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

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SUMMARY

Mercury remains an important water quality concern in the Everglades. As such, the Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (SFWMD or District) continue to lead the South Florida Mercury Science Program (SFMSP)[4] 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 *2006 South Florida Environmental Report – Volume I* serves to update the previously reported findings (SFWMD 1999–2005), with supporting data and other technical information on mercury provided in the appendices to this chapter.[5]

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[4] 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 International University, University of Miami, University of Michigan, University of Wisconsin, Texas A&M University, Louisiana State University, the Smithsonian Institution, Florida Electric Power Coordinating Group, and the National Oceanic and Atmospheric Administration.

[5] Appendices 2B-1 2B-2, and 4-4 of the *2006 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 meet 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, 2000–2004 Everglades Consolidated Reports, and the 2005 South Florida Environmental Report (SFWMD 1999–2005).

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

- Atmospheric deposition of inorganic mercury accounts for greater than 95 percent of the external load of mercury (Hg) to the Everglades.
- Inorganic mercury is converted to methylmercury (MeHg), a highly toxic form of mercury, by naturally occurring sulfate-reducing bacteria (SRB). Sites of mercury methylation include soil surface "flocs" and to a lesser extent, periphyton mats. Once deposited, inorganic mercury is converted to MeHg over a period of hours to days.
- MeHg production is highly influenced by the rate of supply of atmospherically derived mercury.
- A higher fraction of newly atmospherically deposited Hg is methylated in surface soils than is native (old) Hg, indicating that Hg newly deposited to the Everglades surface is more bioavailable for methylation than previously deposited pools.
- The effect of sulfur on methylation is determined by the balance between sulfate and sulfide; methylation is generally highest at 2–10 mg/L sulfate in Everglades surface waters where porewater sulfide concentrations are moderate (5 to 150 ppb or µg/L). Sulfur contamination as an important (perhaps limiting) control on Hg methylation in the ecosystem**.**
- The Everglades Agricultural Area (EAA) is an important source of sulfur to the Everglades.
- Dissolved organic carbon (DOC) promotes Hg dissolution, thereby making it available for methylation. Some DOC fractions, in complexing with Hg, may make Hg unavailable for methylation.
- Long-term phosphate additions have not significantly affected the production of MeHg in surface soil flocs.
- Drying and rewetting cycles stimulate the formation of MeHg in the Everglades, in Stormwater Treatment Areas (STAs) and reservoirs. Drying and consequent aeration of soils results in oxidation of sulfide to sulfate. When rewetted, soil sulfate is readily available to Hg-methylating sulfate-reducing bacteria. However, once sulfide (the end product of microbial sulfate reduction) accumulates in soil pore waters, MeHg production rate is reduced.
- Minimizing soil dryout is a management tool that can be used to manage MeHg production. STAs most prone to high MeHg production appear to be those that have not been previously used for agriculture. Very high levels of reduced sulfur in STAs constructed on former agricultural soils, such as the former ENR, inhibit MeHg production through the formation of Hg-sulfide species which are not available to microorganisms for uptake and methylation.
- MeHg strongly bioaccumulates in the aquatic food chain and in fish-eating birds and mammals. Benthic food webs are dominant in the marsh ecosystem and are the main source of MeHg to fish.
- The primary air emissions sources of mercury in South Florida circa 1990 were incineration of municipal and medical wastes. Mercury emissions from incinerators of all types have since declined by approximately 90 percent.

Principal reasons for this decline were pollution prevention activities that resulted in reductions of mercury concentrations in waste, as well as incinerator emissions controls.

- Although at the peak levels of atmospheric deposition of mercury in South Florida circa 1990, the precise proportions of locally derived versus globally derived mercury remain uncertain, the data indicate that in ca. 1990 the majority of mercury deposition to the Everglades originated from sources within South Florida.
- The southern Everglades exhibits strong MeHg production and bioaccumulation and consequently high mercury levels are found in fish and aquatic wildlife. At the peak of mercury deposition and mercury levels in Everglades fish circa 1990, levels were clearly high enough to pose risk of chronic toxicity to fish-eating wildlife. With subsequent declines in Hg concentrations in fish in the WCAs, the threat has decreased, but the mercury risk to humans and wildlife continues to be a water quality concern, especially in Everglades National Park (ENP or Park).
- Monitoring of Everglades fish and wading birds indicates a significant decline in mercury – up to 80 percent – over the period from 1994–2004 in both largemouth bass and great egrets.
- Mercury concentrations in largemouth bass in WCA-1, 2, and 3 have declined by about 40 to 80 percent over the past decade, but remain relatively high compared to the U.S. Environmental Protection Agency's (USEPA's) recommended MeHg fish tissue criterion of 0.3 mg/kg.
- Very high concentrations of mercury (1.2–1.6 mg/kg) in largemouth bass presently are evident in portions of ENP, particularly in the Shark River Slough at sites in the L-67 Extension canal and North Prong Creek. Mercury levels in largemouth bass have not declined in the ENP, but rather have increased over the past 5-6 years, possibly because sulfate levels in the ENP are now optimal for SRB.
- MeHg production and concentrations at the former mercury "hot spot" near site 3A-15 (CA315) 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. Site 3A-15 sulfate concentrations are now well below optimal levels for MeHg-producing SRB.
- Sulfate discharges to the EPA continue. It is possible that hydrological manipulations affecting sulfate concentrations, or drying and rewetting of soils, have contributed to the elevated mercury levels in fish now evident in the Everglades National Park. Enhanced monitoring is needed to track the changing spatial patterns of mercury methylation throughout the system.
- 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 megalopolis area source influence, composed of a myriad of smaller mercury 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 18 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.

- Mercury concentrations in largemouth bass in WCAs declined significantly from the early 1990s to 1998, but have not declined greatly from 1998 to the present. Thus, in the absence of further reductions in larger-scale Hg emissions that impact South Florida, or reductions in sulfate loading to the Everglades, the mercury problem will likely persist, albeit at a lower level than 15 years ago.

Additional findings and issues of continuing concern include the following:

- In 2003 and 2004, annual volume-weighted total mercury (THg) concentrations in rainfall were elevated as compared to previous years (monitoring commenced in 1994) at all three south Florida Mercury Deposition Network sites (i.e., STA1-W, Andytown substation, and the ENP Beard Research Center). Accordingly, wet deposition, a function of both concentration and rainfall, increased at two of the sites, and remains substantially above that in most of the United States.
- There remains a need to determine the relative importance of local, regional, and global atmospheric sources of mercury on mercury levels in fish in the Everglades, to evaluate options for Everglades' mercury reductions.
- Mercury concentrations in largemouth bass in WCA-1, 2, and 3 while having declined by about 40 to 80 percent from the early 1990s to 1998, remain relatively high (mean of means ca. 0.5 mg/kg) compared to the USEPA recommended MeHg fish tissue criterion of 0.3 mg/kg.
- Mercury concentrations in largemouth bass have increased in the ENP since 1998, and very high concentrations (1.2–1.6 mg/kg) are now evident in the Shark River Slough area at sites L67F1 and North Prong Creek. As well and as observed in previous years, for 2004 resident sunfish at site L67F1 had significantly greater mercury burdens than fishes from other Everglades sites. Mean concentration of Hg in sunfish (*Lepomis* spp.) collected at L67F1 in 2004 was 0.44 mg/kg, which is well above both the U.S. Fish and Wildlife Service (USFWS) and USEPA predator protection criteria (See Appendix 2B-1). Because sunfish represent the preferred prey item of many fish-eating species in the Everglades, there is a need to elucidate the cause of elevated mercury levels in the Park.
- Drying and rewetting cycles exacerbate the formation of MeHg in both the STAs and the Everglades. The CERP plan, by reducing the frequency of drying and rewetting cycles, may decrease MeHg production. Aquifer storage and recovery, however, may introduce high-sulfate connate seawater into the Everglades, with potential increased mercury methylation rate.
- Everglades hydrological alterations in recent years may have changed the distribution of sulfate; it appears that the mercury levels in fish have altered geographically. Station 3A-15, the former mercury hot spot, now has low mercury levels, while mercury in fish in the Shark River Slough area of the ENP are high, possibly because sulfate concentrations are optimal for mercury methylation. Additional survey work is recommended to locate the new mercury hot spot(s) in the Everglades, and to verify the causes of elevated mercury.

- Increases in water delivery from the Stormwater Treatment Areas to the Everglades National Park could widen the area of elevated mercury concentrations in fish in the Park if sulfate concentrations in this "new" water are elevated above Everglades' background.
- There is a need to investigate Everglades sulfur biogeochemistry other than as regards mercury methylation. Sulfur as a biologically very active element has forms that are highly toxic (sulfide), and others (sulfate) which will promote eutrophication of the Everglades via liberation of phosphorus from sediments. There is a need to investigate further the effects of sulfur loading from the Everglades Agricultural Area on the Everglades ecosystem.

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 goal of the SFMSP is to provide the FDEP and the District with information to aid in making 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 comments regarding Everglades Consolidated Reports and South Florida Environmental Reports. 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).

Several lines of evidence suggest that environmentally relevant exposure to mercury has had an effect on nesting by long-legged wading birds in the Everglades. First, methylmercury is known to have effects on reproductive success and egg viability in birds. Specifically in white ibis in the Everglades, mercury contamination may be associated with altered hormonal condition, which could lead to disruption of reproduction. The temporal pattern of MeHg contamination also seems to follow fluctuations in numbers of breeding birds during the past century. Finally, since the dramatic reduction in methylmercury contamination in the late 1990s, numbers of breeding wading birds have increased dramatically.

While this information collectively is suggestive of a role for mercury contamination in fluctuations in breeding success and size of breeding population in the Everglades, the evidence remains largely associative. In an effort to directly test the hypothesis that wading bird reproduction is affected at the population level by ambient concentrations of methylmercury in the Everglades, the Florida Department of Environmental Protection (FDEP) and the USFWS have jointly funded an experimental investigation of effects at the University of Florida.

In this research project, the effects of Everglades-appropriate methylmercury doses in food is being measured on the development, endocrine function, growth, foraging abilities, and reproductive success of captive white ibis.

A 13,000-sq-ft free-flight aviary has been constructed in Gainesville, populated with 160 white ibis from the Everglades. These animals were collected as nestlings, and thus their mercury exposure can be controlled nearly throughout their lives. They are likely to first attempt breeding in spring 2007. The birds are divided into large social groups appropriate to the nature of this species, and dosed at 0, 0.3, 0.1 and 0.05 parts per million (ppm) methylmercury wet weight in diet. These doses span the range of concentrations in naturally occurring food items that ibises eat in the Everglades.

Ibis are fed *ad lib* on a diet of pelletized Flamingo Breeder diet (Mazuri Zoo diets). This food is a complete diet with relatively high protein (35 percent) and fat by comparison with typical ibis diets in the wild. The food is dosed uniformly by spraying the pelletized food with an appropriate solution of methylmercury chloride in corn oil at a rate of 25 ml corn oil per kg of feed (dry weight). All birds within a dose group therefore are dosed at the same rate, with total exposure dependent upon appetite. Feathers and blood will be collected from these birds twice per year, when all birds are caught and processed during prescheduled health exams.

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 (a) support atmospheric mercury studies relevant to the mercury control policy in U.S. southeast coastal regions, (b) sponsor studies that directly measure transport of mercury species into Florida, (c) describe and quantify the atmospheric reactions of mercury that facilitate deposition, and (d) employ photochemical grid models to organize the atmospheric processes research into information to support decision making.

For the 2006 SFER, the FDEP will retain the existing Speciated Atmospheric Mercury Study (SAMS) site at Coral Springs and move our second Tekran Hg speciation system to another location, likely Tampa or the ENP. This new alignment is a step toward our desire to have three full mercury speciation supersites in peninsular Florida as a part of the third-generation mercury study (EgHgIII) to come. SAMS collects 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 2008.

As a prelude to this third-generation mercury study, the USEPA has established mercury supersites 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 2005–2008 will add monitoring sites at ENP 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 2001–2005. 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 a 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 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 (Atkeson, et al., 2005). 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.

Additional research on sulfur has commenced to determine the extent to which sulfate loading to the freshwater Everglades — which results in increased sulfide levels in sediments — will affect the growth and photosynthetic responses of *Typha* and *Cladium*; if these responses differ in the two species; and, if this offers an additional explanation for the expansion of cattail (*Typha domingensis*) into areas previously occupied by the historically dominant sawgrass (*Cladium jamaicense)*.

Although most wetland plants can detoxify H_2S in the oxic rhizosphere surrounding the roots the extent of detoxification does differ with the plant species. It has been clearly demonstrated that *Typha* has a significantly greater ability to transport oxygen to its roots and to produce a more extensive oxidized rhizosphere than *Cladium*. Hence, *Cladium* may be more sensitive to H_2S production than *Typha*. The sulfide toxicity experiments will be conducted in WCA-3A-15, in the central Everglades, and will employ mesocosms and sulfate dosing in both *Typha* and *Cladium* dominated sites.

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

The FDEP continues to support a series of studies with the U.S. Geological Survey (USGS) and the Smithsonian Institution. 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, and include an examination of iron cycling on mercury methylation. Further research on the influence of the effects of wetting and drying cycles on MeHg production is currently scheduled for 2005–2006. Results to date are included in Appendix 2B-2 of the *2006 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 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.

TRENDS IN ATMOSPHERIC DEPOSITION OF MERCURY

A continuous record of wet deposition fluxes and concentrations of mercury is available from November 1993 through December 2004 collected from the Beard (ENP) Research Center (MDN Site FL11) (**Figure 2B-1**) as part of the Florida Atmospheric Mercury Study (FAMS) from 1993–1996 (Pollman et al., 1995, Guentzel 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 1996–2004 (available at http://nadp.sws.uiuc.edu/mdn). This report includes two more years of data since the last 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., 2005). Using analysis of variance (ANOVA) to account for the effects of both seasonal dynamics and rainfall volume on mercury concentrations (Atkeson et al., 2005). Using analysis of variance (ANOVA) to account for the effects of both seasonal dynamics and rainfall volume on mercury concentrations, Atkeson et al. (2005) concluded that volume-weighted mean (VWM) mercury concentrations declined by approximately 3 nanograms per liter (ng/L) due to factors other than these two variables. The magnitude of this decline – approximately 25 percent from 1993 through 2002 for samples collected at the Beard (ENP) Research Center – was 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).

The trend of declining concentrations of Hg in wet deposition noted by Atkeson et al. (2005) appears, however, to have plateaued. Annual VWM concentrations (calculated as a 12-month running average concentration) have increased from a minimum value of approximately 10 ng/L in late 2002 through early 2003 to concentrations in excess of 16 ng/L by mid-2004 (**Figure 2B-2**). These annual average VWM concentrations are the highest that have been observed during the period of record at the Beard Research Station. Inspection of the weekly MDN data for 2003 and 2004 showed that there were a series of five weeks that had concentrations exceeding 50 ng/L – the highest weekly or monthly concentrations in the period of record. For four of these samples, some debris had been noted in the collector, but the degree of contamination was insufficient for MDN to flag and invalidate these samples. Likewise, analysis of the same weekly samples for major cations and anions at the co-located NADP rainfall collector did not suggest any obvious degree of contamination or disturbance.

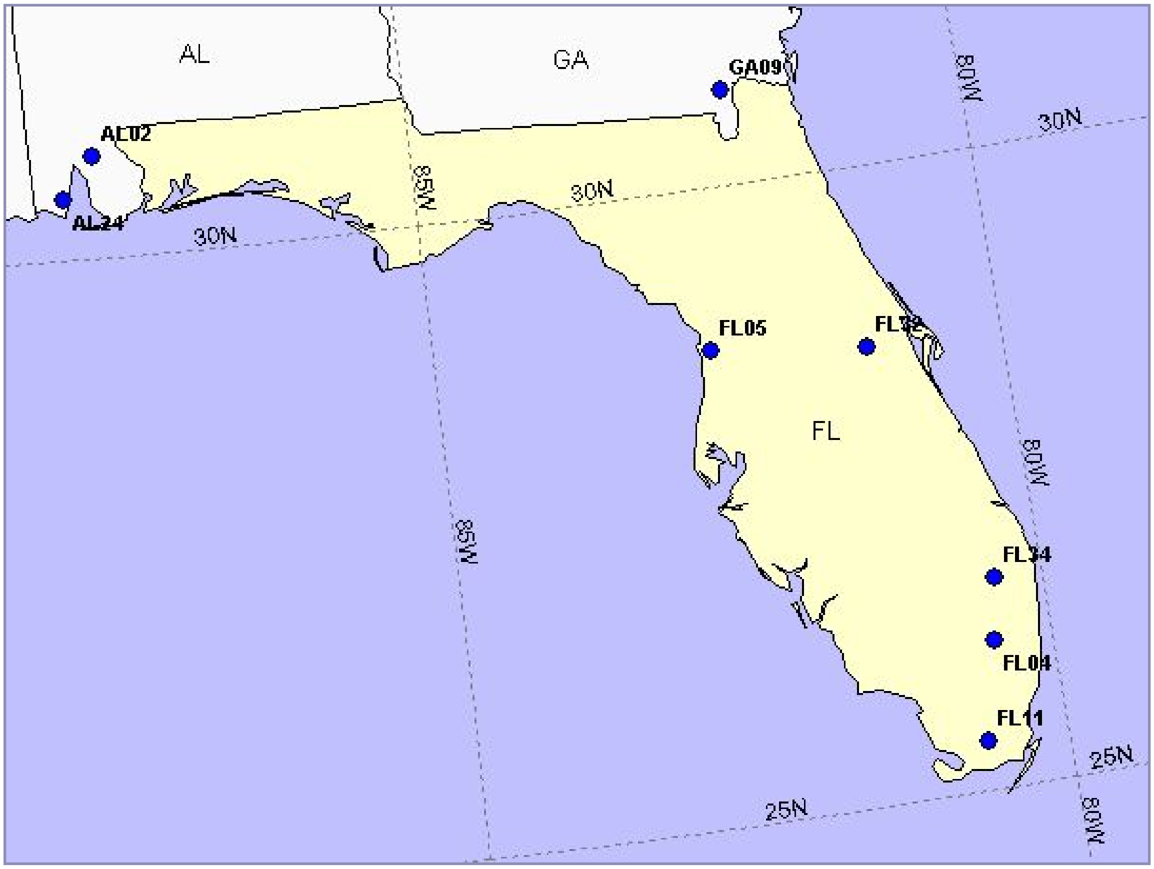

Figure 2B-1. The National Atmospheric Deposition Program (NADP) Mercury Deposition Network's (MDN's) Florida sampling sites (FL34 Everglades Nutrient Removal Project, FL04 Andytown, FL11 Everglades National Park-Research Center or Beard Research Center). (http://nadp.sws.uiuc.edu/sites/sitemap.asp?net=MDN&state=fl)

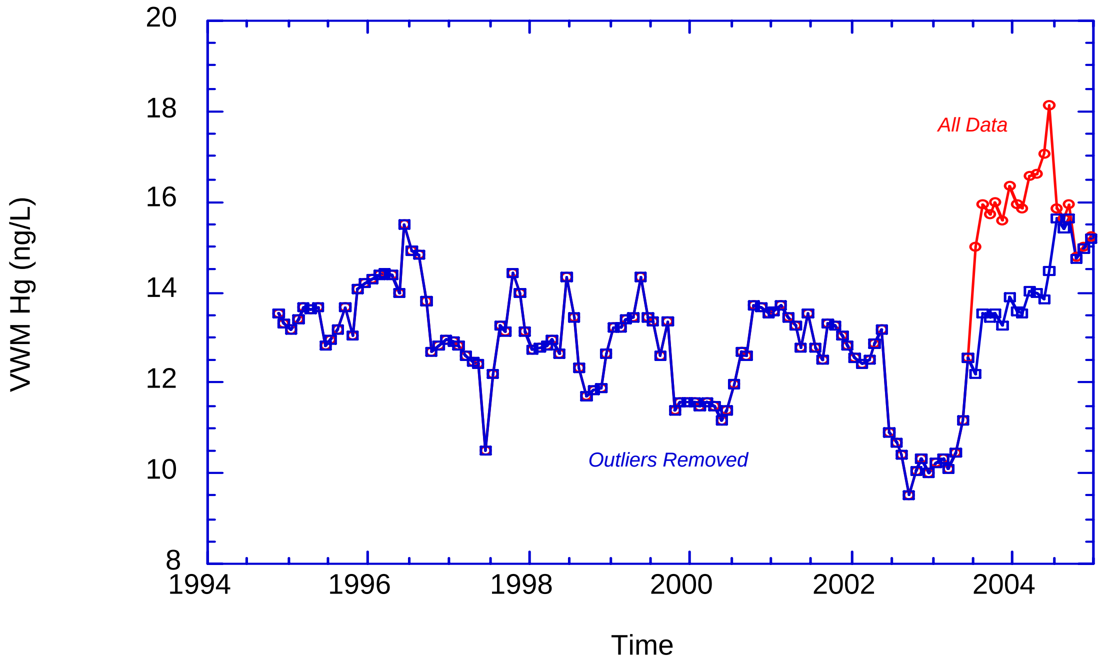

Figure 2B-2. Running annual volume weighted mean Hg concentrations (presented monthly) observed at MDN site FL11, Beard Research Station, Everglades National Park, 1993–2004. Two curves are presented, the first (red) curve includes all the data for each week reported by MDN; the second (blue) curve excludes all weeks when the volume weighted mean concentration of Hg exceeded 50 ng/L. Data from Guentzel et al. (2001) for 1993 through 1996, and MDN for 1996 through 2004.

Annual VWM Hg at the other two south Florida MDN sites (stations at the ENR Project, MDN Site FL34 and the Florida Power and Light Andytown substation, MDN Site FL04) show similar trends to those at the Beard Research Station (MDN Site FL34) of increasing concentrations in 2003 through mid-2004 (**Figures 2B-3** and **2B-4**). This suggests first that the trends are not an analytical anomaly and second, that the source of the apparent increase impacts the entire Everglades (**Figure 2B-5**). Consequently, wet deposition (flux), which is a function of both concentration and rainfall, also increased in 2003–2004 (**Figure 2B-3**). 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 (**Figure 2B-6**).

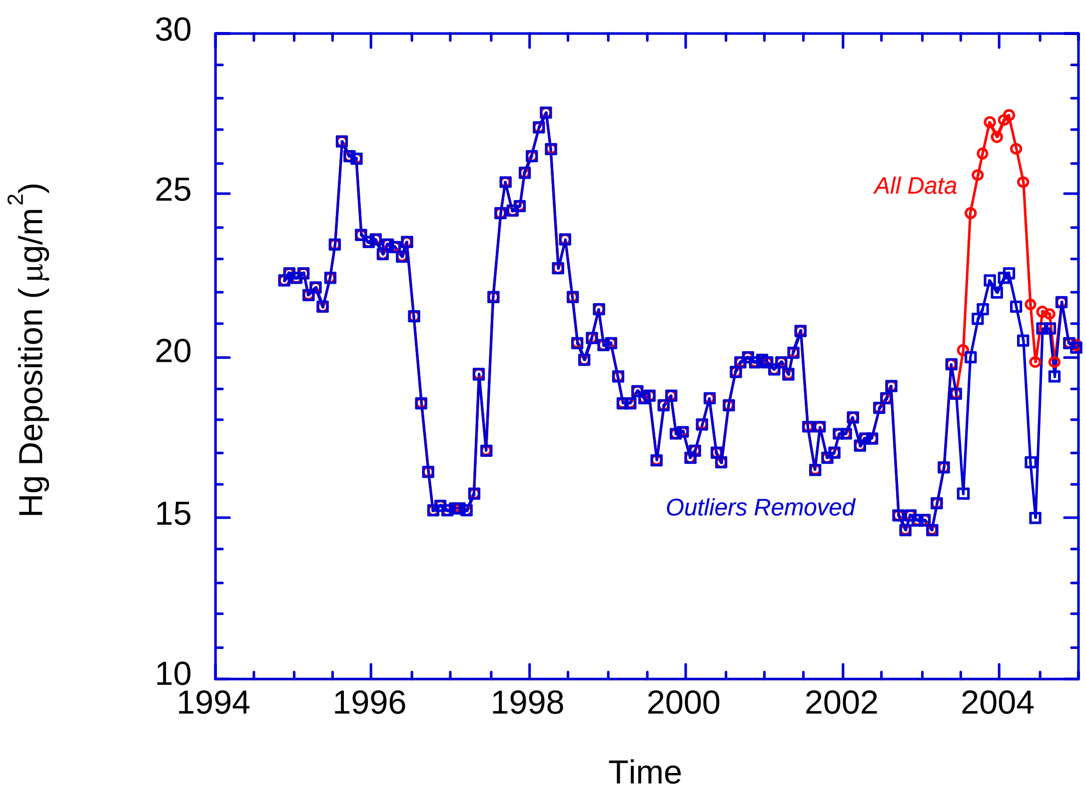

Figure 2B-3. Same as Figure 2B-2, except for running annual wet deposition flux for Hg at Beard Research Center (MDN Site FL11).

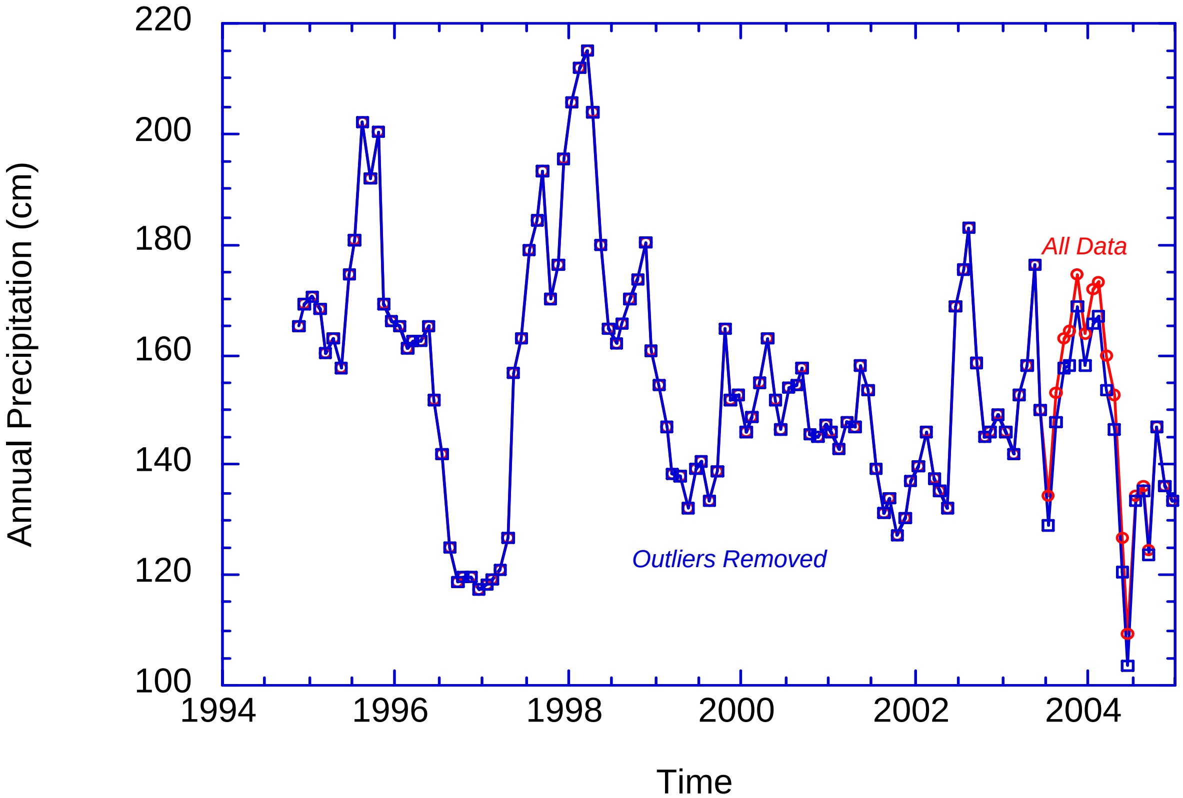

Figure 2B-4. Same as Figure 2B-3, except for running annual precipitation volume at Beard Research Center (MDN Site FL11).

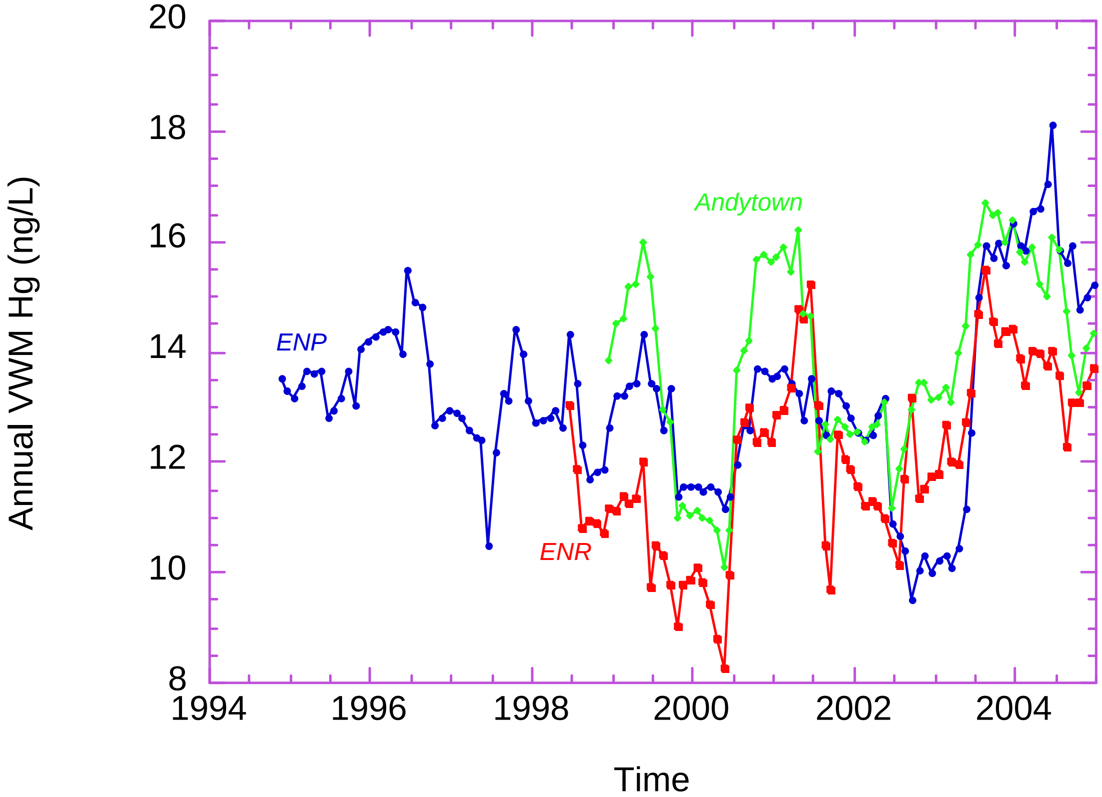

Figure 2B-5. Running annual VWM Hg concentrations in wet deposition at all three South Florida MDN sites.

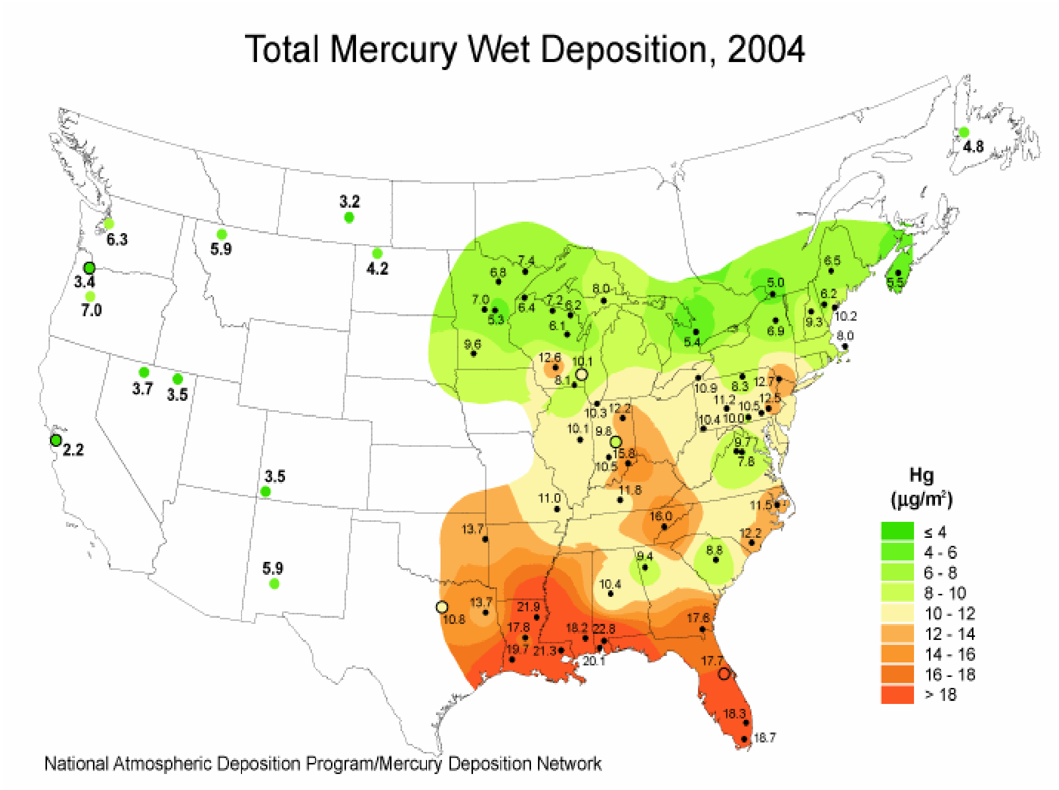

Figure 2B-6. Wet deposition of total mercury (micrograms/m^2) in 2004. Data from National Atmospheric Deposition Program's Mercury Deposition Network (http://nadp.sws.uiuc.edu/mdn/).

CONCENTRATIONS OF MERCURY IN EVERGLADES FISH

Trends in Mercury Concentrations in Everglades Largemouth Bass

Data are available to examine long-term trends in mercury concentrations in largemouth bass (*Micropterus salmoides*) from sites throughout Florida since 1988, including nine sites in the Everglades (Lange et al., 2005). **Figure 2B-7** demonstrates substantial declines in mercury in age 1–2 cohort largemouth bass at most marsh and canal sites in WCAs 2 and 3, with high concentrations still evident in the Everglades National Park.

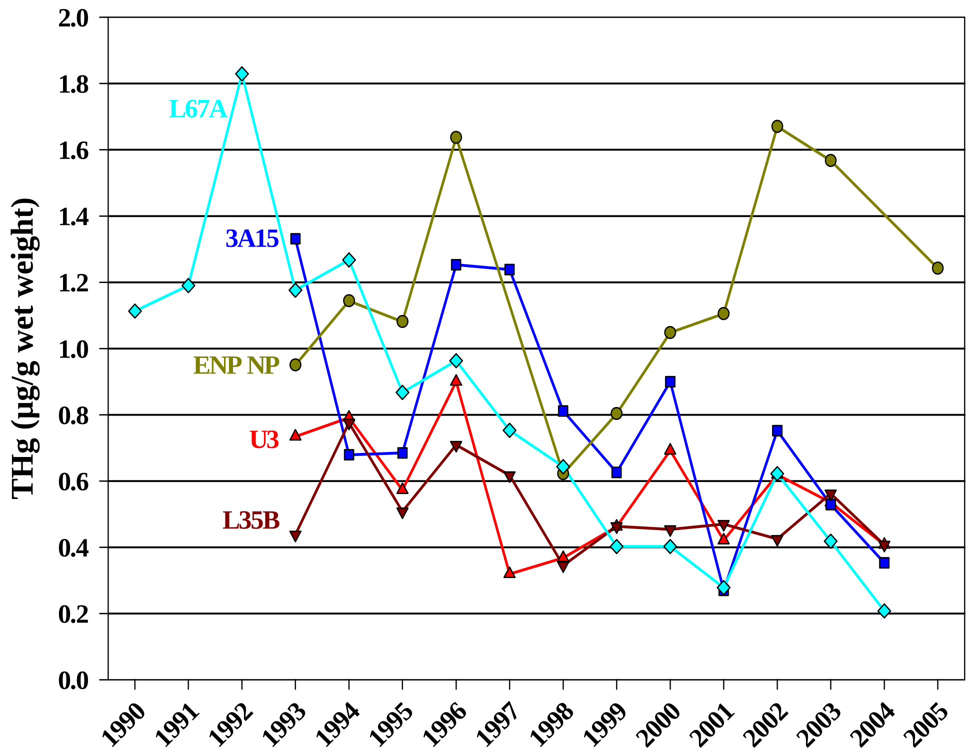

Figure 2B-7. Time series of geometric mean mercury concentrations for largemouth bass (age 1-2 cohort) for five Everglades sites. Sites L-35B and L-67A are canal sites in WCA2 and WCA3, respectively, and sites U3 and 3A-15 represent interior marsh sites located in WCA-2A and WCA-3A, respectively (µg/g = mg/kg = ppm). The ENP site is located in the Everglades National Park (North Prong Creek) in the Shark River Slough.

Largemouth bass, a popular Everglades sport fish, as well as a high trophic level fish, were selected in the late 1980s as a species to monitor as regards 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., 2005) (**Figure 2B-8**).

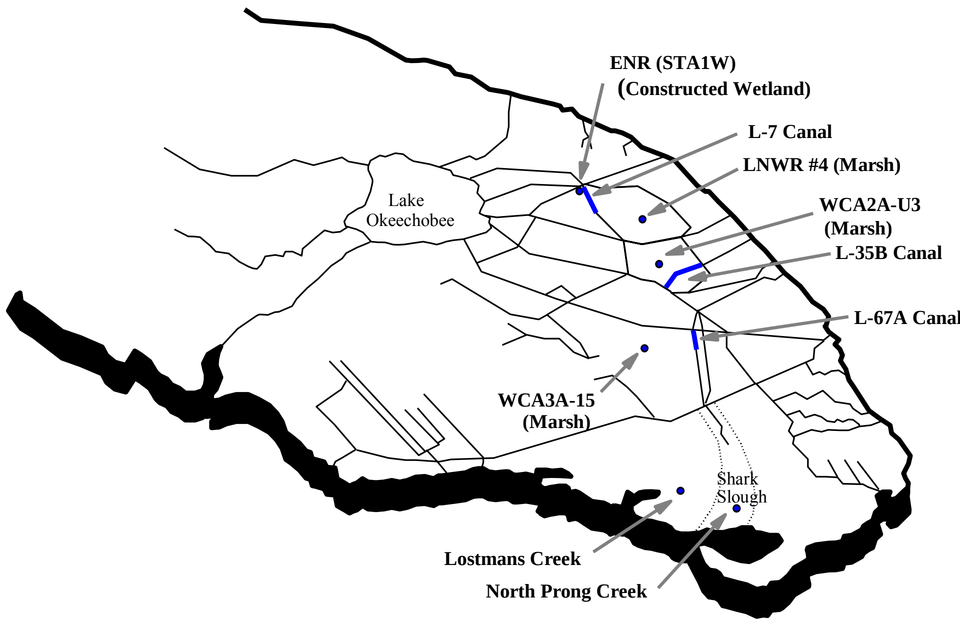

Figure 2B-8. Location of the Florida Fish and Wildlife Conservation Commission long-term monitoring sites in the Everglades Protection Area (EPA) region (Lange et al., 2005).

Mercury concentrations in age-standardized three-year-old largemouth bass in WCAs 1, 2, and 3 while having declined by approximately 40 to 80 percent over the past 10 to 15 years (**Figures 2B-9** through **2B-11**, respectively), remain relatively high (mean of means ca. 0.5 mg/kg) as compared the USEPA proposed 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.

Planned studies on the relative importance of local, regional, and global sources of atmospheric mercury to South Florida will help determine if it is feasible to reduce local atmospheric mercury sources to the extent necessary to meet the USEPA 0.3 mg/kg MeHg or a Florida-specific criterion. It is very possible that measures in addition to reductions in South Florida atmospheric mercury sources, such as reduction in sulfate loading to the Everglades, or reductions in regional or global atmospheric mercury sources, will also be necessary to reach the fish tissue criterion.

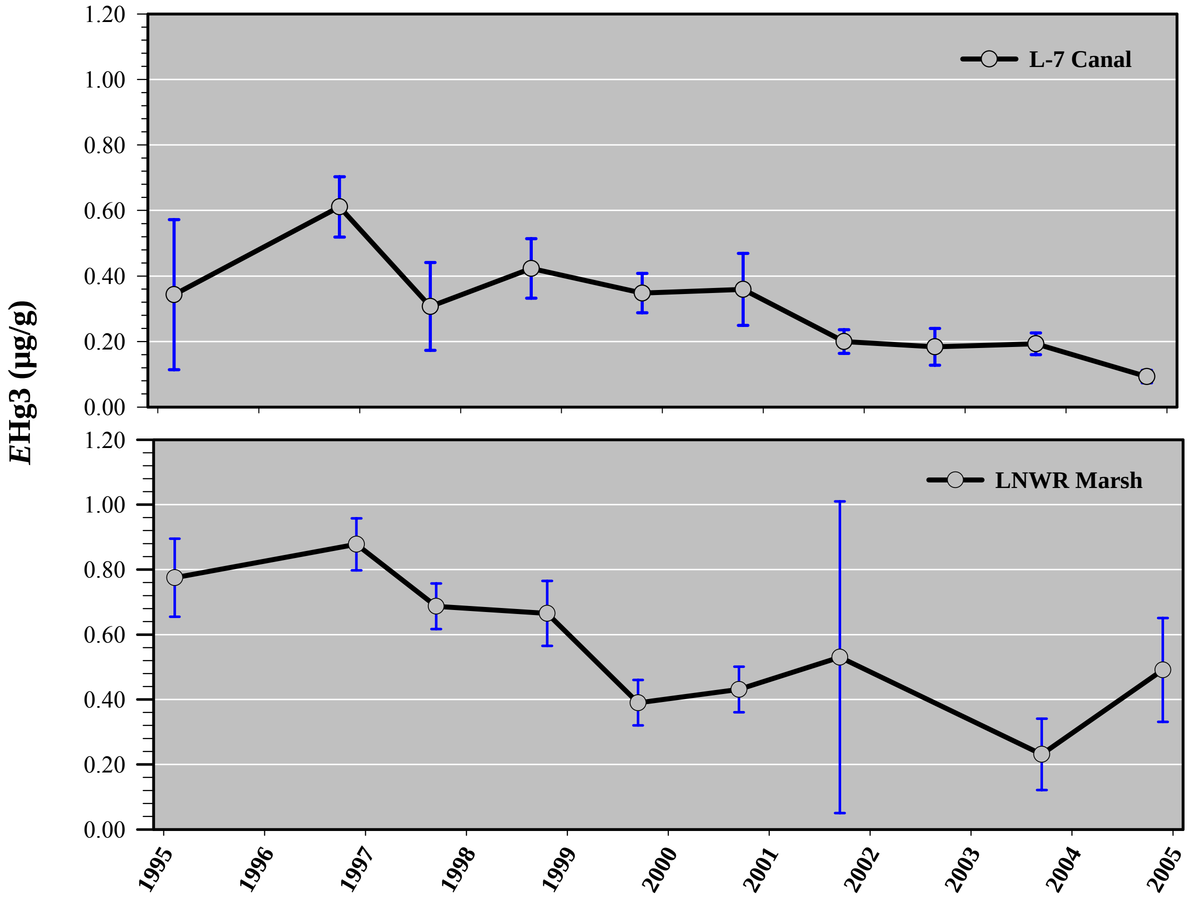

Figure 2B-9. Long-term monitoring sites located in the Loxahatchee National Wildlife Refuge (LNWR) within WCA-1, showing the age-standardized mean mercury concentration for three-year-old largemouth bass (EHg3) (µg/g = mg/kg = ppm) and the 95 percent confidence interval (95% C.I.) (Lange et al., 2005).

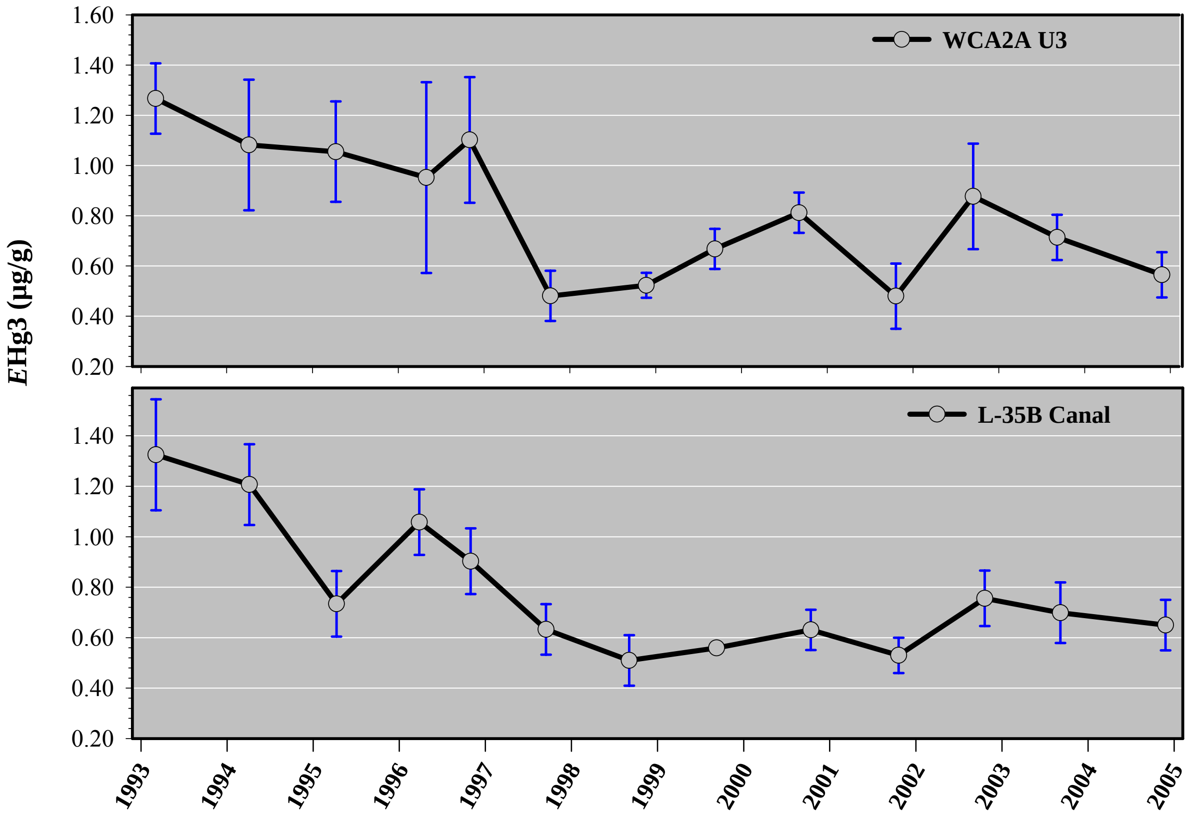

Figure 2B-10. Long-term monitoring sites located in WCA-2 showing the age-standardized mean mercury concentration (EHg3) (µg/g = mg/kg = ppm) for three-year-old largemouth bass and the 95% C.I. (Lange et al., 2005).

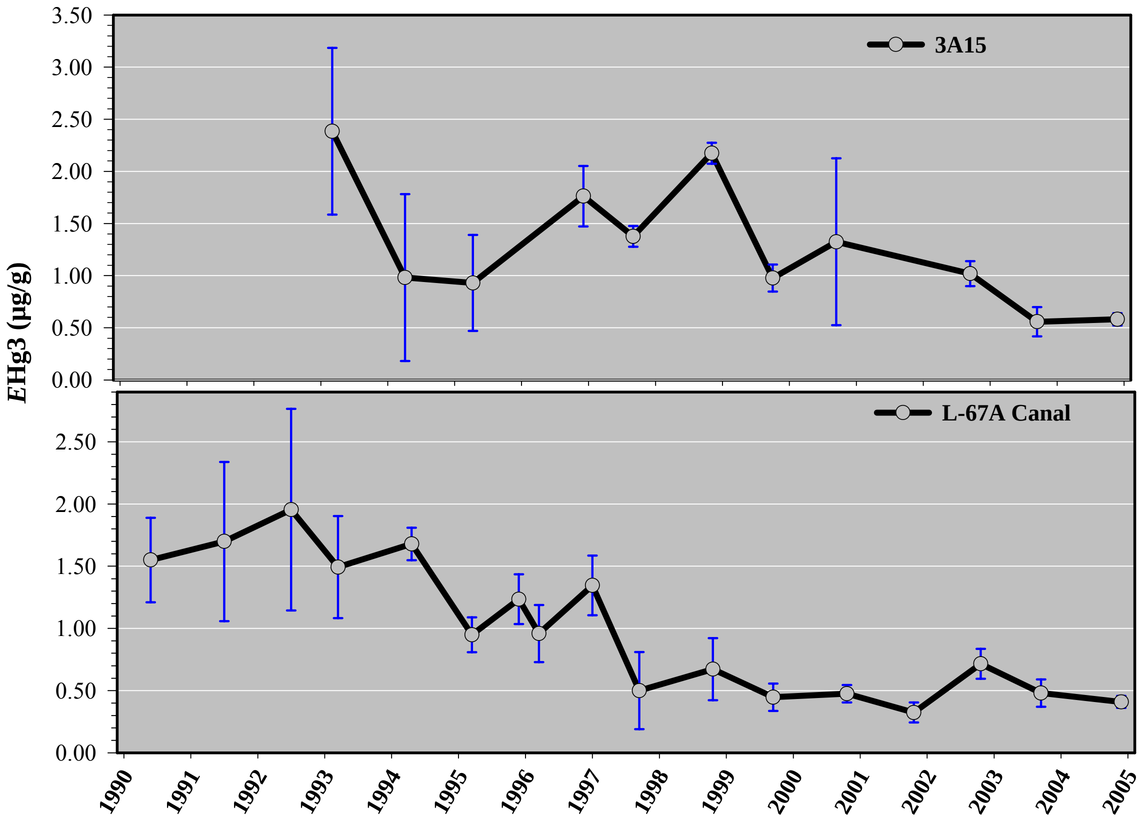

Figure 2B-11. Long-term monitoring sites located in WCA-3 showing the age-standardized mean mercury concentration (EHg3) (µg/g = mg/kg = ppm) for three-year-old largemouth bass and the 95% C.I. (Lange et al., 2005).

Mercury Concentrations in Fish in the Everglades National Park

In contrast to the 40 to 80 percent mercury concentration declines in largemouth bass in WCAs 1, 2, and 3 over the past 10–15 years, declines over the period of record in the Everglades National Park have been smaller (**Table 2B-1**). Recent data indicate that high mercury concentrations – 1.2 and 1.6 mg/kg – in largemouth bass are evident in the ENP, in the Shark River Slough area at sites L67F1 (see Appendix 2B-1) and North Prong Creek, respectively. At the North Prong Creek station (**Figure 2B-12**), mercury concentrations appear to have increased over the past six years.

Sunfish (*Lepomis* spp.) from the northern ENP (L67F1) have also been found to have elevated mercury levels (see Appendix 2B-1). As observed in previous years, for 2004, resident sunfish at site L67F1 had significantly greater mercury burdens than fishes from other Everglades sites. Mean concentration of THg in sunfish collected at L67F1 in 2004 was 0.44 mg/kg. The USFWS has proposed a predator protection criterion of 0.1 mg/kg THg in prey species (Eisler, 1987). 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). Everglades National Park populations of piscivorous avian and mammalian wildlife continue to be at risk of adverse effects from mercury exposure, because sunfish represent the preferred prey item of many fish-eating species in the Everglades. As such, there is a need to elucidate the cause of elevated mercury levels in the Park; a possibility is that sulfate concentrations have not declined in the ENP as much as for other areas, such as WCA-3A-15 (i.e., the former MeHg hot spot), or have increased, either due to natural inputs (e.g., estuarine or tidal influenced sites), sediment drying and rewetting, or due to sulfate loading in stormwater runoff.

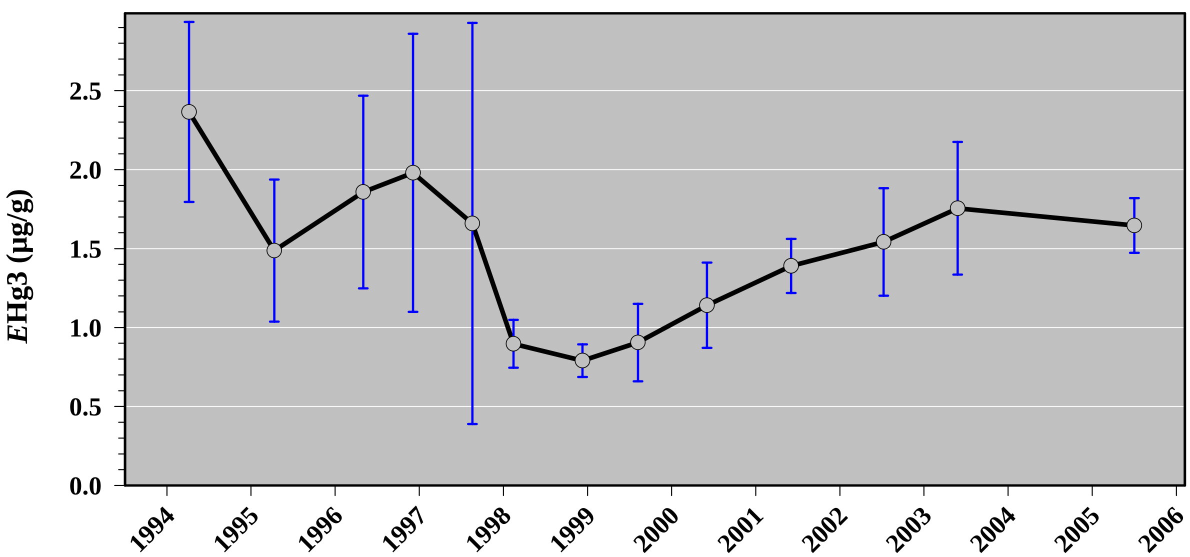

Figure 2B-12. The age-standardized mean mercury concentration (EHg3) (µg/g = mg/kg = ppm) for three-year-old largemouth bass from the North Prong Creek, located in the Lower Shark River Slough in ENP. Error bars show the 95% C.I. (Lange et al., 2005).

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., 2005).

Location	Percent Change	Reported POR
Refuge (WCA-1)		
L-7 Canal	-73	1995–2004
Refuge Marsh	-37	1995–2004
WCA-2A		
WCA-2A U3	-55	1993–2004
L-35B Canal	-51	1993–2004
WCA-3A		
3A-15	-76	1993–2004
L-67A	-74	1990–2004
ENP		
North Prong Creek	-30	1994–2004

EFFECTS OF SULFUR ADDITIONS TO THE EVERGLADES

Freshwater wetlands, especially rainwater-driven ecosystems such as the Everglades, typically have low sulfur loadings and thus minimal concentrations. High concentrations of sulfate-sulfur are evident, however, in surface waters of the northern Everglades. Compared to sulfate concentrations of ≤ 1 mg/L in pristine areas of the Everglades, marshes in portions of the Water Conservation Areas have surface water sulfate concentrations that average nearly 60 mg/L (Bates, et al., 2002; USGS, 2004).

Concentrations of sulfate in Everglades surface waters indicate that canal water draining the Everglades Agricultural Area (EAA) is the principal supplier of sulfate to Everglades marshes (**Figure 2B-13;** Chapter 2A, Figure 2A-11). Results from Bates et al. (2002) implicate agricultural fertilizer as a major contributor of sulfate contamination of the Everglades. Schueneman (2000) however posits that the main source of this sulfate in EAA canals is not applied agricultural sulfate, but instead EAA soil subsidence (mineralization), and inputs of Lake Okeechobee water to EAA canals.

This brings into question the source of the sulfur in EAA peats. The formation of reduced organic sulfur from sulfate via microbial sulfate reduction has been frequently reported (Aamaral, et al., 1993; Rudd et al., 1986; Vile et al., 2003). Carbon-bonded reduced sulfur is generally the dominant end product of sulfate-reduction in freshwater peat soils. ACME data from sulfate reduction rate measurements show this is case at all of ACME sites in the Everglades, including ENR (now STA-1W). As such, much of the sulfur released from mineralizing EAA soils quite possibly originates from application of agricultural sulfur. This hypothesis is also consistent with the stable isotope data (Orem et al., in press).

As regards Lake Okeechobee being a sulfate source, EAA canals generally have higher sulfate levels than Lake Okeechobee, and the Lake may be influenced by sulfate from back-pumping of EAA canal water.

Additionally, stable isotope data ($\delta^{34}S$ of sulfate in surface water) are also consistent with agricultural sulfur and sulfate from other fertilizers and soil amendments used in the EAA as being the principal source of the sulfate in the canals (Bates et al., 2002; USGS, 2004; Orem et al., in press).

In the EAA, especially in sugarcane growing areas, agricultural sulfur (98% S^0), a grade of elemental sulfur, is applied to soils because its oxidation to sulfate acidifies the soil, thus mobilizing applied phosphorus fertilizer and trace metals needed for good crop growth. Orem et al. (in press) postulate that this sulfate is then remobilized from the agricultural soils by rainfall and/or irrigation, transported in runoff to the canals in the EAA, and thence to the EPA in canal water discharge. Sulfate loadings from the EAA continue to be significant (See Chapter 2A, Table 2A-4).

Sulfate, unlike phosphorus, is not removed from waters draining agricultural lands to a significant extent by Everglades plants. Sulfate thus penetrates much further into the Everglades than phosphorus from its point of EAA discharge. As such, while agriculturally derived phosphorus entering the Everglades has caused eutrophication of 6 to 10 percent of the ecosystem, agricultural sulfate loads affect as much as 30 percent of the freshwater Everglades (USGS, 2004).

Sulfate directly affects the rate of mercury methylation by naturally occurring sulfate-reducing bacteria; the end product of metabolism being MeHg, the highly toxic, bioaccumulative form of mercury. For many freshwater wetlands, MeHg does not represent a significant environmental problem because of low sulfate concentrations. The sulfur input from the EAA, however, stimulates MeHg production within the Everglades ecosystem (Gilmour et al., 1992; Gilmour et al., 1998) and is a contributing factor regarding the excessive levels of mercury in Everglades fish and wildlife.

Excess sulfate has concentration-dependent effects with respect to MeHg production: (1) stimulation through increased rate of sulfate reduction and MeHg production by sulfate-reducing bacteria; and (2) inhibition through buildup of excess sulfide, which binds Hg, making it unavailable for methylation. As a result of this dichotomous effect of sulfur on mercury methylation, areas with intermediate concentrations of sulfate exhibit the highest MeHg production. In the Everglades, the highest MeHg concentrations occur where sulfate concentrations in surface water are somewhat higher than background (2–10 mg/L), and where porewater sulfide concentrations are moderate (5 to 150 µg/L or ppb) (Orem et al., 1997).

High sulfide levels in sediments (resulting from sulfate inputs) are not desirable even though they may reduce MeHg production. Sulfide, as undissociated hydrogen sulfide, is water soluble and highly toxic. USEPA guidance documents provide guidance on safe surface water concentrations of sulfide (USEPA, 1976; 1986) and the Criteria Maximum Concentration as then recommended remains at 2.0 µg/L (USEPA, 2004); that is, concentrations in excess of 2.0 µg/L (ppb) “would constitute a long-term hazard to most fish and other aquatic wildlife.”

The USEPA has not yet developed a criterion for sulfide in sediment porewater, though literature values for toxic endpoints for freshwater invertebrates generally range from ca. 20 to 1,000 ppb sulfide (Wang and Chapman, 1999). By comparison, for the Everglades, at sites of high surface water sulfate contamination near EAA canal discharge points, sediment porewater sulfide concentrations range from hundreds to thousands of ppb. Porewater sulfide concentrations at sites distant from canal discharge, but receiving some excess sulfate, range from one to hundreds of ppb. Pristine Everglades sites have porewater sulfide values usually < 0.1 ppb (**Figure 2B-14**). As such, it is a reasonable hypothesis that the toxic effects of elevated sulfide in Everglades porewaters resulting from sulfate contamination from the EAA is causing reduced diversity and abundance of Everglades in fauna.

Sulfur as sulfate can alter the Everglades via other mechanisms. Sulfur is an important element in the biogeochemistry of wetland ecosystems because of the role of sulfate as a terminal electron acceptor in microbial sulfate reduction. Sulfate allows for the metabolism of sedimentary organic matter in the absence of oxygen, and in the process, organically bound phosphorus and nitrogen are released and mobilized into sediment porewaters and then into overlying surface waters.

Lamers et al. (1998) described the phenomenon of “internal eutrophication,” whereby phosphate concentrations in the interstitial water of a freshwater wetland increased considerably as a result of sulfate treatment, and concluded that reduction in nutrient input to a wetland alone may not be sufficient to restore the ecosystem. Preliminary Everglades data show that sulfate additions to surface waters result in increased liberation of phosphorus from sediments and increased sediment porewater and surface water phosphorus concentrations (W.H. Orem, USGS, personal communication).

It has also long been known that sulfide binds with iron, decreasing the abundance of iron forms that can bind with phosphate in sediment, and resulting in release of phosphorus from sediments (Hasler and Einsele, 1948).

Accordingly, the issue of sulfate-induced eutrophication of the Everglades may have to be considered. It is probable that sulfate contamination of the Everglades is hampering Everglades restoration through remobilization of phosphorus in sediments to sediment porewaters and surface waters. It is possible that sulfate is an important factor in liberating phosphorus from sediments in phosphorus-contaminated areas of the Everglades, increasing porewater phosphorus concentrations, and contributing to the replacement of sawgrass by cattail.

The National Academy of Science (NAS, 2005) wrote regarding the Everglades sulfur pollution issue, "The process of eutrophication is exacerbated by interactions with sulfate, which enters the Everglades from anthropogenic atmospheric sources and especially from agriculture…. As limnologists have known for decades, the release of phosphorus (as phosphate ion) from lake sediments can increase significantly when sulfate concentrations are increased. High sulfate concentrations in organic-rich, anoxic water and sediments promote the formation of sulfide. The anoxic conditions and high sulfide levels also promote the reduction of iron oxyhydroxides in sediments leading to the formation of ferrous sulfides. The net effect is to decrease the abundance of iron forms that can bind with phosphate in sediment. High sulfide concentrations also can be toxic to animals and plants, and might explain changes in species composition associated with eutrophic regions in the Everglades. Consideration of the supply and spatial distribution of sulfate within the Everglades should therefore be part of any effort to understand and limit expansion of areas already converted to eutrophic states.”

The matter of sulfur pollution in the Everglades, its effect on geographic distribution of mercury methylation, on phosphorus release from sediments, and on sediment toxicity are in need of much greater research emphasis.

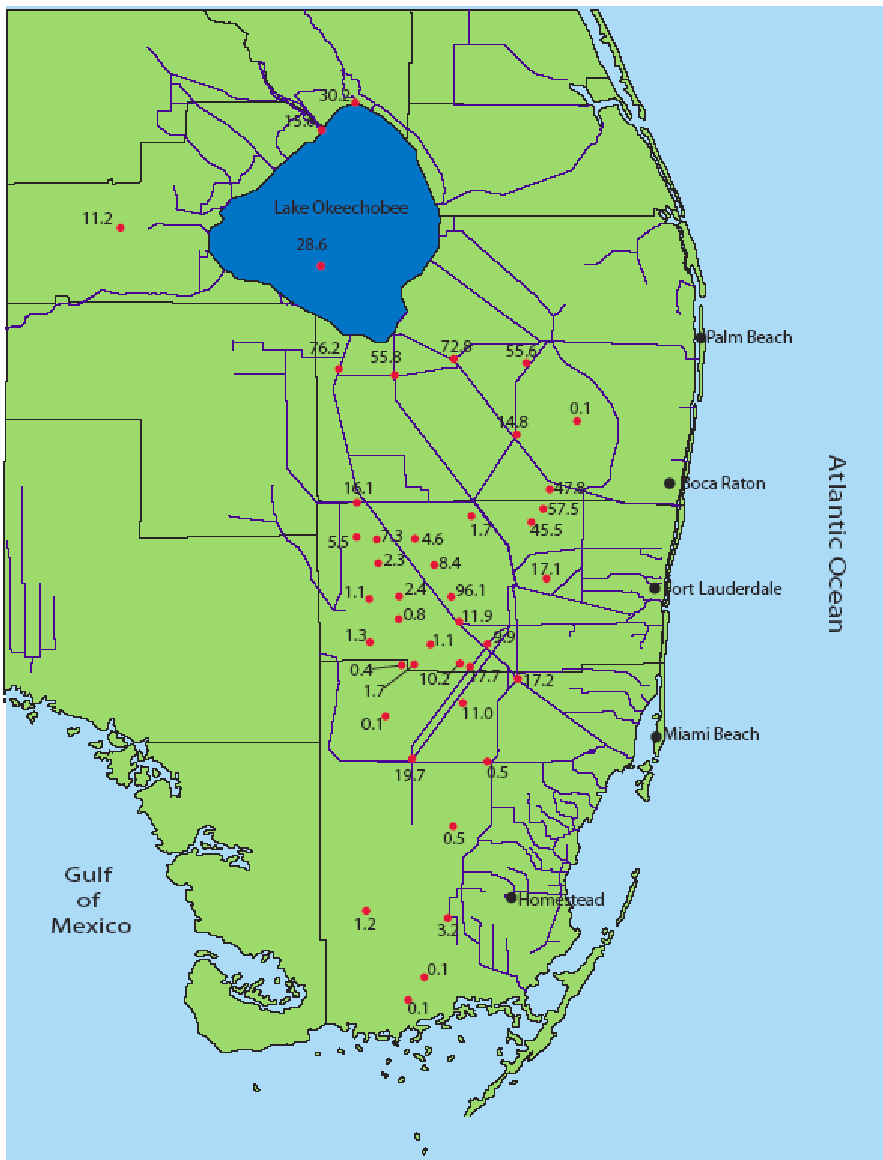

Figure 2B-13. Average sulfate concentrations (mg/L = ppm) in surface water in the South Florida ecosystem, including Lake Okeechobee and its drainage, EAA canals, and the freshwater Everglades, from USGS sampling 1994–2000 (Orem et al., in press).

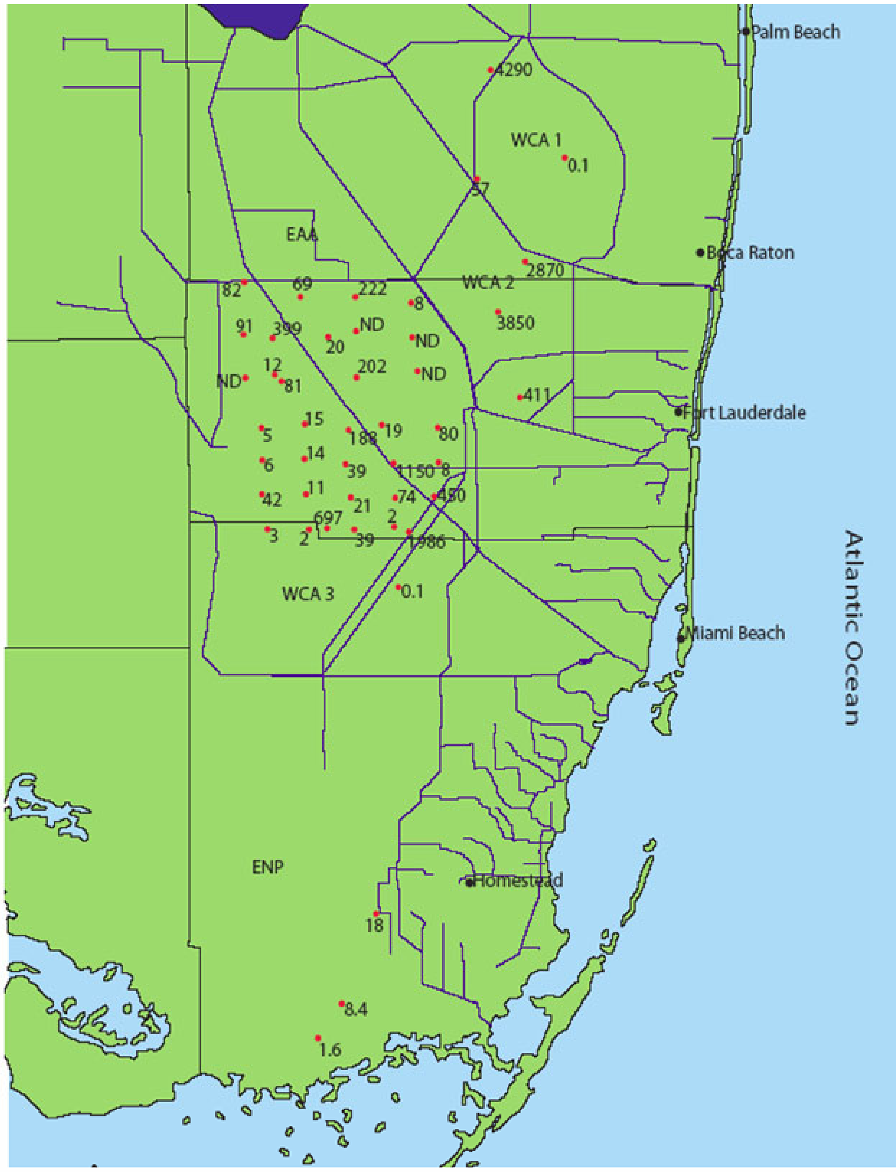

Figure 2B-14. Average sulfide concentrations (µg/L = ppb) in sediment porewater in the northern Everglades, from USGS sampling 1995–2000 (Orem et al., in press).

MERCURY PROGRAM FUTURE ACTIVITIES

For 2006–2007 the FDEP intends to shift focus back to the atmospheric influences of mercury as it continues to view atmospheric deposition as a primary driver of mercury load, methylation, bioaccumulation, and risk in Florida waters and the Gulf of Mexico, albeit cognizant of other influences, particularly the interaction between mercury methylation and sulfur chemistry. Anticipated projects are described below.

Third-Generation Analysis of Mercury Transport and Fate

The largest anticipated effort will be initiation of a joint three-year project with the USEPA Office of Research and Development (ORD) and NOAA Air Resources Laboratory (ARL) to conduct a third-generation mercury transport and fate study[6] to resolve some of the significant uncertainties in scientific studies to date. Tentatively given the moniker of *EgHgIII* (Everglades Mercury III), this project will represent a significant refocusing on gaining a greater understanding of the relative importance of the local, regional, and global scales of mercury influence.

In answer to the questions that this raises, in 2005–2006 the FDEP, USEPA-ORD, Everglades National Park, and NOAA ARL are jointly planning a third-generation study of the atmospheric sources and influences that contribute heavily to the aquatic and biotic problems of mercury bioaccumulation in Florida water. In the coming year, the intent is to review the state of the science of the atmospheric cycle of mercury and, capitalizing on the substantial improvements in monitoring and modeling technologies since the South Florida Monitoring and Modeling Pilot Study (SoFAMMS) study of 1995–1996, return to the field in 2006–2008 for a three-year multisite field study in South Florida.

The FDEP proposes a coordinated effort among the participating agencies that would incorporate sites that should allow gauging the influence of local and regional sources on all of Florida and much of the Gulf of Mexico. The SFWMD provides monitoring support for this effort by its continuing sponsorship of the three Mercury Deposition Network (MDN) sites, which record annual atmospheric mercury deposition load across southern Florida. The intent is to (1) continue the Speciated Atmospheric Mercury supersite at Coral Springs and to support atmospheric mercury studies relevant to the mercury control policy in U.S. southeast coastal

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[6]The *Florida Atmospheric Mercury Study* (FAMS, 1992–1996; principal investigators Gerald Keeler, William Landing and C. Pollman) measured deposition mercury load at nine sites in Florida, establishing the understanding that atmospheric load is the primary source of mercury to Florida waters. FAMS, however, was not conceived as a process study, and had limited power to infer causative factors. In 1995–1996 the USEPA, FDEP, and University of Michigan (Gerald Keeler, principal investigator) conducted a second-generation, intensive, multisite South Florida Monitoring and Modeling Pilot Study (SoFAMMS) that showed strong relationships between local source emitters and tracers collected in rainfall samples. Substantial uncertainty obtained to this study, as it became apparent from the results that key measurements of mercury species were of paramount importance, but techniques to make those measurements were lacking (i.e., the complex speciation of mercury in the samples was hitherto unappreciated of paramount importance in being able to determine source-receptor relationships. As FDEP now contemplates a final set of studies on the atmospheric transport and fate, it is confident that measurement technology can support definitive conclusions. In the interim, FDEP and USEPA have substantially improved measurement technology, now allowing for responsive measurements on reasonable frequencies to be able to draw those relationships.

regions, (2) sponsor direct measurements of the transport of mercury species and related tracers 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 will change in this fiscal year, and one of the two sites there will be relocated to Everglades National Park, where it will serve as a marine background site for the other sites to be emplaced in the coming years.

SAMS remains a key to this effort, continuing to focus on the paramount importance of the speciation of mercury in the atmosphere in controlling the atmospheric 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, the USEPA has established mercury supersites 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 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.

TMDL Program Support

By 2010 the FDEP will require specific information on atmospheric deposition for those impaired waters significantly influenced by atmospheric deposition (i.e., mercury, fixed nitrogen, and perhaps phosphorus). The department is beginning to develop plans for a statewide analysis of these substances which will require both a field and modeling component. The plan is to organize this effort in the coming year and begin field measurements in 2007–2008.

Mercury in Coastal Waters

Excessive concentrations of mercury have been found in all of Florida's coastal waters, affecting over 50 species of commercial or sport-fishing interest. Human health advisories regarding consumption of fish have been issued for several species for all of Florida coastal and marine areas. To begin to develop a better understanding of the effective sources of mercury to marine fish, for the past two years the mercury program has applied for grant funding from the NOAA Office of Human Health Initiatives program, thus far to no avail. This proposed project would address the sources and influences that result in methylmercury formation in the coastal zone, and FDEP will continue to seek support for this activity.

Dry Deposition Processes

The FDEP anticipates award of a two-year EPA Regionally Applied Research (RARE) grant from EPA Region 4 that will focus on the processes that govern the dry deposition of mercury from the atmosphere, a substantial but poorly quantified portion of the total mercury deposition load. Dry deposition studies in general have trailed other aspects of this science because of the minute concentrations and fluxes of mercury species to the earth's surface. Despite the subtlety of this form of deposition, gas and particulate dry deposition occurs continuously, night and day, whereas rainfall at any point occurs for only a few hundred hours per year. Thus the net of dry deposition processes is thought to rival the rainfall load.

The FDEP and USEPA have sponsored two previous field studies, but rapidly evolving measurement technology and modeling techniques should allow for higher resolution analyses since the Florida Everglades Dry Deposition Study of 2000–2001. The capabilities of sampling and analytical instrumentation and computing power have advanced rapidly over the past decade, allowing for more sensitive and specific techniques. This yields higher temporal resolution data which in turn can support more higher-resolution modeling analyses. It was only a few years ago that 24-hour samples were the norm; today we can often obtain semi-continuous or continuous data and in some instances achieve data capture cycles of an hour or less.

In sum, it is believed that the South Florida Mercury Science Program can continue to address the major multimedia aspects of the mercury cycle as it influences Florida. Work is expected to continue until the major scientific uncertainties have been substantially narrowed and applied information and analysis to support department programs is provided.

CONCLUSIONS

- In 2003 and 2004, 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 Beard 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 Mercury Deposition Network.
- There remains a need to determine the relative importance of local, regional, and global atmospheric sources of mercury on mercury levels in fish in the Everglades, and evaluate options for Everglades mercury reductions.
- Mercury concentrations in largemouth bass in WCA-1, 2, and 3, while having declined by about 40 to 80 percent over the past decade, still remain relatively high (mean of means ca. 0.5 mg/kg) compared to the USEPA's recommended MeHg fish tissue criterion of 0.3 mg/kg.
- Mercury concentrations in largemouth bass in WCAs declined significantly from the early 1990s to 1998, but have not declined greatly from 1998 to the present. Thus, in the absence of further reductions in larger-scale Hg emissions that impact South Florida, or reductions in sulfate loading to the Everglades, the mercury problem will likely persist, albeit at a lower level than ca. 15 years ago.
- Mercury concentrations in largemouth bass have increased in the ENP since 1998, and very high concentrations (1.2–1.6 mg/kg) are now evident in the Shark River Slough area at sites L67F1 and North Prong Creek. As well and as observed in previous years, for 2004 resident sunfish at site L67F1 had significantly greater mercury burdens than fishes from other Everglades sites. Mean concentration of THg in sunfish (*Lepomis* spp.) collected at L67F1 in 2004 was 0.44 mg/kg, which is well above both the USFWS and USEPA predator

protection criterion (see Appendix 2B-1). Because sunfish represent the preferred prey item of many fish-eating species in the Everglades, there is a need to elucidate the cause of elevated mercury levels in the Park.

- Drying and rewetting cycles stimulate the formation of MeHg in the Everglades, in Stormwater Treatment Areas (STAs), and in reservoirs. Drying and consequent aeration of soils results in oxidation of sulfide to sulfate. When rewetted, soil sulfate is readily available to Hg-methylating sulfate-reducing bacteria. However, once sulfide (the end product of microbial sulfate reduction) accumulates in soil porewaters, MeHg production rate is reduced.
- Everglades hydrological alterations in recent years may have changed the distribution of sulfate; it appears that the mercury levels in fish have altered geographically. Station 3A-15, the former mercury hot spot, now has low mercury levels, while levels in fish in the Shark River Slough area of the ENP are high, possibly because sulfate concentrations are optimal for mercury methylation. Additional survey work is recommended to locate the new mercury hot spot(s) in the Everglades, and to verify the causes of elevated mercury.
- Increases in water delivery from the Stormwater Treatment Areas to the Everglades National Park could widen the area of elevated mercury concentrations in fish in the Park if sulfate concentrations in this “new” water are elevated above Everglades background.
- There is a need to investigate Everglades sulfur biogeochemistry other than as regards mercury methylation. Sulfur, as a biologically very active element, has forms that are highly toxic (sulfide) and others (sulfate) which will promote eutrophication of the Everglades via liberation of phosphorus from sediments. There is a need to investigate further the effects of sulfur loading from the Everglades Agricultural Area on the Everglades ecosystem.

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