# Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

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## SUMMARY

Mercury and sulfur are Everglades water quality issues of concern due to their elevated concentrations. Mercury is a concern because as methylmercury it is bioaccumulative and neurotoxic — thus it is a threat to fish-eating wildlife and humans. Sulfur is a concern because (1) as sulfate it promotes methylation of mercury, (2) it affects the biogeochemical cycling of numerous elements including phosphorus, and (3) as sulfide, it is toxic to aquatic plants and animals.

The very high mercury concentrations evident in fish and wildlife in the Water Conservation Areas (WCAs) from the late 1980s to the early 1990s have declined substantially; a combination of declining rates of atmospheric mercury deposition and reductions in sulfate concentrations probably account for these declines. Mercury levels in largemouth bass (*Micropterus salmoides*) in the WCAs, however, remain generally above the proposed U.S. Environmental Protection Agency (USEPA) human health criterion for fish consumption, which is 0.3 micrograms per gram (µg/g). In contrast to the mercury reductions in largemouth bass in the WCAs, mercury levels in these fish have increased in Everglades National Park (ENP or Park) and the Holey Land Wildlife Management Area (WMA) in recent years. ENP largemouth bass mercury concentrations of greater than 1 µg/g are currently similar to or greater than those at other known methylmercury hot spots in the U.S. due to a combination of factors including elevated South Florida atmospheric mercury concentrations, high rates of rainfall, favorable conditions in the ENP for methylmercury production, and high bioaccumulation factors. In the ENP, largemouth bass and sunfish mercury levels are both above USEPA wildlife criteria. Options for reducing

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Everglades mercury levels include atmospheric mercury source reduction and sulfate loading reduction.

For sulfur, Everglades Agricultural Area (EAA) canals are a major source of sulfate inputs to the ecosystem, and approximately 60 percent of the Everglades marsh area has sulfate concentrations greater than the Comprehensive Everglades Restoration Plan goal of 1 milligram per liter (mg/L) in surface water. It is probable that broad areas of the Everglades exhibit sulfate concentrations at which increased sulfate levels would enhance (and decreased sulfate concentrations would reduce) methylmercury bioaccumulation. Sulfur may be having detrimental effects beyond promoting mercury methylation, including sulfide toxicity to aquatic plants and animals, and phosphate and ammonium release from sediments. Research to determine the sources of sulfate to the Everglades is planned, and options to reduce loading will be developed from those results.

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)[8] to promote improved understanding of the sources, transformations, and toxicity of mercury in the Everglades, in support of natural resource management decisions. This chapter in the *2008 South Florida Environmental Report – Volume I* (SFER) serves to update previously reported findings in earlier consolidated reports, with supporting data on mercury provided in the Chapter 3A and 3C appendices in this volume.[9]

[8] This partnership of federal, state, and local interests includes the FDEP, the District, the USEPA Office of Research and Development and Region 4, the Florida Fish and Wildlife Conservation Commission, the Smithsonian Environmental Research Center, and the U.S. Geological Survey. Other collaborators associated with the SFMSP are the U.S. Fish and Wildlife Service, National Park Service, U.S. Army Corps of Engineers, University of Florida, Florida International University, University of Miami, University of Michigan, University of Wisconsin, Texas A&M University, Louisiana State University, Florida Gulf Coast University, Florida Electric Power Coordinating Group, and the National Oceanic and Atmospheric Administration.

[9] Appendices 3A-1, 3A-2 3A-3, 3A-4, 3B-1, 3B-2, and 3B-3 of this volume 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 2005–2007 South Florida Environmental Reports).

## NEW FINDINGS

New findings and issues of continuing concern summarized below are drawn from this chapter and from related appendices.

- Mercury concentrations in largemouth bass in WCA-1, WCA-2, and WCA-3 while having declined by about 30–70 percent from levels in the late 1980s and early 1990s, remain generally above the USEPA-recommended MeHg fish tissue criterion of 0.3 μg/g, with 67 percent of the largemouth bass sampled in WCAs in 2006 exceeding the USEPA criterion — for 2006, the WCA median mercury concentration in largemouth bass was 0.40 μg/g (range; 0.07–3.1 μg/g; n = 215).
- One-hundred percent of the largemouth bass sampled in Shark River Slough in the ENP during 2007 exceeded the USEPA human health fish tissue criterion and the USEPA wildlife criterion for trophic level 4 (TL 4) fish (0.346 μg/g). Mercury concentrations in largemouth bass have increased in the ENP since 1999, and very high concentrations (1.1–1.4 μg/g) are now evident in the Shark River Slough area at site L67F1 near the L67 Extension canal and at North Prong Creek. As observed in previous years, for 2006 resident sunfish (*Lepomis* spp.) at site L67F1 had high mercury levels.
- Mean concentration of mercury in sunfish collected at L67F1 in the ENP in 2006 remains above the U.S. Fish and Wildlife Service (USFWS) predator protection criterion and USEPA wildlife criterion for trophic level 3 (TL 3) fish (0.1 and 0.077 μg/g respectively); sunfish represent the preferred prey item of many fish-eating species in the Everglades.
- There is a trend of increasing mercury levels in largemouth bass and sunfish in the Holey Land WMA; the mean mercury concentration in largemouth bass was 0.86 μg/g for 2006, a level that may pose a threat to fish-eating wildlife.
- Great egret (*Casmerodius albus*) feather mercury concentrations for Everglades colonies increased from an average of 6 mg/kg in 2006 to 10 mg/kg in 2007.
- A study currently under way on white ibises (*Eudocimus albus*) exposed to Everglades-relevant mercury levels indicates that the control group had significantly more nests with eggs and higher productivity than MeHg dosed groups.
- Analysis of 1994 to 2002 atmospheric mercury wet deposition data suggested a declining trend in deposition in South Florida; expanding the dataset through 2005 negated the trend, and the addition of data through 2006 again reveals a downward trend in atmospheric mercury wet deposition at site FL11 (Beard Research Center) in the ENP of 2 nanograms per liter (ng/L) in the mercury signal, equivalent to about 15 percent of the mean value over the period of record.
- The increase in mercury wet deposition from early 2003 through mid-2004 in South Florida may be an explanation for the subsequent increases in mercury in Everglades fish and birds at some sites.
- Uranium tracer results suggest that deep groundwater is not a major sulfate contributor to EAA canals — thus, sulfur isotope data, sulfate/chloride ratios, sulfate concentration trends before and after drought, and uranium tracer studies

from the available dataset all point to limited deep groundwater sulfate contribution to EAA canals.

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 rapidly than could have been accomplished individually by either the FDEP or the District. The goal of the SFMSP is to provide the FDEP, the District, and the federal government with information to aid in making mercury-related decisions about the Everglades Construction Project and Comprehensive Everglades Reconstruction Project, as well as other restoration efforts, on the schedule required by the Everglades Forever Act.

# PREVIOUS FINDINGS

This section summarizes findings from the collaborative SFMSP effort and is in response to the 2007 SFER Panel's request to summarize key findings on mercury from previous SFER chapters for reference.

## Mercury in Everglades Fish and Wildlife

- Methylmercury (MeHg) strongly bioaccumulates in the Everglades aquatic food chain, approaching bioaccumulation factors of $10^7$ for largemouth bass (*Micropterus salmoides*). MeHg further bioaccumulates in fish-eating birds and mammals. Benthic invertebrates are the main source of MeHg to fish (USEPA, 1997b; Cleckner et al., 1998; Loftus et al., 1998; Hurley et al., 1998 Fink and Rawlik, 2000; Rumbold et al., 2001; Frederick et al., 2005).
- Mercury (Hg) levels in fish at sites in the WCAs declined about 30–70 percent from levels of the late 1980s and early 1990s to present levels, but WCA-wide median concentrations are little changed from 1998 to the present (Lange, 2007).
- Mean MeHg concentrations in largemouth bass in WCAs remain generally higher than the USEPA-derived MeHg fish tissue criterion of 0.3 μg/g (USEPA 2001; Lange, 2007).
- Very high concentrations of mercury ( >1 μg/g) in largemouth bass are presently evident in portions of the ENP, particularly in the Shark River Slough at sites near the L-67 Extension canal and North Prong Creek. (Lange, 2007; Rumbold et al., 2007; Appendix 3B-1 of this volume).
- The WCAs and the ENP (totaling about 2 million acres) remain under fish consumption advisories for protection of human health, and mercury levels in ENP fish indicate that fish-eating (piscivorous) birds would experience exposures above the acceptable methylmercury dose; mammalian wildlife also may be at risk (FDOH, 2006; Fink and Rawlik, 2000; Frederick et al., 2005; Rumbold et al., 2007).
- Dramatic declines in mercury concentrations in feathers of wading birds beginning in 1998 have been accompanied by increases in numbers of nesting birds (2 to 5 times over 1998–2006, depending on species). It is not clear whether the mercury decline is related to the increase in nesting birds, and controlled

studies are needed to isolate the effect of mercury from the myriad conditions that affect bird nesting in the field (Frederick et al., 2005).

- A risk assessment of MeHg exposure to three piscivorous wildlife species (bald eagle, wood stork, and great egret) foraging at a MeHg hot spot in the northern ENP indicated a 98–100 percent probability that these birds would experience exposures above the acceptable dose (the no-observed-adverse-effect level). Moreover, the likelihood that these birds would experience exposures above the lowest-observed-adverse-effect level ranged from a 14 percent probability for the wood stork to a 56 percent probability for the eagle (Rumbold et al., in press.)

## Mercury Sources to the Everglades

- Atmospheric deposition of inorganic mercury accounts for greater than 95 percent of the external load of mercury to the Everglades (Landing et al., 1995; USEPA, 1996; Guentzel et al., 1998, 2001).
- Due to a combination of elevated rainwater mercury concentrations and the high annual rainfall in South Florida, wet total-mercury deposition to the Everglades remains substantially greater than that for most other regions monitored in the U.S. (NADP, 2007).
- The primary air emissions sources of mercury in South Florida circa 1990 were from municipal and medical waste incinerators. 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 (RMB, 2002; Atkeson et al., 2005).
- Atmospheric mercury contributions from local (South Florida) sources are estimated to have declined from 51 percent of total atmospheric sources in 1991, to 21 percent in the observation period spanning from 1995 through 1996, and 9 percent in 2000 (Pollman et al., 2005b; Pollman et al., 2007).
- Presently, though anthropogenic point source atmospheric emissions of mercury from South Florida are calculated to be a small fraction ($< 10$ percent) of peak historical levels (circa 1990) (Pollman et al., 2005a, 2007), South Florida mercury sources remain poorly quantified. Despite the substantial earlier reductions, an updated emissions inventory of South Florida atmospheric mercury sources is required to evaluate management options for reducing fish tissue mercury to safe levels.

## Mercury and Sulfur Biogeochemistry in the Everglades

- The Everglades mercury problem, more aptly termed a methylmercury problem, results from a relatively high rate of atmospheric deposition of mercury combined with biogeochemistry. While levels of inorganic mercury are low in the Everglades compared to sites with point-source industrial mercury discharge, efficient biogeochemical conversion of inorganic mercury to MeHg in the Everglades leads to higher MeHg levels in fish than is found at many mercury-contaminated industrial sites, in part due to inputs of sulfate to the ecosystem (Gilmour et al., 1992; Gilmour et al., 1998; Benoit et al., 1999; Cleckner et al., 1999; Krabbenhoft et al., 2000; Rumbold and Fink, 2006).

- Variation in MeHg concentration in Everglades sediments and in fish is better explained by differences in rate of mercury methylation than by variation in inorganic mercury in sediments. The correlation between inorganic mercury and MeHg concentrations in sediments in the Everglades is weak; across the Everglades, total mercury concentrations in surface sediments vary by a factor of approximately three, while MeHg concentrations vary by a factor of over 100 (Gilmour et al., 1998, 2000, 2004a; Cleckner et al., 1999; Benoit et al., 1999, 2003; Krabbenhoft et al., 2000; Rumbold and Fink, 2006).
- The slope of the relationship between inorganic mercury and MeHg levels in surface sediments varies among sites, reflecting differences in environmental conditions affecting rate of mercury methylation (Gilmour et al., 1998, 2000, 2004a; Benoit et al., 1999; Cleckner et al., 1999; Krabbenhoft et al., 2000; Rumbold and Fink, 2006).
- Inorganic mercury is converted to MeHg, a highly toxic and bioaccumulative form of mercury, by naturally occurring sulfate-reducing bacteria. 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 (Benoit et al., 2003).
- MeHg production is highly influenced by the rate of supply of atmospherically derived mercury (Orihel et al., 2006; Paterson et al., 2006; Munthe et al., 2007).
- At multiple locations across the Everglades Protection Area (EPA), namely the WCAs and the ENP, net mercury methylation and bioaccumulation responded linearly to single-dose mercury loads up to twice the annual atmospheric mercury wet deposition rates (Gilmour et al., 2007a).
- A higher fraction of newly atmospherically deposited inorganic mercury is methylated in surface soils than is native ( > 2 months old) mercury, indicating that mercury newly deposited to the Everglades is more bioavailable for methylation than previously deposited pools (Orihel et al., 2006; Paterson et al., 2006).
- The effect of sulfur on methylation is determined by the balance between sulfate and sulfide; mercury methylation rate is high at 2–20 mg/L sulfate in Everglades surface waters where sediment porewater sulfide concentrations are moderate (5–150 ppb, or µg/L) (Gilmour et al., 2007a).; sulfide begins to repress mercury methylation at concentrations above about 300 ppb in porewater (Benoit et al., 2003; Gilmour et al., 1998). Sulfate contamination is an important factor in mercury methylation in the ecosystem (Benoit et al., 1999, 2001, 2003; Gilmour et al., 2007a).
- Dissolved organic carbon (DOC) promotes inorganic mercury dissolution, thereby making it available for methylation. Some DOC fractions, in complexing with mercury, may make mercury unavailable for methylation (Drexel et al., 2002; Haitzer et al., 2003; Aiken et al., 2003).
- Long-term phosphate additions have not significantly affected the production of MeHg in surface soil flocs (Atkeson and Axelrad, 2004; Gilmour et al., 2004a).
- Drying and rewetting cycles stimulate the formation of MeHg in the Everglades and in Stormwater Treatment Areas (STAs). Drying and consequent aeration of soils results in oxidation of sulfide to sulfate. When rewetted, soil sulfate is readily available to mercury-methylating sulfate-reducing bacteria. However,

once sulfide (an end product of microbial sulfate reduction) accumulates to high levels in soil porewaters, MeHg production rate is reduced (Fink, 2003; Gilmour, 2003; Gilmour et al., 2004b; Rumbold and Fink, 2006).

- Minimizing soil dry-out can aid in managing MeHg production. STAs most prone to high MeHg production appear to be those not previously used for agriculture. Very high levels of reduced sulfur in soils at STAs that were constructed on former agricultural soils inhibit MeHg production through the formation of mercury-sulfide species that are not available to microorganisms for uptake and methylation (Fink, 2003; Gilmour, 2003; Gilmour et al., 2004b; Rumbold and Fink, 2006).
- MeHg production and concentrations at the former mercury "hot spot" at site 3A-15 in WCA-3 have declined substantially since 1993, and these declines correlate best with reductions in sulfate concentrations in surface waters at this site. Site 3A-15 sulfate concentrations are now below optimal levels for methylation of mercury by sulfate-reducing bacteria (Axelrad et al., 2005).
- Sulfate continues to be discharged from the EAA to the Everglades. It is possible that hydrological manipulations affecting sulfate concentrations, or drying and rewetting of soils, or for the southern ENP, natural tidal influences, have contributed to the elevated mercury levels in fish now evident in the ENP. Enhanced monitoring is needed to track the changing spatial patterns of mercury methylation throughout the system (Gilmour et al., 2007a, b).
- It is probable that broad areas of the Everglades Protection Area (EPA) currently exhibit sulfate concentrations at which increased sulfate levels would enhance, and decreased sulfate concentrations would reduce, net MeHg accumulation in soils, and hence MeHg accumulation in biota (Gilmour et al., 2007a).

## Sulfur Levels, Sources and Effects in the Everglades

- Surface water sulfate concentrations in northern Everglades[10] marshes can reach about 100 times the Comprehensive Everglades Restoration Plan (CERP) goal of 1 mg/L, averaging about 40 to 70 mg/L in WCA-2 compared to $\leq$ 0.1 mg/L in parts of the ecosystem further south and away from canal discharges (Bates et al., 2002; Orem, 2004; Gilmour et al., 2007b; Scheidt and Kalla, 2007).
- Highest surface water sulfate concentrations across the EPA (excluding marine-influenced sites) were observed in EAA canal water; sulfate concentrations averaged over 70 mg/L and levels approaching 200 mg/L were intermittently observed (Bates et al., 2002; Orem, 2004; Gilmour et al., 2007b; Orem et al., in press).
- Approximately 60 percent of the Everglades marsh area has sulfate concentrations greater than the CERP goal of 1 mg/L in surface water (Scheidt and Kalla, 2007).
- EAA canals are a major source of sulfur to the Everglades (Bates et al., 2002; Fink and Rawlik, 2000; Orem, 2004; Orem et al., in press), and data are consistent with the hypothesis that EAA agricultural sulfur applications and legacy agricultural sulfur in EAA peat soils released through mineralization are the principal sources, but not the only significant sources, of sulfate to the

[10] In this chapter, northern Everglades refers to the northern Everglades Protection Area

Everglades. There is a need to determine a sulfur mass balance for the Everglades (see Appendix 3B-2 of this volume).

- Preliminary research results indicate that cattail (*Typha domingensis*) may be more tolerant of elevated sulfide levels in sediments than is sawgrass (*Cladium jamaicense*); growth rate of sawgrass as measured in a short-term assay was reduced by sulfide concentrations that are evident in WCA-2 (approximately 7 mg/L sulfide in porewater), while cattail growth rates were not significantly reduced at this sulfide concentration (Gilmour et al., 2007b).
- Preliminary research indicates that sulfate may promote phosphate and ammonium release from Everglades sediments (Gilmour et al., 2007b).

# MERCURY IN EVERGLADES FISH AND WILDLIFE

## MONITORING MERCURY

Mercury is monitored in the Everglades due to its toxicity. The toxicity of mercury is critically dependent upon its chemical state, with some forms being much more toxic than others. In fish, mercury is present predominantly in the form of methylmercury (MeHg) which is known to be neurotoxic and highly bioaccumulative. Bloom (1992) reported that virtually all (> 95 percent) of the mercury in muscle tissue from largemouth bass is in the form of MeHg.

The greatest threat of mercury to humans and wildlife populations results from the ingestion of contaminated fish. When mercury was first monitored in the Everglades in the late 1980s, some of the highest mercury levels in fish in the nation were revealed. Options for monitoring mercury trends in the Everglades include sampling of water, sediments or periphyton for mercury or MeHg, or monitoring mercury in fish where it is predominantly in the form of MeHg.

Generally, monitoring of mercury concentrations in fish is preferable because of the ease of sampling and analysis, and the general lack of contamination concerns relative to monitoring mercury in other media, such as surface water. Additionally, monitoring of mercury in fish provides a more accurate depiction of waterbody impairment — impairment meaning mercury is interfering with a waterbody's designated use of "fishable" — because elevated mercury levels in fish making it unsafe to consume these fish. Sampling of total mercury or MeHg in Everglades surface waters is not an adequate surrogate for sampling fish, because mercury concentrations in water are poor predictors of mercury levels in fish (Scheidt and Kalla, 2007).

Florida's existing freshwater water-quality criterion for mercury is a surface water concentration of 12 nanograms per liter (ng/L) total mercury — a criterion derived to limit methylmercury bioconcentration in fish to less than the FDA fish safety level of 1 mg/kg (1 μg/g) (http://www.cfsan.fda.gov/~comm/haccp4x5.html) (Florida Rule 62-302, Surface Water Quality Standards, at http://www.dep.state.fl.us/legal/Rules/rulelistnum.htm). This value is rarely exceeded in Everglades surface waters; for the four U.S. Environmental Protection Agency (USEPA) Regional Environmental Monitoring and Assessment Program's Everglades samplings from 1995 to 2005, the 12 ng/L total mercury water quality criterion was exceeded for only six of 733 samples, all in the dry season where water depth was approximately 20 cm or less (Scheidt and Kalla, 2007).

As compared to the water quality criterion for mercury of 12 ng/L, the overall 1995–2005 median for total mercury across the Everglades is 2.0 ng/L, as it was for the November 2005 sampling where no sample reached the value of the water quality criterion (**Figure 3B-1**) (Scheidt and Kalla, 2007). Nonetheless, Everglades fish tissue mercury concentrations reach levels of human health concern in over two million acres of the Everglades and have prompted the Florida Department of Health (FDOH) to issue fish consumption advisories (FDOH, 2006), which the Florida Department of Environmental Protection (FDEP) interprets as signifying impairment of the water body.

The FDOH currently advises anglers fishing in the WCAs to limit consumption of eight sport fish species [largemouth bass (*Micropterus salmoides*), Mayan cichlid (*Cichlasoma urophthalmus*), yellow bullhead (*Ameiurus natalis*), spotted sunfish (*Lepomis punctatus*), bowfin (*Amia calva*), bluegill (*Lepomis macrochirus*), gar (*Lepisosteus platyrhincus*), and redear sunfish

(*Lepomis* spp.)]. Moreover, FDOH guidance regarding largemouth bass exceeding 14 inches in length and all sizes of bowfin and Florida gar is "no consumption" (FDOH, 2006). Furthermore, for protection of human health, the FDOH (2006) recommends "no consumption" of largemouth bass, bowfin, and gar from the entire Shark River Slough region of the ENP, and extremely limited consumption of an additional five sport fish species (Mayan cichlid, redear sunfish, bluegill, spotted sunfish, and yellow bullhead).

The USEPA has advised states on procedures to develop fish tissue criteria for mercury (USEPA, 2001), and the FDEP is evaluating options for revising its mercury water quality criterion.

Largemouth bass (LMB), a popular Everglades sport fish and a high trophic level predator with ubiquitous distribution in the Everglades, were selected in the late 1980s for monitoring MeHg bioaccumulation, thus allowing for tracking of mercury trends and assessment of the effectiveness of management actions in reducing Everglades mercury levels.

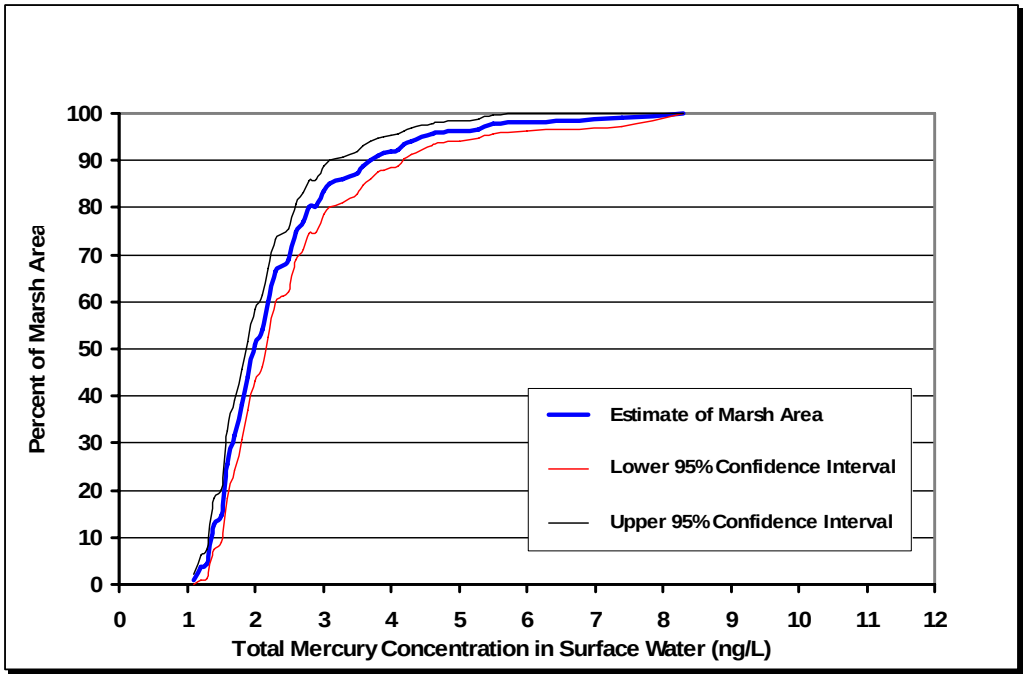



**Figure 3B-1.** Cumulative distribution function for concentration of total mercury in surface water (ng/L) versus percent Everglades marsh area, November 2005 (wet season), (Scheidt and Kalla, 2007).

## MERCURY IN FISH

Mercury concentrations in LMB from the WCAs declined between 1988, when monitoring began, and 2006, reaching their lowest levels in 2001 with a system-wide median concentration of 0.30 micrograms per gram, or µg/g (range; 0.07–1.3 µg/g; n = 151) (**Figure 3B-2,** top panel). Mercury levels in LMB have since increased, reaching a median concentration of 0.40 µg/g (range; 0.07–3.1 µg/g; n = 215) in 2006. Although mercury levels in largemouth bass in WCAs declined 77 percent between 1988 and 2006, 67 percent of the largemouth bass sampled in the WCAs during 2006 exceeded the USEPA nationally recommended fish tissue mercury criterion of 0.3 µg/g.

Mercury concentrations in LMB from the Shark River Slough in the ENP have for the past decade been significantly higher than those from LMB in the WCAs, with median concentrations exceeding 1.0 µg/g during most years since 1989 (**Figure 3B-2,** lower panel). In 2007, the system-wide median concentration (represented only by site North Prong Creek in 2007) was 1.40 µg/g (range; 0.45–2.70 µg/g; n = 21). One-hundred percent of the largemouth bass sampled in Shark River Slough in ENP (sites L67F1 and North Prong Creek) during 2006 and 2007 exceeded the USEPA fish tissue mercury criterion (n = 61; minimum = 0.45 µg/g).

In an effort to monitor long-term trends at both local and regional scales within the Everglades, mercury levels in LMB have been monitored along a transect of sites established through Stormwater Treatment Area 1 West (STA-1W); WCA-1, WCA-2, and WCA-3; Holey Land Wildlife Management Area (WMA); and the ENP since the early 1990s (**Figure 3B-3**). The periods of record (POR) and number of sampling events vary among sites due to differences in initial sampling dates and inability to collect LMB samples during some years. Spatial and temporal trends for these long-term monitoring stations are reported in **Table 3B-1** and **Figures 3B-4** through **3B-10**. To allow comparison of spatial and temporal trends both within and among sites, LMB mercury levels were standardized to an expected age-3 mercury concentration (EHg3) by regression of mercury against LMB age for each long-term monitoring site (**Table 3B-1** and **Figures 3B-4** through **3B-10**).

Mercury concentrations for EHg3 for the most current year sampled ranged between 0.08 µg/g in STA-1W and 1.35 µg/g in North Prong Creek in Everglades National Park. The average EHg3 for the 10 sites was 0.72 µg/g (**Table 3B-1**). Maximum EHg3 concentrations occurred between 1992 and 1997 at all sites except Holey Land, which reached its highest EHg3 in the most recent sampling year, 2006. Excluding Holey Land, there has been an average decline in EHg3 of 41 percent across all sites between the maximal years in the mid-1990s and the most recent sampling year. Declines ranged between 31 percent and 67 percent for the nine sites.

Throughout the LMB mercury monitoring project, the spatial distribution of mercury has remained consistent with increasing mercury bioaccumulation moving from north to south in the EPA (**Table 3B-1**). Data indicate that at the time of maximal EHg3, and for the most recent sampling years, the highest levels of mercury in LMB have occurred in the ENP. Although the declines from the very high levels of mercury in LMB in the mid-90s are encouraging, temporal trends at individual sites indicate some potential increasing trends.

In WCA-1, WCA-2, and WCA-3 (**Figures 3B-4** through **3B-6**), there have been consistent declines from maximal to current EHg3. At two sites in WCA-1, declines were 32 and 42 percent; in WCA-2, declines were 38 and 40 percent. The greatest declines, 64 and 67 percent, were observed at two sites in WCA-3 where in the early 1990s EHg3 was ≥ 2.0 µg/g. Over the past three to four years however, increases in EHg3 have been observed for these WCA sites. Between

2004 and 2006 (three sample years), EHg3 has increased an average of 79 percent at the WCA sites. The greatest increase was observed in WCA-1 (**Figure 3B-4**) where EHg3 increased 283 percent to 0.36 µg/g in the L-7 canal and 22 percent to 0.60 µg/g in the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge) marsh (**Table 3B-1**). Recent increases in mercury bioaccumulation do not bring current levels to near those measured in LMB during the mid-1990s, but they do represent a trend of increased MeHg exposure for piscivorous wildlife and humans.

Of greatest concern are the temporal trends experienced at three sites with the highest current year mercury concentrations (EHg3); Holey Land, North Prong Creek, and Lostmans Creek. The period of record for these sites is generally shorter than for those located in the WCAs, and maximum EHg3 concentrations could potentially have occurred prior to commencement of sampling. However, it is evident that trends differ at these sites from those observed at the WCA sites.

At the canal site in the Holey Land WMA, the maximum EHg3 occurred in the most recent sampling year (**Table 3B-1**) and between 1999 and 2006 EHg3 has increased by 196 percent, reaching 0.86 µg/g in 2006 (**Figure 3B-7**). Similarly, at site North Prong in the Shark River Slough in the ENP, EHg3 increased 94 percent from its lowest concentration in 1998 to that in 2003. Since 2003, EHg3 has declined slightly, reaching 1.35 µg/g in 2007, which is well in excess of the USEPA fish tissue mercury criterion of 0.3 µg/g. There has been a modest increase in EHg3 in recent years at the Lostmans Creek site, which lies north of the Shark River Slough within the drainage basin of Big Cypress National Preserve (**Figure 3B-8**). Although no LMB were collected between 2001 and 2006, the current year EHg3 (2007), corresponding to an increase of 47 percent since 2000, is near the maximal EHg3 of 1.02 µg/g from 1997 (**Table 3B-1**). Trends at all three sites have shown general increases in recent years, approaching maximum concentrations at their respective sites. Furthermore, the two sites in ENP, Lostmans and North Prong Creeks, have consistently shown the highest mercury levels in the Everglades and for the state of Florida.

SFWMD sampling has confirmed a trend in recent years of increasing mercury in fish [mosquitofish (*Gambusia holbrooki*), sunfish, and LMB] in the Holey Land WMA and at site L67F1 in the Shark River Slough ENP (see Appendix 3B-1 of this volume).

In STA-1W, the EHg3 within treatment cell 3 has remained relatively constant during the POR (**Table 3B-1**) ranging between 0.05 and 0.12 µg/g between 1995 and 2007 (**Figure 3B-9**). No trends are evident and these concentrations represent some of the lowest mercury levels found in fish from the Everglades, including from the other STAs (Rumbold et al., 2007). Mercury concentrations in age 1 and 2 cohort LMB were evaluated as these fish represent a shorter mercury bioaccumulation integration period than EHg3 LMB. Similar to the EHg3 data, mean mercury concentrations in age 1 and 2 cohort LMB in the WCAs and Holey Land WMA are all near 0.6 µg/g (range; 0.57–0.69 µg/g) while in Shark River Slough in the ENP, the mean mercury concentration was 1.14 µg/g (**Figure 3B-10**).

Fish-eating avian and mammalian wildlife continue to be at risk of adverse effects from mercury exposure in particular in the Shark River Slough area of the ENP as mercury concentrations in TL 3 sunfish and TL 4 LMB (age 1 and 2 cohort and EHg3), exceed established USFWS (0.1 µg/g) (Eisler, 1987) and USEPA wildlife criteria levels (TL 3, 0.077 µg/g; TL 4, 0.346 µg/g) (USEPA, 1997a). Sunfish, which are at TL 3 (*L. gulosus* at TL 4; Loftus et al., 1998), exceeded the TL 3 criterion at all Everglades sites sampled by the SFWMD and approached or exceeded the TL 4 criterion at half of the sites (see Appendix 3B-1 of this volume). Largemouth bass exceeded the TL 4 criterion at both Shark River Slough sites in the ENP in 2006/07; North Prong Creek mean mercury concentration in LMB from age cohort 1–2 was 1.14 µg/g and EHg3 was 1.4 µg/g; for L67F1, LMB mean EHg3 was 1.13 µg/g (see Appendix 3B-1 of this volume).

**Table 3B-1**. Trends in age-standardized mercury levels in largemouth bass ($EHg_3$) for various periods of record (POR) at 10 long-term monitoring sites in the Everglades. Percent change contrasts the highest observed $EHg_3$ (maximum) with the most recent $EHg_3$ (current) and is reported as the percent change. Sites are aligned from north to south and $EHg_3$ is reported as µg/g = mg/kg = ppm).

| Location/Site | Reported POR | Sample Events | Maximum EHg3 (Year) | Current EHg3 (Year) | % Change From Maximum |
|---|---|---|---|---|---|
| | | | | | |
| **Stormwater Treatment Area 1W** | | | | | |
| Treatment Cell 3 | 95-06 | 13 | 0.12 (1996) | 0.08 (2006) | -31 |
| **ARM Loxahatchee National Wildlife Refuge** | | | | | |
| L-7 Canal | 95-06 | 12 | 0.61 (1996) | 0.36 (2006) | -42 |
| LNWR Marsh | 95-06 | 12 | 0.88 (1996) | 0.60 (2006) | -32 |
| **Holeyland WMA** | | | | | |
| Holeyland Canal | 96-06 | 11 | 0.86 (2006) | 0.86 (2006) | NA |
| **Water Conservation Area 2A** | | | | | |
| WCA2A-U3 Marsh | 93-06 | 15 | 1.27 (1993) | 0.76 (2006) | -40 |
| L35B Canal | 93-06 | 16 | 1.33 (1993) | 0.83 (2006) | -38 |
| **Water Conservation Area 3A** | | | | | |
| L67A | 90-06 | 20 | 1.96 (1992) | 0.71 (2006) | -64 |
| WCA3A-15 Marsh | 93-06 | 14 | 2.39 (1993) | 0.79 (2006) | -67 |
| **Everglades National Park** | | | | | |
| Lostmans Creek | 95-07 | 9 | 1.02 (1997) | 0.92 (2007) | -10 |
| North Prong Creek | 94-07 | 15 | 2.37 (1994) | 1.35 (2007) | -43 |
| **Average** | | | | **0.72** | **-41** |

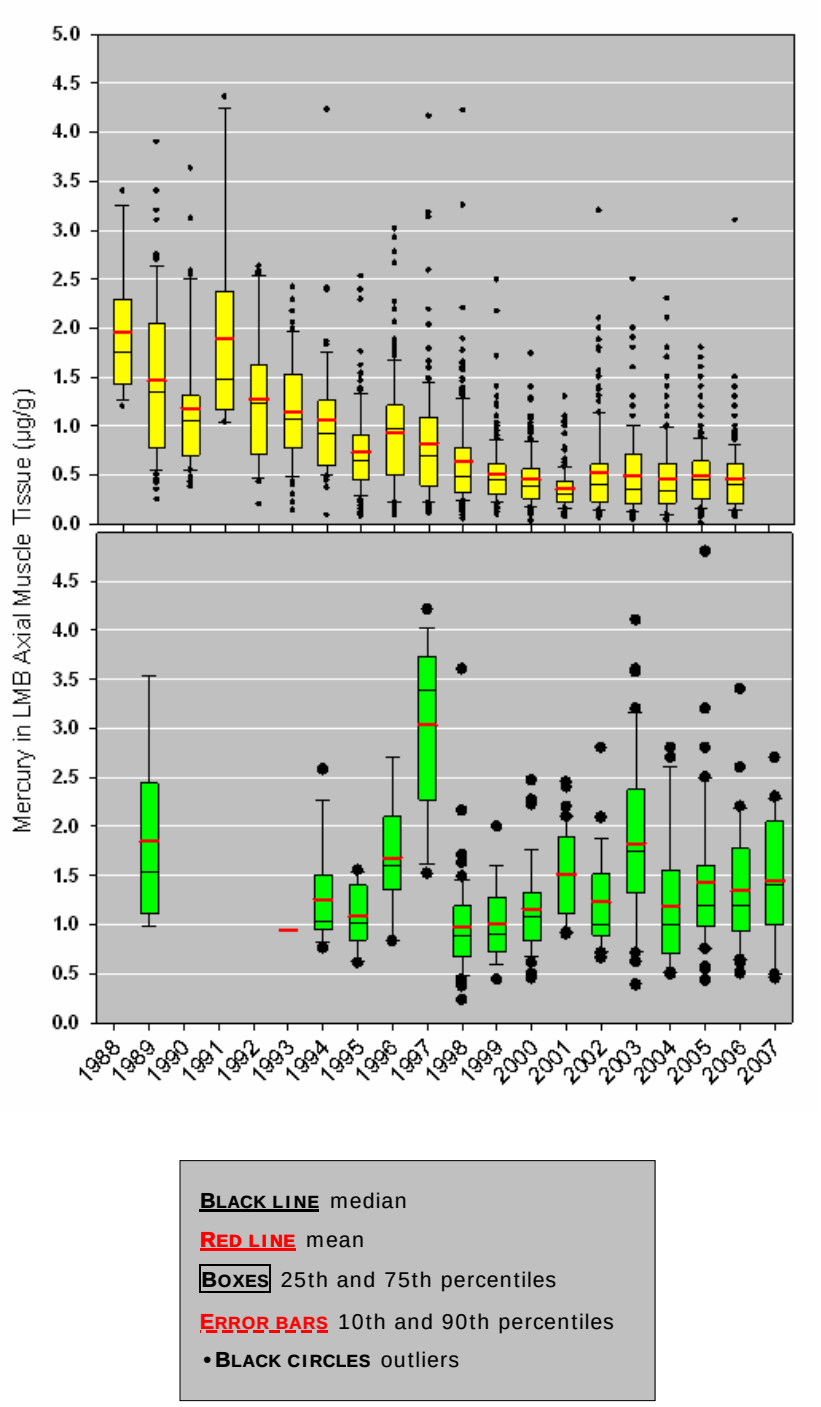
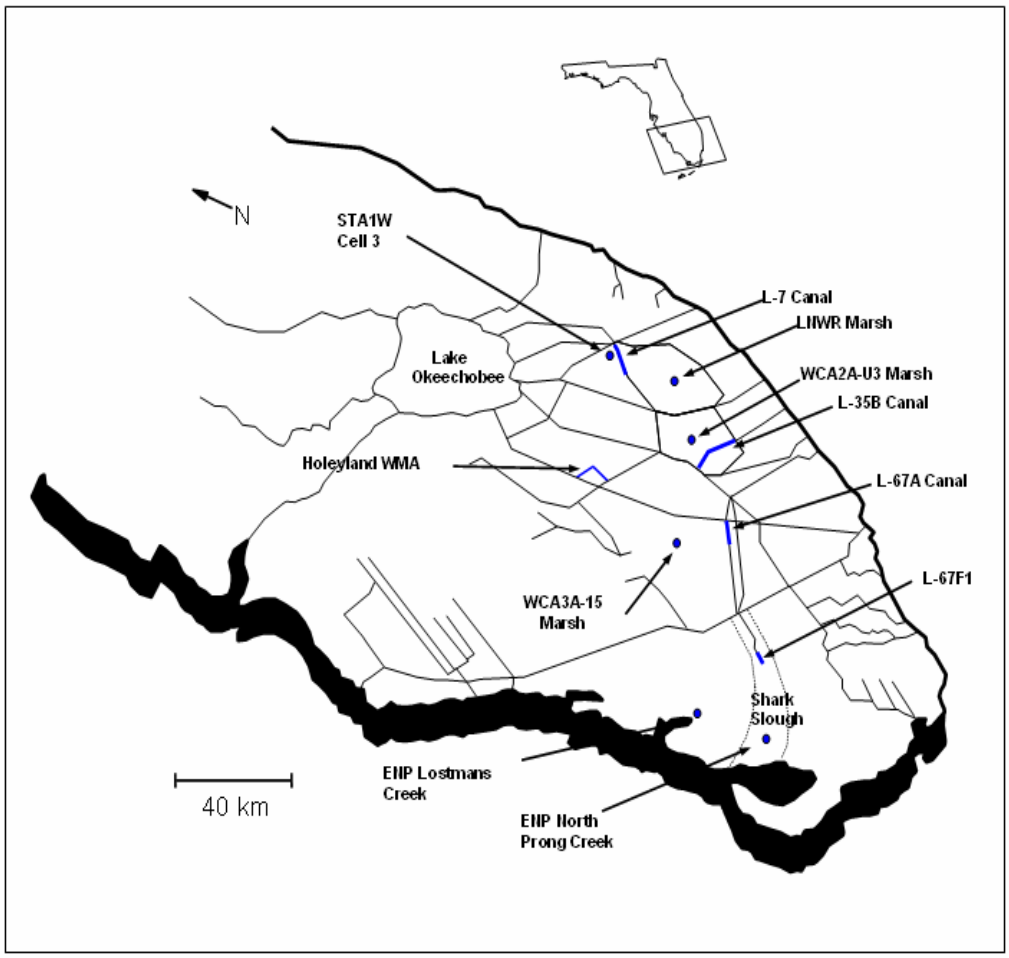



**Figure 3B-2.** Annual summaries of mercury concentrations in 2,529 largemouth bass collected between 1988 and 2006 from canals and marsh sites in Water Conservation Areas 1, 2, and 3 (WCA-1, WCA-2, and WCA-3) (top panel) and for 391 largemouth bass (LMB) collected between 1988 and 2007 from the Shark River Slough (at North Prong Creek and site L67F1) in the ENP (bottom panel). Mercury is reported as µg/g = mg/kg =ppm.




**Notes:**
- STA-1W contains Cell 3
- WCA-2 contains the L-35B canal and WCA-2A-U3
- Holey Land WMA is sampled in its perimeter canal
- Lostmans Creek and North Prong Creek are part of the ENP
- WCA-1 contains the L-7 canal and Refuge marsh site
- WCA-3 contains the L-67A canal and WCA-3A-15

**Figure 3B-3**. Location of 10 long-term monitoring locations in the Everglades Protection Area.

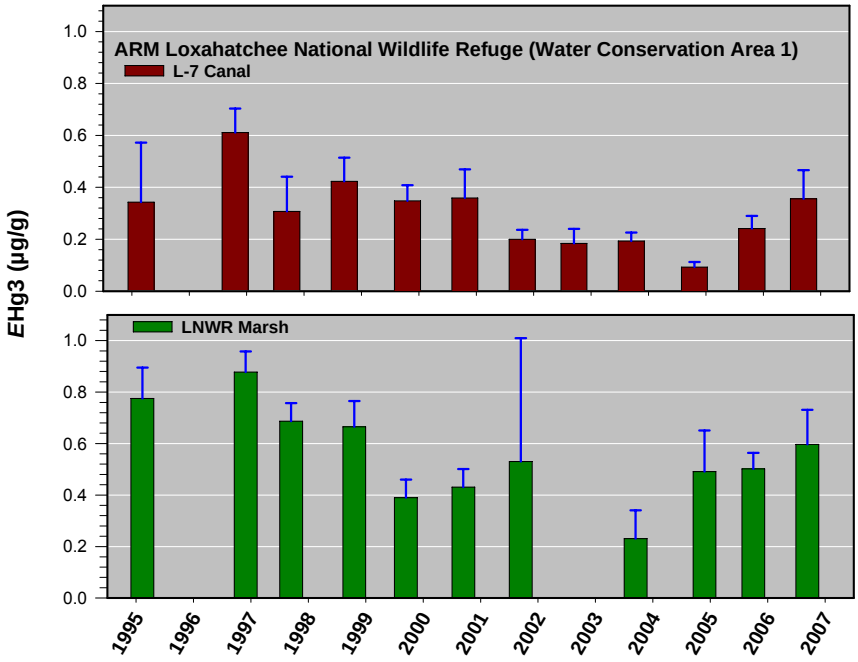



**Figure 3B-4.** Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval (95% C.I.) in LMB at long-term monitoring sites located within the Arthur R. Marshall Loxahatchee National Wildlife Refuge.

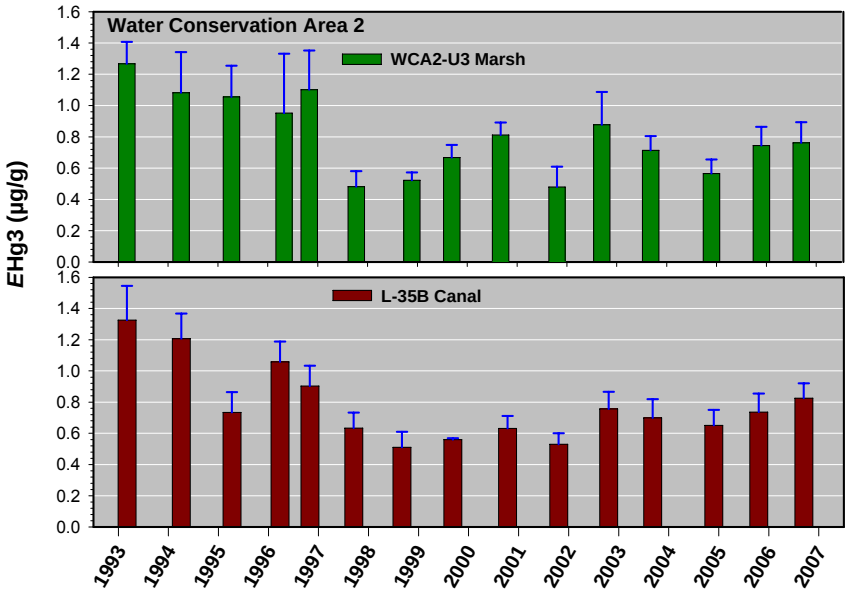



**Figure 3B-5.** Age-standardized mercury concentration (EHg3) and the 95% C.I. in LMB at long-term monitoring sites located within WCA-2.

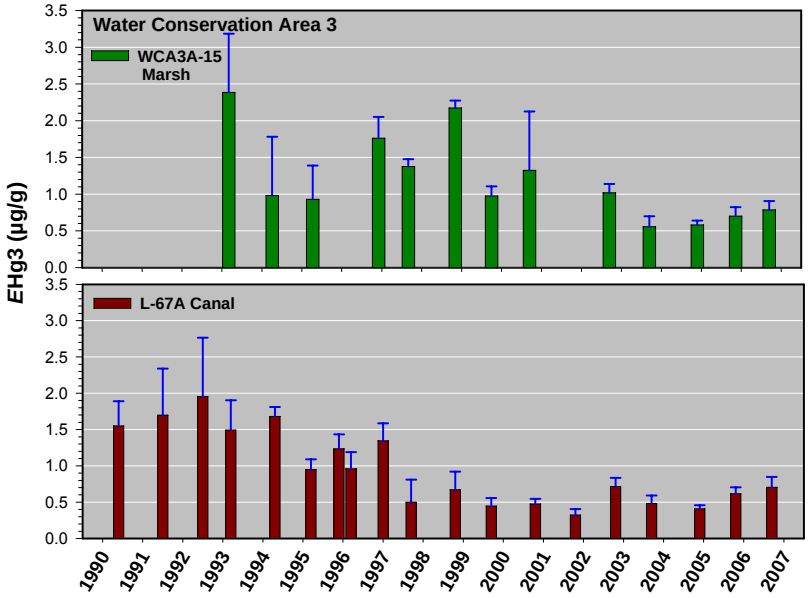



**Figure 3B-6.** Age-standardized mercury concentration (EHg3) and the 95% C.I. in LMB at long-term monitoring sites located within WCA-3.

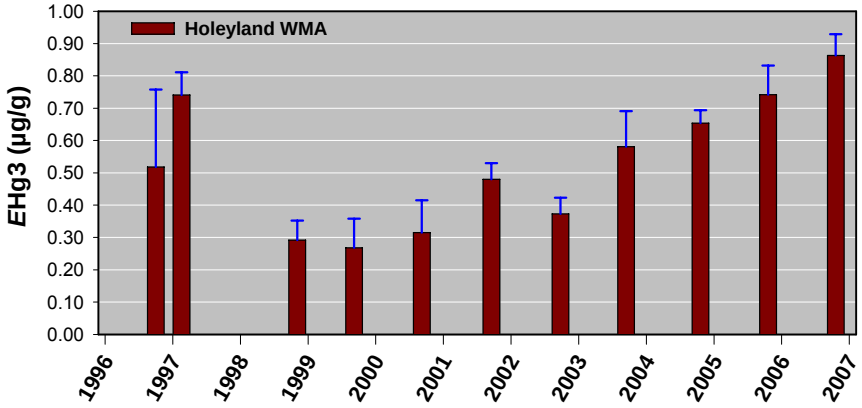



**Figure 3B-7.** Age-standardized mercury concentration ($EHg_3$) and the 95% C.I. in LMB from the perimeter canal in Holey Land Wildlife Management Area (WMA).

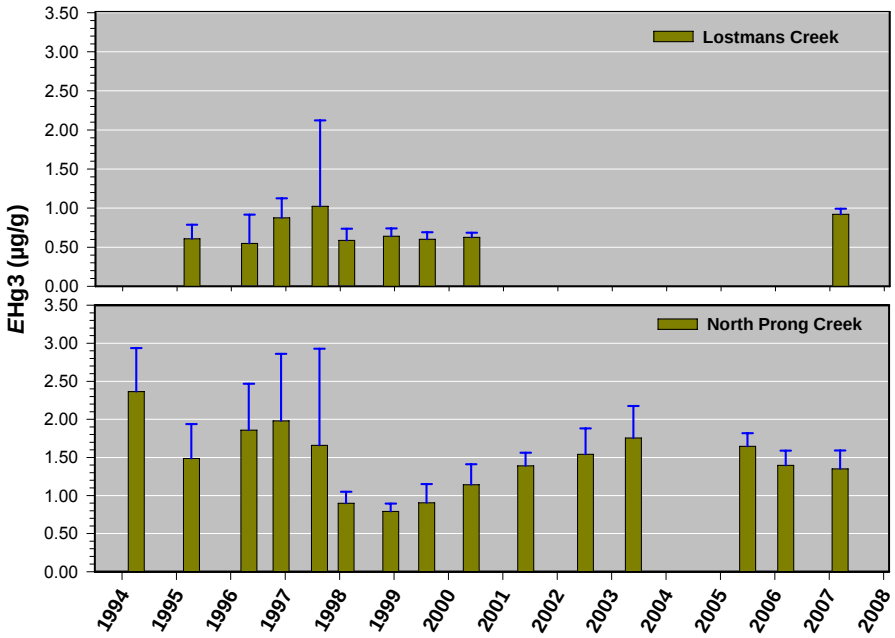



**Figure 3B-8.** Age-standardized mercury concentration (EHg3) and the 95% C.I. in largemouth bass from Lostmans Creek and North Prong Creek in Everglades National Park.

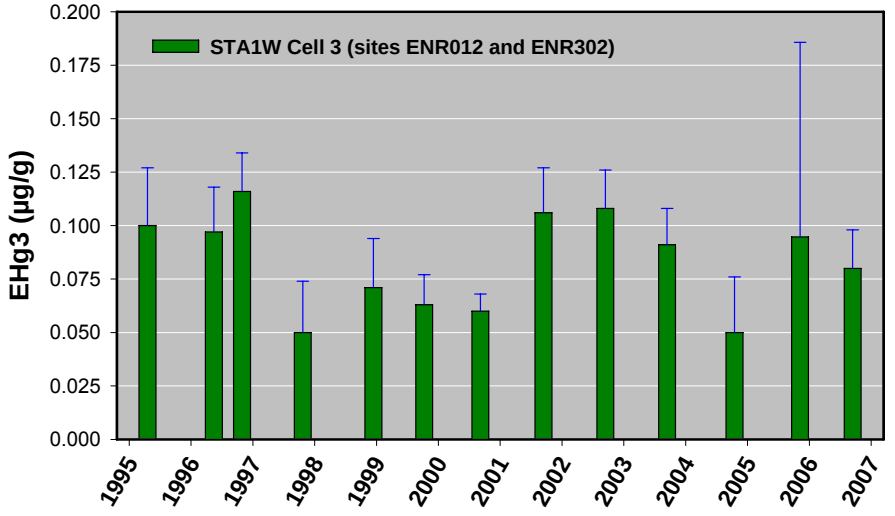



**Figure 3B-9.** Age-standardized mercury concentration (EHg3) and the 95% C.I. in largemouth bass at long-term monitoring sites located within Stormwater Treatment Area 1 West (STA-1W) Cell 3.

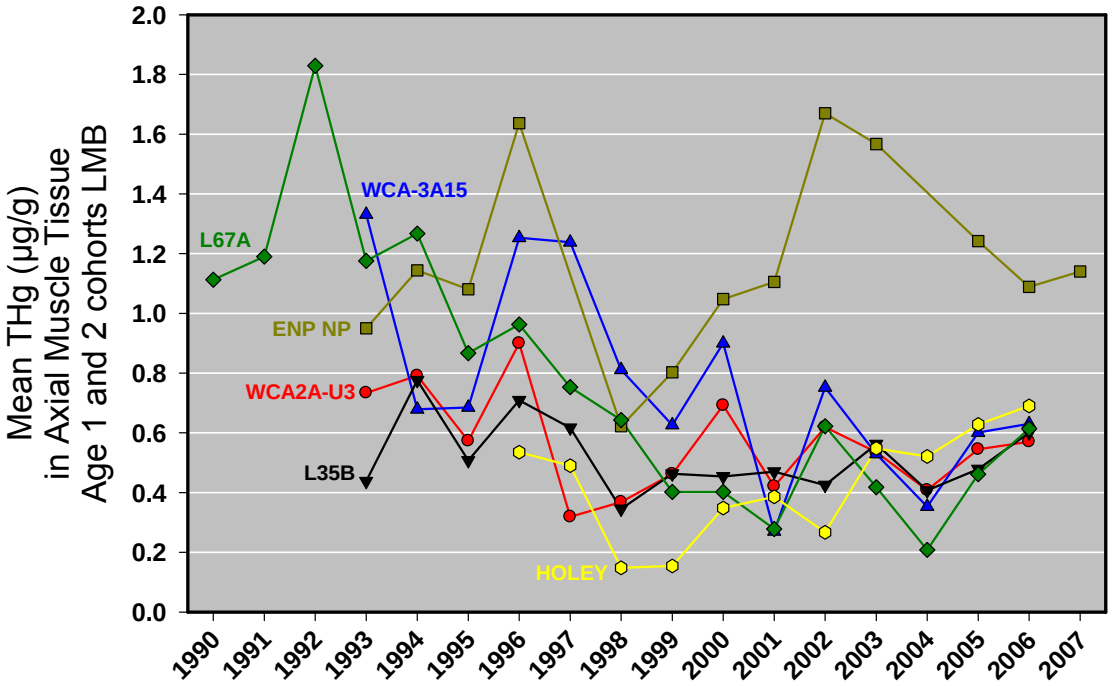



**Figure 3B-10.** Time series of geometric mean mercury concentrations (µg/g) for LMB (age 1-2 cohort) for six Everglades sites. Sites L-35B and L-67A are canal sites in WCA-2 and WCA-3, respectively; sites U3 and 3A-15 represent interior marsh sites located in WCA-2A and 3A, respectively. The ENP NP site is in the ENP (North Prong Creek) and site HOLEY is within the WMA.

## MERCURY IN FISH-EATING BIRDS

Feathers of great egret (*Ardea alba*) nestlings were collected between 1994 and 2007 from colonies in the freshwater Everglades. From 1994 to 2000, all showed strongly declining mercury concentrations, a mean of 73 percent decline averaged across colonies, similar to the decline in mercury in largemouth bass in the WCAs (**Figures 3B-2,** top panel; **3B-11;** and **3B-12**; see also Appendix 3B-1 in this volume).

Comparisons of great egret feather mercury concentrations between 2007 and previous years are somewhat hampered because 2007 was a very dry year and the birds were not able in many cases to nest in the same locations as in previous years—or in some instances by the time the chicks were large enough to sample feathers from, water depth did not allow for sampling via airboat.

However, three colonies allow direct comparisons: Tamiami West, L-67, and Cypress City **(Figure 3B-11)**. Mercury in 2007 was 1.8 times that in 2006 for the first two colonies and for Cypress City mercury was 2.2 times that in 2005. By comparison with the mean of the past five years, L-67 was 1.4 times the average, and Tamiami West 2.4 times the average.

Although the number of direct comparisons is somewhat small, the data are evidence of an uptick in mercury contamination in the birds. Exactly what may be causing this is not clear — early 2007 was relatively dry and mercury and sulfur biogeochemistry could be explanatory, however a mercury increase was not seen in other recent dry years such as 2001 Another possible explanation for the increase in mercury in feathers is the increase in atmospheric mercury wet deposition from early 2003 through mid-2004 (Axelrad et al., 2006; 2007). Annual averages of mercury in colonies suggest that Everglades egrets have gone from around 6 milligrams per kilogram (mg/kg) in feathers in 2006 to approximately 10 mg/kg for 2007.

In summary:

- Current mercury levels in largemouth bass at sites in the WCAs are about 30–70 percent lower than levels of the late 1980s and early 1990s, but concentrations have not varied greatly from year to year from 1998 to the present, and mercury concentrations remain generally higher than the USEPA recommended MeHg human health fish tissue criterion of 0.3 μg/g. Sixty-seven percent of samples exceed the criterion.
- Very high concentrations of mercury ( > 1 mg/kg) in LMB are presently evident in portions of the ENP (mean of 0.86 μg/g) and have increased in recent years in the Holey Land WMA.
- The WCAs and the ENP remain under fish consumption advisories for protection of human health, and mercury levels in fish in the ENP threaten fish-eating birds and mammalian wildlife.
- Annual averages of mercury in great egret feathers suggest that Everglades egrets have gone from around 6 mg/kg in 2006 to approximately 10 mg/kg for 2007.

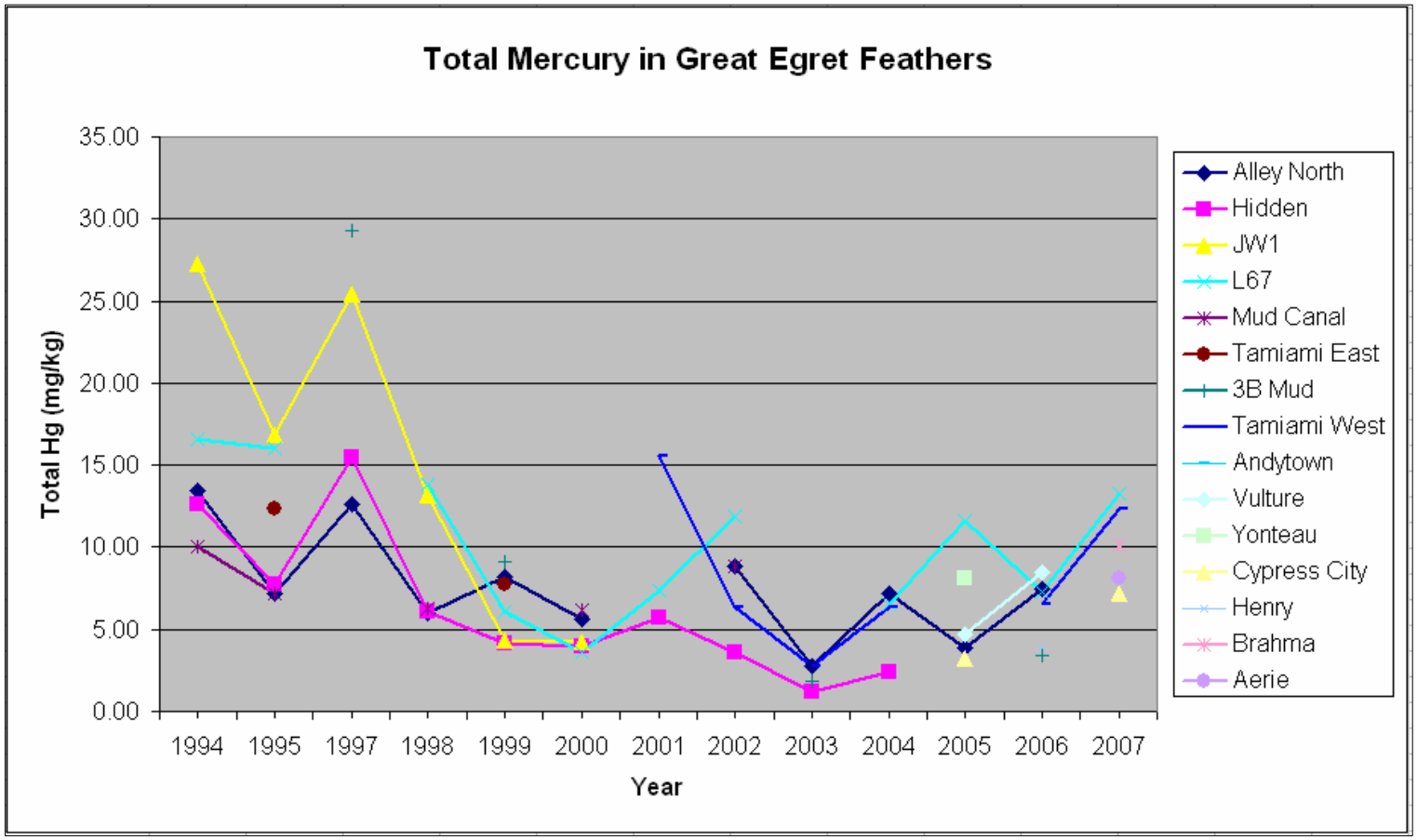



**Figure 3B-11.** Mercury concentrations (mg/kg) in feathers in great egret nestlings at various colony locations in the Everglades from 1994 to 2007. Discontinuities in the period of record reflect years when a colony site was abandoned or otherwise not used (Frederick et al., 2002).

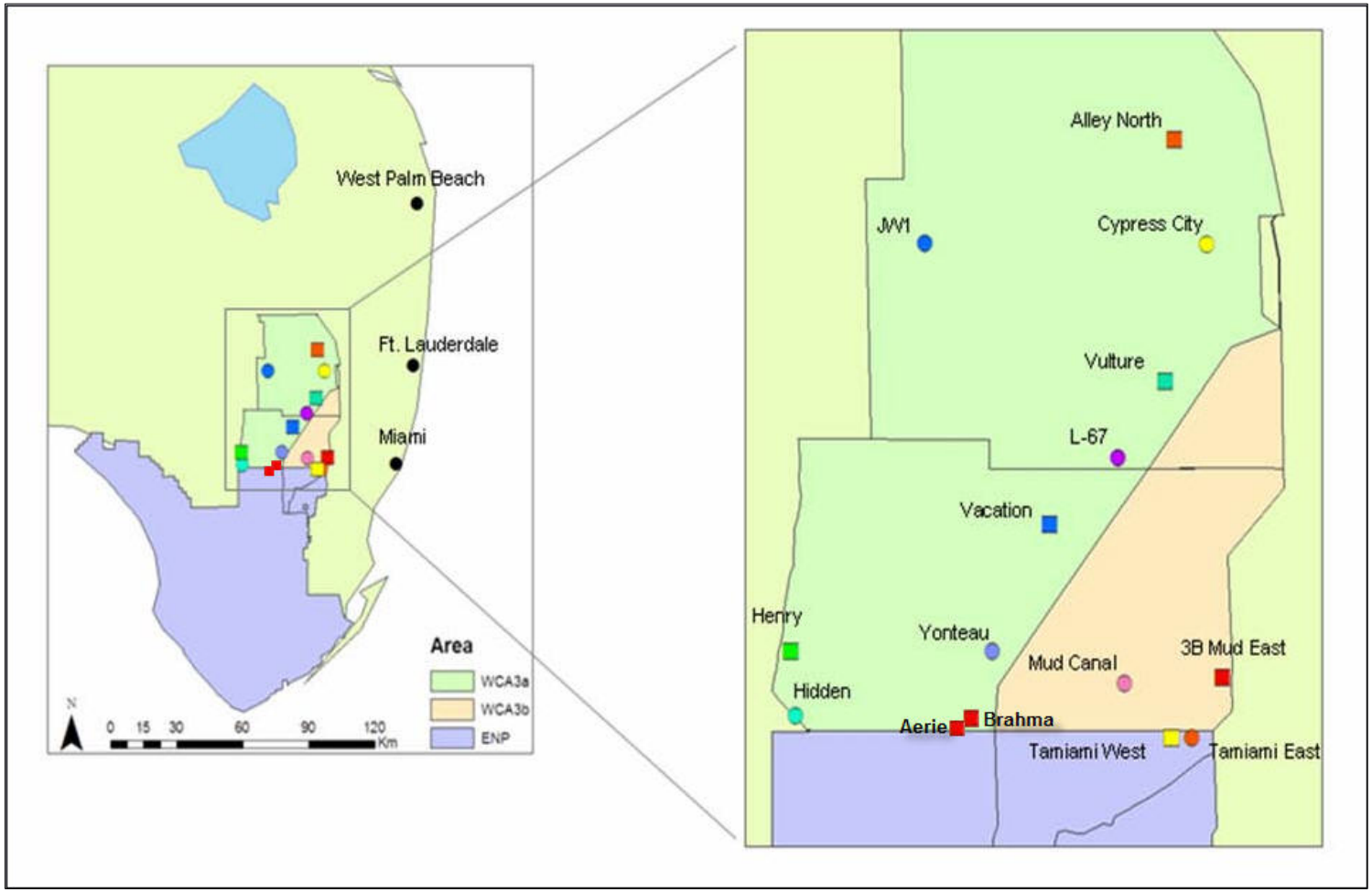



**Figure 3B-12.** Great egret colony locations where feathers from nestlings were sampled from 1994 to 2007.

# ATMOSPHERIC DEPOSITION OF MERCURY TO THE EVERGLADES

Atmospheric deposition of inorganic mercury accounts for greater than 95 percent of the external load of mercury to the Everglades (USEPA, 1996) and MeHg production is highly influenced by the rate of supply of atmospherically derived mercury (Orihel et al., 2006; Paterson et al., 2006; Munthe et al., 2007; see also Appendix 3B-1 of this volume).

In 2005, Atkeson et al. concluded that volume-weighted mean (VWM) mercury concentrations in wet deposition falling within the Everglades had declined by approximately 3 nanograms per liter (ng/L), or approximately 25 percent, between late 1993 and the end of 2002 due to factors other than seasonal dynamics and changes in precipitation. The magnitude of this decline was more than could be ascribed to larger-scale sources alone (i.e., 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).

Axelrad et al. (2006 and 2007) subsequently examined whether there had been a continuing decline in atmospheric deposition of mercury in the Everglades beyond 2002 by extending the period of record through 2004. Their analyses showed that an increase in mercury wet deposition and annual VWM concentrations from early 2003 through mid-2004 essentially negated the overall declines that had been observed previously from late 1993 through 2002.

Weekly wet deposition data are now available for Mercury Deposition Network (MDN) site FL11 at the Beard Research Center at the ENP from 1996 through 2006 (NADP, 2007). When coupled with monthly-integrated samples collected at that site from November 1993 through December 1996 as part of the Florida Atmospheric Mercury Study (FAMS) (Pollman et al., 1995; Guentzel et al., 1998; Guentzel et al., 2001), there is an essentially continuous period of record of wet deposition from November 1993 through 2006. This is particularly notable because, with the exception of sites located in Ely, MN and Underhill, VT, FL11 has the longest period of record monitoring mercury in wet deposition in the United States.

As part of the MDN, wet deposition monitoring for mercury also is available for three other sites: FL04 (Andytown); FL34 (Everglades Nutrient Removal Project site); and FL97 (Everglades-western Broward County) (**Figure 3B-13**). Only two of these additional sites are currently active (FL34 and FL97), and one (FL97) has been active since only November 2006 (see Appendix 3B-1 of this volume). The remaining site, FL04, was discontinued in mid-October 2006. As the primary objective of this analysis is to examine for temporal trends in the mercury wet deposition signal to the Everglades, only data from FL11, FL04, and FL34 were used.

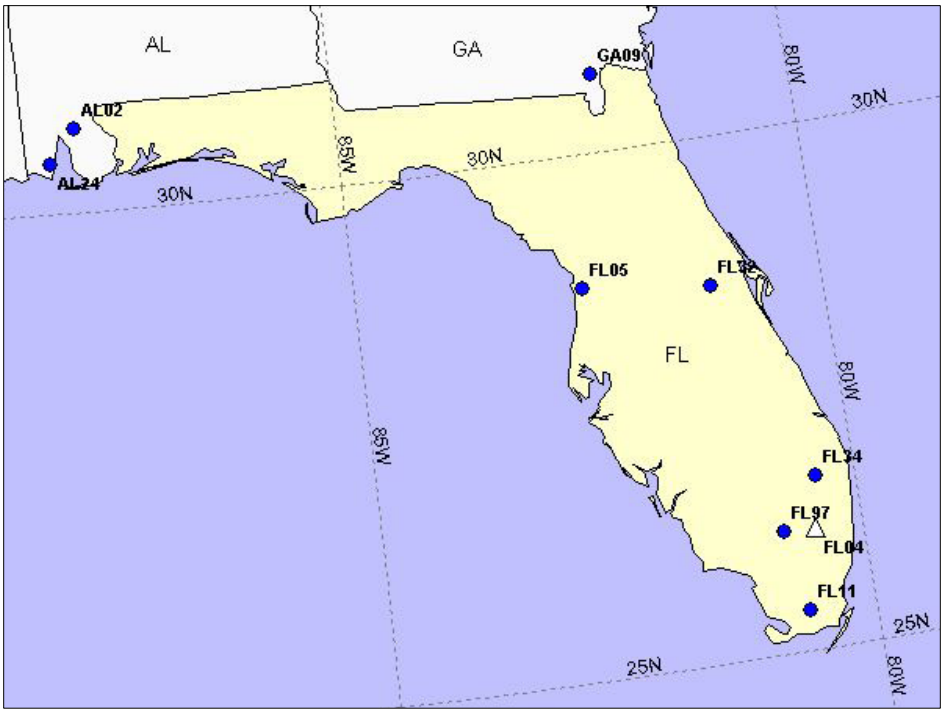



**Figure 3B-13.** The National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) South Florida total mercury wet deposition sampling sites: FL04 Andytown, FL34 Everglades Nutrient Removal Project, and FL11 in the ENP at the Beard Research Center (NADP, 2007).

Weekly data from each of these three sites were downloaded from the MDN web site for the entire period of record available (i.e., through the end of 2006 for FL11 and FL34 and through mid-October 2006 for FL04). Only data that were identified by MDN as valid were used, and the analysis was restricted to observations that had contemporaneous, valid measurements of both rainfall depth and mercury concentration to avoid artifacts in computing VWM concentrations that would arise in using a dataset that comprised non-paired observations of rainfall depth and concentration. The MDN data were then composited on a monthly basis and the data for site FL11 combined with the FAMS monthly data. Monthly samples overlapping across the two studies in 1996 for precipitation and mercury deposition were volume-averaged.

Temporal trends in mercury deposition are presented for all three South Florida sites (**Figure 3B-14**). As noted by Axelrad et al. (2006), annual fluxes of Hg in wet deposition are most closely related to precipitation, and secondarily to changes in the mercury concentration in the rain because of the greater degree of relative variance in precipitation. Thus the wettest years generally also correspond to the years with the highest fluxes of Hg in wet deposition (**Figure 3B-15**), with the notable exceptions of mid-2002 through mid-2003 and mid-2005 through mid-2006, which were comparatively wet years but showed only a modest annual Hg deposition flux. Likewise, as also noted by Axelrad et al. (2006), the mercury deposition flux in mid- to late 2003 was quite high relative to the precipitation flux. These variations appear likely due to changes in regional source contributions (Axelrad et al., 2006), although a more definitive analysis would require more sophisticated source-receptor modeling that lies beyond the scope of this effort.

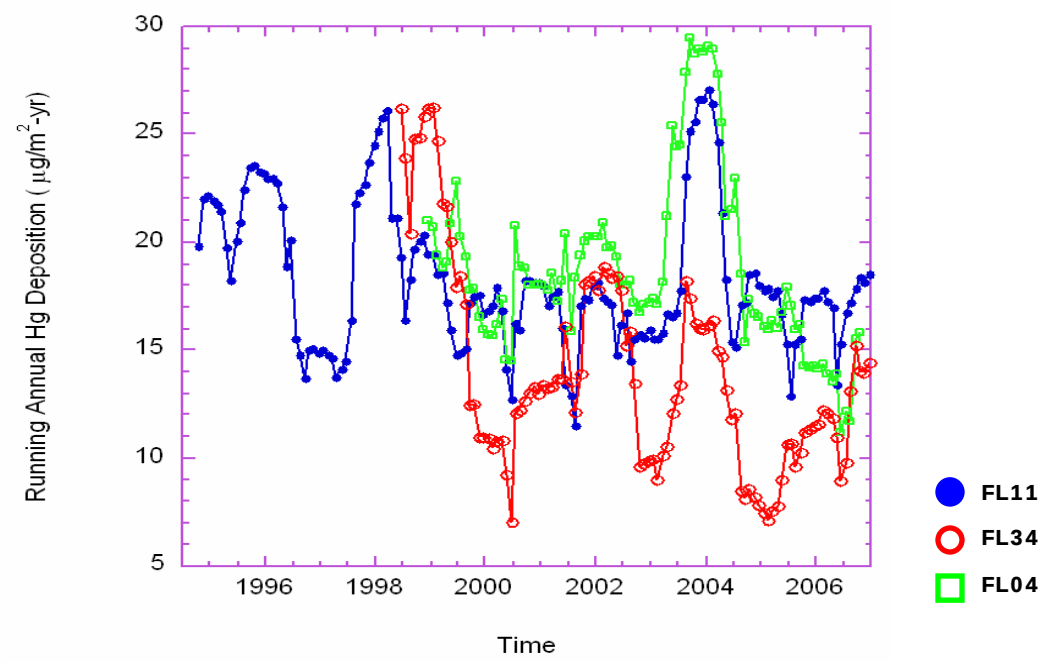



**Figure 3B-14**. Running annual fluxes of mercury in wet deposition in South Florida, 1994 through 2006. Fluxes are calculated monthly based on the current month and previous 11 months of data. Period of record (POR) extends from October 1994 through December 2006.

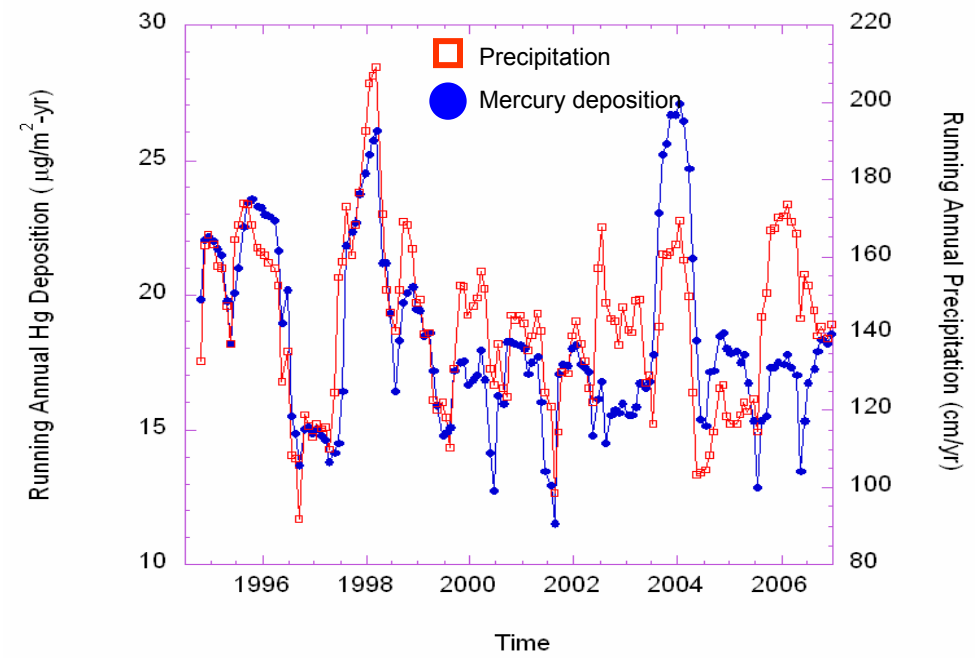



**Figure 3B-15.** Running annual fluxes of precipitation and mercury in wet deposition, MDN site FL11 (ENP), October 1994 through December 2006. Fluxes are calculated monthly based on the current and previous 11 months of data.

Similar to analyses conducted in previous consolidated reports, analysis of variance (ANOVA) was used to assess whether any changes in the mercury wet deposition signal had occurred at FL11 as a function of time that were unrelated to changes in precipitation flux. In addition, because the wet deposition of mercury in South Florida so clearly has a large seasonal component (Guentzel et al., 2001; see also **Figure 3B-16**), seasonal dynamics were factored out using the month the samples were collected to account for the seasonal effect. The ANOVA was then conducted accounting for both of these two effects, and the resultant residuals were then regressed against time to determine significance of trend (**Figures 3B-17** and **3B-18**). Although the slope is downward (m = -0.075 ng/L-yr), the trend is not significant (p = 0.5764).

The results of the ANOVA were tested for the influence of outliers on the direction and significance of the trend. The residuals from the ANOVA were correlated with time and outliers identified based on the calculated Mahalanobis distance (SAS Institute, Inc., 1998). Five months were eliminated as outliers: November 1996, April 1998, July 2003, October 2003, and December 2004. The ANOVA was then rerun after the outliers were removed from the data set. The resultant analysis shows a reinforced downward trend (slope, m = -0.155 ng/L-yr; **Figure 3B-18**) that is now significant (p = 0.0526). This strengthening of the downward trend in the mercury signal compared to the analysis conducted by Axelrad et al. (2006) of data through 2005 is due to a much weaker Hg signal in wet deposition in 2006. Similar reductions in the mercury signal in mid-2005 through mid-2006 were observed at sites FL04 and FL34 (not shown).

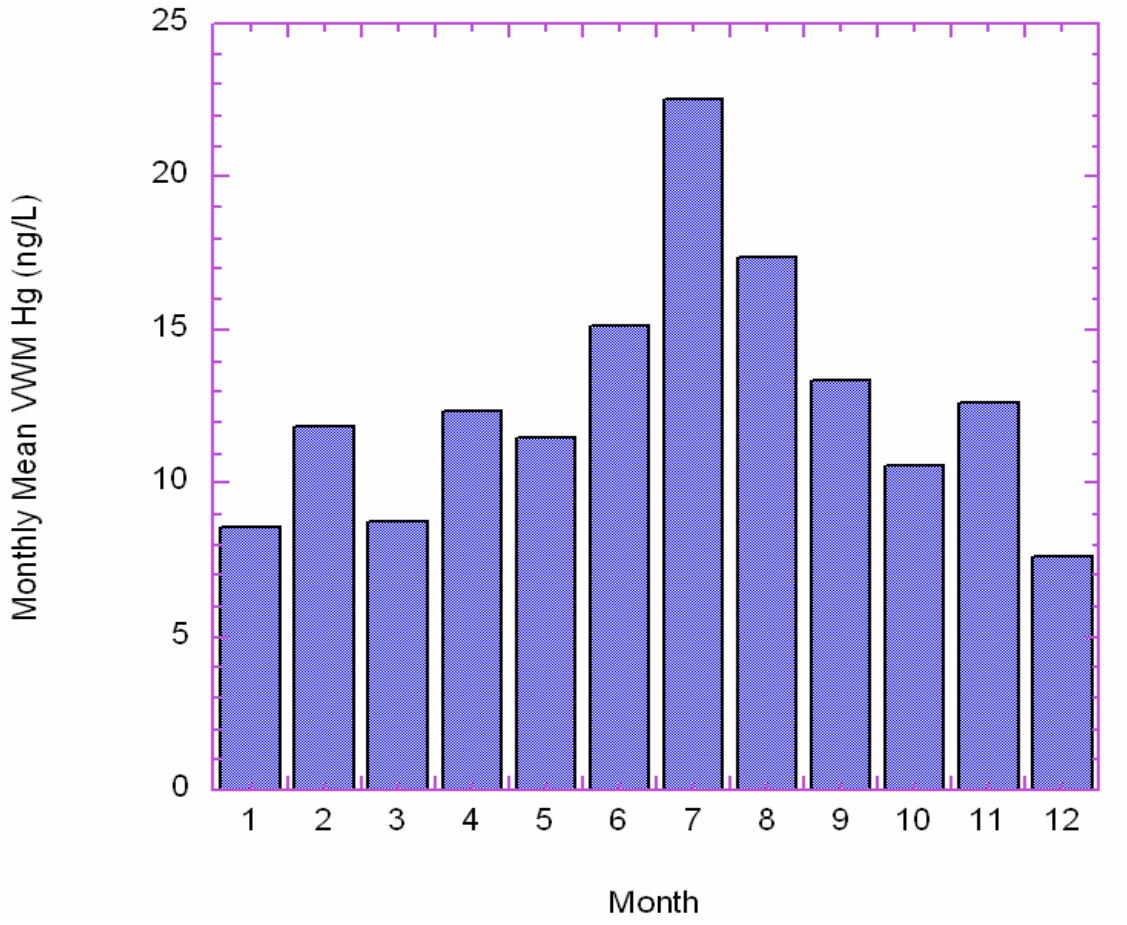



**Figure 3B-16.** Monthly VWM mercury concentrations (ng/L) at FL11 (ENP) averaged by month (1-12) across the entire POR: November 1993 through December 2006.

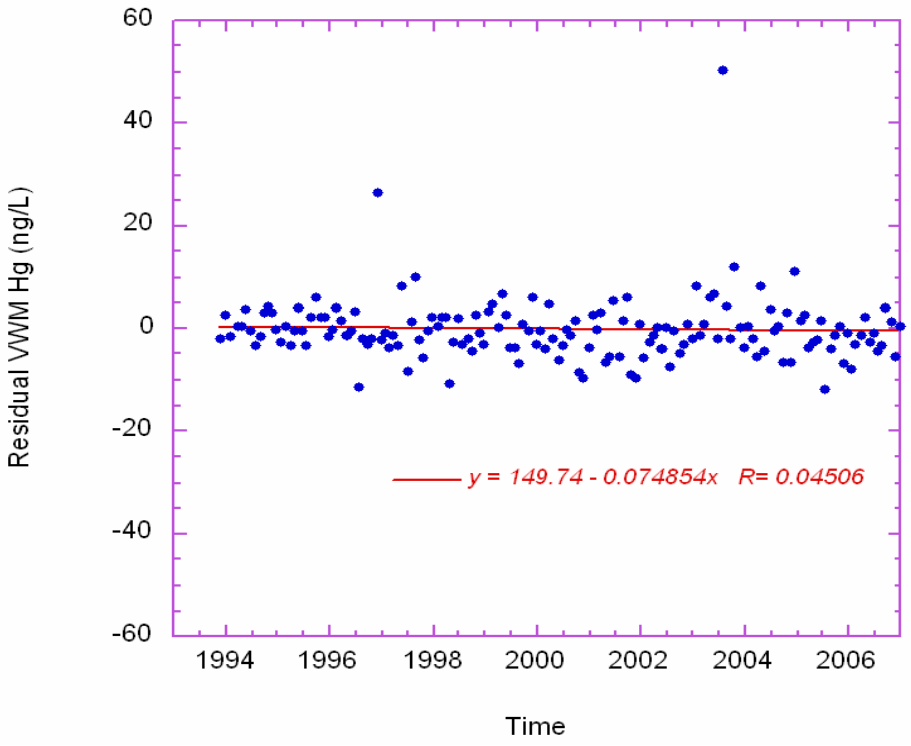



**Figure 3B-17.** Time-series plot of the analysis of variance model residuals (observed minus predicted) used to predict monthly volume-weighted mean (VWM) concentrations of mercury in wet deposition as a function of precipitation and seasonal dynamics at site FL11 (ENP). Data include all monthly observations.

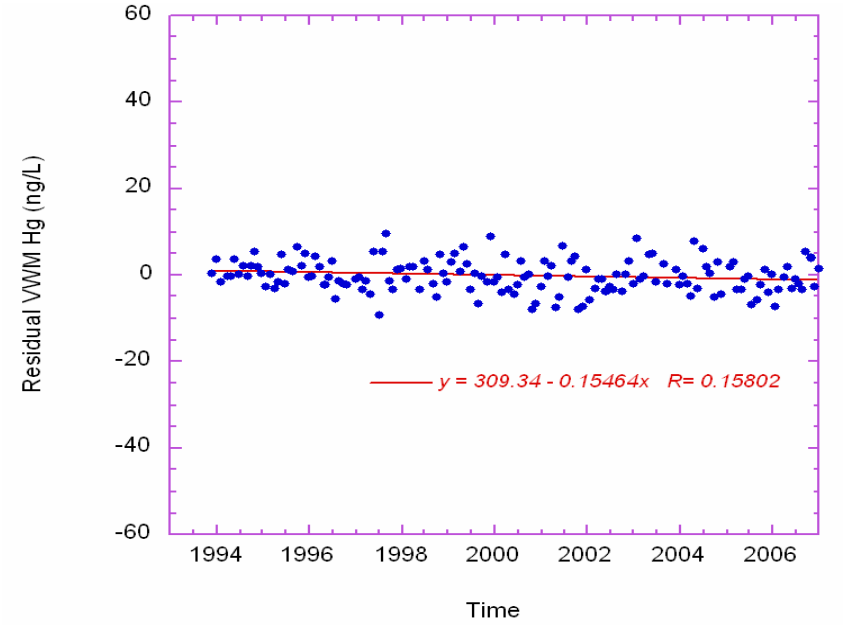



**Figure 3B-18.** Same as **Figure 3B-17**, except that outliers based on Mahalanobis distance were removed prior to conducting trend analysis.

Temporal trends in annual VWM concentrations for all three sites were generally similar during 1998 through 2006 (**Figure 3B-19**) and suggest that the factors contributing the strongest to the overall mercury signal in wet deposition were larger in scale than local sources. Pollman et al. (2007) reached a similar conclusion based on an analysis of trends in wet deposition at FL11 conducted in concert with an analysis of declining mercury accumulation rates in sediment cores collected from Lake Annie in south central Florida north of Lake Okeechobee and declines in total gaseous mercury concentrations observed by Slemr et al. (2003). Pollman et al. (2007) calculated that contributions from local sources had declined from 51 percent in 1991 to 21 percent in 1995–1996 and 9 percent in 2000.

In conclusion, as noted in the analyses conducted in the previous two years by Axelrad et al. (2006, 2007), the significant declines in the mercury signal in wet deposition falling in the EPA that were first observed by Atkeson et al. (2005) from 1993 through 2002 are no longer statistically supported when the period of record is extended further toward the present. However, wet deposition of mercury between mid-2005 and mid-2006 was somewhat lower than expected given the amount of precipitation and, after factoring out the effects of both seasonal (monthly) dynamics and precipitation, this was reflected in a general overall but weak trend of a declining mercury signal over the period of record.

The trend in the wet deposition signal is sensitive to a handful of deposition of events. Elimination of five months from the period of record objectively identified as outliers (out of a total n of 156 months) resulted in a statistically significant decline that would have equated to a reduction of 2.0 ng/L (about 15 percent of the period of record mean) in the wet deposition signal between late 1993 and the end of 2006 if these outlying events did not occur.

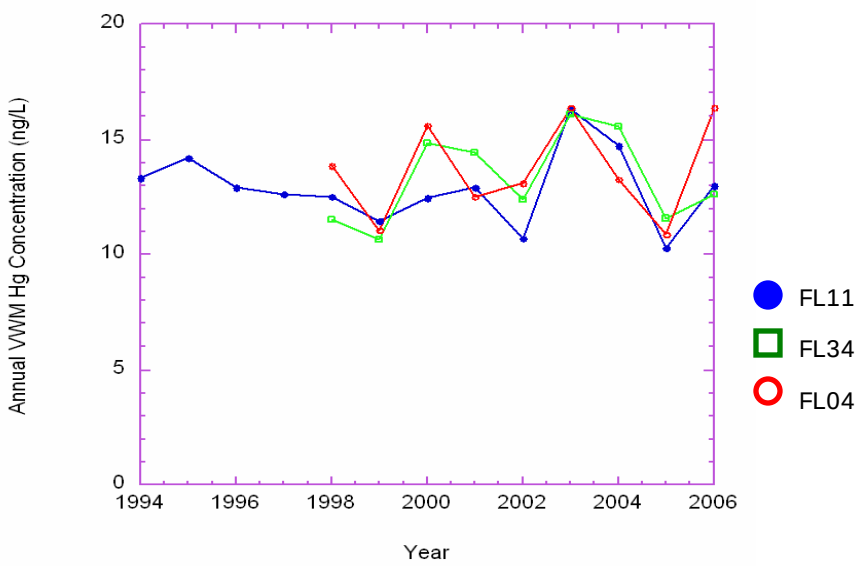



**Figure 3B-19.** Annual VWM concentrations of Hg (ng/L) in wet deposition in South Florida.

The previous work of Axelrad et al. (2007) suggests that these singular events tend to be regional in nature [at least for the high deposition events in 2003 that were largely responsible for eliminating the downward trend initially observed by Atkeson et al. (2005)], and this indication is further supported by the similar temporal patterns in monthly volume weighted mercury concentrations observed across the three south Florida MDN sites with the longest period of record. Clearly, in terms of trying to manage and mitigate mercury loadings to the Everglades via atmospheric deposition, it is thus critically important to understand the nature of these singular events — not only in terms of their source and magnitude of emissions, but also in terms of their quantitative relationship with the Everglades as a receptor.

In one such event, the increase in mercury wet deposition and annual VWM concentrations from early 2003 through mid-2004 in South Florida, an explanation for some of the increases in mercury in Everglades fish and birds at some sites may be found. The mercury wet deposition increase over this period corresponds well with the increases in mercury in largemouth bass that occurred from 2003–2006 at the marsh site in WCA-1; WCA-1 being a rainfall driven system with low sulfate levels in its interior (Axelrad et al., 2007). This suggests that increases in mercury methylation rate in WCA-1 were unlikely to have caused the increases in mercury in fish, leaving increases in mercury wet deposition as the better hypothesis for this site.

In summary:

- Atmospheric deposition of inorganic mercury accounts for more than 95 percent of the external load of mercury to the Everglades and due to a combination of elevated rainwater mercury concentrations and the high annual rainfall in South Florida, wet total-mercury deposition to the Everglades remains substantially greater than that for most other regions monitored in the U.S. (**Figure 3B-20)**.
- VWM mercury concentrations in wet deposition falling within the Everglades had declined by approximately 3 ng/L, or about 25 percent, between late 1993 and the end of 2002 due to factors other than seasonal dynamics and changes in precipitation.
- An increase in mercury wet deposition and annual VWM concentrations from early 2003 through mid-2004 essentially negated the overall declines that had been observed previously from late 1993 through 2002.
- The most recent values, between mid-2005 and mid-2006, for wet deposition of mercury at site FL11 (ENP) 2006 were lower than expected given the amount of precipitation and, after factoring out the effects of both seasonal dynamics and precipitation; for the period late 1993 through 2006, a reduction of 2.0 ng/L (about 15 percent of the POR mean) in the wet deposition signal (VWM) for FL11 (in the ENP) was detected.
- The primary point-source air emissions 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.
- Mercury atmospheric deposition contributions from South Florida local sources are estimated to have declined from 51 percent of total mercury atmospheric sources in 1991, to 21 percent in 1995–1996, to 9 percent in 2000.
- The increase in mercury wet deposition from early 2003 through mid-2004 in South Florida may be an explanation for the subsequent increases in mercury in Everglades fish and birds at some sites.

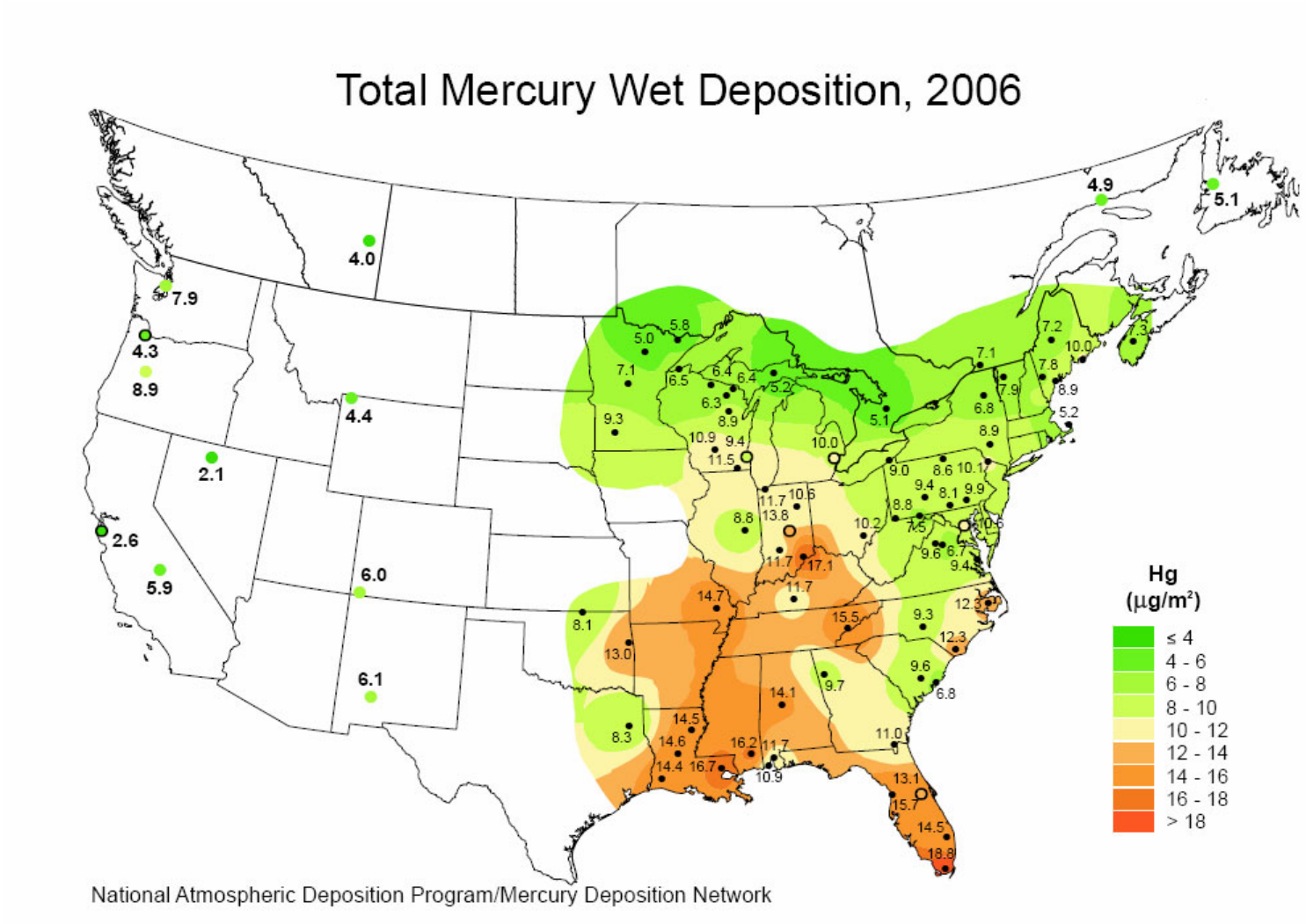



**Figure 3B-20.** Wet deposition of total mercury (µg/m$^2$) in 2006. Data from National Atmospheric Deposition Program's Mercury Deposition Network (NADP, 2007).

# SULFUR LEVELS, SOURCES AND EFFECTS ON THE EVERGLADES

## SULFUR LEVELS AND SOURCES

Sulfate-reducing bacteria (SRB) are the major producers of methylmercury in aquatic ecosystems and methylation of inorganic mercury by SRB is dependant on sulfate availability (Ekstrom et al., 2003; Gilmour et al., 2004b). The effect of sulfur on mercury methylation in the Everglades is determined by the balance between sulfate ($SO_4^{2-}$) and sulfide ($S^{2-}$); mercury methylation rate has been found to be high at 2–20 mg/L sulfate in Everglades surface waters where sediment porewater sulfide concentrations are moderate (5–150 µg/L) (Gilmour et al., 2007a); sulfide begins to repress mercury methylation at concentrations above about 300 µg/L in porewater (Benoit et al., 2003; Gilmour et al., 1998).

Sulfate contamination is an important factor in causing increased mercury methylation in the Everglades (Benoit et al., 1999; 2001, 2003; Bates et al., 2002; Gilmour et al., 2007a). At present, it is probable that broad areas of the Everglades exhibit sulfate concentrations at which increased sulfate levels would enhance, and decreased sulfate concentrations would reduce net MeHg accumulation in soils and hence MeHg accumulation in fish, birds and mammals (Gilmour et al., 2007a).

To date, the USEPA has not issued any guidance regarding water quality criteria for sulfate, and the state of Florida has no such water quality criteria; the Comprehensive Everglades Restoration Plan (CERP) goal for sulfate in surface water is 1 mg/L — background sulfate in the Everglades may be ≤ 0.1 mg/L (Scheidt and Kalla, 2007; Weaver et al., 2007). At 1 mg/L sulfate in Everglades surface water however, data indicate that microbial sulfate reduction and MeHg production rates would be low due to sulfate limitation, and sediment porewater sulfide levels would only be in the tens of µg/l, minimizing both sulfide toxicity to aquatic plants and animals and internal eutrophication — phosphate and ammonium release from sediments (Gilmour et al., 2007a, b).

Managing sulfate inputs to the Everglades is a potential option for reducing MeHg bioaccumulation, and to accomplish this, determination of the major sources of sulfate to the Everglades is critical (see Appendix 3B-2 of this volume). In evaluating sulfate sources to the Everglades, the highest surface water sulfate concentrations across South Florida (excluding marine-influenced sites) have been observed in Everglades Agricultural Area (EAA) canals; sulfate concentrations averaged over 70 mg/L and levels approaching 200 mg/L were intermittently observed (Bates et al., 2002; Orem, 2004; Gilmour et al., 2007b). Previous work (Bates et al., 2001 and 2002; Orem, 2004; Gilmour et al., 2007b) has shown that water with very elevated sulfate concentrations (about 100 times background) is entering the northern Everglades from EAA canal discharge; for WCA-2, sulfate averaged about 40 to 70 mg/L compared to < 1 mg/L in parts of the ecosystem further south and away from canal discharges (Bates et al., 2002; Axelrad et al., 2007; Gilmour et al., 2007b; Weaver et al., 2007; also, see Chapter 3A of this volume).

Based on these sulfate concentration data, it may be concluded that much of the sulfate entering the Everglades originates from EAA canals. While elevated levels of sulfate are also found in Lake Okeechobee, suggesting the lake may also be a major source of sulfate to the Everglades, sulfate levels in the lake are usually significantly lower than those in the canals within the EAA — the lake has an annual average sulfate concentrations less than half that in EAA canals (approximately 30 mg/L versus 70 mg/L) (Bates et al., 2002). Sulfate from EAA canals penetrates well into the Shark River Slough of the ENP (Scheidt and Kalla, 2007) (**Figure 3B-21**), and in the southern ENP, there appears to be occasional seawater — and sulfate — intrusion, due to natural tidal influences (Ted Lange, Florida Fish and Wildlife Conservation Commission, personal communication).

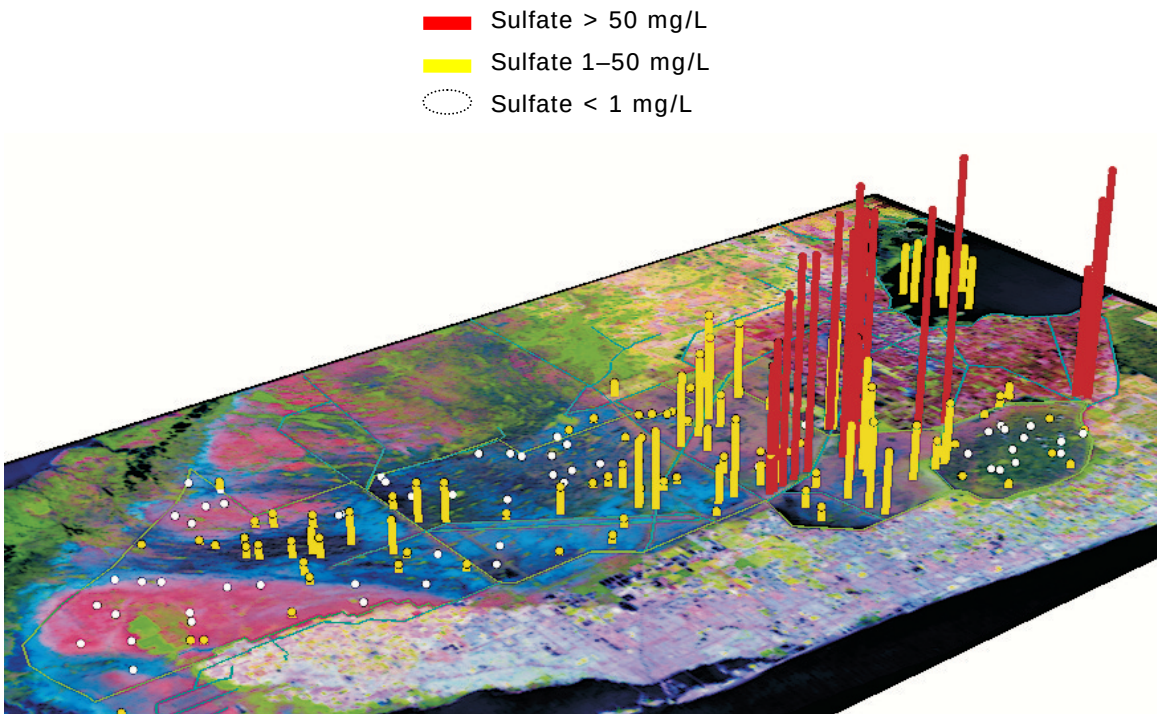



**Figure 3B-21.** Surface water sulfate concentrations across the EPA for the November 2005 (wet season) (Scheidt and Kalla, 2007).

The question then becomes, what is the dominant source of the sulfate to EAA canals? This question has also been examined in previous studies (Bates et al., 2001, 2002; Orem, 2004; Axelrad et al., 2007; Gilmour et al., 2007b). Examining potential sources, rainfall contains too little sulfate to represent a significant source to EAA canals; though rainfall is likely a major source of sulfate to pristine areas of the Everglades far removed from canal sources (Bates et al., 2002). Dry deposition of sulfate is also unlikely to be a major source. Shallow groundwater (< 9 m depth) often has sulfate concentrations too low to account for the sulfate concentrations observed in the marsh surface water, though at some sites surface water and shallow groundwater exchange may result in near equivalence of sulfate concentrations (Bates et al., 2001, 2002).

However, it is well known that significant amounts of sulfur are used in both soil amendments and fertilizers within the EAA — up to 500 lbs/ac of elemental sulfur is recommended for soil pH reduction but actual use is probably far less (Rice et al., 2006; Schueneman, 2000). While sulfur is applied to the fields in different forms, microbes in the oxidizing soils of the EAA will convert this sulfur to sulfate, and during rain events or irrigation, this sulfate would be readily washed into farm canals and thence into the larger canals within the EAA (Bates et al., 2002). Thus, it seems logical to hypothesize that agricultural sulfur sources are a principal source of sulfate to EAA canals.

Supporting this hypothesis, sulfur isotope studies were conducted by Bates et al. (2002), which concluded that the sulfate in EAA canals has an isotopic composition consistent with that of agricultural sulfur. The isotopic studies were not able to determine whether the agricultural sulfur source was recently applied or legacy sulfur (agricultural sulfur which chemically reacted with and was bound to peat soils and is then released during soil oxidation) but it is likely that both new and legacy agricultural sulfur are contributors to EAA canals.

An alternative potential source of sulfate to canals within the EAA is deep groundwater (connate seawater). Much of the groundwater deeper than 9 m underlying the EAA and the Everglades is saline, and contains a significant amount of sulfate that could account for the high sulfate concentrations in the EAA canals. Bates et al. (2002) examined the sulfur isotopic composition of groundwater in a limited number of samples from STA-1W and WCA-2A. They concluded that, in general, the sulfur isotopic composition of the sulfate in deep groundwater is different from that in canal water. In addition, the chemical composition of the deep groundwater (sulfate/chloride ratio) is very different from that of canal water (**Figure 3B-22**). Thus, based on available data, both sulfur isotope results and sulfate/chloride ratios argue against deep groundwater as a major source of sulfate to EAA canals.

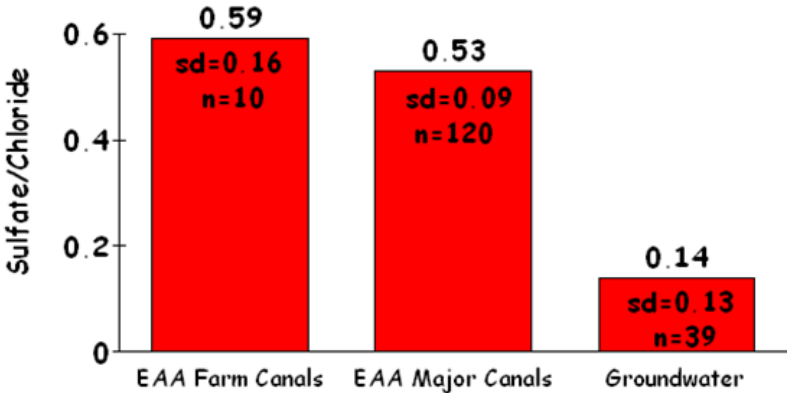



**Figure 3B-22.** Average sulfate/chloride ratios of farm canal water, major canal water, and groundwater in the northern Everglades and EAA. The EAA canal water sulfate/chloride value was calculated from data in Chen et al. (2006).

Another argument against groundwater being a major source of sulfate to EAA canals comes from the observation that sulfate concentrations in the canals tend to decline sharply during drought events (Scheidt et al., 2000; Bates et al., 2002; Axelrad et al., 2007). During drought conditions, the sulfate concentrations in the EAA canals drop to levels observed in Lake Okeechobee. As rain arrives following the drought, sulfate concentrations in the EAA canals have been observed to dramatically increase, from concentrations of 25 mg/L up to 200 mg/L. This observation suggests that during drought conditions, sulfate is not being washed from agricultural fields into EAA canals, but as rain arrives, sulfate on the agricultural fields that has accumulated during the drought event is washed into the canals, producing the exaggerated sulfate levels observed in the canals following a drought or the end of the dry season (**Figures 3B-23a** and **23b**).

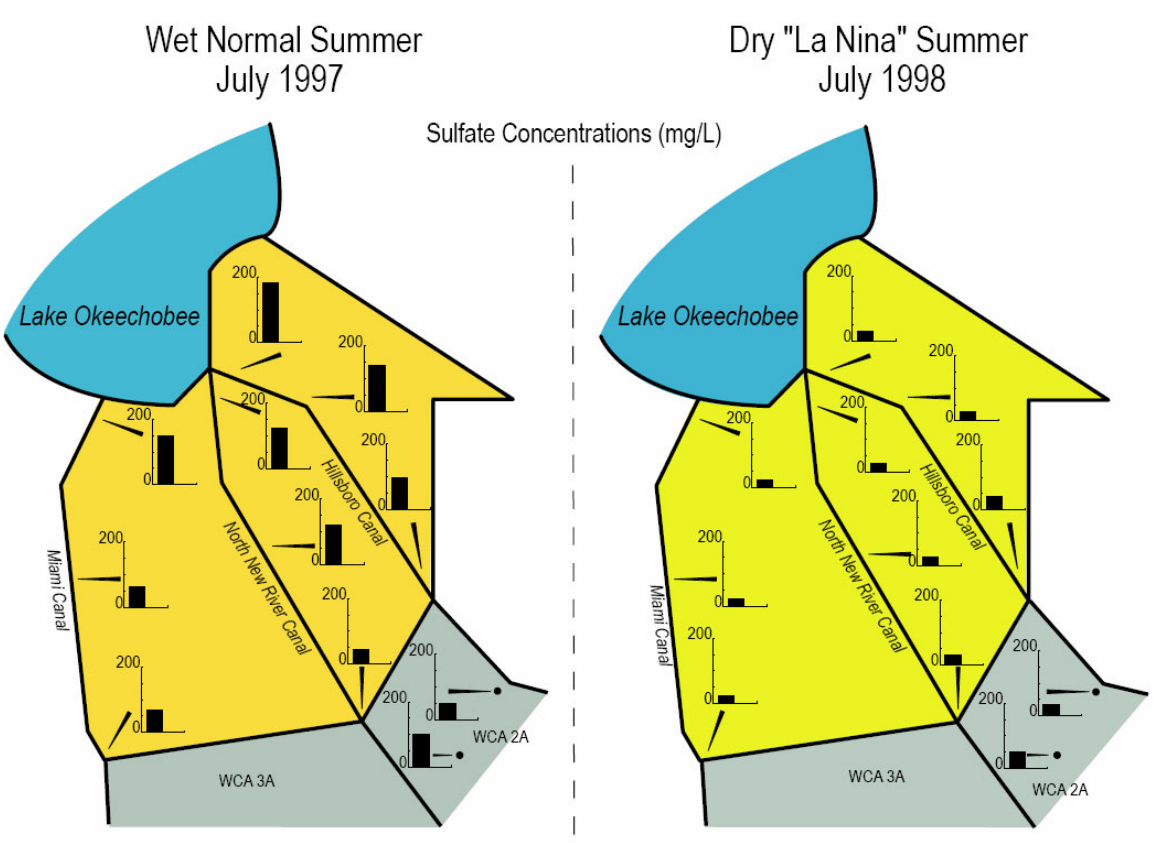



**Figure 3B-23a.** Sulfate concentrations (mg/L) in EAA canals during a normal, wet summer (left) and during a dry "La Nina" summer (right); note the bars indicating higher concentrations in July 1997 than in the following drier summer. (W.H. Orem and A.L. Bates, U.S. Geological Survey, unpublished figure.)

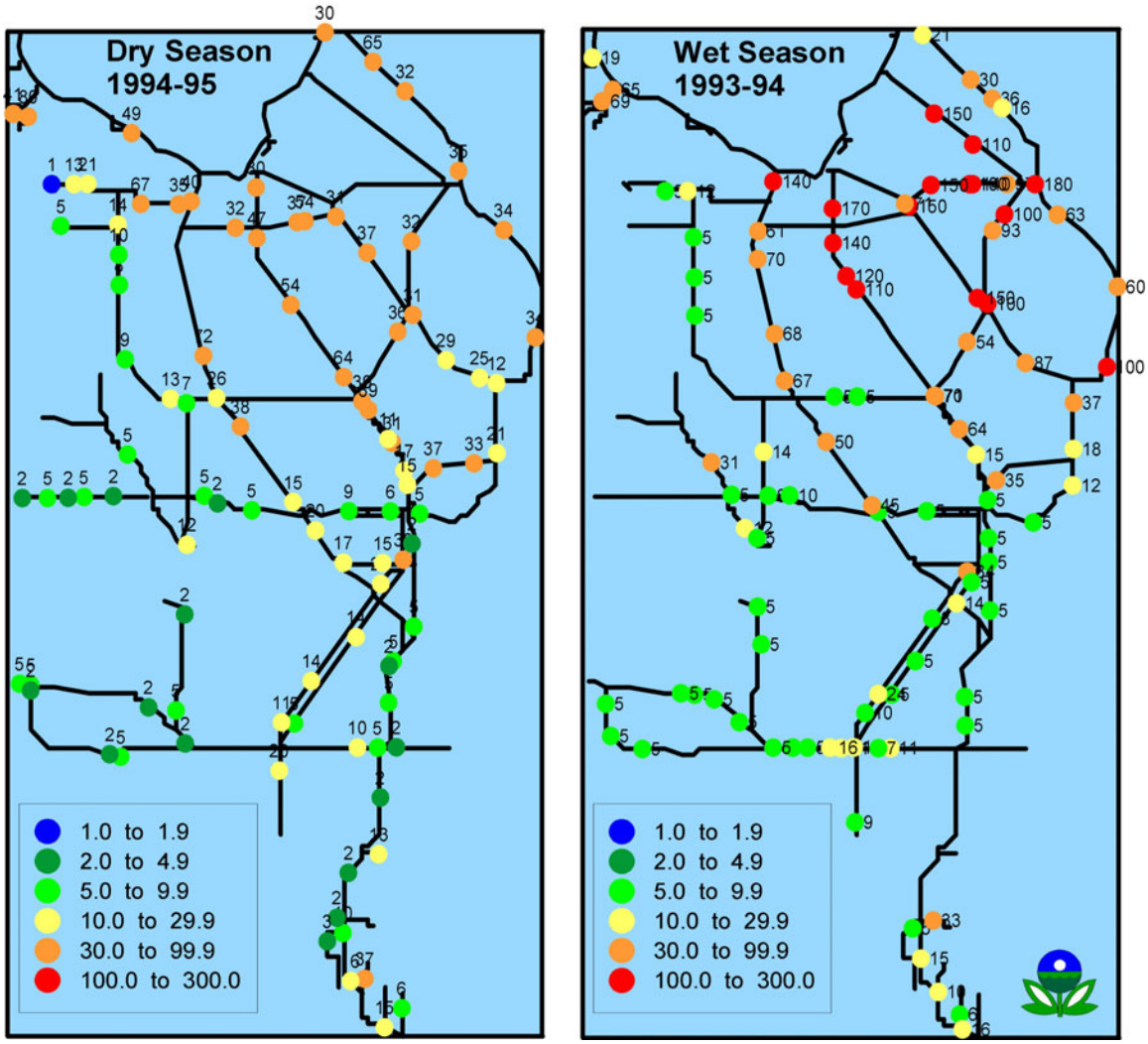



**Figure 3B-23b**. Sulfate concentrations (mg/L) in canal waters from the EAA to the ENP, dry vs. wet season (adapted from Scheidt et al., 2000).

A further argument against deep groundwater being a major source of sulfate to EAA canals comes from uranium concentration and uranium isotopic data ($^{234}U/^{238}U$ activity ratio). Uranium concentration and activity ratio has been used as a geochemical tracer of phosphorus in the Everglades and fluvial systems in central Florida (Zielinski et al., 1999, 2006). Uranium concentration and activity ratio data of groundwater, canal water, and surface water from the Everglades may be used to determine the extent of deep groundwater contribution to canal water.

Average uranium concentration (ppb) and isotopic data ($^{234}U/^{238}U$ activity ratio) for deep groundwater and canal water from the northern Everglades, and surface water from STA-1W and WCA-2A are shown in **Figure 3B-24**. Deep groundwater has significantly higher uranium concentrations than canal water, and thus could account for the concentrations of uranium in the canals. However, the isotopic composition of the groundwater ($^{234}U/^{238}U$ activity ratio of 1.3) is different than that of canal water (0.97). The canal water has a uranium isotopic composition

consistent with a source from phosphorus fertilizer used in the EAA ($^{234}U/^{238}U$ activity ratio = 1.00 ± 0.05) (Zielinski et al., 1999). Similarly, surface water from STA-1W and central WCA-2A has uranium activity ratios consistent with a source from phosphorus fertilizer. It should also be noted that uranium concentration drops from EAA canals to surface water in STA-1W and to surface water in central WCA-2A (see (**Figure 3B-24**). As distance from the source (e.g., EAA phosphorus fertilizer) increases, uranium tends to partition onto particles and settles out of the water column.

The tendency of uranium to partition onto organic-matter rich particles and deposit in the underlying soil in wetlands allows a time-integrated view of changes in uranium in the overlying water column. The uranium concentration (µg/g) and $^{234}U/^{238}U$ activity ratio of soil (peat) from two cores collected in WCA-2A are shown in **Figure 3B-25.** One core site is located 0.3 km from an EAA canal discharge site, and the other site is located 8.3 km further south of the same canal discharge. First, note that the concentration of uranium is significantly higher throughout the upper 25 cm of soil at the site 0.3 km from the canal discharge, consistent with the closer proximity of this location to the source of the uranium (EAA canal water). The profile of uranium concentrations at the 0.3 km distance site shows an increase with depth. Lower concentrations in the upper portion of this core may reflect biodilution of uranium entering the ecosystem by the high production rate of *Typha* (cattail) biomass and subsequent organic matter accumulation in these peat soils. Uranium concentration at the 8.3-kilometer site (sawgrass-dominated) shows a decrease with depth in the soil column.

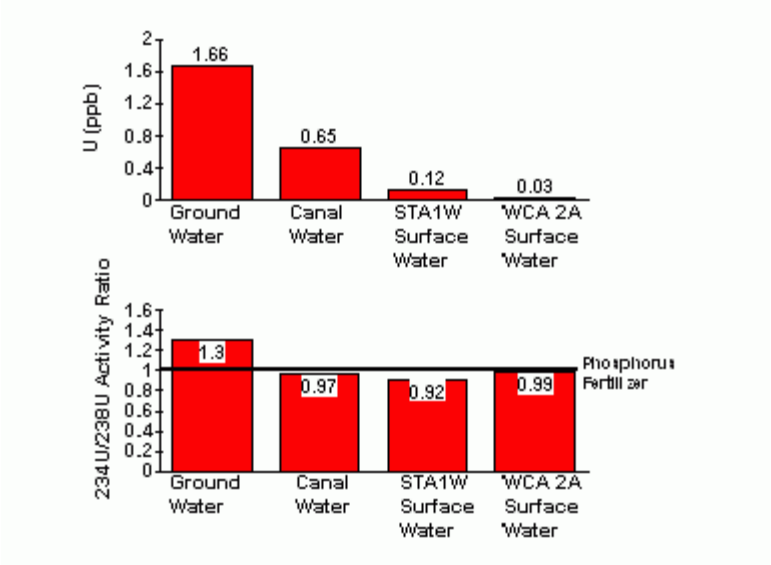



**Figure 3B-24.** Average uranium concentration (ppb) (top figure), and uranium activity ratio ($^{234}U/^{238}U$) (bottom figure), of deep groundwater and canal water from the northern Everglades, surface water from STA-1W, and surface water from WCA-2A. The horizontal black line across the bottom figure is the average uranium activity ratio of phosphorus fertilizer (1.00 ± 0.05) used in the EAA.

The $^{234}U/^{238}U$ activity ratios of soil from the two sites are also quite different. The site 0.3 km from canal discharge has a $^{234}U/^{238}U$ activity ratio for soil that is relatively invariant with depth in the upper 25 cm, and ranges from about 0.97 to 1.00. This is consistent with a source of uranium from phosphorus fertilizer (not groundwater) at this site. In contrast, the site 8.3 km from the canal discharge has a $^{234}U/^{238}U$ activity ratio that is higher (1.0 to 1.2). Only the uppermost interval at the 8.3 km distance site has a uranium activity ratio consistent with a phosphorus fertilizer source.

Overall, the uranium results suggest that deep groundwater is not a major sulfate contributor to EAA canals, and the soil uranium results show that this has been the case for at least 50 years. Thus, sulfur isotope data, sulfate/chloride ratios, sulfate concentration trends before and after drought, and uranium tracer studies from the available dataset all point to limited deep groundwater sulfate contribution to EAA canals. Considering the continued use of sulfur in agriculture, and the geochemical data pointing to agricultural sulfur as the principal source of sulfate to canals, available data support the hypothesis that newly applied sulfur and legacy sulfur in agricultural soil in the EAA is the principle source of sulfate to EAA canal water, and sulfate loading to the Everglades.

While existing data support the hypothesis that EAA canals are the principal source of sulfate to the Everglades, and new and legacy sulfur used in EAA agriculture is the primary source, but not the only significant source of sulfate to EAA canals, additional investigation of the sources of sulfate to EAA canals is warranted to further test this hypothesis.

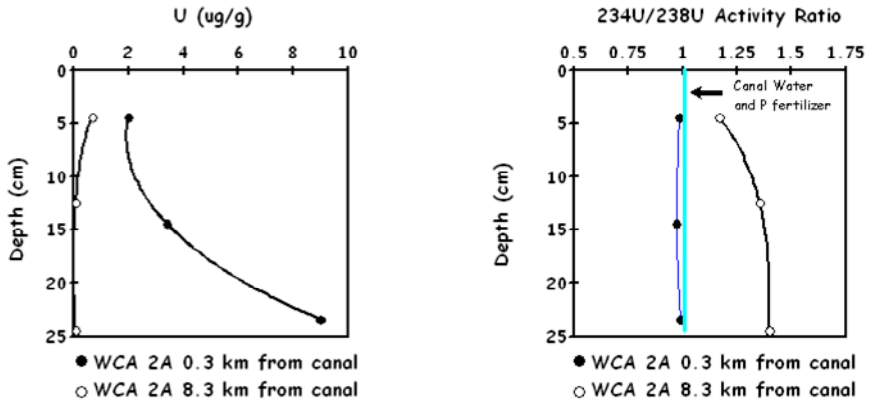



**Figure 3B-25.** Uranium concentration data (µg/g) (left figure), and uranium activity ratio ($^{234}U/^{238}U$) (right figure), of soil (peat) from two cores in WCA-2A, one site 0.3 km from a canal discharge site (●), and the other 8.3 km from a canal discharge site (○). The vertical line in the right figure represents the uranium activity ratio of phosphorus fertilizer used in the EAA.

In summary:

- The highest surface water sulfate concentrations across South Florida (excluding marine-influenced sites) have been observed in EAA canals, and these canals are a significant source of sulfate to the Everglades.
- Though deep groundwater (connate seawater) is a potential source of sulfate to EAA canals, uranium tracer results suggest that this deep groundwater is not a major sulfate contributor, and thus sulfur isotope data, sulfate/chloride ratios, sulfate concentration trends before and after drought, and uranium tracer studies all point to limited deep groundwater sulfate contribution to EAA canals.

## EFFECTS OF SULFUR

Effects of sulfur on the Everglades were discussed in detail in the 2007 SFER – Volume I (Axelrad et al., 2007; Gilmour et al., 2007a, b). These include:

1. **Production of Toxic Methylmercury:** Increasing Everglades sulfate concentrations stimulate methylmercury production by sulfate-reducing bacteria, up to a point, and thereafter excess sulfide, an end-product of bacterial sulfate reduction, inhibits methylmercury production; the ranges over which these processes occur vary by location because of the complex interaction of physical, chemical, and microbiological conditions and the biogeochemical cycles of several elements. It is probable that broad areas of the Everglades currently exhibit sulfate concentrations at which increased sulfate levels would enhance, and decreased sulfate concentrations would reduce, MeHg production (Gilmour et al., 2007a).

2. **Toxic Effects on Aquatic Life**: Sulfide is an end product of bacterial sulfate reduction, and this process is stimulated by sulfate additions to the Everglades. While excess sulfide may inhibit mercury methylation, the negative effects of excess sulfide may be very significant. The build-up of excess sulfide in Everglades soil porewater could reach levels toxic to more sensitive, desirable rooted plants (i.e., sawgrass) but not to less sensitive, undesirable plants (i.e., cattail), and could also prove toxic to aquatic invertebrates. Growth rate of sawgrass as measured in a short-term assay was reduced by sulfide concentrations that are evident in WCA-2 (approximately 7 mg/L sulfide in porewater), while cattail growth rates were not significantly reduced at this sulfide concentration (Gilmour et al., 2007b).

3. **Increased Phosphate Release and Eutrophication**: Excess sulfate may release phosphate from soil to the overlying water column via several mechanisms, potentially increasing the degree of eutrophication and slowing the rate of recovery of the Everglades, a phosphorus-limited ecosystem. Preliminary research indicates that sulfate may promote phosphate and ammonium release from Everglades sediments (Gilmour et al., 2007b).

   ***a.*** In anaerobic sediments and soils, sulfate-reducing bacteria may utilize sulfate as an electron acceptor to metabolize organic matter, thereby releasing phosphate and ammonium (nitrogen) from this organic material; this is termed "internal eutrophication" or "sulfate-mediated eutrophication";

   ***b.*** Sulfate may compete with phosphate for anion adsorption sites on sediments (e.g., $Fe^{+3}$), thereby releasing phosphate;

   ***c.*** Sulfate reduction results in alkalinization (increased pH; decreased acidity) of sediment pore waters thereby providing more suitable conditions for microorganisms to metabolize organic matter, which may further release phosphorus and nitrogen. In contrast, it has been widely demonstrated that acid conditions favor the accumulation of peat (organic matter) which stores phosphorus and nitrogen and thus reduces the threat of eutrophication;

   ***d.*** Sulfate reduction, and the concomitant reduction of Fe (from $Fe^{+3}$ to $Fe^{+2}$) leads to the formation of FeS*x* and may result in a strong decrease in the phosphate-binding capacity of sediments (Lamers et al., 1998; Smolders et al., 2006).

There is now a need to construct an Everglades sulfur mass balance to quantify sources and sinks and to evaluate sources as to their feasibility for reduction through Best Management Practices (BMPs), rerouting of water flow, or other means. There is a need to further investigate the potential toxic effects of sulfide and the role and importance of sulfate in releasing phosphate from Everglades sediments (see Appendix 3B-2 in this volume).

# DISCUSSION

The Everglades has a significant mercury problem; health advisories warning people to limit or avoid consuming fish are widespread, and fish-eating wildlife are overexposed to mercury in some areas of the ecosystem. Everglades sulfate levels also appear problematic from the standpoint of stimulating mercury methylation, with regard to potential sulfide toxicity to plants and animals, and with regard to sulfate-induced liberation of phosphate and ammonium from Everglades soils, potentially counteracting Everglades restoration efforts.

The declines in mercury levels in fish and fish-eating birds from 1990–2000 are heartening, and the mechanism that appears to best account for these declines is a combination of both declining rates of atmospheric mercury deposition and declining concentrations of sulfate. As such, the best options for reducing methylmercury production in the Everglades appear to be reductions in atmospheric deposition of mercury and sulfate loading reduction to the Everglades.

One estimate, however, is that anthropogenic point source atmospheric emissions of mercury from South Florida are presently a small fraction (about 10 percent) of the peak historical levels of circa 1990, and despite this, mercury deposition to the Everglades remains high compared to other U.S. sites. If in fact local atmospheric mercury emissions have been reduced by 90 percent from levels of circa 1990, this would leave little scope for source reductions through regulation in Florida or the United States. However, urban South Florida may contribute a myriad of small mercury sources to the atmosphere, and these remain poorly quantified. Despite the substantial earlier local source atmospheric mercury emission reductions, an updated emissions inventory of South Florida is required and is being planned, and there remains a need to determine the relative importance of local/regional/global and wet/dry atmospheric mercury deposition sources to identify and develop opportunities for reducing mercury deposition to the Everglades. The FDEP, as part of its state-wide atmospheric mercury Total Maximum Daily Load (TMDL) Program, plans to determine quantities and sources of wet and dry atmospheric mercury deposition to South Florida.

Similarly, a sulfur mass balance for the Everglades would allow for identification of sulfate sources amenable to controls (through BMPs, control technologies, rerouting of water flow, or other means) for reducing mercury methylation rates and reducing other negative ecological effects of sulfate. Also, continued research into the effects of sulfate loading to the ecosystem on mercury methylation rates, sulfide toxicity to plants and animals, and phosphate release from Everglades sediments is needed.

## RESEARCH PROGRESS

The following research needs were identified in peer-review comments regarding Everglades Consolidated Reports (ECRs) and South Florida Environmental Reports (SFERs). An update on the progress made with respect to each of the research needs is presented below.

**1. Quantify the no-effect level for Everglades fish-eating bird dietary exposure to methylmercury to support development of a water quality criterion (2000 ECR).**

The effects of methylmercury in birds have been researched for over 40 years, but the effects of sublethal exposure in wild birds remain poorly understood, particularly in the context of typical daily challenges in the wild, and mercury toxicity may vary greatly among bird species (Rumbold, 2005). A study was designed to identify the potential effects of environmentally realistic mercury exposure on development and reproduction in a carnivorous wetland bird under controlled conditions. The work has also been designed to establish a lowest observed adverse effect level (LOAEL) for effects of MeHg on development and reproduction in these animals (Frederick et al., 2007).

The approach in this study is to raise and maintain white ibises in captivity on controlled diets containing different levels of methylmercury, and to examine these birds for treatment effects on health, survival, appetite, behavior, endocrine function and, as they mature, reproductive success. The global hypothesis examined is that MeHg contamination at the levels chosen (0.05, 0.1, and 0.3 mg MeHg/kg ww in diet) has negative effects upon development, survival and breeding of ciconiform birds. The choice of dose levels was based largely on the mercury values of predominant prey items in the diet of free-ranging Everglades ibises established in the mid-1990s (Loftus, 2000).

During spring 2005, a 1,233 $m^2$ (13,000 sq ft) aviary was constructed in Gainesville, FL, and populated with 30-to-40 day old ibis chicks from two colonies in Florida, randomly placed into one of the four dose groups. In 2005 and 2006, it was found that (1) food consumption was higher in controls than other dose groups during the three months following initiation of dosing — control group birds ate more — but that there was no significant effect after that date; (2) in an experiment designed to test the ability of young birds to forage and learn about novel foraging situations, significant effects of habitat complexity and time on foraging efficiency were found (i.e., the birds were challenged and became more efficient over time). Although mercury dose group was also a significant effect, the effect was not linear or even consistent with dose (control and high-dose groups were similarly low in efficiency, medium and low groups were significantly higher). Also not found were: (3) effects of dose group on blood hematocrit levels, survival of juveniles, mass gain, or body measurements.

Nearly all of the birds did breed in their first year (two years old is typical age for first breeding in the wild), probably as a result of the artifact of captivity and the lack of adults to exert a suppressive effect on reproduction by young birds. Control birds bred significantly earlier than all dose groups, and produced 37 percent more nests and 22–40 percent more eggs than did any of the dosed groups. All groups showed male-male homosexual pairings but the control group showed the lowest rate of male-male pairings and no female-female pairings (Frederick et al., 2007).

Between 2006 and 2007, feather mercury concentrations remained largely unchanged in control-, low- and medium-dose groups, with feather mercury concentration increasing with increased MeHg exposure via food. The high-dose group almost uniformly increased in mercury

concentration between 2006 and 2007, by an average of 23 mg/kg fw. One possible explanation for this increase is that at high doses birds tend to run out of mercury storage "pools" in muscle and organs and birds have limited ability to excrete mercury, resulting in higher circulating blood levels and feather mercury levels. This supports previous studies that suggest the dynamics of mercury retention change at higher dose levels in birds.

In an effort to understand the possible effects of mercury exposure on development of ibis endocrine systems, fecal samples from individually identifiable birds were collected between June 2005 and January 2006. Steroid hormones (estradiol, testosterone, corticosterone) or their breakdown products from these fecal samples were extracted and measured. Using repeated measures general linear models, a set of candidate models were tested to explain variation in endocrine expression. The control group showed significantly lower estradiol and corticosterone metabolite levels than the other groups. While these data suggest an effect of methylmercury, the effect observed was not linear with respect to exposure level. No significant effect of sex on expression of any of the hormones was found, even in the control group, suggesting that there is little sexual differentiation in hormones during this period. Steroid hormones may therefore not be a very sensitive endpoint for endocrine disruption in juvenile birds. However, it is possible that the nonlinear response of corticosterone levels may be interpretable as contaminant stress.

During the 2007 breeding season, reproduction was monitored in several ways. Pairing and nest information were monitored daily, and courtship, nesting (112 hours) and parental behavior (272 hours) weekly for all groups. Over 2,500 fecal samples were collected for hormone information on a weekly basis. To facilitate the latter, a novel method of identifying fecal samples to individual without the use of direct observation was developed. Individual birds were fed baits (small fishes typically used as food supplements), that were in turn stuffed with particular combinations of small colored beads (cf 0.5 mm diameter). The beads passed the gut along with feces and allowed accurate individual identification of fecal splays. Hormone samples from all breeding detecting endocrine differences due to treatment. Hormone samples are currently being analyzed for testosterone, estradiol, and corticosterone; behavioral information is also presently being analyzed.

Although there were roughly equal numbers of total nesting attempts in each dose group this year, a significantly greater percentage of the nests (18–28 percent more) that were initiated in the control group resulted in egg laying than in the mercury dose groups. There were no significant differences among the mercury-dosed groups in proportion of nests resulting in eggs. In addition, the numbers of fledglings per nest start were significantly higher in the control group than in any of the mercury dosed groups, and no significant differences among mercury dosed groups were observed in this measure. No differences were found in mean clutch size among any of the groups, nor were significant differences in egg hatchability found.

Unlike in 2006, there were no significant differences in mean egg laying date, either for all nests, or for first nesting attempts (n = 39 to 46). The most consistent difference between the groups was the degree of homosexual pairings. The control group had only one male-male pairing (less than 2 percent), whereas low-, medium- and high-dose groups showed 27 percent, 43 percent, and 44 percent of males engaging in homosexual pairings, respectively. The proportional differences in male homosexual pairings within mercury dose groups were not significant, but proportion of pairings that were homosexual in all mercury dose groups were significantly higher than the control.

Male-male pairings were concentrated in the early part of the breeding season, and about half of the initially homosexual males paired later in the season with females. Male-male pairings were not related to a shortage of females. In fact, the highest level of homosexuality was observed

in the high dose cage, where there was a female-biased sex ratio. Although no eggs were ever laid in male-male nests, male-male pairings occupied a very large proportion of the total pair-days. Females in reproduction were therefore inversely related to homosexual pairings, largely in relation to mercury dose. It is not clear whether this was brought about by male homosexual preference or lack of female receptivity to males. Proportionally, the control group had significantly more heterosexual pair-days than any other group, and there were significant differences in this measure among mercury groups that suggested a dose-related response. In contrast, there were no female-female pairs in any dose group in 2006, and only one in 2007, in the high-mercury dose group.

The lack of female breeding is probably the most likely mechanism by which the control group had more nests with eggs and higher productivity than the other groups. There are two mechanisms by which male homosexual pairing and lack of female breeding might occur: males might have homosexual preferences and females are thus ignored, or females might be unreceptive. Better understanding of the mechanism could be gained through analysis of nest stage-specific hormones and behavior.

Breeding and pairing information were also analyzed by individual feather mercury levels, within groups. No evidence was found that homosexual males showed higher mercury values than heterosexual males within groups, nor that female nest success was related within groups to female feather mercury burden. While there are several possible flaws in this analysis, at least there was no evidence for a threshold effect for a relationship between mercury exposure and either homosexual behavior or nest success. However, this could easily have been masked in a within-group analysis by group-related dynamics.

Although the fecal hormone metabolite samples are yet to be analyzed, the sample sizes suggest excellent potential for examining effects of either group mercury or individual mercury on endocrine function, while controlling for the effects of time and nesting stage. As weekly information on reproductive and parental behavior are available, future analyses may also offer a chance to evaluate relationships between endocrine expression during the breeding season and both homosexual tendencies and other reproductive behaviors.

### 2. Quantify "global versus local" atmospheric mercury sources to South Florida to better define options for reducing mercury levels in Everglades biota (2002 ECR).

In support of FDEP programs, the Mercury Program continues to pursue resolving uncertainties in the emissions, fate, and transport of mercury in the environment. Beginning in 2007/2008, the Mercury Program proposes to initiate a statewide project to provide atmospheric deposition load estimates across Florida in support of the FDEP's TMDL Program.

Present plans suggest that to encompass the Florida domain will require establishing four mercury monitoring "Supersites" and two satellite daily event "precipitation-only" sites to provide adequate "ground truth" information to support the application of an atmospheric photochemical grid model analysis to project atmospheric deposition loads across the Florida landscape (see **Figure 3B-26**).

The measurement program will employ a wide variety of advanced monitoring instrumentation to provide high spatial and temporal resolution data. The data collected will support an atmospheric spatial modeling analysis to estimate the atmospheric deposition load of mercury, nitrogen, and phosphorus to Florida watersheds and waterbodies. In addition, rainfall and fine and coarse particulate samples will subjected to analysis by multi-element techniques

(e.g., energy dispersive x-ray fluorescence and high resolution inductively coupled plasma mass spectrometry) to provide information to drive both dispersion and receptor models (CMB, PMF, etc.).

One of the competent photochemical grid modeling systems, such as the National Oceanic and Atmospheric Administration/U.S. Environmental Protection Agency Community Model for Air Quality or other similar tool, will be employed to subsume the relevant emission and ambient data, then cast deposition isopleths on Geographic Information Systems (GIS) coverages (maps) and interpolate atmospheric deposition across Florida. Model output is envisioned to provide GIS coverages to cast deposition isopleths across the state-wide modeling domain.

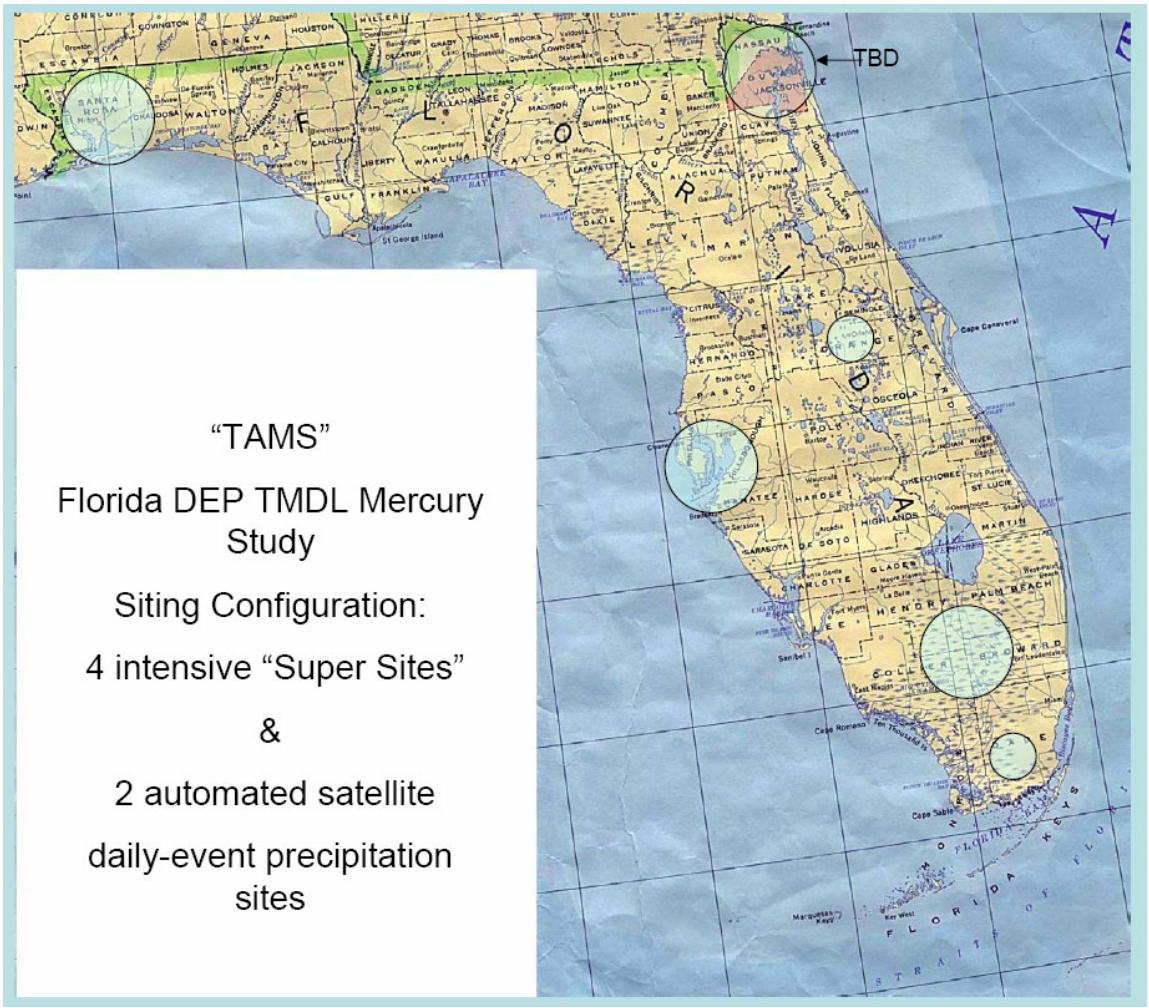



**Figure 3B-26.** Proposed future location of four mercury monitoring "Supersites" (large circles) and two satellite daily event "precipitation-only" sites (small circles).

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

Efforts to link the E-MCM to a diagenetic transport-reaction model capable of predicting the depth distribution of mercury (Hg) methylation as a function of soil biogeochemistry, are reported in Appendix 3B-3 of this volume.

Mercury cycling models have not adequately captured the complex interactions between methylmercury (MeHg) production and the sulfur cycle. In the Everglades, and in many other ecosystems, the sulfur cycle is a primary control on net MeHg production and bioaccumulation (along with inorganic mercury inputs and organic matter availability) (Compeau and Bartha, 1985; Gilmour, et al., 2007b).

As such, the SFWMD has supported efforts to capture the biogeochemical relationships between the mercury and sulfur cycles, and to link these to the E-MCM.

The mercury model supported by the Mercury Program is Tetra Tech's Everglades Mercury Cycling Model, a mechanistic simulation model that runs on Windows™-based computers (Tetra Tech, 1999, 2002). Using a mass balance approach, the model predicts time-dependent concentrations for three forms of mercury: inorganic Hg(II), methylmercury and elemental mercury. Mercury concentrations in the atmosphere are input as boundary conditions to calculate fluxes across the air/water interface (gaseous, wet deposition, dry particle deposition, deposition of reactive gaseous mercury). Model compartments include the water column (dissolved and particular phases), three macrophyte species (cattails, sawgrass, water lilies), four sediment layers and a food web. The simplified food web consists of detritus, periphyton, phytoplankton, zooplankton, benthos, shrimp, mosquitofish (*Gambusia*), bluegill/warmouth sunfish (grouped together), and largemouth bass.

The E-MCM includes algorithms to represent microbial methylation of mercury, but it has been unresolved how to best link methylation in E-MCM to sulfur cycling. Once methylation in the E-MCM is linked to sulfur cycling, the model would be available to help predict how ecosystem restoration and resulting sulfate concentrations could affect MeHg production and bioaccumulation in the EPA.

To link methylation in E-MCM to sulfur cycling, a diagenetic transport-reaction model capable of predicting the depth distribution of Hg methylation as a function of soil biogeochemistry was developed. Diagenetic models are numerical simulations of the post-burial decomposition of organic matter via a sequence of microbial fermentative and respiratory processes. In these models, microbial organic matter oxidation is driven by the vertical flux of oxidants (i.e., oxygen, nitrate, and sulfate) into sediments and soils. A diagenetic transport-reaction model that is capable of predicting the depth distribution of Hg methylation as a function of soil biogeochemistry through equations based on first principals.

To explore how the diagenetic Hg and sulfur cycling model could be used to improve the ability of the E-MCM to predict responses to changing sulfate concentrations in the Everglades, the model was applied to several sites within STA-3/4 (Cells 1–3), WCA-2A (sites U3 and F1), and WCA-3A (site 3A-15) using detailed biogeochemical field data from the Aquatic Cycling of Mercury in the Everglades (ACME) study. In addition, the model was used to generate input values for E-MCM simulations of the response of site 3A-15 to decreases in sulfate input over the last 10 years (1995–2005).

The diagenetic model was first applied to sites U3 and F1 in WCA-2A, and then to site 3A-15 in WCA-3A. Site 3A-15 has been studied for over a decade through the ACME study and other programs. Surface water sulfate concentrations have dropped during that decade, along with MeHg levels in water, sediments and fish. The diagenetic model was calibrated to fit observed downcore data from 1996 through 1998, and then used to predict depth-integrated sulfate reduction rates and MeHg concentrations over the full decade. Model outputs accurately predicted the concomitant declines in sulfate reduction rate and MeHg production at site 3A-15 over time, providing mechanistic support for the hypothesis that sulfate declines are driving at least part of the observed decline in MeHg at this site. The model can now be applied to predict the distribution of MeHg across the EPA under changing sulfate loading scenarios (please see Appendix 3B-3 of this volume).

Another goal was to create models can reproduce MeHg concentrations across the large sulfate and sulfide gradients found in the Everglades; 3A-15 is a low sulfate site where sulfide concentrations have been low throughout the study period. In order to predict MeHg concentrations at high sulfide sites, the model required empirically-fit routines for either Hg speciation and/or methylation routines, suggesting that our current understanding of Hg complexation chemistry is insufficient to model from first principals.

**4. Research biogeochemical controls on mercury methylation (2001 ECR).**

Significant progress has been made in our understanding of biogeochemical controls on mercury methylation through U.S. Geological Survey (USGS) and the Smithsonian Institution research supported by the FDEP and the SFWMD. Findings are noted earlier in the *Previous Findings Highlighted, Mercury and Sulfur Biogeochemistry in the Everglades* section of this chapter. The USGS plans further mercury biogeochemical research, as detailed below in the *Mercury Program Future Activities* section.

**5. Determine sulfur sources to and effects on the Everglades (2006 SFER – Volume I).**

The Everglades is contaminated by sulfate originating in the EAA, and there remains a need to derive a sulfur mass balance to confirm the sources of sulfur to EAA canals. Sulfur is a biologically very active element, and sulfate is essential for the dominant Everglades producer of MeHg: sulfate-reducing bacteria. It is probable that broad areas of the EPA exhibit sulfate concentrations at which increased sulfate levels would enhance (and decreased sulfate concentrations would reduce) net MeHg accumulation in soils and hence, MeHg accumulation in fish, birds, and mammals, and human exposure to mercury from consuming Everglades fish. Apart from sulfate promoting methylation of mercury, sulfate may promote eutrophication of the Everglades via liberation of phosphorus from sediments, while sulfide has long been known to be toxic to plants and animals. Preliminary data indicate that cattail may be more tolerant of elevated sulfide than is sawgrass, and sulfate may liberate phosphate from Everglades sediments.

The SFWMD and the FDEP are currently discussing a sulfur research program to address questions about sulfur sources and effects (see Appendix 3B-3 in this volume). Proposed projects include a sulfur budget for the EPA with quantification of all sulfur inputs including sulfur release from mineralization of peat soils, and determination of the relationship between sulfate concentration and "internal eutrophication" — that is, phosphate and ammonium release from sediments in STAs and in the EPA.

# FUTURE ACTIVITIES OF THE MERCURY PROGRAM

## Mercury, Sulfur and Dissolved Organic Carbon Research

Over the past decade, a consortium of agencies lead by the USGS conducted the Aquatic Cycling of Mercury in the Everglades Project on biogeochemical factors contributing to the high levels of mercury in Everglades biota. Work conducted under Phases I and II of ACME was reported on in previous SFERs.

A new three-year USGS project will seek to extend our knowledge of the factors controlling methylmercury production in the Everglades, with specific attention to geographic areas where Everglades restoration may affect methylmercury production and bioaccumulation. Because work under ACME Phases I and II was largely conducted in the WCAs, USGS will direct future efforts towards Everglades areas where less research has been conducted, in particular, federally managed lands.

The overall objective of this next phase of research is to extend understanding of interactions between mercury, sulfate, and dissolved organic carbon (DOC) as they influence MeHg production to areas of the Everglades that are anticipated to receive increased water delivery from sulfate-rich EAA runoff or high-sulfate Aquifer Storage and Recovery waters, including ENP, Big Cypress National Preserve (BCNP), and Loxahatchee National Wildlife Refuge (LOX).

Several areas of work will be conducted in 2007-08: (1) sampling surveys in interior marshes where the ACME project has only sporadic or no data; (2) surveys in coastal areas, particularly the southern mangroves that interface Florida Bay, the bay has system-wide warnings for high levels of mercury in game fish; (3) completion of the sulfide toxicity mesocosm study; and, (4) planning for a final set of mesocosm experiments in regions of the Everglades where the previous mesocosm tests may not have direct transferability, such as the marl regions of the ENP, and sandy regions of BCNP.

Field surveys will be conducted in the ENP, BCNP, and LOX. Field surveys in BCNP will examine potential impacts of the diversion of waters with elevated sulfate concentration from the L28 feeder canal into the Preserve as part of restoration efforts, which may result in increased MeHg production in BCNP. The coastal zone of the ENP and the southwest coast will also receive increased freshwater flow from restoration activities, but the impacts on MeHg production and bioaccumulation are unknown. One important goal of the field studies in the coastal zone will be to determine the relative importance of MeHg flux from the freshwater Everglades, compared to in situ production of MeHg in coastal sediments.

Mesocosms will be used to examine the effects of changing environmental conditions (increased mercury, sulfate and DOC loading, changes in hydroperiod, drought/fire) on MeHg production. The mesocosm work is intended to validate field observations, and to provide data for the prediction of the response of the environment to future conditions. Planned mesocosm studies will examine how environments in the ENP, BCNP, and LOX respond to changing freshwater inputs with variable water quality characteristics, with respect to MeHg production and bioaccumulation. Results will allow prediction of how different ecotones in the Greater Everglades ecosystem will respond to changes in water flux, and increased flux of mercury, sulfate and DOC. Of particular importance will be changes in MeHg production and bioaccumulation, redox conditions (from sulfide buildup in anoxic soils), and DOC and nutrient recycling (from increases in sulfate reduction rates).

This study is directly relevant to three overarching restoration questions in the U.S. Department of Interior (USDOI) science plan, including:

1. What actions will improve the quantity, timing, and distribution of clean fresh water needed to restore the South Florida ecosystem?
2. What actions will restore, protect, and manage natural resources on USDOI lands in South Florida?
3. What actions will recover South Florida's threatened and endangered species?

### State-wide Mercury Total Maximum Daily Load Program

The Mercury Program continues to pursue resolving uncertainties in the emissions, fate, and transport of mercury in the environment. Beginning in 2007/2008, the Mercury Program proposes to initiate a state-wide project to provide atmospheric deposition load estimates across Florida in support of the FDEP TMDL Program.

### Mercury in Coastal Waters

Excessive concentrations of mercury have been found in fish for all of Florida's coastal waters, affecting numerous species of commercial or sport-fishing interest. Human health advisories regarding consumption of marine fish have been issued for over 50 species and there are no-consumption advisories for several species for all of Florida's coastal waters. Floridian's exposure to methylmercury is predominantly via consuming marine fish. The Mercury Program has applied for grant funding to determine the sources of mercury to the Gulf of Mexico and the most important sites of mercury methylation in the Gulf, thus far to no avail. The FDEP will continue to seek support for this activity. In sum, the South Florida Mercury Science Program continues to progress toward the goal of resolving the multimedia nature of the mercury cycle as it influences Florida.

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