Chapter 2B: Mercury Monitoring, Research and Environmental Assessment in South Florida

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SUMMARY

Mercury remains one of the major water quality concerns for the Comprehensive Everglades Restoration Plan. Consequently, the Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (District or SFWMD) continue to lead the South Florida Mercury Science Program (SFMSP)[1] to improve understanding of the sources, transformations, toxicity, and fate of mercury in the Everglades. The SFMSP seeks to provide scientific information on environmental cycling of mercury at local, regional, and global levels to better support decision making in South Florida. General information on the nature of the environmental mercury cycle has been presented in previous Everglades Consolidated Reports. This chapter in the *2005 South Florida Environmental Report – Volume I* serves to update the previously reported findings, with supporting data and other technical information on mercury provided in the appendices to this chapter.[2]

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[1] This partnership of federal, state, and local interests includes the FDEP, the District, the U.S. Environmental Protection Agency Office of Research and Development and Region 4, the Florida Fish and Wildlife Conservation Commission, and the U.S. Geological Survey. Other collaborators associated with the SFMSP are the U.S. Fish and Wildlife Service, U.S. Park Service, U.S. Army Corps of Engineers (USACE), University of Florida, Florida State University, Florida International University, University of Miami, University of Michigan, University of Alabama, Texas A & M University, Oak Ridge National Laboratory, the Smithsonian Institution, Florida Power and Light, Florida Electric Power Coordinating Group, the Wisconsin Department of Natural Resources, the Electric Power Research Institute, and the National Oceanic and Atmospheric Administration.

[2] Appendices 2B-1, 2B-2, 2B-3, and 4-4 of the *2005 South Florida Environmental Report – Volume I* provide additional details to meet the Everglades Forever Act (EFA) requirement that the District and the FDEP shall annually issue a peer-reviewed report regarding the mercury research and monitoring program that summarizes all data and findings. Appendices 2B-1 and 4-4 of this volume meets the reporting requirements of the EFA, as well as specific permits issued by the FDEP to the District. Additional detailed scientific information can be found in the specific chapters on mercury monitoring and assessment presented in the 1999 Everglades Interim Report and 2000–2004 Everglades Consolidated Reports.

Previous findings from this collaborative effort on mercury include the following:

- Although the precise proportions of locally derived versus globally derived mercury remain uncertain, the data indicate that at the time of peak levels of atmospheric deposition of mercury in South Florida in the late 1980s and early 1990s, the majority of mercury deposition to the Everglades originated from sources within South Florida.
- Methylmercury (MeHg), a highly toxic form of mercury, is primarily produced in sediments by naturally occurring, sulfate-reducing bacteria (SRB). MeHg strongly bioaccumulates in the aquatic food chain and in fish-eating birds and mammals.
- MeHg production is highly influenced by the rate of supply of atmospherically derived mercury and by sulfur and dissolved organic carbon (DOC) concentrations. Inorganic mercury newly deposited from the atmosphere is converted to MeHg over a period of hours to days.
- The southern Everglades exhibits strong MeHg production and bioaccumulation and, therefore, high mercury levels are found in fish and wildlife. At the apparent peak of mercury in Everglades biota in the late 1980s and early 1990s, these levels were high enough to pose risk of chronic toxicity to wildlife. Subsequent declines in body burdens have eased this concern, but mercury risk to humans and wildlife continues to be a water quality concern.
- The primary emissions sources of mercury in South Florida circa 1990 were incineration from both municipal solid waste and medical waste. Mercury emissions from incinerators of all types have declined by approximately 90 percent since the late 1980s. Principal reasons for this decline were pollution prevention activities that resulted in reductions of mercury concentrations in waste, as well as incinerator emissions controls.
- Monitoring of Everglades fish and wading birds indicates a significant decline in mercury over the period from 1994–2003 in both largemouth bass and great egrets by about 60 to 80 percent. Mercury levels in largemouth bass have not declined in Everglades National Park (ENP or Park), or may even have increased over the past five years, for reasons that remain obscure.
- Despite substantial declines in recent years, mercury levels in Everglades largemouth bass generally remain well above the 0.3 milligrams per kilogram (mg/kg) human-health fish tissue criterion proposed by the U.S. Environmental Protection Agency (USEPA).
- Environmental mercury models for the Everglades have been developed and incorporate the latest findings from atmospheric and aquatic research. Results substantiate a strong relationship between atmospheric mercury load to the Everglades and mercury levels in top predator fish. Increasing focus on the role of sulfate as it influences mercury cycling has led to concomitant efforts to incorporate sulfur cycling in the Everglades Mercury Cycling Model.
- Aquatic system modeling analyses indicate that the response times of the Everglades to changes in atmospheric load are short. Modeling analyses suggest that significant benefits can be expected within a decade of sustained load reductions, with the ultimate benefits occurring within about 30 years.

Monitoring data suggest that the Everglades has responded to decreased mercury emissions from South Florida. Trend monitoring confirms these reductions, which appear to take effect more rapidly than model predictions.

Additional findings over the past year include the following:

- In 2003, annual volume-weighted total mercury (THg) concentrations in rainfall were elevated as compared to previous years - monitoring commenced in 1994 - at all three Everglades monitoring stations (e.g., stations at the Everglades Nutrient Removal Project, Florida Power and Light's Andytown substation, and the ENP's Baird Research Center). Accordingly, wet deposition (flux), which is a function of both concentration and rainfall, increased at two of the sites, and remained substantially greater than most other regions in the United States monitored by the National Atmospheric Deposition Program's Mercury Deposition Network.
- MeHg production and concentrations at the former mercury "hot spot" near site 3A-15 in Water Conservation Area 3 (WCA-3) have subsided substantially since 1993, correlating with declines in mercury emissions, sulfate, and DOC concentrations in surface waters at this site. Currently, site 3A-15 sulfate concentrations are well below optimal levels for MeHg-producing SRB.
- Research continues to highlight the importance of the interactions of mercury deposition, sulfur, and DOC on MeHg production and concentrations in Everglades biota.
- Sulfate continues to be discharged from the Everglades Agricultural Area to the Everglades at high rates. However, high sulfate concentrations are no longer evident at site 3A-15. It is likely that flow changes resulting from the Stormwater Treatment Areas coming online and/or other hydrological manipulations have caused the mercury hot spot to be relocated, possibly to the ENP. Enhanced monitoring is needed to track the changing spatial patterns of mercury throughout the system.
- Mercury concentrations in largemouth bass in WCA-1, 2, and 3 have declined by about 40 to 80 percent over the past decade, but still remain relatively high (0.2–0.7 mg/kg) compared to the USEPA's recommended MeHg fish tissue criterion of 0.3 mg/kg. Very high concentrations of mercury in bass remain evident in some portions of the ENP, specifically at the L-67 Ext canal and North Prong and Lostman's Creek sites.
- Presently, anthropogenic point source emissions of mercury from South Florida are calculated to be a small fraction (about 7 percent) of peak historical levels. However, the South Florida area source influence, composed of a myriad of smaller mercury emissions sources, remains poorly quantified. Some evidence suggests that local source influences are no longer declining (e.g., the total number of medical waste incinerators in Florida has rebounded from a low of two to eighteen statewide, with eight in South Florida). Despite the substantial earlier reductions, a micro-emissions inventory of South Florida may be required to identify and develop Best Management Practices, if the proposed USEPA's fish tissue mercury water quality criterion is to be attained.

- Changes in mercury concentrations in largemouth bass appear to have stabilized at most Everglades sites post-1998. Thus, in the absence of further reductions in larger-scale emissions that impact South Florida, the mercury problem will likely persist, albeit at a lower level than 10 to 15 years ago, unless alternative means for mitigating MeHg bioaccumulation in the food chain are elucidated and implemented. The most promising remaining means of managing MeHg may be by controlling sulfate loading to the Everglades.

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

RESEARCH PROGRESS

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

1. Quantify the no-effect level for wading bird dietary exposure to methylmercury (MeHg) to support a revised numerical Class III water quality standard (2000 ECR).

   The Florida Department of Environmental Protection (FDEP), with potential support from the U.S. Fish and Wildlife Service (USFWS), plans to fund a multigenerational feeding study of mercury effects on fish-eating birds. A captive colony of white ibis (*Eudocimus albus)* will be established in Gainesville, Florida for controlled experimental studies. It is planned that the aviary will be constructed in time for the 2005 spring breeding season.

   The proposed research seeks to test whether MeHg concentrations at ambient levels in the South Florida environment are likely to cause developmental or reproductive impairment in white ibis (a representative carnivorous wetland bird). Although this is not designed as a titration study, the work also seeks to define a threshold at which any effects occur. Although effects have been examined in numerous field studies of many birds, the results are nearly always confounded by uncontrolled effects of weather, environment, and mobile unmarked individuals. Developmental and reproductive effects have been clearly established in a captive situation for ducks, but the literature indicates that enormous variation exists in susceptibility across species. This uncertainty leads to very wide confidence margins in risk assessments and equivocal support for any particular regulatory policy.

   The research approach used in this study is to establish experimental groups of captive birds in a 135-foot diameter aviary, allowing for controlled dosing and isolation of sources of variation. Ibises will be brought into captivity as piping eggs or day-old chicks, and reared to reproductive age (approximately 22 months) in the aviary setting. A minimum of two breeding seasons is considered necessary for appropriate experiments because large variation is typical of first-time breeders.

Endpoints for Phase 1 of this research include white ibis food consumption, bird mass gain over time, fledging mass, health indicators (packed red blood cell volume, white blood cell counts, body fat, immune response), behavioral indicators (activity levels, shade-seeking, exploratory behavior, hunting behavior), and mortality during periods of severe weather. In Phase 2, which is not yet funded, reproductive outcome and reproductive behavior endpoints will be examined.

2. Quantify “global versus local” and “new versus old” sources of mercury (2001 ECR) from receptor relationships of mercury (2002 ECR).

   The FDEP and the U.S. Environmental Protection Agency (USEPA) continue to (1) support atmospheric mercury studies relevant to the mercury control policy in U.S. southeast coastal regions, (2) sponsor studies that directly measure transport of mercury species into Florida, (3) describe and quantify the atmospheric reactions of mercury that facilitate deposition, and (4) employ photochemical grid models to organize the atmospheric processes research into decision making. The operation of two sites in the Speciated Atmospheric Mercury Study (SAMS) project by the Broward County Air Quality Division is continuing. This project focuses on the paramount importance of the speciation of mercury in the atmosphere in controlling the transport and fate of mercury. SAMS makes highly time-resolved measurements of all known forms of atmospheric mercury and associated tracer species. It is expected that this measurement and modeling project will continue through 2006. As a prelude to this ‘Third-Generation Mercury Study’ (EgHgIII), the U.S Environmental Protection Agency (USEPA) has established mercury ‘super sites’ in Ohio and Hawaii to assess and contrast the impacts of the emissions and transport among the handful of intensive mercury monitoring sites worldwide. This joint study by the USEPA and the FDEP envisioned for 2005 and 2006 will add monitoring sites at Everglades National Park (ENP or Park) and Tampa, Florida as part of a nascent, global network. Coordinated analyses among these sites will provide improved data, tools, and understanding in the effort to resolve the question of the importance of long-distance transport of mercury into Florida.

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

   Research aimed at defining both the details of the mercury methylation process and its quantitative relationships with factors that influence this process is important to understanding what controls the effective net production of MeHg in the aquatic system. The South Florida Mercury Science Program (SFMSP) has devoted significant effort to this topic from 2001–2004. A specific focus has been to organize the work around the requirements of the Everglades Mercury Cycling Model, while incorporating qualitative and quantitative information as it becomes available into this evolving model and providing a more robust tool for evaluating management options. The data from field studies are being fed directly into model formulation and testing. The results are then used to calibrate and test the E-MCM in order to simulate the effects of various hydrology, water quality, or restoration activities.

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

Increasing focus on the role of sulfate as it influences MeHg production has led to concomitant effort to incorporate sulfur cycling in the E-MCM. The coupling of mercury cycling to sediment biogeochemical processes is complex, involving issues related to mercury bioavailability and the relative propensity of different principle bacterial functional groups and genera within those groups to methylate inorganic mercury [Hg(II)]. The goal of the modeling component of this project is to incorporate information on the biogeochemical characteristics of Everglades sediments with experimental and observational information on sediment mercury geochemistry and microbial transformation into a diagenetic, transport-reaction mode. This model will be used to predict the depth distribution of mercury methylation as a function of sediment biogeochemical zonation, and the relative abundance and physiological-biochemical properties of different functional groups of microorganisms.

The potential role of sulfate has also been underscored through extensive modeling with the E-MCM of recent historical trends of mercury concentrations in largemouth bass in the Everglades over approximately the past decade. This modeling has examined the cause and effect relationship between changes in atmospheric deposition, sulfur, dissolved organic carbon (DOC), and phosphorus dynamics as the possible drivers for the observed declines in largemouth bass mercury concentrations. The modeling effort has taken advantage of our current state-of-the-art understanding of trophic state interactions with the mercury cycle. The model hindcasting suggests that sulfate trends may have contributed as significantly as changes in atmospheric inputs of mercury to the observed biota trends. It also illustrates that the role of sulfur (i.e., the sulfate/sulfide redox couple) in mercury methylation needs to be further investigated and quantified.

4. Research geochemical controls on mercury methylation (2001 ECR).

   The FDEP continues to support a series of studies with the U.S. Geological Survey and the Smithsonian Institute. Field mesocosm experiments using stable-isotope and other tracer techniques have been used to examine the interactions between mercury, sulfur, and DOC, and methylation rates of "old versus new" mercury. Field work began with deployment of mesocosms in spring 2001; field experiments are presently scheduled through June 2006. Further research on the influence of the effects of wetting and drying cycles on MeHg production is currently scheduled for 2005–2006. Research and monitoring on MeHg production in Stormwater Treatment Areas (STAs) is included in Appendix 2B-2 of the *2005 South Florida Environmental Report – Volume I* (SFER).

5. Collect data on trends of mercury in Florida (2002 ECR).

   Long-term trends of mercury in Everglades fish and wading birds are presented in this chapter. Continued collection of these data provides a demonstration of the effects of changes in mercury deposition, water chemistry, and water flow on mercury exposure of fish and wildlife.

LINKING DECLINES IN LOCAL ATMOSPHERIC EMISSIONS TO MERCURY CONCENTRATION DECLINES IN EVERGLADES BIOTA

Multiple lines of evidence demonstrate that the mercury concentrations in fish and wading birds in the Everglades have declined sharply over the past decade (Atkeson et al., 2003). Declines in mercury levels in biota were preceded by a long-term rise in mercury emissions beginning in the mid twentieth century, which peaked circa 1990, and subsequently declined by 90 percent by 2000. Given that atmospheric sources of wet and dry deposition are accepted as the major sources of mercury to the Everglades (Stober et al., 2001), and because local emissions have been inferred to be the predominant source of mercury deposited in South Florida rainfall including the Everglades, it has been hypothesized that the decline in local emissions was the primary driver for the biotic response over the past 10 to 15 years (Dvonch et al., 1999; Atkeson et al., 2002).

In order to have a clear causal link between declining local emissions of mercury and biotic response, there needs to be proven evidence in several areas. First, there must be unambiguous evidence that declines in local emissions have occurred. Second, there needs to be proof that declining local emissions have produced significant declines in the fluxes of mercury delivered to the Everglades in atmospheric deposition. Third, the declines in mercury concentrations in biota need to be unambiguous. Fourth, there needs to be proof that quantitatively links the resultant declines in atmospheric deposition to the observed biota declines, both in terms of the timing and the magnitude of the decline. These points are the subject of the following four sections.

Trends in Local Emissions of Mercury

Two separate analyses have been recently conducted to examine whether there have been declines in local mercury emissions. RMB Consulting & Research, Inc. (2002) used a direct approach where a historical emissions inventory was compiled from 1980–2000 for Southeast Florida (i.e., Broward, Dade, and Palm Beach counties). Emissions were estimated from plant operational data and emission factors typical for the source under consideration. These three counties were selected as the regions containing sources most likely to be important local contributors to mercury deposition in the Everglades and South Florida. The second analysis (Husar et al., 2002) in turn used an inferential, or indirect, approach where the trend in local emissions was inferred by reconstructing a mass balance on the flows of mercury ascribed to various use categories or major economic sectors. This latter analysis (1850–2000) first focused on mercury use on a national scale, then performed a statewide analysis of Florida, and finally concluded with a regional analysis for Broward, Dade, and Palm Beach counties.

Similar results were obtained by both groups of researchers. The emissions estimates (RMB Consulting & Research, Inc., 2002) indicated very large changes occurred from 1980 through 2000 as a function of the major combustion sources in South Florida: power generation, sugar industry, and incineration of municipal and medical wastes (**Figure 2B-1**). Total emissions were quite low from 1980–1982, and then increased in 1983 by 3.5 times above 1982 levels, when both municipal waste combustors (MWC) and medical waste incinerators (MWI) came online. Local emissions continued to increase through the 1980s until 1991. The material flows analysis (Husar et al., 2002) suggests an earlier peak in local emissions occurring circa 1984, followed by a sharp monotonic decline to 1991. Both analyses indicate that local emissions declined by greater than 90 percent from the peak emission period to the present. The overwhelming fraction of the emissions reduction was due to reductions in emissions by both MWIs and MWCs in response to regulatory changes.

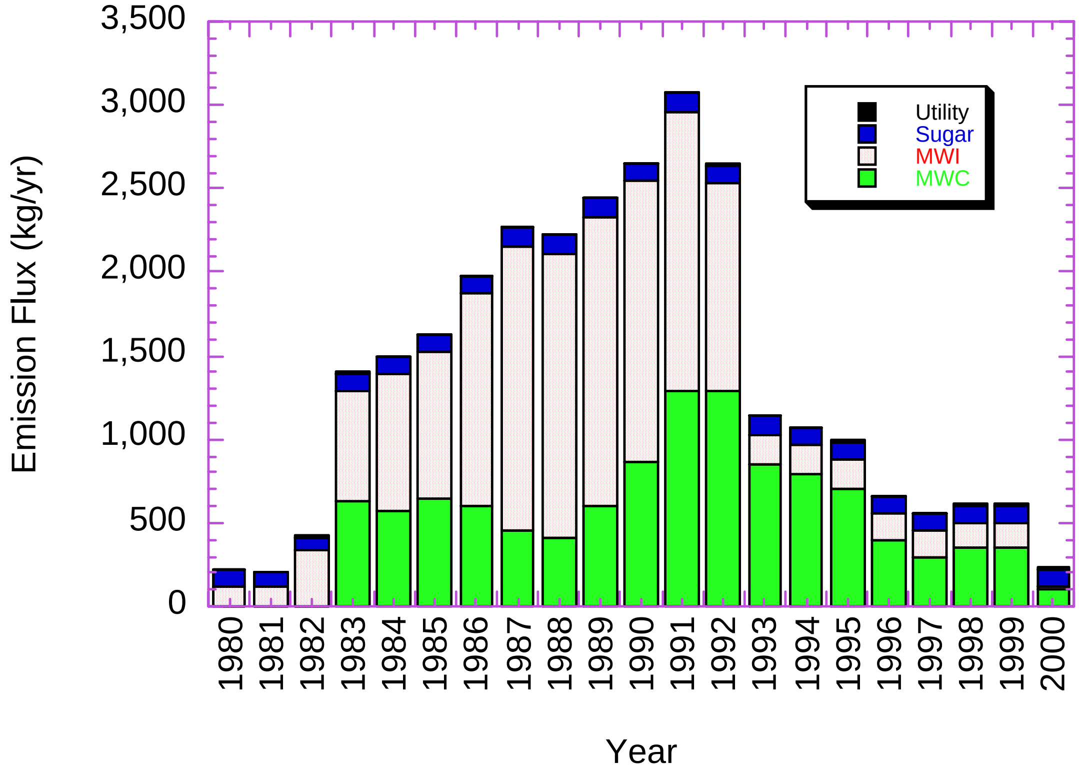

Figure 2B-1. Annual atmospheric mercury emissions in South Florida from 1980–2000, estimated as a function of major combustion source category (RMB Consulting & Research, Inc., 2002). Sources include power generation facilities (utility), municipal waste combustors (MWC), medical waste incinerators (MWI), and sugar refineries (sugar). Note that utility emissions are too small to be discernable in this graphic.

Trends in Atmospheric Deposition of Mercury

A continuous record of wet deposition fluxes and concentrations of mercury generally are available for samples from November 1993 through December 2002 collected from the Beard Research Center in the ENP as part of the Florida Atmospheric Mercury Study (FAMS) from 1993–1996 (Pollman et al., 1995, Guentzel et al., 1995; Guentzel et al., 2001) and the National Atmospheric Deposition Program's (NADP's) Mercury Deposition Network (MDN) from 1996–2002 (http://nadp.sws.uiuc.edu/mdn). Statistical analysis of the wet deposition fluxes for mercury was performed from these ENP samples to determine whether trends can be related to changes in the atmospheric signal or are related to changes in rainfall patterns (Atkeson et al., 2004). Using an analysis of variance (ANOVA) to account for the effects of both seasonal dynamics and rainfall volume on mercury concentrations, it was determined that volume-weighted mean mercury concentrations declined by approximately 3 nanograms per liter (ng/L) due to factors other than these two variables (Atkeson et al., 2004). The magnitude of this decline (approximately 25 percent) is more than can be ascribed to larger-scale sources alone (particularly, global sources) during this time, estimated between 7 and 11 percent, based on trends in ambient air concentrations of total gaseous mercury in the northern hemisphere between 1990 and 1999 (Slemr et al., 2003).

However, annual volume-weighted mean concentrations in 2003 increased at all three South Florida sites (stations at the ENR Project, Florida Power and Light's Andytown substation, and ENP's Baird Research Center) compared to previous years since monitoring was initiated in 1994 (Appendix 2B-1 of the 2005 SFER – Volume I). Consequently, wet deposition (flux), which is a function of both concentration and rainfall, also increased in 2003. Wet atmospheric loading of total mercury (THg) to the Everglades Protection Area (EPA) was estimated to range from 161 to 258 kilograms per year, or kg yr^{-1} (Appendix 2B-1); the upper range exceeding loading estimates for 1994 (238 kg yr^{-1}) and 1995 (206 kg yr^{-1}). Due to a combination of elevated concentrations and the high annual rainfall in South Florida, wet THg deposition to the Everglades remains substantially greater than most other regions monitored by the NADP's MDN (see **Figure 2B-2**).

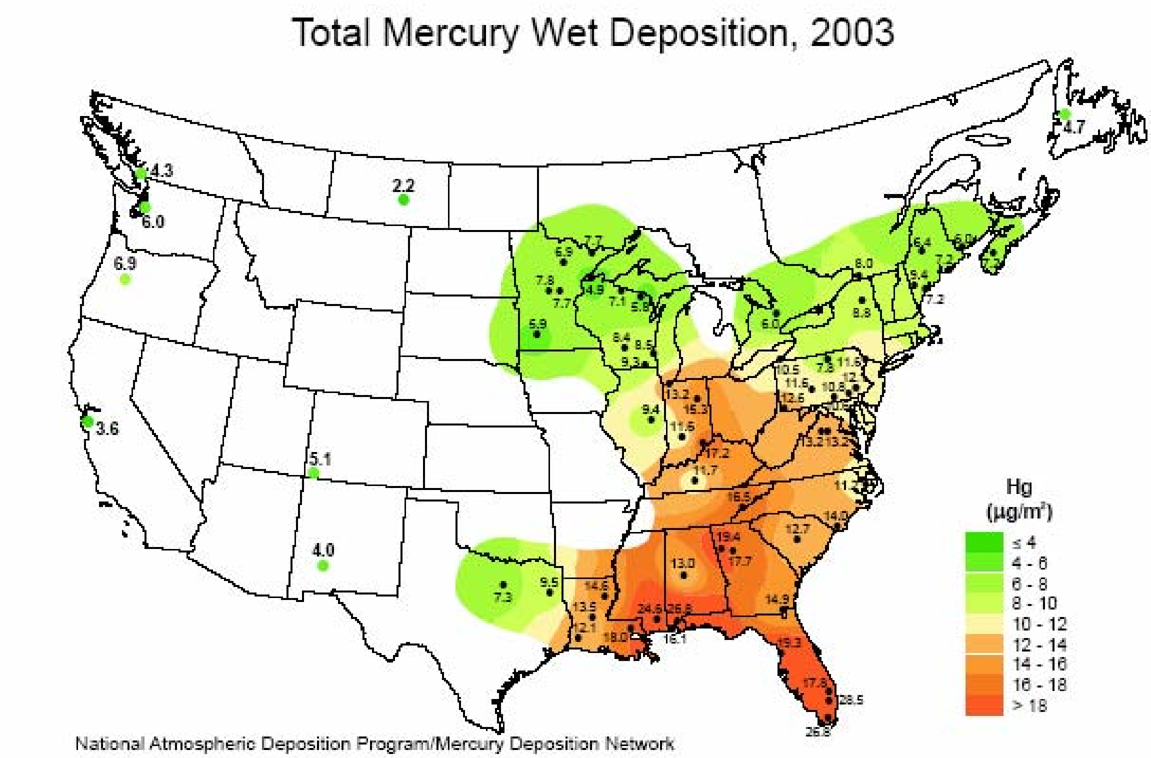

Figure 2B-2. Wet deposition of total mercury in 2003. Data from National Atmospheric Deposition Program's Mercury Deposition Network (http://nadp.sws.uiuc.edu/mdn/).

Trends in Mercury Concentrations in Everglades Biota

Two data sets are available to examine long-term trends in mercury concentrations in biota in the Everglades: (1) data analyzing tissue mercury concentrations in largemouth bass (*Micropterus salmoides*) from sites throughout Florida since 1988, including nine sites in the Everglades (Lange et al., 2003); and (2) data examining mercury concentrations in great egret (*Ardea alba*) chick feathers throughout Florida since 1994, including seven sites in South Florida (Frederick et al., 2001). Research was done to analyze the significance of the temporal trends in both data sets through 2000 using the non-parametric Mann-Kendall Slope Test-of-Sign (Pollman et al., 2002). This monitoring was supplemented and expanded in terms of sampling locations, and targeted species or life stages in 1998 through the District's monitoring program (Appendix 2B-1; Rumbold et al., 2001 and 2002).

In general, the statistical analysis of Pollman et al. (2002) substantiated the overall robustness of declining trends in both largemouth bass and great egret chick mercury concentrations. The largemouth bass data were tested separately for each site and age cohort. Of the total of 72 age cohort site combinations, 19 showed significant declines ($p = 0.05$), 22 showed no trend, 28 had insufficient data to test for significance, and three showed an increasing trend. Of the nine sites monitored with the Everglades, only the fish at site U3 in Water Conservation Area 2A (WCA-2A) showed an increasing trend, apparently due to a highly localized effect both in time and space, such as peat burning and oxidation that occurred in the Everglades following the intense drought and drydown in May and June 1999 (Pollman et al., 2002).

Great egret chick feather data from all seven sites (Frederick et al., 2001) also was tested for trend significance. During trend significance analysis, the time frame spanned by the great egret study extended from 1994–2001 (Pollman et al., 2002). Additional data have since been collected, and the full POR now extends to 2003 (**Figure 2B-3**). Four of the seven great egret nestling sites (Alley, Hidden, J-W1, and L-67) studied showed significant downward trends through 2001 (Frederick et al., 2001). Subsequent data collected for 2002 and 2003 further substantiate the overall robustness of the downward trend. Consistent with the largemouth bass results from the same region (**Figure 2B-4**), results from great egret colonies located in the mid Everglades indicate over an 80-percent decrease in mercury concentrations from 1994–2003. Although these downward trends may be cause for optimism, additional concerns do remain, as discussed in the following sections.

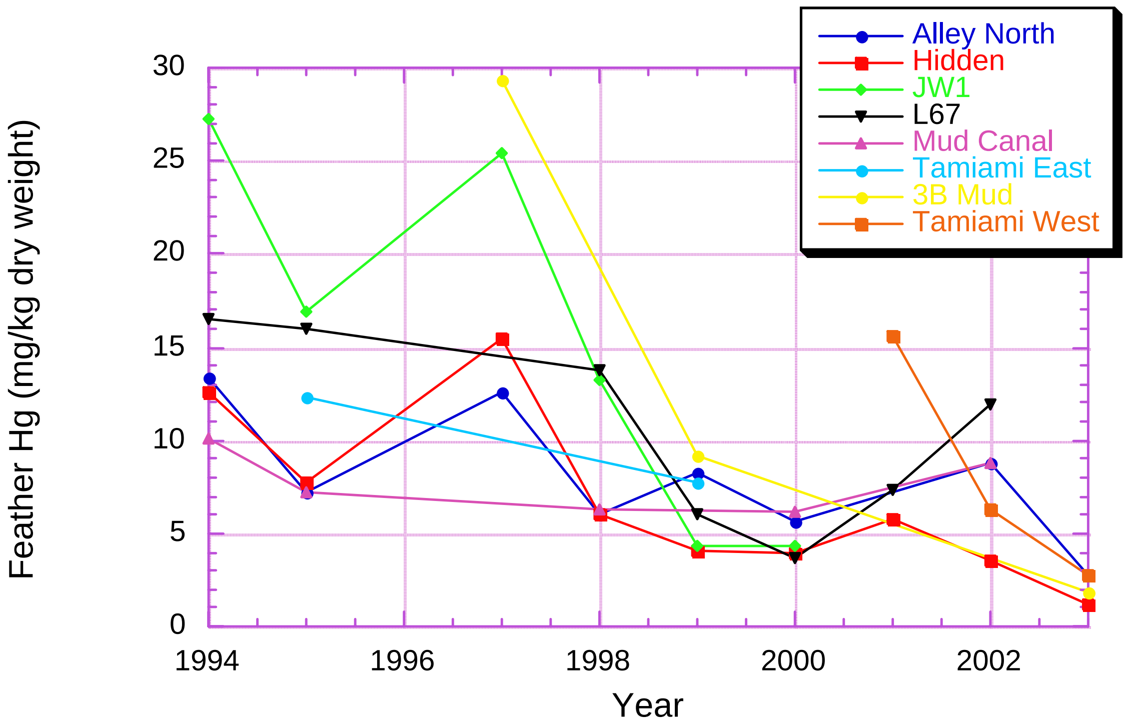

Figure 2B-3. Mercury concentrations in great egret nestlings at various colony locations in the Everglades from 1994–2003. From unpublished data (Frederick, 2003). Discontinuities in the period of record (POR) reflect years when a colony site was abandoned or otherwise not used (Frederick et al., 2001).

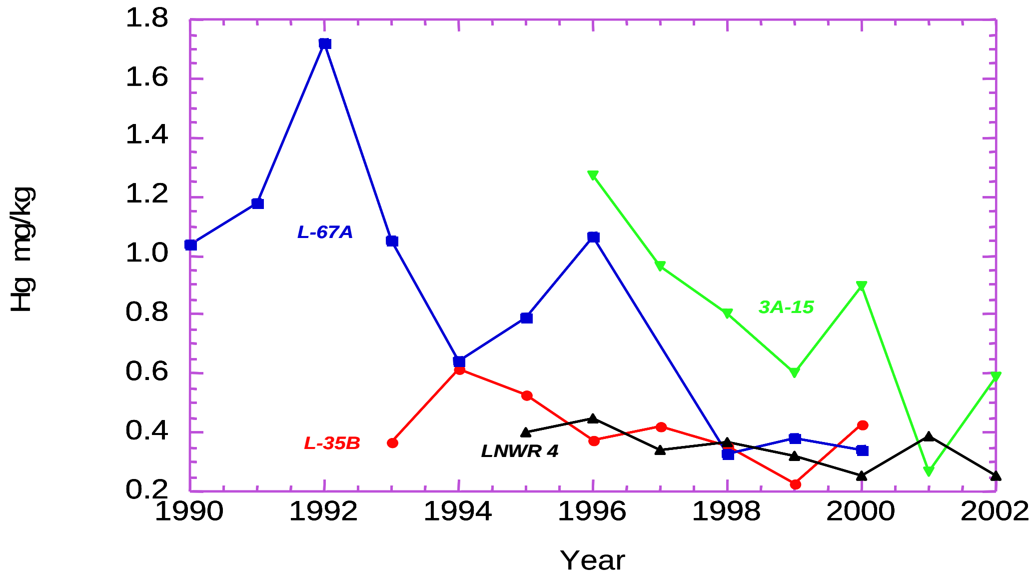

Figure 2B-4. Time series of geometric mean mercury concentrations in largemouth bass (age 1–2 cohort) for four sites in the Everglades. L-67A and L-35B are canal sites in WCA-3 and WCA-2, respectively; 3A-15 and LNWR-4 are interior marsh sites located in WCA-3A and the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge) (within WCA-1), respectively.

Links between Reductions in Local Mercury Emissions and Mercury Concentrations in Biota

Atkeson et al. (2004) used the E-MCM (Harris et al., 2003) to examine whether the observed changes in mercury concentrations in largemouth bass can be explained, both with respect to timing and magnitude, by changes in atmospheric loadings of mercury. The model hind-cast simulations were conducted at site 3A-15, which has long been a mercury hot spot in the central Everglades, and which has also experienced recent declines in largemouth bass mercury concentrations. Atkeson et al. (2004) constructed a simplified deposition trajectory for mercury between 1900 and the present, based on historical fluxes and enrichment ratios of mercury accumulation (pre-1900 and circa 1990) measured by Rood et al. (1995), ambient wet deposition fluxes measured in 1995–1996, and dry deposition fluxes estimated for the same year (Keeler et al., 2001). Consistent with the trends observed at the ENP, the trajectory (**Figure 2B-5)** also assumed that mercury deposition continued to decline after 1996 by about 25 percent.

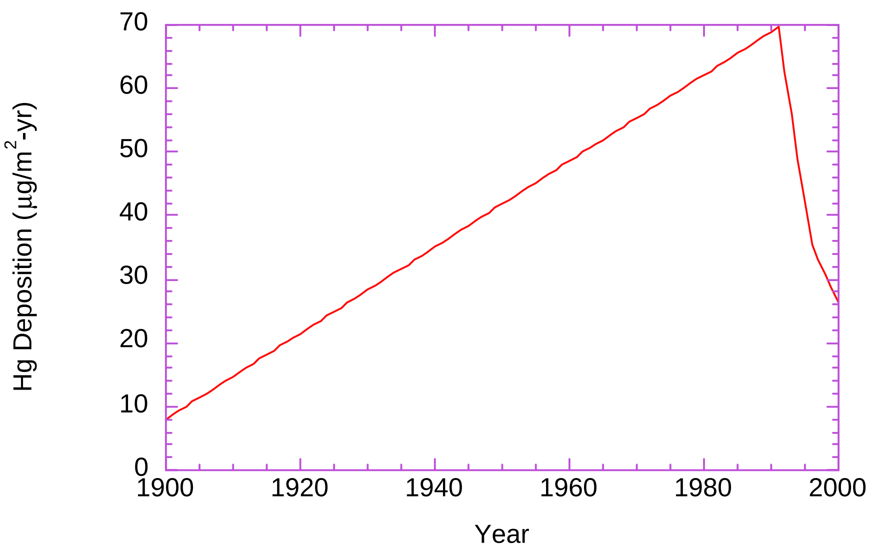

Figure 2B-5. Total (wet plus dry deposition) mercury deposition trajectory used in the Everglades Mercury Cycling Model (E-MCM) model hind-cast (Atkeson et al., 2004).

The hind-cast results indicate that the assumed declines in atmospheric inputs can explain nearly 60 percent of the observed decline in observed trends in largemouth bass mercury concentrations, a predicted 48-percent decline versus an observed 75-percent decline (**Figure 2B-6**). Likewise, the predicted timing of the biota decline is concordant with the observed results. The fraction of the observed decline unexplained by the model hind-cast may reflect several factors. First, the reconstructed deposition trajectory may reflect an underestimation of the effects local sources historically exerted on mercury deposition rates in the Everglades. For example, the simulation assumes that the decline in deposition from 1991–2000 was 62 percent, compared to an approximate 75-percent decline in biota. Given the essential linearity of the long-term response of the model (Harris et al., 2001), the hind-cast at most would predict a 62-percent decline. Second, the depth of surficial sediments actively exchanging with the water column assumed by Atkeson et al. (2004) may have been overestimated. Reducing the exchange depth would bring the slope of the predicted response closer to the slope of the deposition trajectory, which in turn is nearly coincident with the slope of the observed biotic response. Third, the larger observed response may also reflect changes in other environmental variables during the same period, in particular declining surface water sulfate concentrations observed at the site which can influence rates of MeHg production (Pollman et al., 2004). The effects of these other variables need to be examined more carefully before more definitive conclusions on causality can be reached.

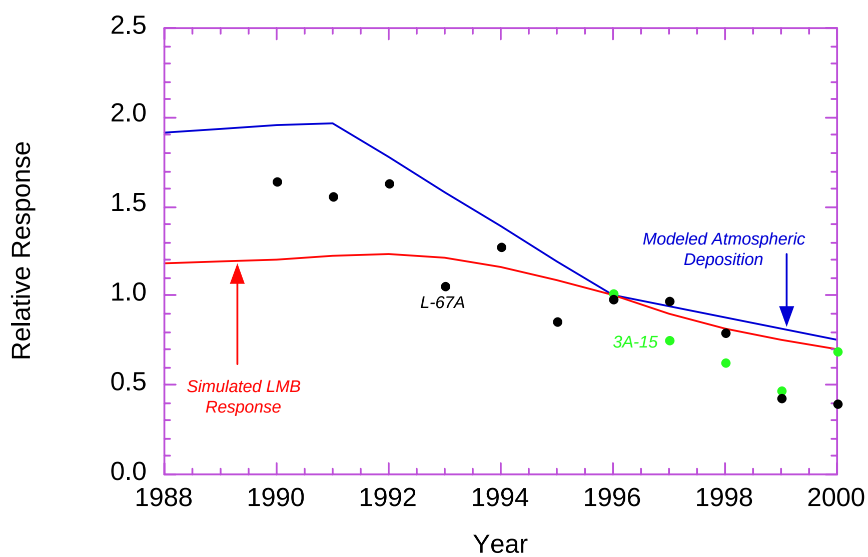

Figure 2B-6. E-MCM simulation hindcast of changes in mercury concentrations in largemouth bass age-1 cohorts at site 3A-15, in response to assumed changes in atmospheric deposition. Analysis assumes that the depth of surficial sediments actively exchanging inorganic mercury [Hg(II)] is 1 cm. Shown are normalized (relative to 1996) changes in atmospheric deposition inputs, observed concentrations in largemouth bass (filled circles) for both 3A-15 and the L-67A canal located approximately 20 km east of site 3A-15 (Atkeson et al., 2004).

CONCENTRATIONS OF MERCURY IN EVERGLADES FISH

Concentrations of Mercury in Everglades Largemouth Bass Relative to Acceptable Levels

Largemouth bass, a popular Everglades sport fish, as well as a high trophic level fish, were selected in the late 1980's as a species to monitor as regards to mercury pollution. A number of long-term monitoring sites for tracking mercury concentrations in largemouth bass were established across the Everglades as early as 1990 (Lange et al., 2004) (**Figure 2B-7**). Mercury concentrations in largemouth bass in WCA-1, 2, and 3, while having declined by approximately 40 to 80 percent over the past 8 to 13 years (**Figures 2B-8** through **2B-10**, respectively), remain relatively high (about 0.2 to 0.7 milligrams per kilogram, or mg/kg) as compared to human health considerations for consumption of fish. The USEPA has proposed a criterion of 0.3 mg/kg MeHg in fish tissue for the protection of human health related to the consumption of freshwater and estuarine fish. As such, the mercury levels in largemouth bass in WCA-2, WCA-3, and the ENP generally remain well above the USEPA's recommended criterion. Additional information on this criterion can be found on the USEPA's Website at http://www.epa.gov/fedrgstr/EPA-WATER/2001/January/Day-08/w217.htm.

Mercury levels in fish tissues must also be assessed for risk to wildlife. The U.S. Fish and Wildlife Service (USFWS) has proposed a predator protection criterion of 0.1 mg/kg THg in prey species (Eisler, 1987). In the Mercury Study Report, the USEPA proposed 0.077 mg/kg and 0.346 mg/kg of MeHg for trophic level (TL) 3 and 4 fish, respectively, for the protection of wildlife (USEPA, 1997). When results of the Florida Fish and Wildlife Conservation Commission (**Figures 2B-8** through **2B-10**) and District monitoring programs (Appendix 2B-1) are evaluated using these criteria, it is evident that certain Everglades' populations of piscivorous avian and mammalian wildlife continue to be at risk of adverse effects from mercury exposure. This conclusion is consistent with a recent ecological risk assessment that focused on STA-2 as well as other reference areas in the Everglades (Rumbold, in press). This assessment found that current exposures continue to exceed effects thresholds. Simulations indicated MeHg exposures were greatest in the northern ENP (see discussion below). In fact, the probability of exceeding the lowest-observed-adverse-effects level in the northern ENP suggested a high likelihood that some adverse effects may be expected. At the same time, an uncertainty analysis of that risk assessment underscored the need for additional studies to quantify the no-effect level for wading birds.

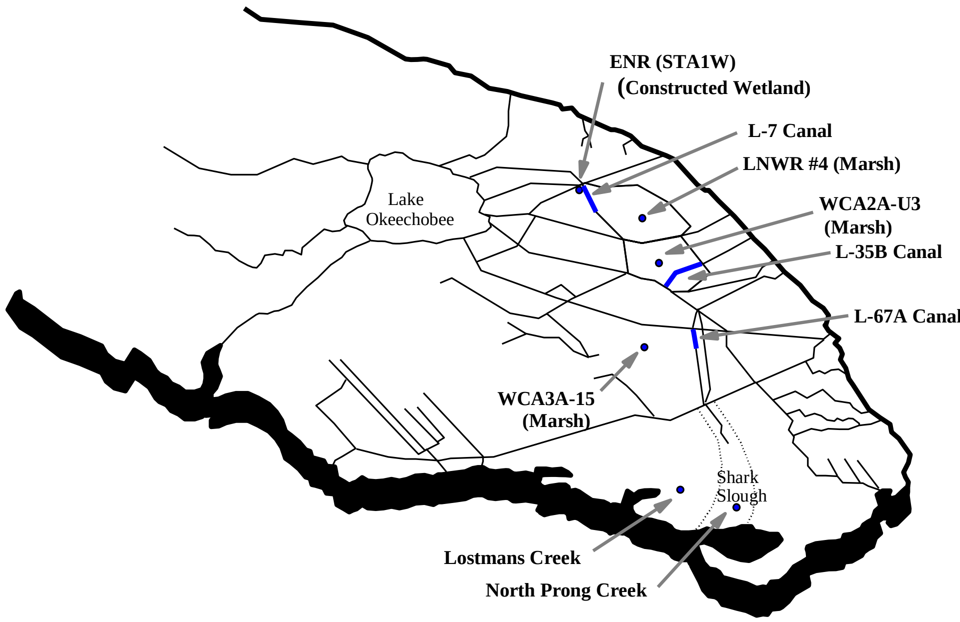

Figure 2B-7. Location of the Florida Fish and Wildlife Conservation Commission long-term monitoring sites in the Everglades Protection Area (EPA) region (Lange et al., 2004).

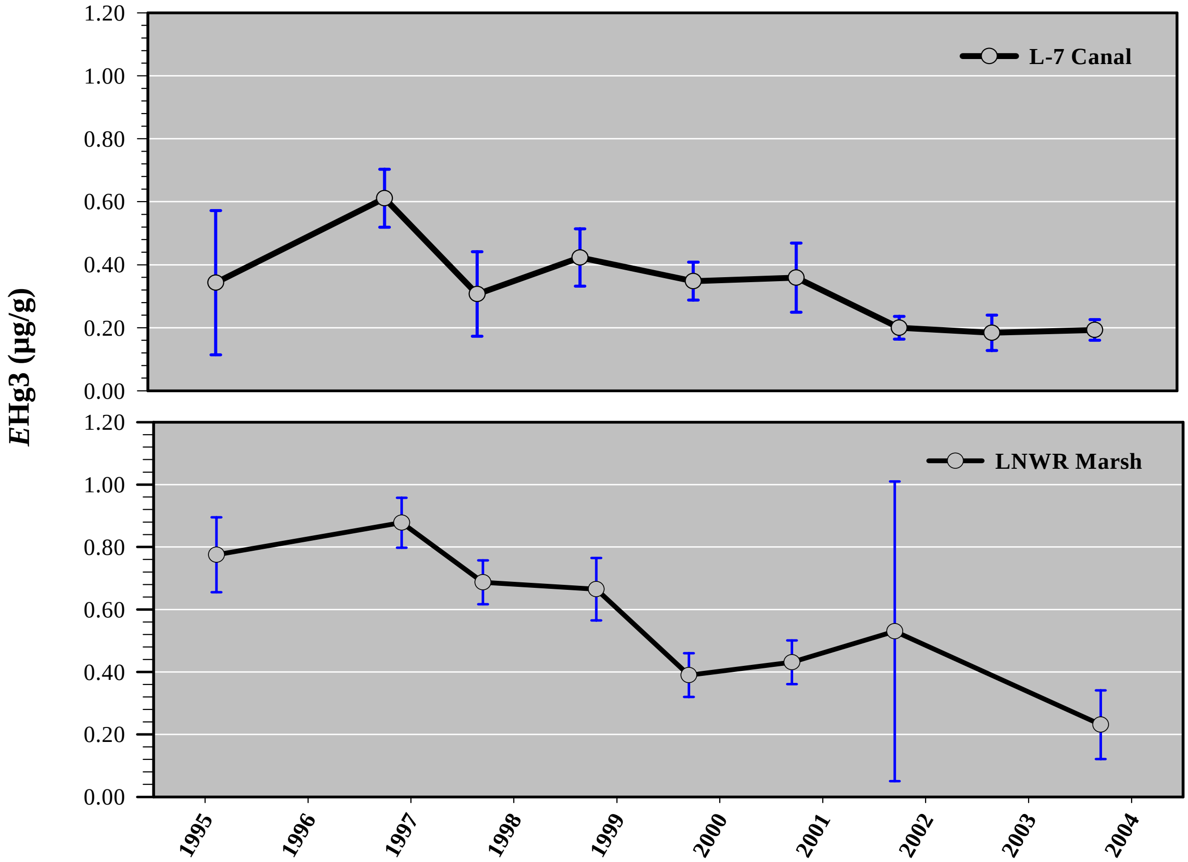

Figure 2B-8. Long-term monitoring sites located in the Refuge (within WCA-1), showing the age-standardized mercury concentration for three-year-old largemouth bass (EHg3) and the 95-percent confidence interval (95% C.I.) (Lange et al., 2004).

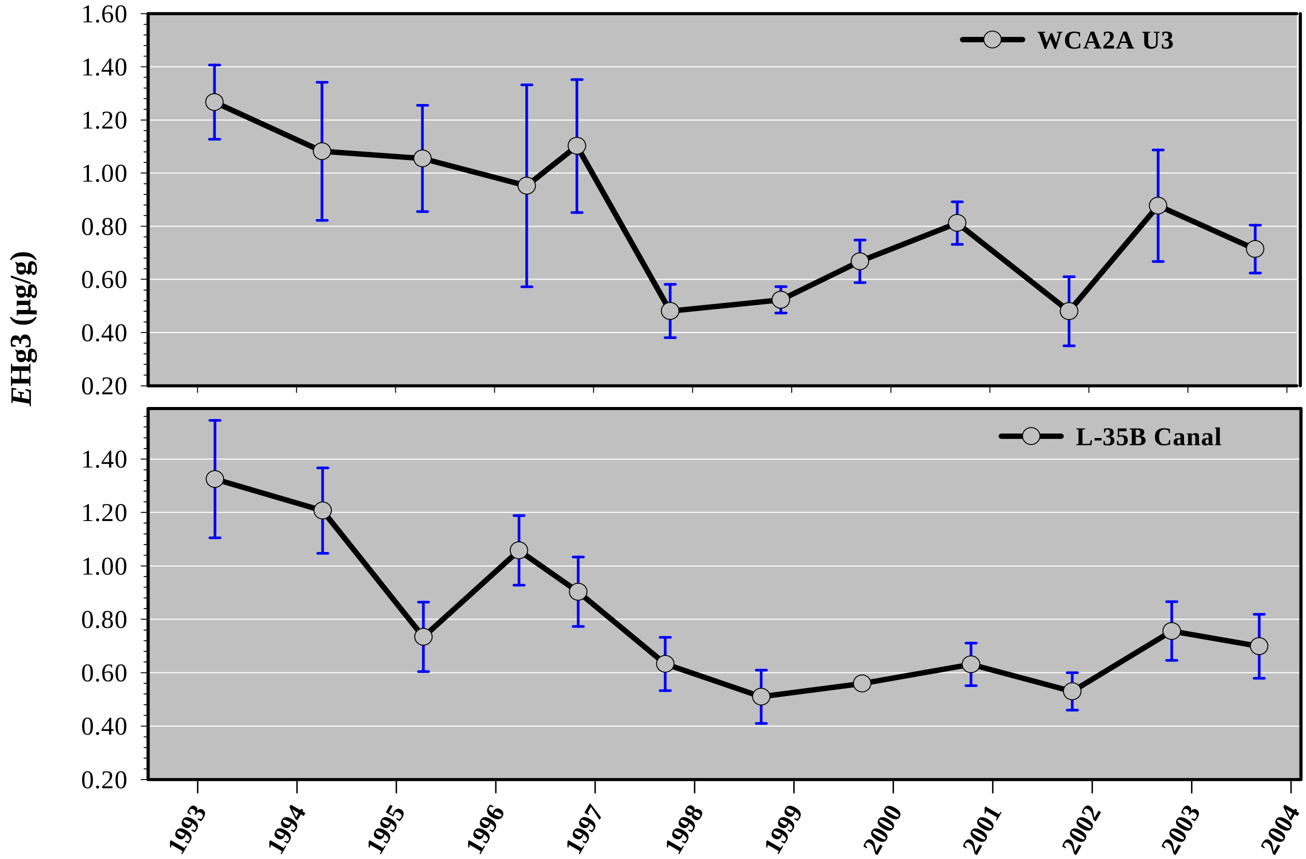

Figure 2B-9. Long-term monitoring sites located in WCA-2 showing the age-standardized mercury concentration (EHg3) for three-year-old largemouth bass and the 95% C.I. (Lange et al., 2004).

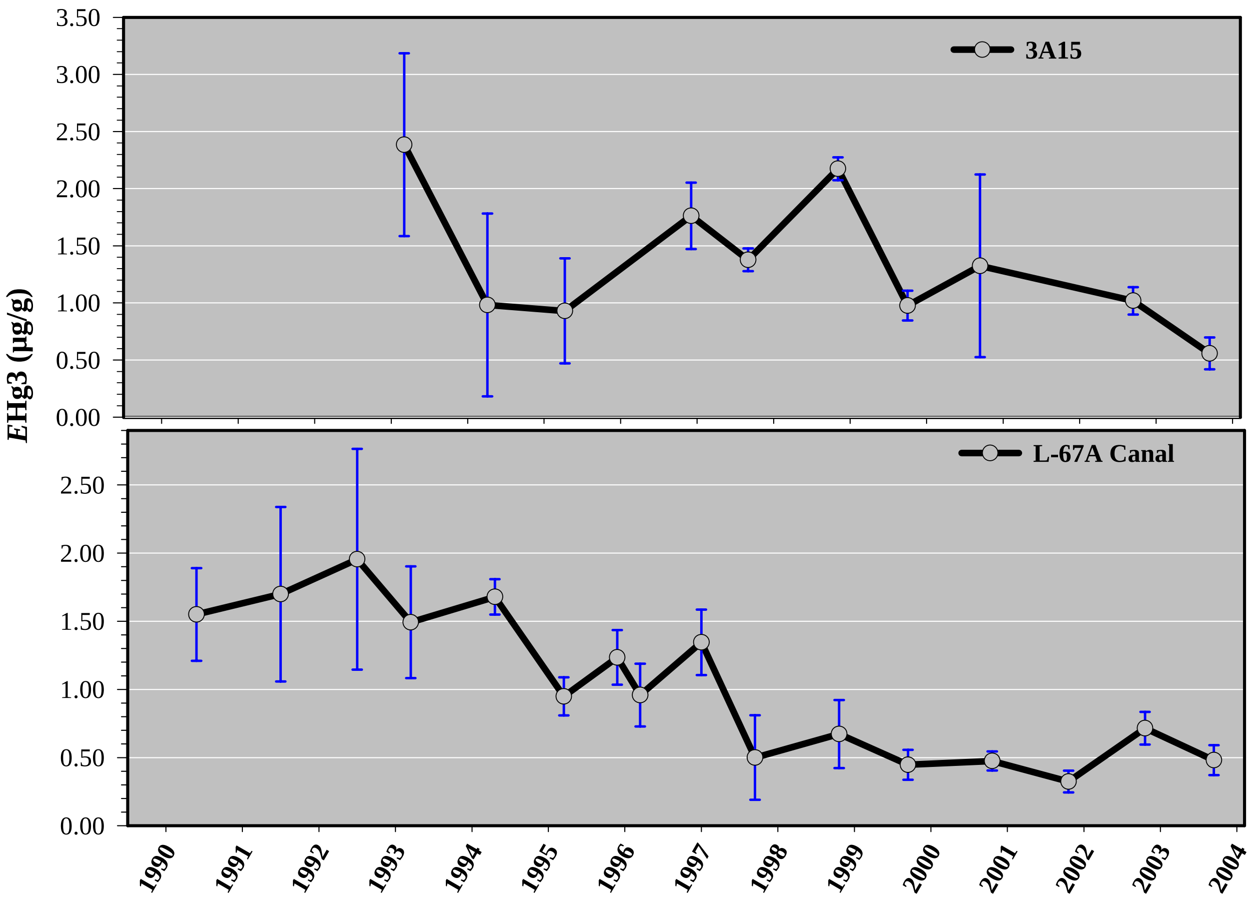

Figure 2B-10. Long-term monitoring sites located in WCA-3 showing the age-standardized mercury concentration (EHg3) for three-year-old largemouth bass and the 95% C.I. (Lange et al., 2004).

Concentrations of Mercury in Fish in the Everglades National Park

Mercury concentrations in largemouth bass in WCA-1, 2, and 3 have declined by about 40 to 80 percent over the past 8 to 13 years. In contrast, mercury declines in the ENP have been small or non-existent. Bass and sunfish from the northern ENP (L67F1) have been found to have elevated mercury levels in recent years (peaking at 1.6 mg/kg and 0.65 mg/kg, respectively; see Appendix 2B-1). Further south, at the North Prong Creek station (**Figure 2B-11**), mercury concentrations appear to have increased over the past 5 to 6 years, with the most recent concentrations peaking at approximately 1.7 mg/kg mercury in largemouth bass (**Table 2B-1**). Elevated mercury levels also persist in fish from eastern Florida Bay (Evans et al. 2003, cf. Strom and Graves, 2001). These elevated levels are not limited to fish, as alligators from the ENP have also been reported to have elevated Hg levels compared to those in the WCAs (Rumbold et al., 2002).

A methylmercury hot spot had been identified in the northern ENP in 1994–1995 by USEPA's Regional Environmental Monitoring and Assessment Program (see Figure 8.55 in USEPA, 1998). This raises the question why the ENP has not experienced the same declines as the WCAs. One possibility is that sulfate concentrations have not declined in the ENP as much as other areas such as WCA-3A-15 (i.e., the former MeHg hot spot), either due to natural inputs (e.g., estuarine or tidal influenced sites), or due to sulfate loading in stormwater runoff.

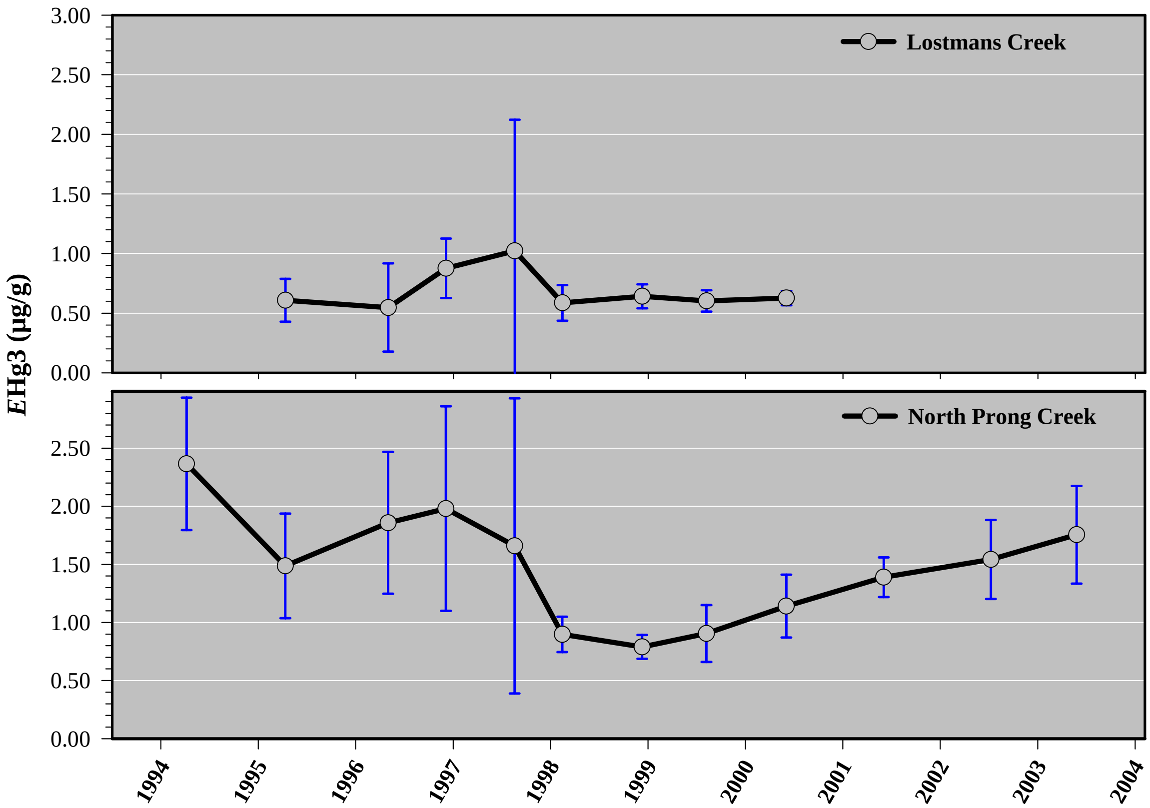

Figure 2B-11. Long-term monitoring sites located in the ENP showing the age-standardized mercury concentration (EHg3) for three-year-old largemouth bass and the 95% C.I. (Lange et al., 2004).

Table 2B-1. Long-term monitoring sites located in WCA-1, 2, and 3, and the ENP, showing the station location, the sampling period of record (POR), and percent change over the POR in age-standardized median mercury concentration for three-year-old largemouth bass (Lange et al., 2004).

Location	Percent Change	Reported POR
Refuge (WCA-1)		
L-7 Canal	-44	1995–2003
Refuge Marsh	-70	1995–2003
WCA-2A		
WCA-2A U3	-44	1993–2003
L-35B Canal	-47	1993–2003
WCA-3A		
3A-15	-77	1993–2003
L-67A	-69	1990–2003
ENP		
Lostman's Creek	+03	1995–2000
North Prong Creek	-26	1994–2003

Where are the Mercury "Hot Spots" in the Everglades?

For several years, site 3A-15 in WCA-3 was identified as the MeHg hot spot in the Everglades, with high MeHg production levels and elevated concentrations in water, sediment, and fish. It is evident that MeHg concentrations in largemouth bass have recently declined at site 3A-15 (**Figure 2B-10**), with this station having experienced the largest decline of all Everglades stations in fish MeHg concentrations (77 percent from 1993–2003). Data also indicate that in recent years, THg concentrations in the water column at site 3A-15 have declined, but MeHg concentrations have declined at an even steeper rate (**Figure 2B-12**).

Corresponding with this trend in MeHg concentrations are declines in sulfate (**Figure 2B-13**) and DOC concentrations (**Figure 2B-14**). It is now likely that sulfate concentrations at site 3A-15 are suboptimal for MeHg production by sulfate-reducing bacteria (SRB). Reductions in sulfate concentrations at site 3A-15 in recent years may account for a substantial proportion of the largemouth bass MeHg concentration declines that are not explained by declines in atmospheric inputs of mercury.

The importance of sulfate related to MeHg production in the Everglades has been previously summarized in Atkeson and Axelrad (2004) and Appendix 2B-3 of the 2005 SFER – Volume I. Recent mercury and sulfate data suggests that sulfate control has efficacy for MeHg production control in the Everglades now that local mercury emission sources to the atmosphere have been reduced, so that further reductions may not provide substantial benefit for reducing fish mercury concentrations.

Data continue to suggest that there is high sulfate loading to the EPA from the Everglades Agricultural Area (EAA), with sulfate concentrations in canals leading from the EAA 100 times greater than those in the historical Everglades (see Figure 2A-13). MeHg production was formerly highest at the leading edge of the sulfate contaminate plume at station 3A-15. With the rerouting of water flow in the Everglades in recent years as a result of the STAs coming online and other hydrological alterations, it is highly probable that the MeHg hot spot has relocated, possibly to the southern end of WCA-3 or to the northern area of the ENP. Additional survey work is recommended to locate the new MeHg hot spot(s) in the Everglades.

Additional water quality monitoring of sulfate concentrations and loads to the Everglades is warranted in order to determine the importance of sulfate in mercury methylation rates. Sulfate monitoring is conducted at most EPA inflow structures on a quarterly basis with the exception of STA discharges, which are sampled biweekly. However, available sulfate data is insufficient to estimate loadings or flow-weighted concentrations. **Figure 2B-15** provides a summary of mean annual sulfate concentrations in EPA inflows (see Figures 2A-1 through 2A-5) since 1990, based on the best available information. Due to the low sampling frequency, particularly for the pre-STA historical period, there is substantial uncertainty associated with the quantification of annual inflow sulfate levels. This uncertainty, which is reflected by the wide-ranging 95-percent confidence intervals (95% C.I.) shown in **Figure 2B-15**, limits the ability to detect changes over time. Over the period of record, there may have been decreases in sulfate levels in WCA-3 and ENP inflows; however, the among-year differences are within the range of statistical uncertainty. Loading information is needed to more fully understand observed interior marsh mercury and sulfate patterns and trends. Quantification of sulfate loading rates would require increased monitoring frequencies. At a minimum, monitoring would need to be conducted on a monthly basis across all inflow structures. Ideally, the sampling should be conducted at the same frequency as total phosphorus (i.e., monthly, or biweekly, when flowing).

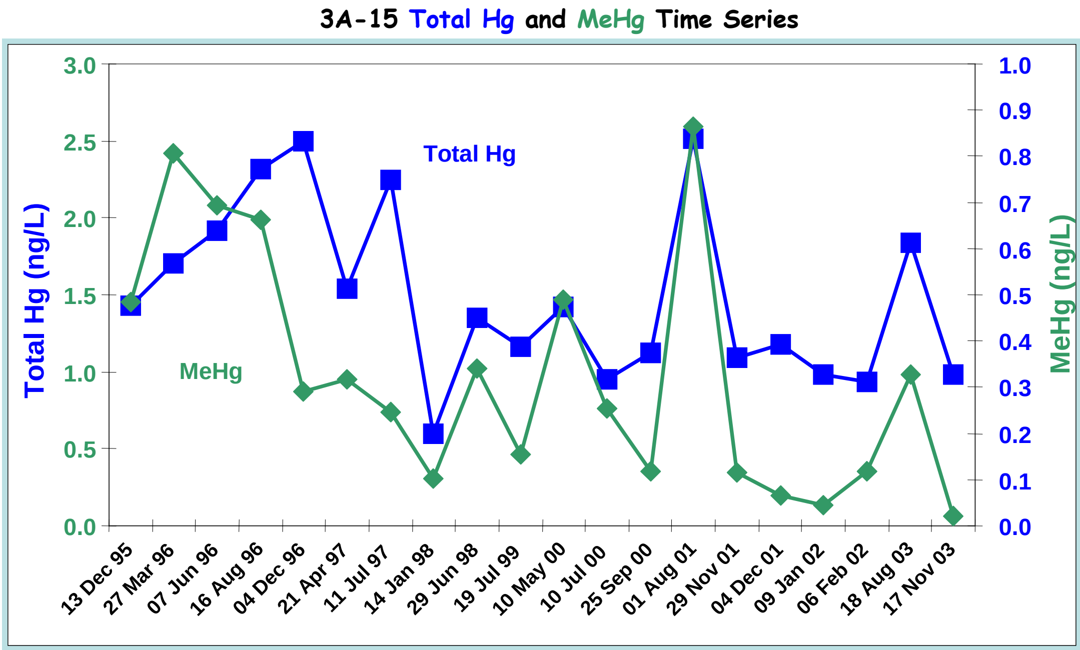

Figure 2B-12. Total mercury and methylmercury concentrations (ng/L) in the water column at site 3A-15 from 1995–2003 (Krabbenhoft et al., 2004).

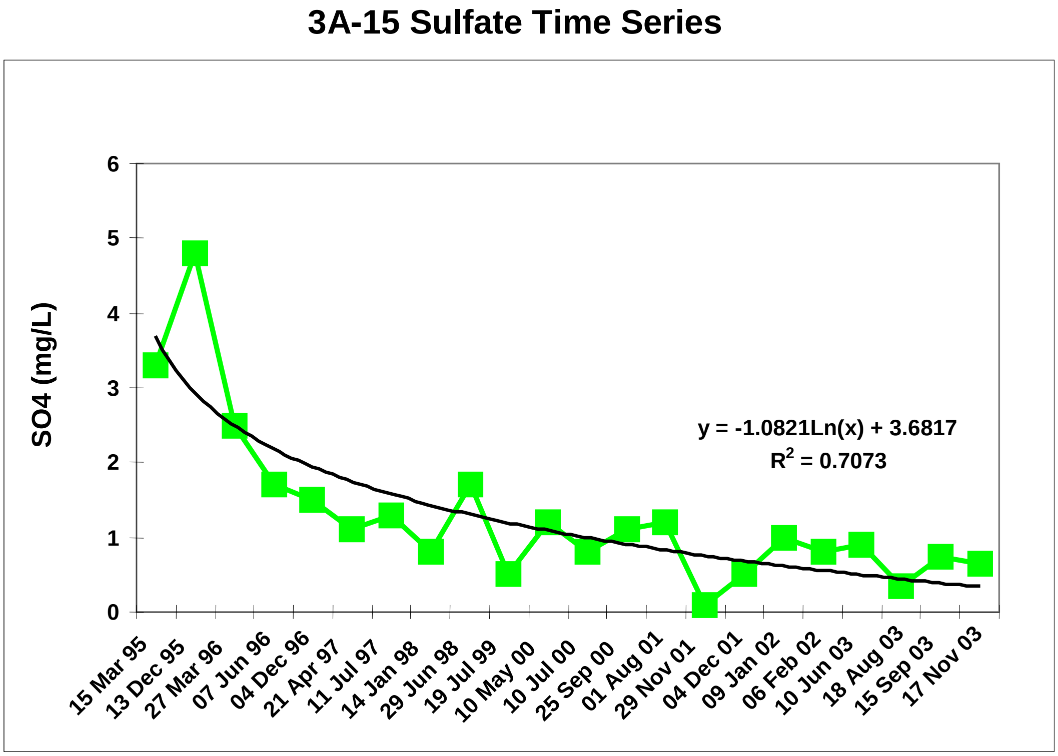

Figure 2B-13. Sulfate concentrations (mg/L) in the water column at site 3A-15 from 1995–2003 (Krabbenhoft et al., 2004).

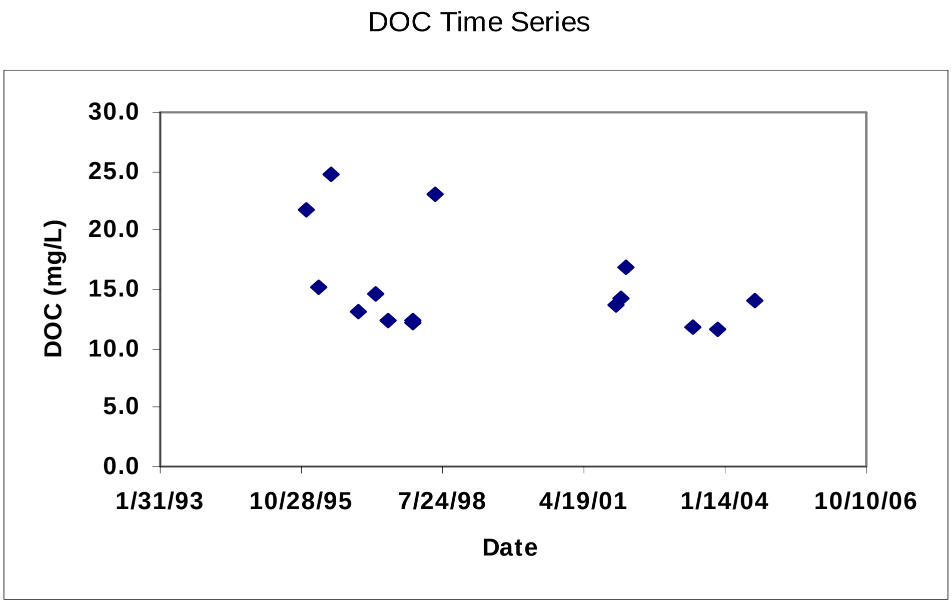

Figure 2B-14. Dissolved organic carbon concentrations (mg/L) in the water column at site 3A-15 from 1995–2003 (Krabbenhoft et al., 2004).

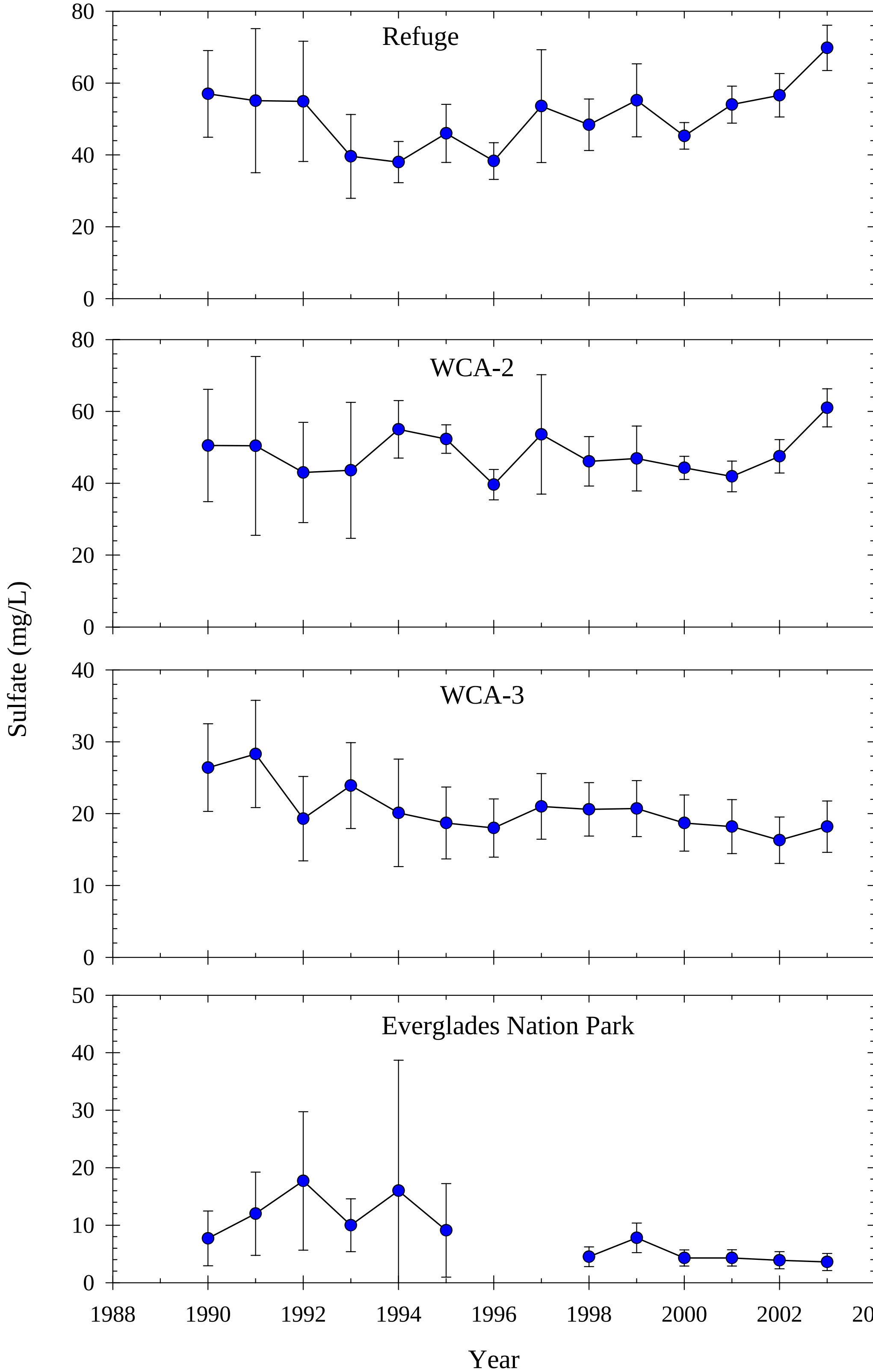

Figure 2B-15. Mean ± 95% C.I. annual sulfate concentrations (mg/L) in EPA inflows.

CONCLUSIONS

As a result of a series of various local, national, and international initiatives, mercury usage in North America has declined by approximately 90 percent since 1990. In addition, environmental controls have been developed and implemented for MWIs and MWCs, which have resulted in emissions declines in excess of 95 percent for both of these source-related sectors.

It is clear that significant declines in mercury concentrations in both largemouth bass and wading birds have occurred in the Everglades over the past 10 to 15 years. Moreover, based on model hind-casting, these declines appear to be largely related to changes in local mercury emissions and associated reductions in atmospheric loadings to the Everglades.

Mercury concentrations in largemouth bass in WCA-1, 2, and 3, while having declined by about 40 to 80 percent over the past eight to 13 years, remain relatively high (about 0.2 to 0.7 mg/kg) compared to the USEPA's proposed fish tissue criterion (0.3 mg/kg MeHg for the protection of human health). Mercury levels in largemouth bass in the ENP also generally remain well above the USEPA's recommended criterion.

From 1993–1998, site 3A-15 in WCA-3 was the MeHg hot spot in the Everglades, with high MeHg production levels and elevated concentrations in water, sediment, and fish. MeHg concentrations in largemouth bass have declined at site 3A-15 in recent years, with this station having experienced the largest decline of all Everglades stations in fish MeHg concentrations (77 percent from 1993–2003). Reduced mercury emissions explain about 60 percent of this decline, with declining sulfate concentrations possibly explaining much of the remainder.

With the rerouting of water flow in the Everglades in recent years as a result of the STAs coming online and other hydrological alterations, it is highly probable that the MeHg hot spot has relocated, possibly to the southern end of WCA-3 or to the northern area of the ENP, where sulfate concentrations may be optimal for SRB. Additional survey work is recommended to locate the new MeHg hot spot(s) in the Everglades.

Further reductions in local emissions of mercury may not result in further reductions in mercury concentrations in Everglades fish to desirable levels for consumption by humans or wildlife. This is because current emissions are both a small fraction (approximately 7 percent) of peak historical levels and also are now very likely a minor contributor to the current loadings of atmospheric mercury to the Everglades.

The changes in mercury concentrations in fish and wading birds appear to have stabilized at most sites after 1998, or even increased in fish in the ENP. Thus, in the absence of further reductions in larger-scale mercury emissions that impact South Florida, the mercury problem in this region will likely persist, albeit at a lower level than 10 to 15 years ago, unless alternative means for mitigating MeHg bioaccumulation in the food chain are elucidated and implemented. The most promising remaining means of managing MeHg in the Everglades may be by controlling sulfate loading.

LITERATURE CITED

Atkeson, T.D. and D.M Axelrad. 2004. Chapter 2B: Mercury Monitoring, Research and Environmental Assessment. G. Redfield, ed. In: *2004 Everglades Consolidated Report*, South Florida Water Management District, West Palm Beach, FL.

Atkeson, T.D., D.M. Axelrad, C.D. Pollman and G.J. Keeler. 2003. Integrating Atmospheric Mercury Deposition with Aquatic Cycling in the Florida Everglades: An Approach for Conducting a Total Maximum Daily Load Analysis for an Atmospherically Derived Pollutant. Integrated Summary, Final Report prepared by the Florida Department of Environmental Protection, University of Michigan Air Quality Laboratory, and Tetra Tech Inc., Lafayette, CA.

Atkeson, T.D. and C.D. Pollman. 2002. Trends of Mercury in Florida's Environment: 1989–2001. Presented at the 23rd ACS National Meeting, April 7-11, 2002, Orlando, FL.

Atkeson, T.D., C.D. Pollman and D.M. Axelrad. In Press. International Workshop on Harmonization of Mercury Measurement Methods and Models to Assess Source-Receptor Impact on Air Quality and Human Health. May 23–26, 2004, Maratea, Italy. Kluwer Academic Press.

Dvonch, J.T., J.R. Graney, G.J. Keeler and R.K. Stevens. 1999. Utilization of Elemental Tracers to Source Apportion Mercury in South Florida Precipitation. *Env. Sci. Technol.*, 33: 4522-4527.

Eisler, R. 1987. Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. *U.S. Fish and Wildlife Service Biological Report*, 85(1.10).

Evans, D.W., P.H., Crumley, D.G., Rumbold and S. Niemczyk. 2003. Mercury in Fish from Eastern Florida Bay. Presented at the 2003 Joint Conference on the Science and Restoration of the Greater Everglades and Florida Bay Ecosystem. Palm Harbor, FL. April 13–18, 2003. Available at http://conference.ifas.ufl.edu/jc/FB.pdf [July 26, 2004].

Frederick, P.C., M.G. Spalding and R. Dusek. 2001. Wading Birds as Bioindicators of Mercury Contamination in Florida: Annual and Geographic Variation. *Env. Toxicol. Chem.*, 21: 262-264.

Guentzel, J.L., W.M. Landing, G.A. Gill and C.D. Pollman. 1995. Atmospheric Deposition of Mercury in Florida: The FAMS Project (1992–1994). *Water, Air, and Soil Pollution*, 35: 393-402.

Guentzel, J.L., W.M. Landing, G.A. Gill and C.D. Pollman. 2001. Processes Influencing Rainfall Deposition of Mercury in Florida. *Environ. Sci. Technol.*, 35: 863-873.

Harris, R., C. Pollman, D. Hutchinson and D. Beals. 2001. Florida Pilot Mercury Total Maximum Daily Load (TMDL) Study: Application of the Everglades Mercury Cycling Model (E-MCM) to Site WCA 3A-15. Report prepared for the U.S. Environmental Protection Agency and the Florida Department of Environmental Protection. Submitted by Tetra Tech, Inc., Lafayette, CA.

Harris, R., D. Beals, D. Hutchinson and C. Pollman. 2003. Mercury Cycling and Bioaccumulation in Everglades Marshes: Phase III Report. Final Draft Report submitted to Florida Department of Environmental Protection. Tetra Tech, Inc., Lafayette, CA.

Keeler, G.J., F.J. Marsik, K.I. Al-Wali and J.T. Dvonch. 2001. Modeled Deposition of Speciated Mercury to the SFWMD Water Conservation Area 3A, June 22, 1995 through June 21, 1996, Project Description and Results. The University of Michigan Air Quality Laboratory, Ann Arbor, MI.

Husar, J.D. and R.B. Husar. 2002. Trends of Anthropogenic Mercury Mass Flows and Emissions in Florida. Final Report, Lantern Corporation, Clayton, MO.

Krabbenhoft, D., W. Orem, G. Aiken and C. Gilmour. 2004. Unraveling the Complexities of Mercury Methylation in the Everglades: The Use of Mesocosms to Test the Effects of "New" Mercury, Sulfate, and Organic Carbon. 7th International Conference on Mercury as a Global Pollutant, June 27–July 2, 2004, Ljubljana, Slovenia.

Lange, T.R., R. Richard, B. Sargent and E. Lundy. 2003. Fish Tissue Monitoring Report. Florida Fish and Wildlife Conservation Commission, Environmental Research Institute, Eustis, FL.

Lange, T.R., R. Richard and B. Sargent. 2004. Annual Fish Mercury Monitoring Report, July 2004. Long-Term Monitoring of Mercury in Largemouth bass from The Everglades and Peninsular Florida. Florida Fish and Wildlife Conservation Commission, Eustis, FL.

Pollman, C.D., G.A. Gill, W.M. Landing, J.L. Guentzel, D.A. Bare, D. Porcella, E. Zillioux and T. Atkeson. 1995. Overview of the Florida Atmospheric Mercury Study (FAMS). *Water, Air, and Soil Pollution*, 80: 285-290.

Pollman, C.D. and D.B. Porcella. 2002. Trends in Mercury Emissions and Concentrations in Biota in South Florida: A Critical Analysis. Final Report to the Florida Electric Power Coordinating Group. June 19, 2002.

Pollman, C.D., R. Harris, D.B. Porcella and D. Hutchinson. 2004. Have Changes in Atmospheric Deposition Caused Concomitant Changes in Largemouth Bass Concentrations in the Florida Everglades – A Model Hind-cast Analysis. 7th International Conference on Mercury as a Global Pollutant, June 27 through July 2, 2004, Ljubljana, Slovenia.

Rood, B.E., J.F. Gottgens, J.J. Delfino, C.D. Earle and T.L. Crisman. 1995. Mercury Accumulation Trends in Florida Everglades and Savannas Marsh Flooded Soils. *Water, Air, and Soil Pollution*, 80: 981-990.

RMB Consulting & Research, Inc. 2002. Atmospheric mercury emissions from major point sources – Broward, Dade, and Palm Beach Counties, 1980–2000. Draft Final Report, RMB Consulting & Research, Inc., Raleigh, NC.

Rumbold D.G. In press. A Probabilistic Risk Assessment of the Effects of Methylmercury on Great Egrets and Bald Eagles Foraging at a Constructed Wetland in South Florida. *Human and Ecological Risk Assessment.* April 2005.

Rumbold D.G., L.E. Fink, K.A. Laine, S.L. Niemczyk, T. Chandrasekhar, S.D. Wankel and C. Kendall. 2002. Levels of Mercury in Alligators (*Alligator Mississippiensis*) Collected along a Transect through the Florida Everglades. *Sci. Total Environ*., 297: 239-252.

Rumbold D.G., S.L. Niemczyk, L.E. Fink, T. Chandrasekhar, B. Harkanson, K.A. Laine. 2001. Mercury in Eggs and Feathers of Great Egrets (*Ardea albus*) from the Florida Everglades. *Arch. Environ. Contam. Tox.*, 41: 501-507.

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

SFWMD. 2000. 2000 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 2001. 2001 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 2002. 2002 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 2003. 2003 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

SFWMD. 2004. 2004 Everglades Consolidated Report. South Florida Water Management District, West Palm Beach, FL.

Slemr, F., E. Brunke, R. Ebinghaus, C. Temme, J. Munthe, I. Wängberg, W. Schroeder, A. Steffen and T. Berg. 2003. Worldwide Trend of Atmospheric Mercury since 1977. *Geophysical Research Letters*, 30 (10): 1516.

Strom, D.G. and G.A. Graves. 2001. A Comparison of Mercury in Estuarine Fish between Florida Bay and Indian River Lagoon, Florida, U.S.A. *Estuaries*, 24: 597-609.

Stober, Q.J., K. Thornton, R. Jones, J. Richards, C. Ivey, R. Welch, M. Madden, J. Trexler, E. Gaiser, D. Scheidt and S. Rathbun. 2001. South Florida Ecosystem Assessment: Phase I/II – Everglades Stressor Interactions: Hydropatterns, Eutrophication, Habitat Alteration, and Mercury Contamination (Summary). U.S. Environmental Protection Agency Region 4 Science and Ecosystem Support Division, Water Management Division, and Office of Research and Development. EPA-904-R-01-002.

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

USEPA. 1998. South Florida Ecosystem Assessment. Volume 1, Final Techincal Report: Phase 1 Monitoring for Adaptive Management: Implication for Ecosystem Restoration. U.S. Environmental Protection Agency, Athens, GA, Region 4 and Office of Research and Development. EPA-904-R-98-002.