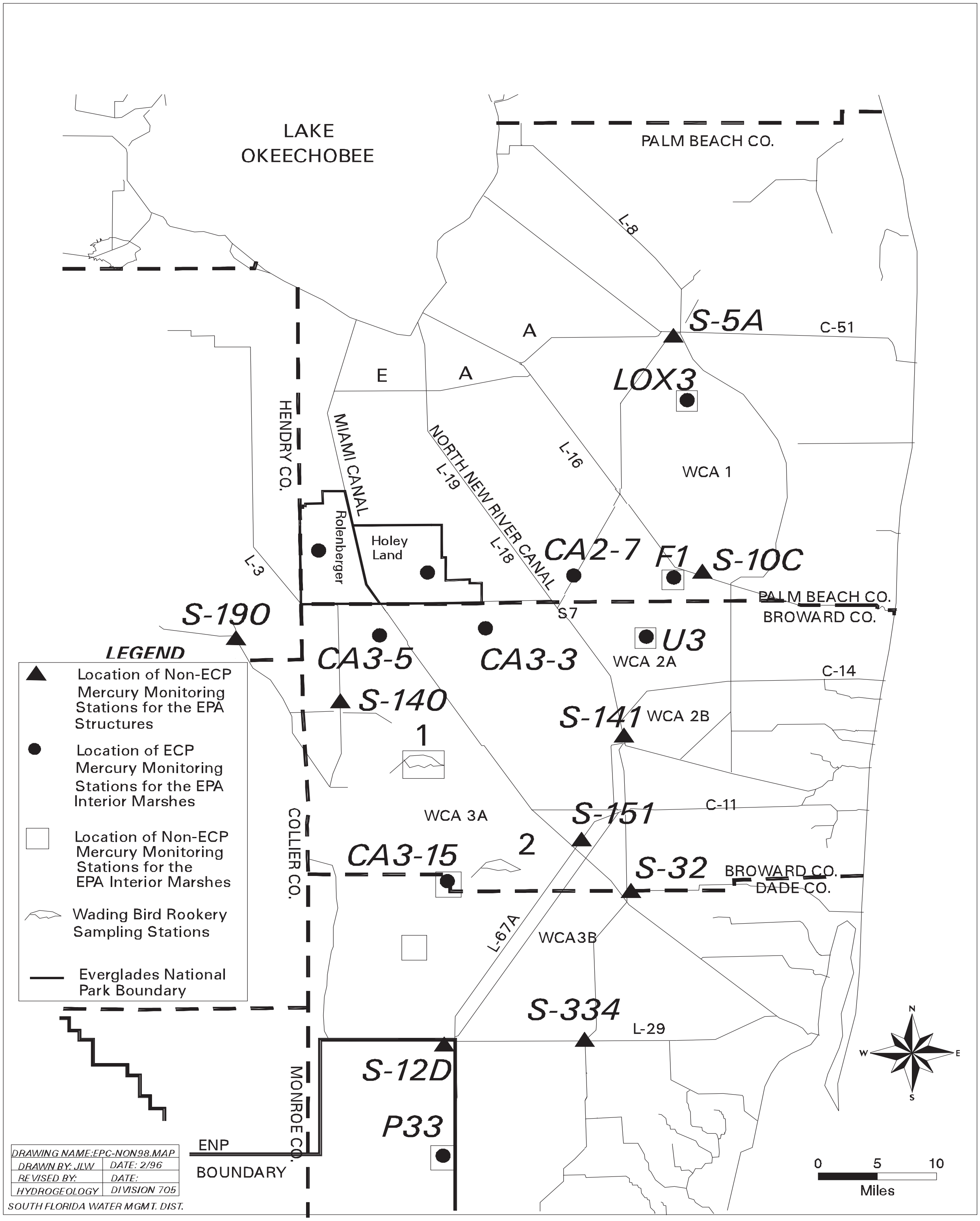

Figure 7-6. Proposed ECP/non-ECP EFA permit mercury monitoring sites.

- Beginning January 1, 2000, the District and the DEP are to issue an annual, peer-reviewed report regarding the research and monitoring program that summarizes all data and findings. The report shall identify water quality parameters, in addition to phosphorus, which exceed state water quality standards or are causing or contributing to adverse impacts in the Everglades Protection Area.

  This will be done by the scheduled date under Research and Monitoring Project 8, see ***Chapter 1****.*

- By December 31, 2001, the research and monitoring program should allow evaluation of existing state water quality standards applicable to the Everglades Protection Area. See above.

  The District and DEP believe this deadline will be met for the fish and wildlife component of the criterion if funding is sufficient (see above).

- In establishing limits for permits to discharge into the Everglades Protection Area, the DEP is required to use the best available information to prevent an imbalance in the natural populations of aquatic flora or fauna in the Everglades Protection Area, and to provide a net improvement in the areas already impacted.

  Phosphorus reduction in EAA discharges will reduce the extent of eutrophication in the impacted areas and improve the balance of natural populations of biota. In the preceding section, the District and DEP have shown that phosphorus reduction in WCA-2A will not result in an increase in wading bird risks from methylmercury exposures to levels of concern. Therefore, with appropriate safeguards, the ECP will result in a net improvement to the already impacted areas.

Specific Actions Under Way or Completed by the DEP and the District

The DEP and the District are cooperating in the development of schedules and strategies to provide compliance with the existing mercury water quality standards to the maximum extent practicable, as manifested in permits for the operation of the STAs and the non- ECP structures. The District and the DEP are cooperating in the development of a long-term strategy for the recovery and protection of the Everglades from its mercury problem to protect human health and Everglades wildlife, including the American Alligator, Wood Stork, otter, and Florida Panther. To implement this strategy, the DEP will issue long-term compliance permits to meet revised WQSs by December 31, 2006. Specific Department and District accomplishments to date in the development of the information and tools for the implementation of this strategy are summarized below.

DEP

- Through its Office of Mercury Coordinator, facilitated cooperative funding of a state-federal-Private partnership to determine the effects of emissions source controls, establish water quality criteria, and determine if management of water quality and quantity can reduce mercury bioaccumulation.
- Continued to support work on understanding the effects of mercury on fish and wildlife, including wading bird exposure and toxicology studies by the University of Florida and panther mercury residue studies for the Game and Fish Commission.
- Funded research to develop a method for directly measuring Reactive Gaseous Mercury, a major unknown in mercury source control.

- Constructed a mercury-free ('clean”) laboratory and acquired an ultra-trace analysis capability for total mercury.
- Quantified pre-industrial and present-day mercury input rates to the Everglades.
- Co-funded a statewide mercury atmospheric deposition network, the Florida Atmospheric Mercury Study (FAMS), with seven stations in South Florida.
- Evaluated mercury emissions at three local sources in Broward and Miami-Dade Counties.
- Implemented regulations to control emissions from municipal solid waste incinerators, a possible source of Everglades mercury, which have resulted in a 65% reduction in mercury emissions from these sources. The USEPA has since adopted similar regulations.
- Co-funded top-predator fish sampling in the ENR Project, District canals, and interior marsh sites by the Florida Game and Fresh Water Fish Commission (FGFWFC).
- Supported mercury monitoring and research studies in the ENR Project by providing analytical services through its own laboratory and by contract.
- Issued permits under the EFA that provide information about mercury inputs into the Everglades Protection Area from the District's Stormwater Treatment Areas (STAs) and non-ECP structures.
- Evaluated wading bird mercury exposures and toxic effects.
- Tightened hazardous waste disposal regulations to limit mercury wastes. This has had the effect of encouraging commercial and industrial facilities to minimize or eliminate mercury from their products and processes.
- The Florida Solid Waste Act of 1993 banned mercury from many commercial products such as household batteries. Recycling of other mercury containing items was mandated.
- Pollution prevention activities have been implemented at both the state and national level to decrease mercury use at its source. In July 1998, for example, USEPA and the American Hospital Association signed an agreement to minimize uses of mercury in hospitals. This should help resolve the problem of high mercury emissions from medical waste incinerators, a possible source of Everglades mercury. The DEP will help implement this agreement.

<u>District</u>

- Conducted biweekly monitoring at seven District structures in 1994-1997 in partnership with the USEPA Region 4.
- Supported USGS in its Everglades mercury research projects under the Aquatic Cycling of Mercury in the Everglades (ACME) program.
- Participated in the FAMS program by sponsoring a site at the ENR Project.
- Since start-up in August 1994, conducted mercury monitoring, research, and modeling studies at the Everglades Nutrient Removal (ENR) Project, a prototype filter marsh, with in-kind support from the DEP’s analytical laboratory and a $219,292 Section 319 grant from USEPA Region 4.
- Co-funded top-predator fish sampling in ENR Project by FGFWFC.

- Assisted USEPA's Office of Research and Development in developing a wetlands mercury cycling model that links the phosphorus and mercury cycles.
- Evaluated the potential for the ECP to create new mercury risks in the filter marshes or to exacerbate the downstream mercury risks in the Everglades to support the preparation of the PEIS for the ECP.
- Implemented an extensive mercury monitoring program in the STAs and the Everglades Protection Area to provide ongoing corroboration that the ECP and non-ECP structures will not cause or contribute to a significant new mercury problem or exacerbate an existing mercury problem in the Everglades.
- Evaluated Everglades canals and interior marsh waters for compliance with the state's existing mercury Class III Water Quality Standard (WQS) and concluded that the WQS of parts per trillion is not being routinely exceeded anywhere in the canal or marsh waters of the Everglades.
- Prepared an Everglades mercury baseline report that will incorporate data collected by or for USEPA (i.e., the USEPA *Everglades Mercury Study*), USGS, and others to define the pre-ECP conditions against which to measure the mercury-related effects of construction and operation of the ECP works and structures.

The District and the DEP will continue to apprise the Legislature of the progress of the multi-agency effort to understand and solve the Everglades mercury problem through the updated status summaries in the Everglades Peer-Reviewed Report.

Conclusions

What is the significance of the Everglades mercury problem?

- Mercury is a National and Florida problem, but bioaccumulation of mercury in Everglades sport fish is the highest in Florida.
- The state has issued advisories for no fish consumption (> 1.5 ppm) or limited consumption (0.5 - 1.5 ppm) for all of the Everglades and Big Cypress National Preserve and eastern Florida Bay, but high mercury residues have not been found in local sport fishers participating in a study conducted by the Centers for Disease Control in Atlanta.
- High mercury residues have been detected in wading birds, but effects on their populations have not been documented.
- High mercury residues have been detected in alligators and otters, but the effects on these populations have not been studied.
- Recent studies indicate that mercury levels in panthers have fallen substantially, but panthers that prey on raccoons that have been exposed to high mercury in their diets could be at an increased risk.

- The USEPA study of mercury in the Everglades did not detect waters that exceeded the state Class III WQS of 12 ng/L in the District's canals or the interior marshes in the period 1993-1997. District data collected in 1997-1998 confirm this status.

Can the sources of Everglades mercury be controlled?

- Mercury deposition rates to the Everglades have increased about five-fold on average over the last century.
- While the STAs are expected to remove between 50% and 75% of the mercury loads from EAA runoff, the Everglades will still be subjected to atmospheric deposition, which contributes more than 95% of the new mercury load to the Everglades.
- The contribution to present-day methylmercury production and bioaccumulation of historically deposited inorganic mercury recycled from Everglades peat is the focus of Everglades studies by the USGS, the Academy of Natural Sciences, and the University of Wisconsin.
- There is as yet no scientific consensus on the relative contributions of local and global air emissions sources to the new mercury entering the Everglades.
- The U.S. State Department has added mercury to the global environmental agenda for priority global source reduction.

Can management of water quality and quantity reduce Everglades mercury risks to acceptable levels?

- The rates of production and bioaccumulation of methylmercury in the Everglades are influenced by meteorology, hydrology, water chemistry, and ecology.
- Excess phosphorus could affect methylmercury production and bioaccumulation by:

  -- increasing areas devoid of dissolved oxygen where sulfate-reducing bacteria thrive but where the sulfide that some believe poisons the methylation process also accumulates.
  -- increasing the production of plant biomass and plant decay products, net plant biomass settling, and net peat accretion, resulting in higher mercury settling and dilution rates.
  -- altering aquatic plant and animal communities, trophic relationships, and critical paths of methylmercury bioaccumulation.

- Water flow rate and depth determine the hydraulic residence time, which affects particle settling and the accumulation of contaminants in water, sediment, and biota, and water depth affects the penetration of sunlight, which, in turn, affects benthic periphyton production, elemental mercury production, and methylmercury decomposition, as well as influencing water column turnover and reoxygenatation.

How will the Everglades Construction Program affect mercury risks?

- Using available data, baseline mercury risks have been calculated for wading birds feeding exclusively in WCA-2A downstream of the S-10 structures in the minimally impacted zone below 10 ppb total phosphorus. The District and DEP conclude that they are below the level of immediate concern.

- Based on the above analysis, the District and DEP have concluded that restoring the impacted zone in WCA-2A to the minimally impacted condition with total phosphorus concentrations less than 10 ppb will not expose wading birds feeding exclusively in that area to a significant increase in mercury risk. However, for birds feeding exclusively in the "hot spots" in WCA-3A prior to the ECP, methylmercury risks may be of concern.
- USEPA's Everglades Mercury Cycling Model is undergoing further development to incorporate the iron and sulfur cycles to address the potential positive effects of changes in water quality and quantity to be brought about by the ECP, as predicted by other District models.

What is the status of District and DEP efforts to understand and solve the mercury problem?

- The Florida Class III Water Quality Standard (WQS) for total mercury cannot be considered fully protective of the Everglades. The DEP continues to fund research to support the promulgation of new mercury WQSs, if needed, including wading bird exposure and toxicology studies by the University of Florida and panther mercury residue studies for the Game and Fresh Water Fish Commission.
- The DEP and the District have cooperated in the development of schedules and strategies to provide compliance with the existing mercury water quality standards to the maximum possible extent, as manifested in EFA permits for the operation of the STAs and the non-ECP structures.
- Contrary to the hypotheses set forth in challenges to the ENR Project NPDES permit, the results of four years of District studies demonstrate that the ENR Project:

  -- outflow concentrations were always less than inflow concentrations for both total mercury and methylmercury on an annual average basis and did not exceed the Florida Class III Water Quality Standard for total mercury.
  -- mercury concentrations in sediments are not at hazardous levels and are declining.
  -- fish have less mercury than those found anywhere else in the Everglades system.
  -- removed between 50 and 75% of the total mercury and methylmercury entering through the inflow pump on an annual average basis.
  -- fish from the interior and outflow have lower mercury concentrations than at the inflow and L-7 reference site, with but a few exceptions.
  -- exhibited a complex relationship between phosphorus in water and mercury in fish.

- The DEP and the District are cooperating in the development of a long-term strategy for the recovery and protection of the Everglades from its mercury problem to meet the new WQS, to protect human health, and restore the full use of the sport fishery and Everglades wildlife, including the alligator, woodstork, otter and Florida panther.
- To implement this strategy, the DEP will issue long-term compliance permits to meet revised WQSs by December 31, 2006.

Recommendations

For the next and succeeding annual reports required by the EFA (373.4592(4)(d)6., F.S.), the District and the DEP will address Everglades mercury concerns by preparing a Mercury Assessment Plan for the Everglades that sets forth, by agency, the current status of the mercury programs and funding, together with additional actions required and an estimated timetable for completion at a specified level of funding for the following activities:

- Develop water quality criteria for mercury and methylmercury that, when met, will prevent impairment of the existing and designated beneficial uses of Everglades waters;
- Estimate the relative contributions to the Everglades mercury problem caused by activities that are potentially controllable under Florida law; activities that are potentially controllable under other U.S. jurisdictions; man-induced, non-abatable causes including those not controllable by any U.S. jurisdiction; and natural causes; and
- Estimate the benefits to be achieved by additional controls on activities that are potentially controllable under Florida law.

Decisions regarding further regulatory activities will be based on the DEP’s assessment of the weight of evidence of the data relating to these three efforts.

Timelines

The Mercury Assessment Plan will reflect the District’s and DEP’s commitment to joint sponsorship of this effort and will be completed during 1999. Until the plan funding recommendations are prepared, the District and DEP should continue their present level of effort in the areas of risk assessment and new water quality criteria development, source attribution, biogeochemical research, bioaccumulation studies and modeling. When the plan has been prepared, the appropriate level of effort should be determined. To the extent appropriate, implementation of this plan by the District and DEP should be through the multi-agency South Florida Mercury Science Program.

Findings on the Everglades Mercury Problem

- The State has issued public health advisories for no or limited fish consumption for all of the Everglades, Big Cypress, and eastern Florida Bay, which limits the recreational uses of these waters.
- There is a significant mercury problem in the Everglades Protection Area.
- Most new mercury arriving in the Everglades comes from the atmosphere. However, the role of local air emissions is not known with certainty at this time.
- Water quality and quantity can affect mercury bioaccumulation, and the relative effects must be considered through continued monitoring, research and modeling.

- An ecological risk assessment indicates that the Everglades Construction Project will not significantly increase the methylmercury risk to the Everglades wading birds to levels of concern.
- The Florida Class III standard for mercury does not appear to protect fish and wildlife from mercury bioaccumulation to problematic levels in the EPA.
- Research and monitoring in the EPA should continue under the multi-agency South Florida Mercury Science Program to fill information gaps on management options.

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