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

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SUMMARY

The very high mercury concentrations evident in fish and wildlife in Everglades Water Conservation Areas (WCAs) in the late 1980s to early 1990s have declined substantially; a combination of declining rates of atmospheric mercury deposition and reductions in Everglades sulfate concentrations probably account for these declines. However, mercury levels in fish in the WCAs still remain generally above the proposed U.S. Environmental Protection Agency (USEPA) human health criterion for fish consumption. In contrast to the mercury reductions in WCAs, mercury levels in fish have increased in the Everglades National Park (ENP or Park) and the Holey Land Wildlife Management Area (WMA) in recent years. ENP fish mercury concentrations are currently similar to or greater than at other known methylmercury (MeHg) hot spots in the U.S., and are well above USEPA wildlife criteria. Options for reducing mercury levels include atmospheric mercury source reduction and sulfate loading reduction. Everglades Agricultural Area (EAA) canals are a major source of sulfate inputs to the ecosystem. Approximately 60 percent of the Everglades marsh area has sulfate concentrations greater than historical levels, and this may be having detrimental effects beyond promoting mercury methylation, including sulfide toxicity to plants and phosphate release from sediments. 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

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Program (SFMSP)[12] 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 *2007 South Florida Environmental Report* (SFER) serves to update previously reported findings (1999–2006 Everglades Consolidated Reports and SFERs), with supporting data on mercury and sulfur provided in the appendices to this chapter.[13]

PREVIOUS FINDINGS HIGHLIGHTED

Previous findings from this collaborative SFMSP effort are summarized below.

Mercury in Everglades Fish and Wildlife

- Methylmercury strongly bioaccumulates in the Everglades aquatic food chain — approaching bioaccumulation factors of 10^7 for largemouth bass (*Micropterus salmoides*) — and 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., 1999; Fink and Rawlik, 2000; Rumbold et al., 2001; Frederick et al., 2005).
- Mercury levels in fish at many sites in the Everglades WCAs have declined about 30–70 percent from levels of the late 1980s and early 1990s, but have not declined greatly from 1998 to the present (Lange, 2006).
- Mean MeHg concentrations in largemouth bass in WCAs remain higher (ca. 0.5 milligrams/kilogram, or mg/kg) than the USEPA-recommended MeHg fish tissue criterion of 0.3 mg/kg (kg (Federal Register. 2001; Lange, 2006).
- Very high concentrations of mercury (1.1–1.4 mg/kg) 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. Mercury levels in largemouth bass have increased over the past 6–7 years, possibly because sulfate levels in the ENP are now in the optimal range for sulfate-reducing bacteria (SRB) to convert inorganic mercury to MeHg (Lange, 2006; Rumbold et al., 2007).
- The WCAs and the ENP (totaling about 2,000,000 acres) remain under fish consumption advisories for protection of human health, and mercury levels in fish threaten piscivorous birds and mammalian wildlife (FDOH, 2006; Fink and Rawlik, 2000; Frederick et al., 2005; Rumbold et al., In Review).

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12 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 (USGS). 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.

13 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 and 2006 SFERs).

- Dramatic declines in mercury concentrations in feathers of wading birds beginning in 1998 have been accompanied by increases in numbers of nesting birds (2–5 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).

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, 2006).
- The primary air emissions sources of mercury in South Florida ca. 1990 were incineration of municipal and medical wastes. Mercury emissions from incinerators of all types have since declined by approximately 90 percent. Principal reasons for this decline were pollution prevention activities that resulted in reductions of mercury concentrations in waste, as well as incinerator emissions controls (RMB, 2002; Atkeson et al., 2005).
- Although the precise proportions of locally versus globally derived mercury at the peak levels of atmospheric deposition of mercury in South Florida (ca. 1990) remain uncertain, the data analyses indicate that the majority of mercury deposition to the Everglades at that time originated from sources within South Florida (Pollman et al., 2005b).
- Presently, anthropogenic point source atmospheric emissions of mercury from South Florida are calculated to be a small fraction (about 10 percent) of peak historical levels (ca. 1990) (Pollman et al., 2005a). However, 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; 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 SRB. Sites of mercury methylation include soil surface "flocs" and to a lesser extent, periphyton mats. Once deposited, inorganic mercury is converted to MeHg over a period of hours to days (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., In Press).
- 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; methylation is generally highest at 2–20 mg/L sulfate in Everglades surface waters where porewater sulfide concentrations are moderate (5–150 ppb or µg/L). Sulfate contamination is an important factor in mercury methylation in the ecosystem (Benoit et al., 1999, 2001, 2003; Gilmour et al., 2007a).
- The EAA is an important source of sulfate to the Everglades (Bates et al., 2002; Fink and Rawlik, 2000; Orem, 2004; Orem et al., In Press).
- 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., 2002; 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 correlating with calculated declines in South Florida mercury emissions, as well as to declines in sulfate and DOC concentrations in surface waters at this site. Site 3A-15 sulfate concentrations are now well below optimal levels for methylation of mercury by sulfate-reducing bacteria (Axelrad et al., 2005).
- The mechanism that appears to best account for the declines in fish tissue mercury concentrations at the former WCA-3 mercury hot spot, site 3A-15, is a combination of both declining rates of atmospheric mercury deposition and declining concentrations of sulfate (Pollman et al., 2005a).
- 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, 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).

NEW FINDINGS HIGHLIGHTED

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

- Seventy-one percent of the largemouth bass sampled in WCAs in 2005 exceeded the USEPA fish tissue criterion. Mercury concentrations in largemouth bass in WCA-1, 2, and 3 while having declined by about 30–70 percent from levels in the late 1980s and early 1990s, remain relatively high (ca. 0.5 mg/kg) compared to the USEPA-recommended MeHg fish tissue criterion of 0.3 mg/kg.
- One-hundred percent of the largemouth bass sampled in Shark River Slough in the ENP during 2005 and 2006 exceeded the USEPA fish tissue criterion. Mercury concentrations in largemouth bass have increased in the ENP since 1999, and very high concentrations (1.1–1.4 mg/kg) are now evident in the Shark River Slough area at site L67F1 near the L67 Extension canal and at North Prong Creek. As well and as observed in previous years, for 2005 resident sunfish (*Lepomis* spp.) at site L67F1 had significantly greater mercury burdens than fishes from other Everglades sites. Mean concentration of mercury in sunfish collected at L67F1 in 2005 remains above the U.S. Fish and Wildlife Service (USFWS) predator protection criteria (Rumbold et al., 2007). Because sunfish represent the preferred prey item of many fish-eating species in the Everglades, there is a need to elucidate the cause of elevated mercury levels in the Park.
- There has been a trend of increasing mercury levels in largemouth bass and sunfish in the Holey Land WMA; the resulting mercury levels in fish have reached levels that may pose a threat to fish-eating wildlife (Rumbold et al., 2007).
- A study is currently under way on white ibises exposed to Everglades-relevant mercury levels. Early results show (1) white ibis eggs are considerably more vulnerable to embryonic death than are duck eggs — the commonly used piscivorous bird toxicology standard, and (2) captive ibises eating diets without mercury have in their first year have nested significantly earlier, and

produced 57 percent more nests and 37 percent more eggs than birds receiving Everglades-relevant mercury doses. Although these results suggest effects of relatively low mercury exposure, they are preliminary and cannot be considered conclusive.

- 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 northern ENP, indicated the likelihood was very high, ranging from 98–100 percent probability, that these birds would experience exposures above the acceptable dose (the no-observed-adverse-effect level, or NOAEL). Moreover, the likelihood that these birds would experience exposures above the lowest-observed-adverse-effect level (LOAEL) ranged from a 14 percent probability for the wood stork to 56 percent probability for the eagle (Rumbold et al., In Review)
- Broad areas of the Everglades Protection Area (EPA), namely the WCAs and the ENP, 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.
- At multiple locations across the EPA, net mercury methylation and bioaccumulation responded linearly to single-dose mercury loads up to twice the annual atmospheric mercury wet deposition rates.
- There was no significant trend from 1994 through 2005 in atmospheric mercury wet deposition at site FL11 (Beard Research Center) in the ENP, while in contrast mercury levels in largemouth bass at the North Prong site in the ENP have generally increased from 1999 to 2006, almost doubling over that period to ca. 1.4 mg/kg. Inasmuch as FL11 appears to have the most pronounced trend (decline) over time of the three South Florida MDN sites, but that trend is not statistically significant, it is evident that FL34 and FL04 have no trend in Hg wet deposition for their period of record either.
- EAA canals are a major source of sulfur to the Everglades, 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 source — but not the only significant source — of sulfate to the Everglades. There is a need to determine a sulfur mass balance for the Everglades.
- As well, there is a need to investigate Everglades sulfur biogeochemistry other than as regards mercury methylation. Sulfur is a biologically very active element and has forms that are known to be highly toxic (sulfide) to plants and animals, and other forms (sulfate) which have been well demonstrated to promote eutrophication in fresh waters, and could exacerbate the Everglades phosphorus problem via liberation of phosphate from sediments.
- Preliminary research results indicate that that cattail (*Typha domingensis*) may be more tolerant of elevated sulfide than is sawgrass (*Cladium jamaicense*), and that sulfate liberates phosphate from Everglades sediments. If these results are confirmed through planned follow-up research, it would suggest that sulfur, as well as phosphorus, promotes replacement of native sawgrass by invasive cattail in the Everglades.

The monitoring, research, modeling, and assessment studies described in this chapter and appendices were coordinated among the collaborators in the SFMSP. This group of agencies, academic and private research institutions, and the electric power industry has advanced the understanding of the Everglades mercury problem more effectively and 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, the Comprehensive Everglades Restoration Program (CERP), as well as other restoration efforts, on the schedule required by the Everglades Forever Act.

MERCURY IN EVERGLADES FISH AND WILDLIFE

Largemouth bass, 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 mercury bioaccumulation, thus allowing for assessment of the effectiveness of management actions in reducing Everglades mercury levels. Data are available from 1988 to 2005 from sites in WCAs 1, 2, and 3 and the ENP (to 2006) for examination of Everglades spatial and temporal trends in mercury levels in largemouth bass. Data are for total mercury in fish; Bloom (1992) reported that virtually all (>95 percent) of the mercury in muscle tissue from largemouth bass is methylmercury.

For the Everglades WCAs, median concentrations of mercury in largemouth bass have declined about 70 percent over the past 14 years **(Figure 3B-1 top panel**), reaching their lowest levels in 2005 with a system wide median concentration of 0.45 µg/g (range; 0.01–1.8 µg/g; n = 216) (µg/g = mg/kg = ppm). In contrast, in Shark Slough in the ENP, median concentrations have approached or exceeded 1.0 mg/kg during the past 17 years (**Figure 3B-1 bottom panel)**, reaching 3.4 mg/kg in 1997. In 2006, the systemwide median was 1.2 mg/kg (range; 0.64–2.6 mg/kg; n = 20).

Although these substantial declines observed in the WCAs represent an encouraging trend, most fish — 71 percent of largemouth bass sampled in WCAs in 2005 — continue to exceed the U.S. Environmental Protection Agency's (USEPA) recommended MeHg fish tissue criterion of 0.3 µg/g (Federal Register, 2001). During 2005 and 2006, all fish collected from the Shark River Slough exceeded the USEPA MeHg fish tissue criterion.

The Florida Department of Health (FDOH) currently advises anglers fishing in the WCAs to limit consumption of eight species of sport fish (largemouth bass, Mayan cichlid, yellow bullhead, spotted sunfish, bowfin, bluegill, gar, and redear sunfish). Moreover, FDOH guidance regarding largemouth bass exceeding 14 inches in length and all sizes of bowfin (*Amia calva*) and Florida gar (*Lepisosteus platyrhincus*), 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 species of sport fish (Mayan cichlid, redear sunfish, bluegill, spotted sunfish, and yellow bullhead).

As early as 1988, eight long-term monitoring sites were established to track Everglades spatial and temporal trends in largemouth bass mercury concentrations (**Figure 3B-2**) (Lange et al., 2005). Such monitoring allows comparison of standardized fish mercury concentrations among years at specific locations within the ecosystem.

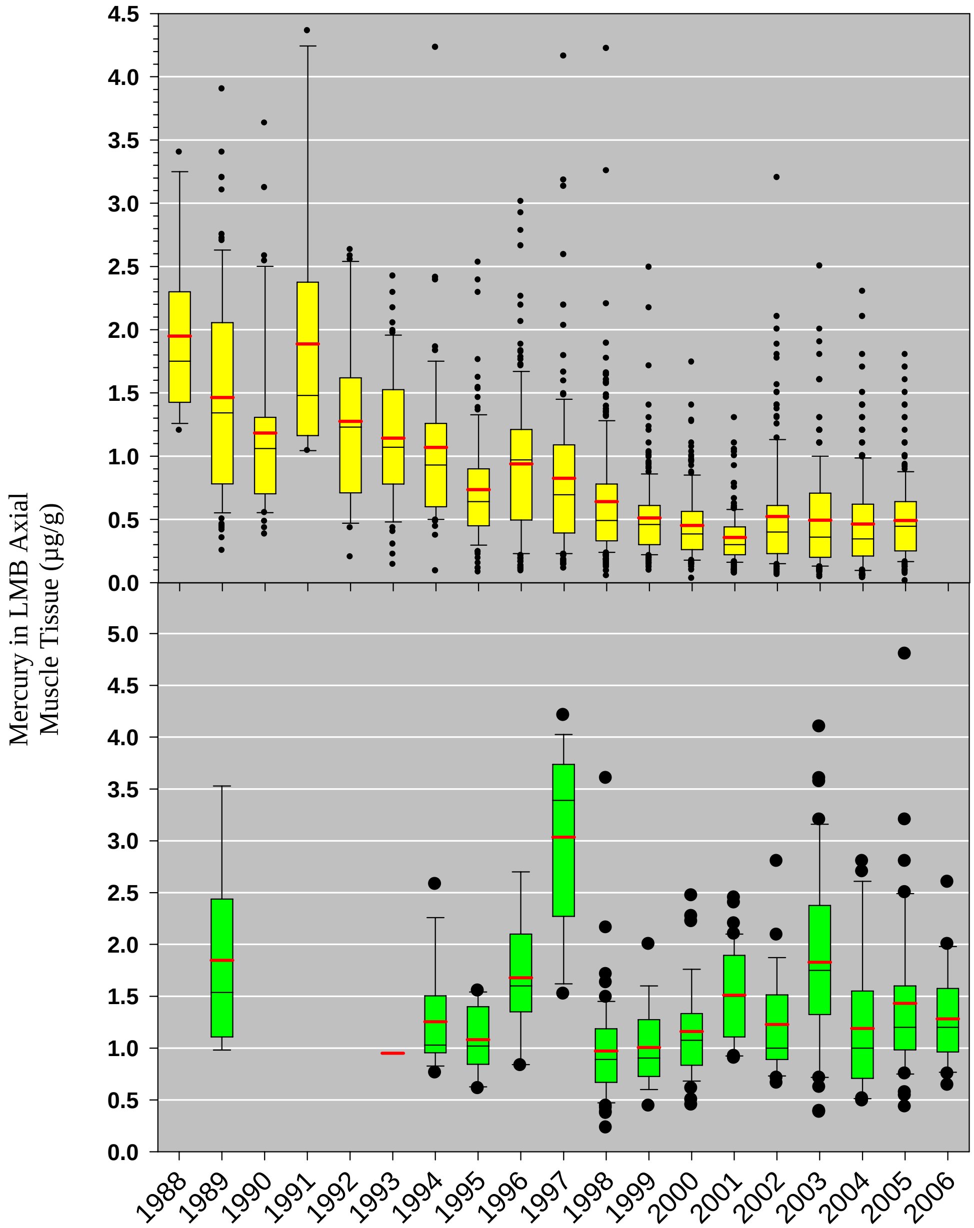

Figure 3B-1. Annual summaries of mercury concentrations in 2,314 largemouth bass *(Micropterus salmoides)* collected between 1988 and 2005 from canals and marsh sites in Water Conservation Areas (WCAs) 1, 2, and 3 (top panel) and for 371 largemouth bass collected from the Shark River Slough (at North Prong Creek and site L67F1) in Everglades National Park (ENP) (bottom panel). Each panel shows the median (black line), mean (red line), 25th and 75th percentiles (boxes), 10th and 90th percentiles (error bars) and outliers (black circles). Mercury is reported as µg/g = mg/kg = ppm.

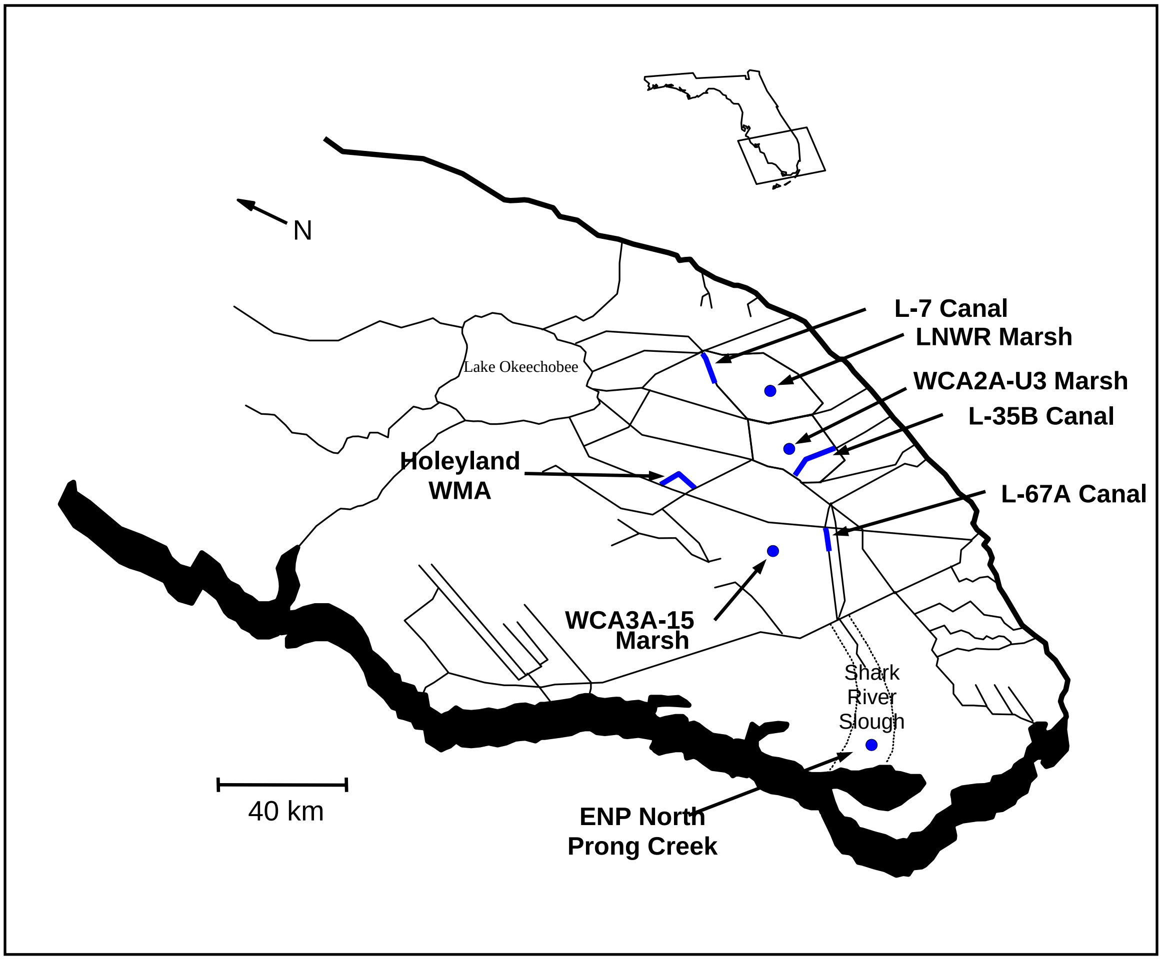

Figure 3B-2. Location of eight long-term monitoring locations in the Everglades Protection Area (EPA). The L-7 Canal and Loxahatchee National Wildlife Refuge (LNWR) Marsh site are located in the LNWR (WCA-1). Sites L-35B Canal and WCA-2A-U3 are located in WCA-2 and sites L-67A Canal and WCA-3A-15 are located in WCA-3. Holey Land Wildlife Management Area (WMA) is sampled in its perimeter canal while site North Prong Creek is located near the terminus of the Shark River Slough in the ENP. Sites represent a north-south transect through the EPA.

Comparing the highest observed levels over time to present levels, declines in mercury levels in largemouth bass from the eight long-term monitoring sites in the WCAs averaged 46 percent, with a range from "no change" (NC) in the Holey Land WMA (**Figure 3B-7**), to a 68 percent decline at site L67A Canal (**Figure 3B-5**). Declines were observed at all sites within the WCAs, ranging from 42 to 71 percent (**Table 3B-1**).

Mercury trends over time in largemouth bass at Holey Land WMA and North Prong Creek in Everglades National Park (ENP or Park) (**Figures 3B-6** and **3B-7**) differ from trends for the WCAs (**Figures 3B-3** through **3B-5**). Holey Land WMA and North Prong Creek had period of record minimum concentrations in 1999, followed by increases averaging about 15–20 percent per year (Lange, 2006), in direct contrast to trends in the WCAs over the same period (**Figure 3B-1**). Although, there has been an overall decline in mercury levels at North Prong Creek for the period of record, with the recent upward trend, age-standardized mercury concentrations are in range of the 1.5 µg/g level that was last exceeded in 1997. As is the case for largemouth bass and sunfish (Lange, 2006; Rumbold et al., 2007), there is a mercury hotspot for mosquitofish (*Gambusia affinis*) in the ENP (**Figure 3B-8**).

Regarding the Holey Land WMA, Rumbold (2005) found that a 12 percent increase in mercury in year 2004 largemouth bass (based on the predicted mercury in bass at age-3, or EHg3, method of age standardization) did not differ statistically from 2003 levels, but 2004 levels were greater than all previous years. Similarly, a 14 percent increase in mercury in year 2005 bass was not statistically different from 2004 levels, but 2005 levels were greater than all previous years (Rumbold et al., 2006). Rumbold (2005) speculated that conditions were becoming more favorable for mercury methylation in the Holey Land, though the observed trend could also be a result of increasing complexity in the food web (following hydroperiod changes), thus providing additional steps for biomagnifications. In either case, the resulting mercury burdens are reaching, or have reached, levels that may pose a threat to fish-eating wildlife (Rumbold et al., 2007).

In contrast to data that standardizes mercury concentrations for largemouth bass with varying age distributions (EHg3), annual trends in age 1-2 cohorts of largemouth bass would be expected to represent a sample that integrates mercury over a discreet short period of time, and perhaps offers a better representation of short-term changes in mercury bioavailability.

Mean mercury concentrations in age 1-2 largemouth bass (**Figure 3B-9**) showed declines in mercury concentrations in WCAs 1, 2, and 3, similar to earlier observations of EHg3. However, at sites Holey Land WMA and North Prong Creek, dramatic increases in mercury were observed beginning in 1999 (**Figure 3B-9**). After 2002, concentrations declined somewhat in North Prong Creek and may represent a shift towards less mercury bioaccumulation. Nevertheless, mercury levels remain highly elevated relative to other Everglades sampling areas.

The most current data (EHg3 values from 2005 and 2006) suggest that mercury bioaccumulation increases in largemouth bass are moving further south in the EPA (**Table 3B-1**). The lowest EHg3 was observed in the L-7 Canal in WCA-1, while the highest value was observed at the most southernmost site at North Prong Creek in the ENP. It is apparent that the Shark River Slough in the ENP, as indicated by data from sites North Prong Creek and L67F1 (Rumbold et al., 2007), has a significant mercury problem.

Feathers of great egret (*Ardea alba*) nestlings were collected between 1994 and 2005 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-10** and **3B-11**).

Table 3B-1. Trends in age-standardized mercury levels in largemouth bass (EHg3) for various periods of record (POR) at eight long-term monitoring sites in the Everglades. The percent change contrasts the highest observed EHg3 (maximum) with the most recent EHg3 (current) and is reported as the percent change. Sites are aligned from north to south and EHg3 is reported as µg/g = mg/kg = ppm).

Location	Reported POR	Maximum EHg3 (Year)	Current Year EHg3	% Change From Maximum
WCA1				
L-7 Canal	1995–2005	0.61 (1996)	0.24	-61
LNWR Marsh	1995–2005	0.88 (1996)	0.50	-43
Holey Land WMA				
Holey Land	1996–2005	0.75 (1997)	0.75	NC
WCA2A				
WCA2A-U3 Marsh	1993–2005	1.27 (1993)	0.74	-42
L35B Canal	1993–2005	1.33 (1993)	0.74	-44
WCA3A				
L67A Canal	1990–2005	1.96 (1992)	0.62	-68
WCA3A-15 Marsh	1993–2005	2.39 (1993)	0.70	-71
ENP				
North Prong Creek	1994–2006	2.37 (1994)	1.40	-40
Average			0.71	-46

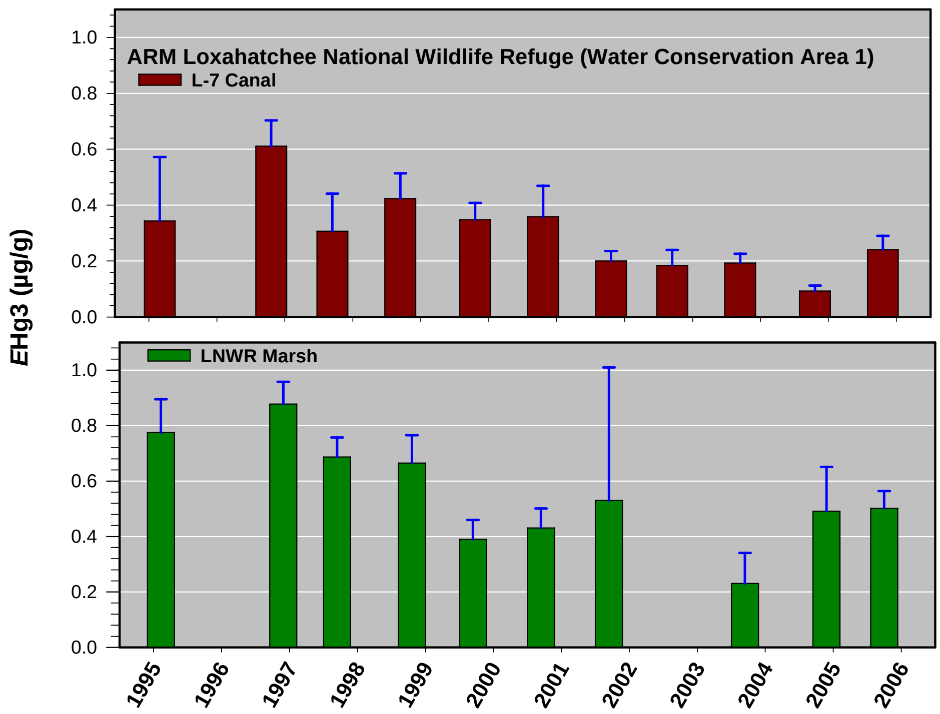

Figure 3B-3. Age-standardized mercury concentration (EHg3) (µg/g = mg/kg = ppm) and the 95% confidence interval (95% C.I.) in largemouth bass at long-term monitoring sites located within the Loxahatchee National Wildlife Refuge (WCA-1).

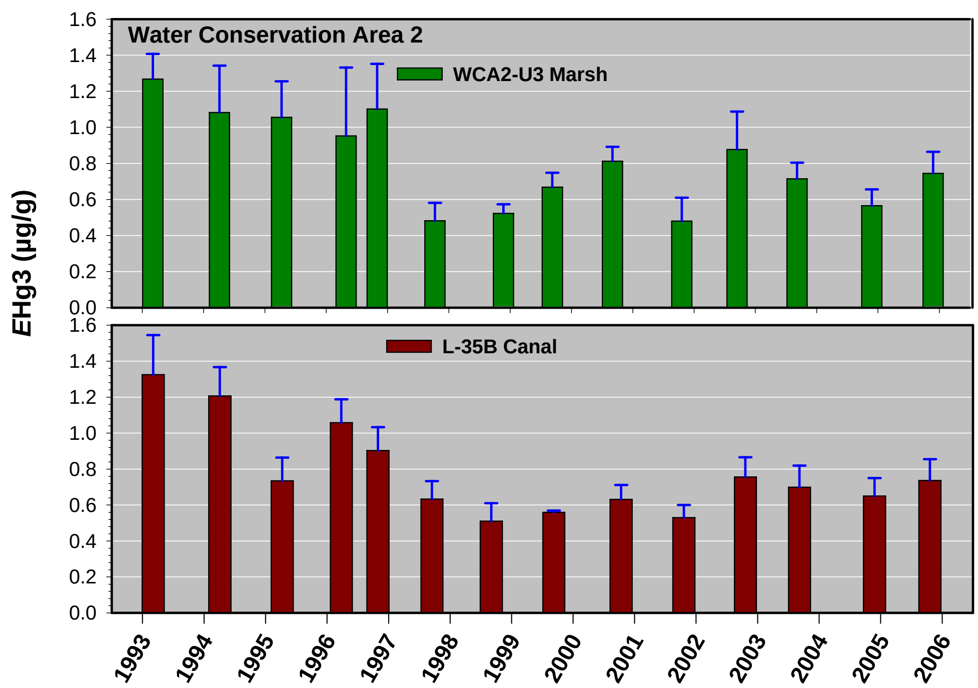

Figure 3B-4. Age-standardized mercury concentration (EHg3) (µg/g = mg/kg = ppm) and the 95% confidence interval (95% C.I.) in largemouth bass at long-term monitoring sites located within WCA-2.

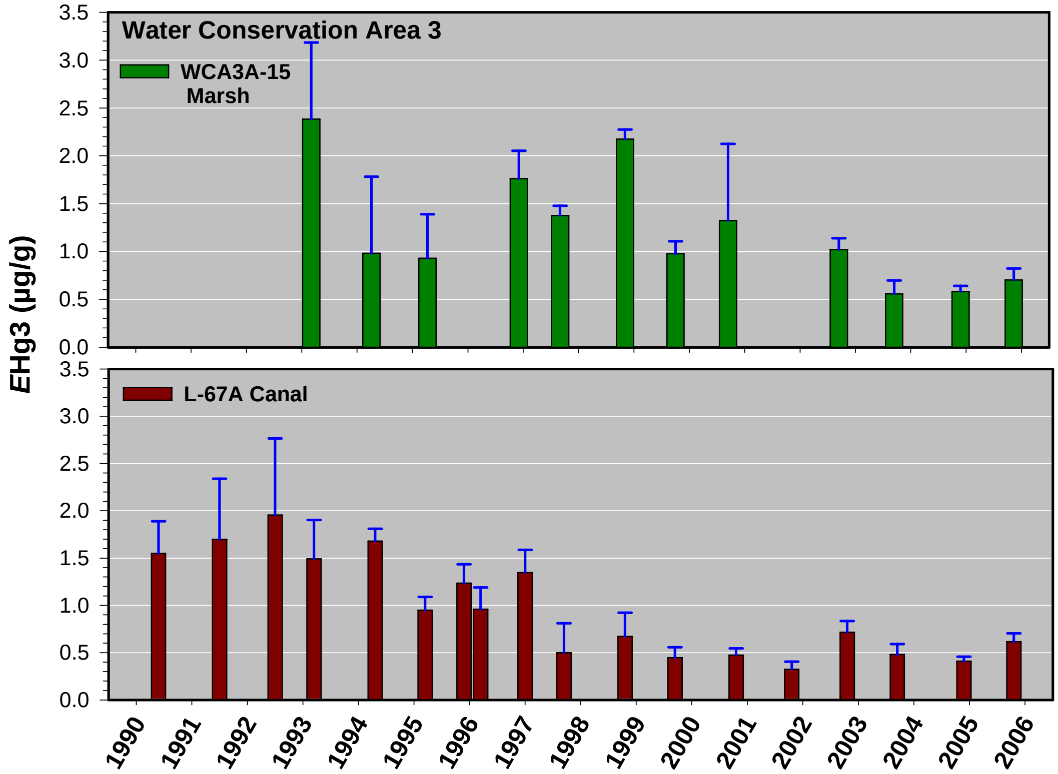

Figure 3B-5. Age-standardized mercury concentration (EHg3) (µg/g = mg/kg = ppm) and the 95% confidence interval (95% C.I.) in largemouth bass at long-term monitoring sites located within WCA-3.

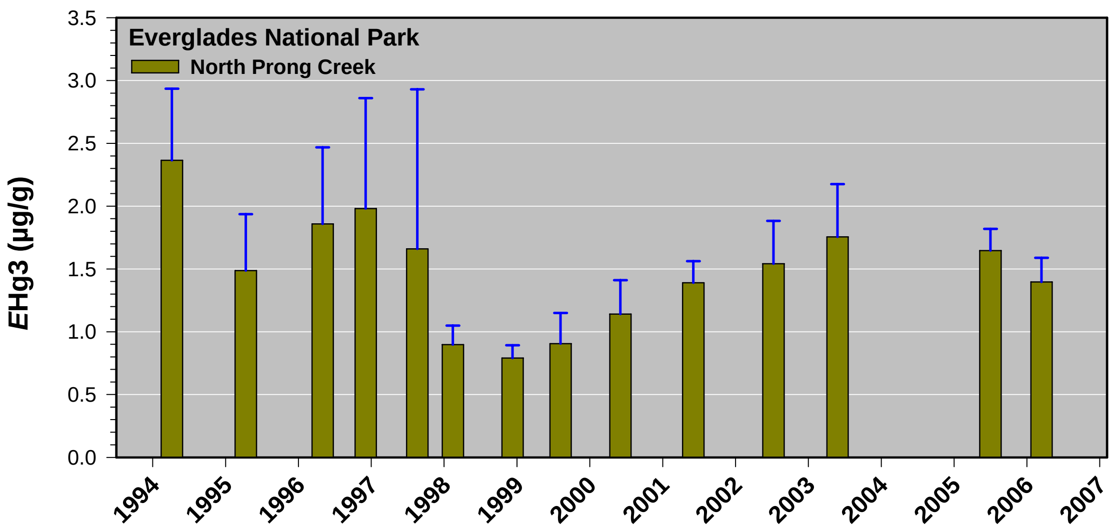

Figure 3B-6. Age-standardized mercury concentration (EHg3) (µg/g = mg/kg = ppm) and the 95% confidence interval (95% C.I.) in largemouth bass from North Prong Creek in Everglades National Park (ENP).

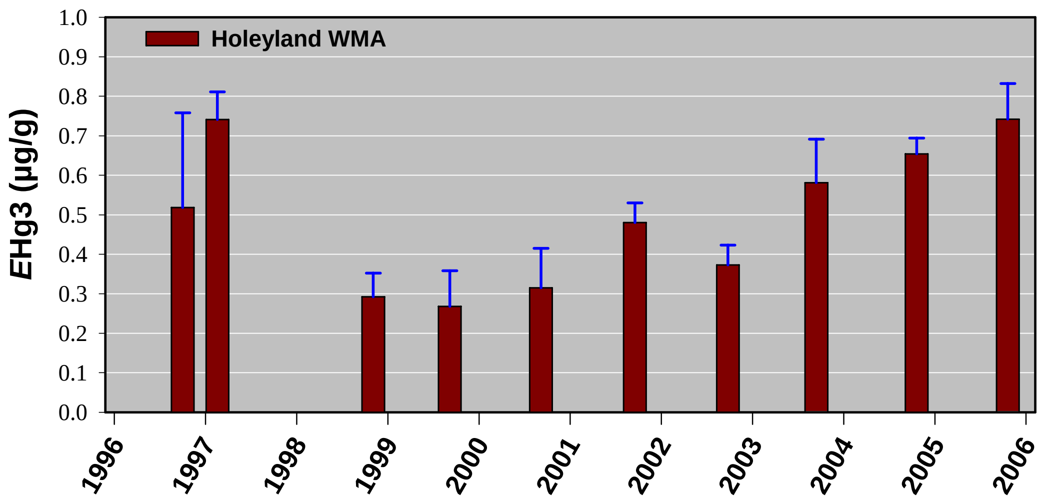

Figure 3B-7. Age-standardized mercury concentration (EHg3) (µg/g = mg/kg = ppm) and the 95% confidence interval (95% C.I.) in largemouth bass from the perimeter canal in Holey Land WMA.

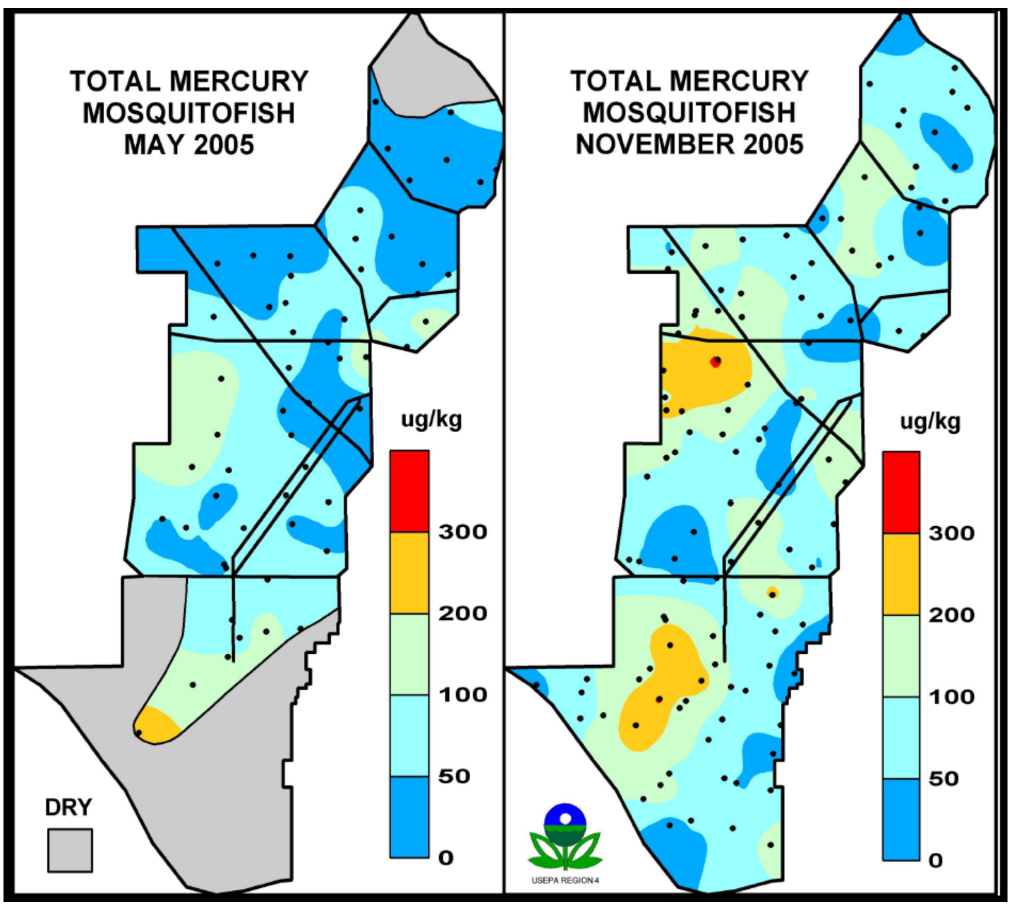

Figure 3B-8. USEPA REMAP sampling of mercury in mosquitofish *(Gambusia affinis)*, wet (November) and dry (May) seasons, 2005.

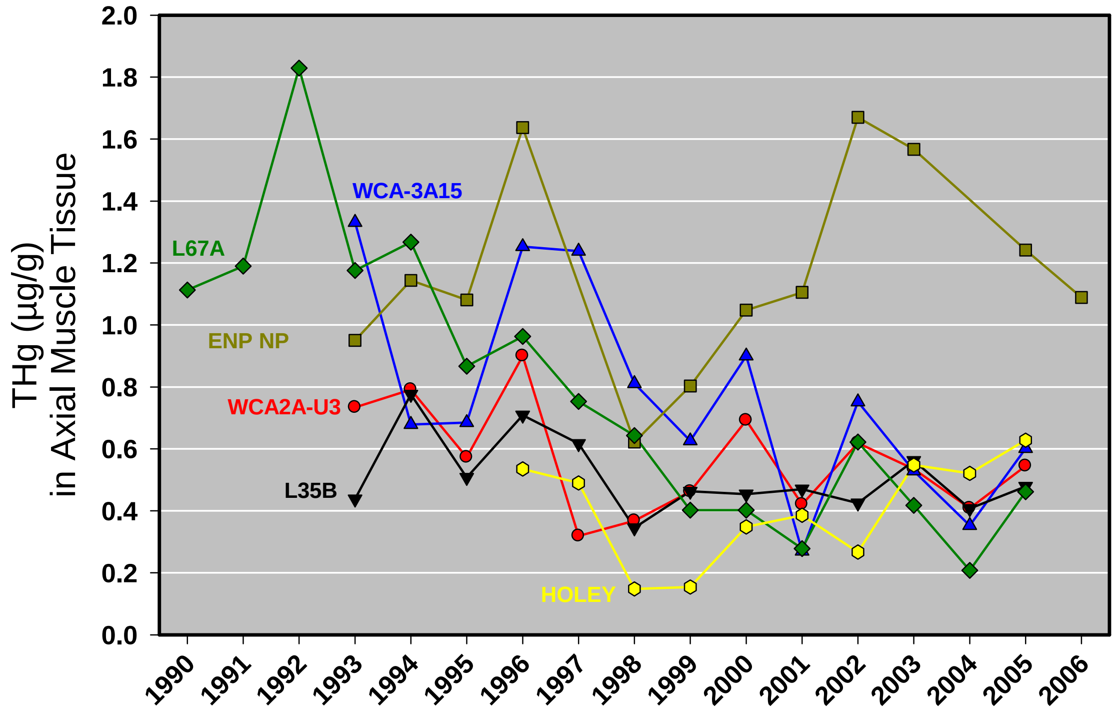

Figure 3B-9. Time series of geometric mean mercury concentrations for largemouth bass (age 1-2 cohort) for five Everglades sites. Sites L-35B and L-67A are canal sites in WCA-2 and WCA-3, respectively and sites U3 and 3A-15 represent interior marsh sites located in WCA-2A and 3A, respectively. The ENP NP site is located in the ENP (North Prong Creek) in the Shark River Slough and Site HOLEY is located in the canal within Holey Land WMA.

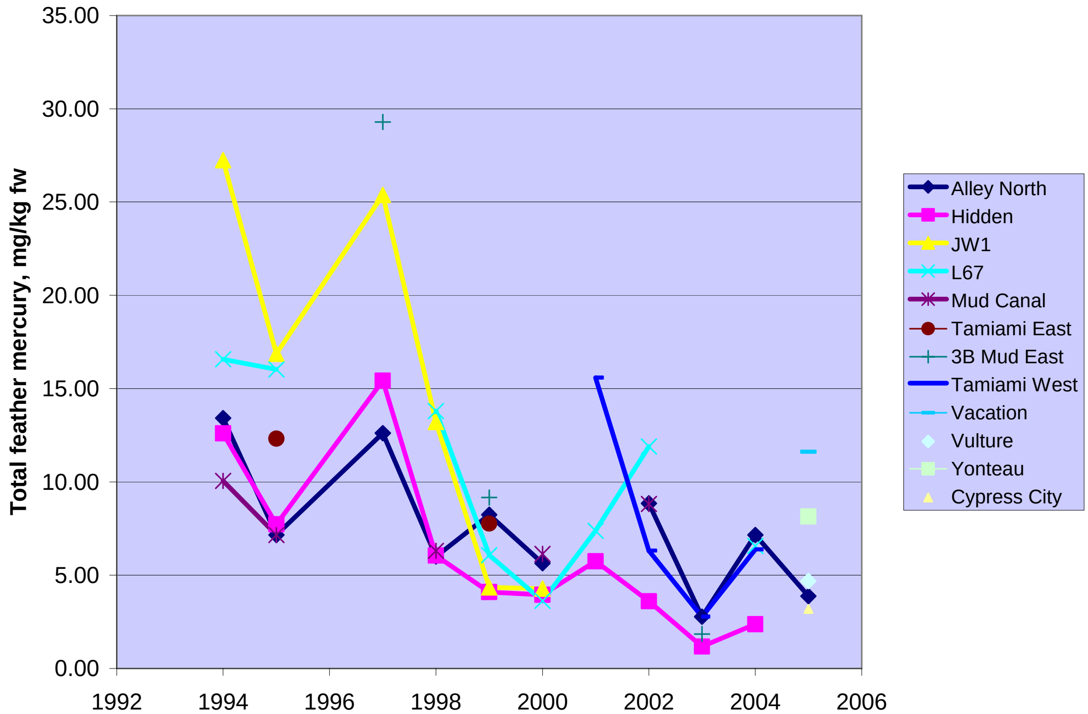

Figure 3B-10. Mercury concentrations in feathers in great egret nestlings at various colony locations in the Everglades from 1994–2005. Discontinuities in the period of record reflect years when a colony site was abandoned or otherwise not used (Frederick, 2006 pers. comm.; Frederick et al., 2002).

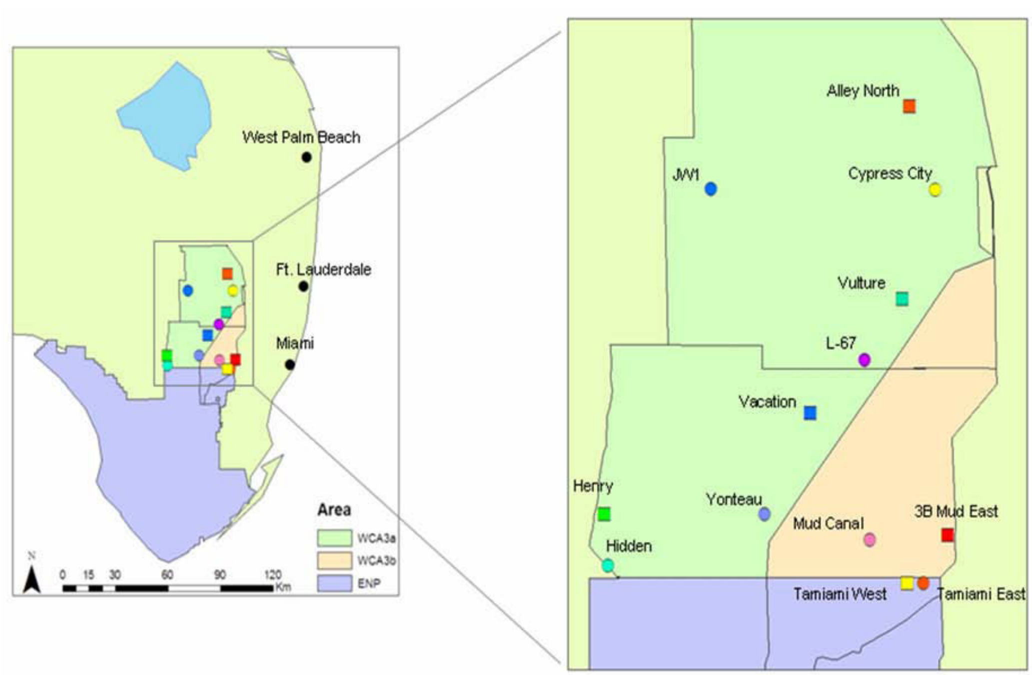

Figure 3B-11. Great egret colony locations where feathers from nestlings were sampled from 1994 to 2005.

Fish-eating avian and mammalian wildlife continue to be at risk of adverse effects from mercury exposure in the Shark River Slough area of the ENP as mercury concentrations in trophic level (TL) 3 and TL 4 species, sunfish and largemouth bass respectively, exceed established USFWS (Eisler, 1987) and USEPA wildlife criteria levels (USEPA, 1997a).

At the North Prong Creek site in the Shark River Slough, the mean mercury concentration in largemouth bass from age cohort 1-2 (TL 4) exceeded 1.2 µg/g in 2006. Likewise, largemouth bass from age cohorts 1-2 collected at site L67F1 in the upper regions of Shark River Slough in 2005 (Rumbold et al., 2007) had a mean concentration of 1.00 µg/g. Mercury concentrations in both populations in the Shark River Slough were well in excess of USEPA's recommended criteria of 0.346 µg/g for the protection of wildlife. Similarly, the mean mercury concentration in bluegill (*Lepomis macrochirus*) collected from site L67F1 was 0.41 µg/g in 2005, exceeding both the USFWS and USEPA criteria for protection of wildlife for TL 3 fish.

Supporting these data suggesting excessive MeHg exposure to wildlife, a probabilistic risk assessment of MeHg exposure to three piscivorous bird species (bald eagle, wood stork, and great egret) foraging at the L67F1 MeHg hot spot in northern ENP indicated a very high likelihood (98–100 percent probability) that these birds would experience exposures above the acceptable dose. Moreover, the likelihood that these birds would experience exposures above the LOAEL ranged from a 14 percent probability for the wood stork to 56 percent probability for the eagle (Rumbold et al., In Review).

The FDEP Class III water quality criterion of 12 nanograms per liter (ng/L) total mercury in fresh waters is not being routinely exceeded anywhere in the EPA. Nevertheless, the sport fishery is under public health advisories and wading birds are exposed to potentially problematic levels of methylmercury in their diets. To help address the mercury problem, the FDEP will develop new mercury criteria to protect human health and wildlife (Redfield, 1999).

In summary:

- Mercury levels in largemouth bass at many sites in the WCAs have declined about 30–70 percent from levels of the late 1980s and early 1990s, but have not declined greatly from 1998 to the present.
- Mean mercury concentrations in largemouth bass in WCAs remain higher than the USEPA recommended MeHg fish tissue criterion.
- Very high concentrations of mercury in largemouth bass are presently evident in portions of the ENP, and mercury levels are increasing 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 threaten piscivorous birds and mammalian wildlife.

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., In Press).

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. (2005) 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 analysis 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 2005 (NADP, 2006). 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 late 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.

MDN data for the three South Florida sites (FL11, FL04, and FL34; **Figure 3B-12**) were downloaded from the MDN web site for the entire period of record available (i.e., through the end of 2005). 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, precipitation depth, and VWM mercury concentrations are presented for all three South Florida sites in **Figures 3B-13** through **3B-15**. Each of the three time series plots is presented as a running annual total (precipitation depth and mercury deposition) or concentration (VWM). Not surprisingly, the deposition flux of mercury is closely related to the precipitation depth — this in part is because the deposition flux of mercury is the product of precipitation depth.

In addition, although mercury deposition flux is also a product of the wet deposition concentration of mercury, it is more closely related to precipitation depth because the degree of variation for the two variables is higher for rainfall (88 versus 61 percent relative standard deviation respectively for rainfall and concentration, respectively, while the interquartile range

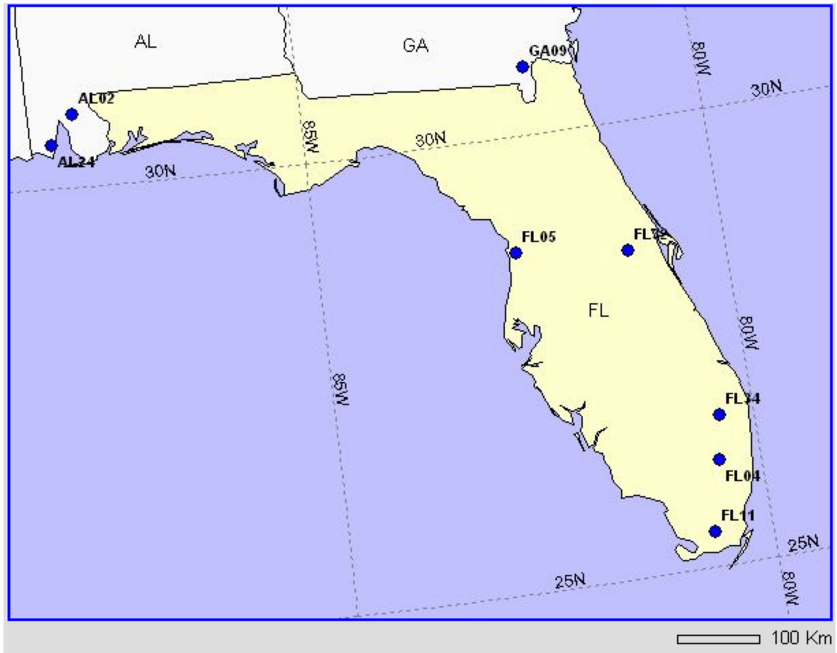

Figure 3B-12. The National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) South Florida total mercury wet deposition sampling sites – FL34 Everglades Nutrient Removal Project, FL04 Andytown, and FL11 Everglades National Park Beard Research Center (NADP, 2006).

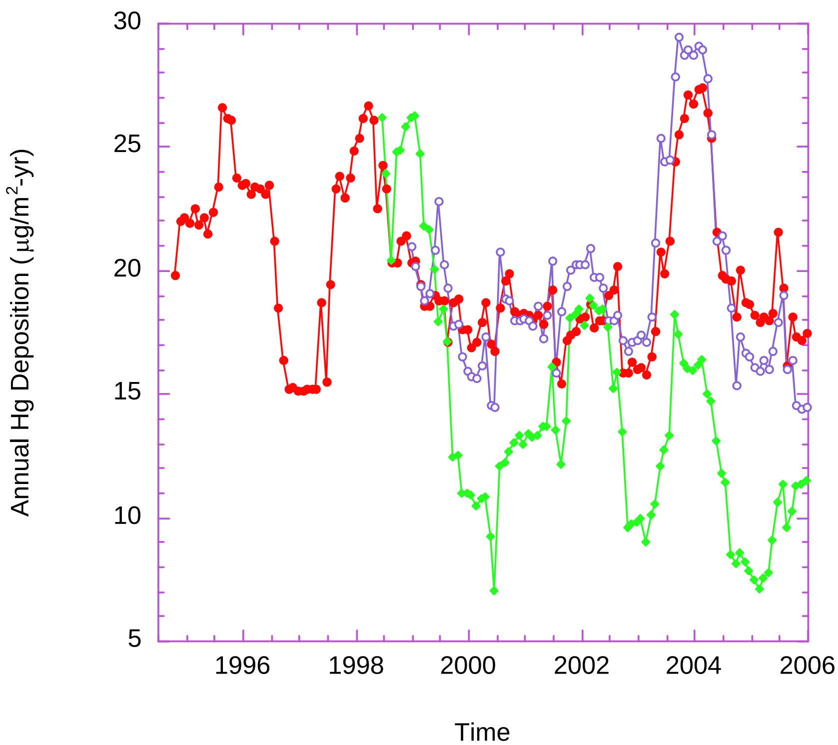

Figure 3B-13. Running annual fluxes of mercury in wet deposition in south Florida, 1995 through 2005. Fluxes are calculated monthly based on the current month and previous 11 months of data. Red closed circles are FL11, blue open circles are FL04, and green closed diamonds are FL34.

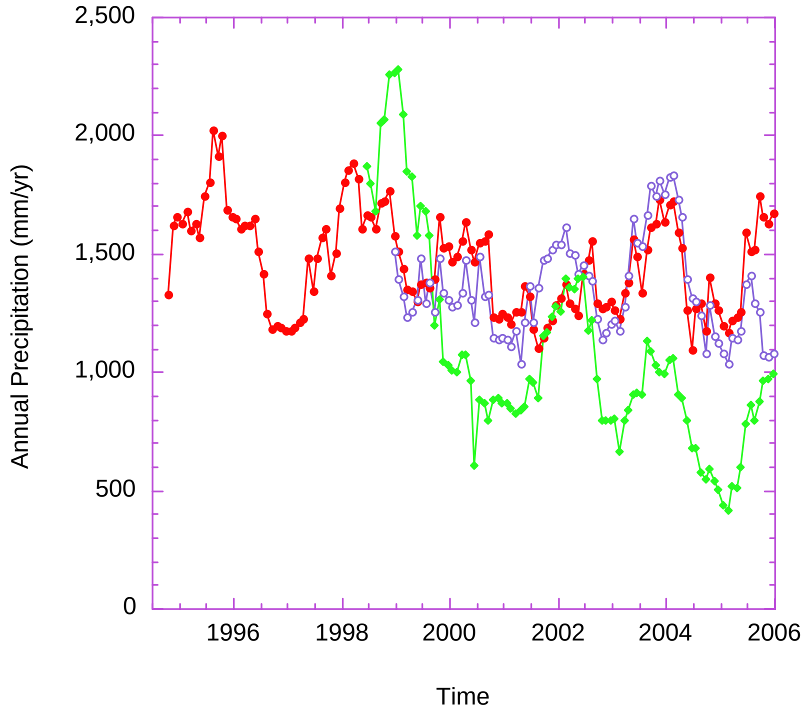

Figure 3B-14. Running annual fluxes of precipitation in south Florida, 1995 through 2005. Fluxes are calculated monthly based on the current month and previous 11 months of data. Red closed circles are FL11, blue open circles are FL04, and green closed diamonds are FL34.

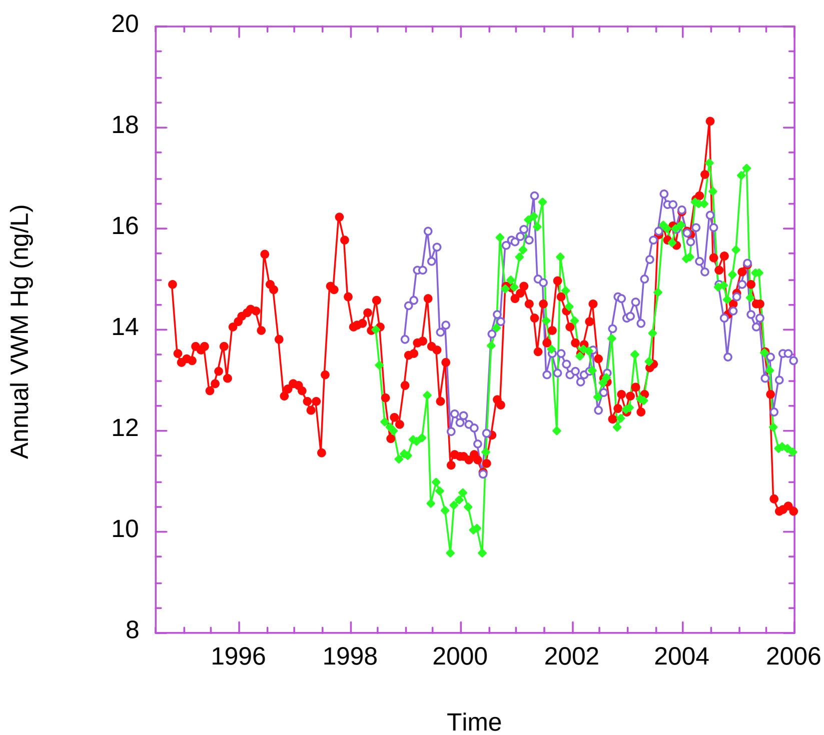

Figure 3B-15. Running annual volume-weighted mean concentration of mercury in wet deposition in south Florida, 1995 through 2005. Fluxes are calculated monthly based on the current and previous 11 months of data. Red closed circles are FL11, blue open circles are FL04, and green closed diamonds are FL34.

for rainfall spans a factor of nearly 6 compared to a factor of only ca. 2 for concentration). Examination of collocated MDN measurements gave no indication of contamination emanating from the site or its locale.

The highest deposition flux for the entire period of record was for a six-month interval between late 2003 and early 2004. During that time, the deposition flux ranged from 24.5 to 27.5 $\mu g/m^2$-yr at site FL11. Similarly high levels during the same period were observed at site FL04 (Andytown) approximately 140 km north of site FL11 (maximum deposition flux of 29.5 $\mu g/m^2$-yr).[14]

What is most notable about this interval of increased deposition was that the increase was not due simply to increased volumes of precipitation; as **Figure 3B-15** illustrates. VWM concentrations of mercury in wet deposition were comparatively elevated during this period as well. As a result, mercury wet deposition fluxes at site FL11 were elevated by an additional 11 percent or more compared to other intervals of coincident high precipitation and wet deposition fluxes (**Figure 3B-16**).

The VWM concentrations for all three sites were remarkably similar during the high-deposition flux interval, and suggest that the factors contributing to this flux were larger in scale than local sources. Further analysis using data from MDN stations across the U.S. for the period (late 2003 and early 2004) when FL11 had an elevated wet deposition mercury signal indicated that all four of the Florida MDN sites considered in the analysis show this elevated mercury signal, but that the elevation was not observed elsewhere in the United States.

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), seasonal dynamics was factored out by fitting the monthly VWM data to a form of sinusoidal model similar to that previously used by Atkeson et al. (2005). 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. Not surprisingly given the magnitude of deposition that occurred in 2003, virtually no long trend in the mercury wet deposition signal can now be discerned (slope = -0.003 ng/L-yr; $p = 0.987$).

Because mercury deposition between March and August 2003 was anomalously high compared to monthly fluxes observed in other years **(Figure 3B-17**), the ANOVA was revised to help determine whether the high deposition fluxes during this period were responsible for eliminating the declining trend seen prior to 2003. In revising the analysis, data from March through August 2003 — the period of elevated wet deposition mercury signal — was eliminated from the time series. The seasonal model to predict seasonal dynamics then was revised to reflect the changes in the dataset.

The residuals from the revised ANOVA are plotted as a function of time in **Figure 3B-18**. The downward trend was strengthened by removing the six months of 2003 in question, but the overall 1996–2005 trend in mercury wet deposition at FL11 (Beard Research Center) at ENP is still not significant (slope = -0.149 ng/L-yr, with 95 percent UCL and LCL on slope equal to +0.110 and -0.407 ng/L-yr, respectively; $p = 0.245$). As FL11 appears to have the most pronounced trend over time as well as the longest period of record of the three South Florida MDN sites, it is evident that FL34 and FL04 have no trend in mercury wet deposition for the period of record either.

[14] Lower fluxes were observed during the same interval at FL34 due to lower recorded precipitation volumes that, between 2002 and 2005, totaled only 56–63 percent of the amounts measured at sites FL11 and FL04, respectively.

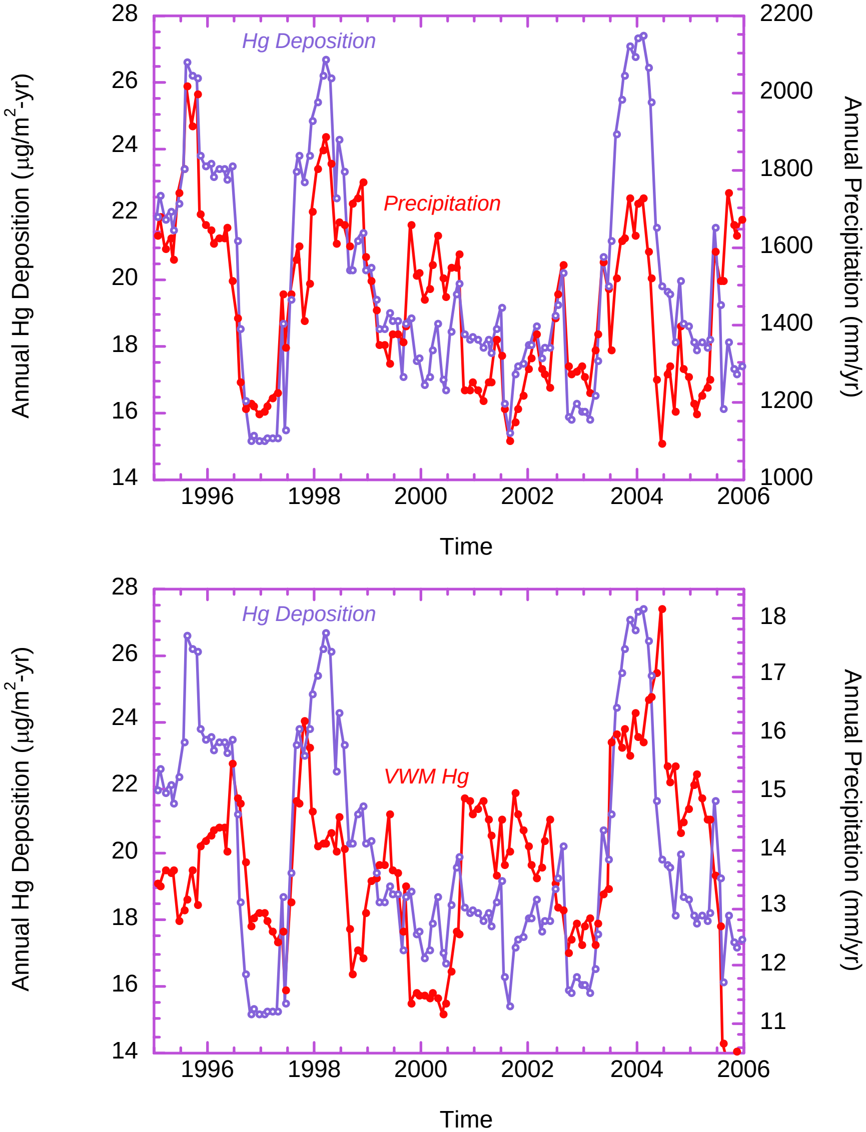

Figure 3B-16. Annual running totals for Hg wet deposition and precipitation fluxes (upper panel) and Hg wet deposition fluxes and VWM Hg concentrations in wet deposition (lower panel) for site FL11.

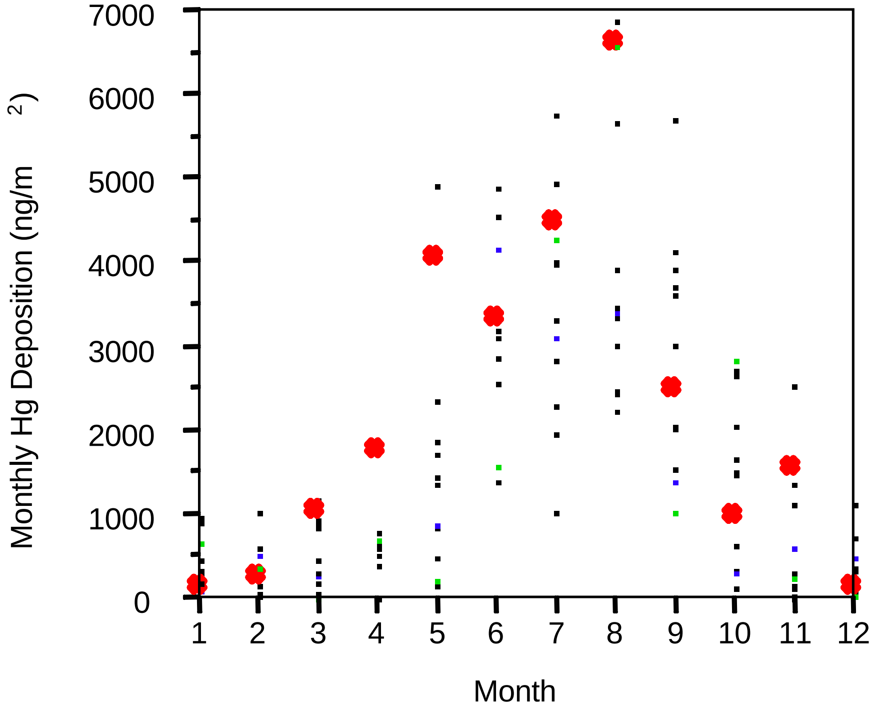

Figure 3B-17. Monthly wet deposition fluxes observed at site FL11 (November 1993 – December 2005. Red markers highlight deposition that occurred in 2003.

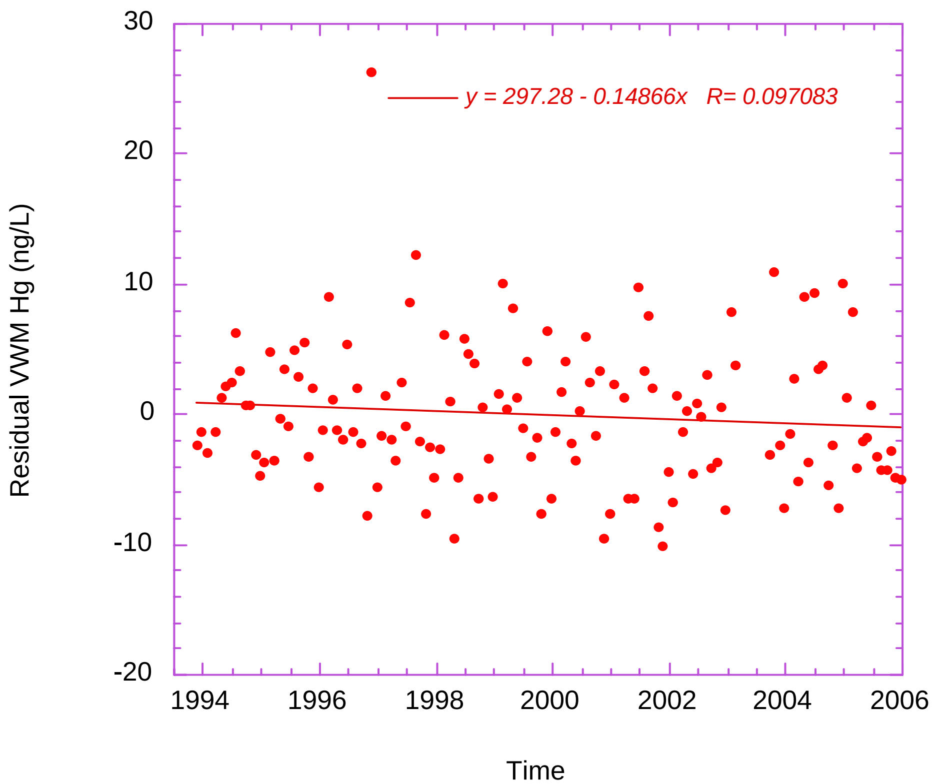

Figure 3B-18. Time series plot of the analysis of variance model residuals (observed – predicted) used to predict monthly VWM concentrations of Hg in wet deposition as a function of precipitation and seasonal dynamics at site FL11. Data include all monthly observations except the high deposition period, March–August 2003.

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-19**).
- The primary air emissions sources of mercury in South Florida ca. 1990 were incineration of municipal and medical wastes. Mercury emissions from incinerators of all types have since declined by approximately 90 percent.
- Although at the peak levels of atmospheric deposition of mercury in South Florida ca. 1990, the precise proportions of locally derived versus globally derived mercury remain uncertain, the data analyses indicate that the majority of mercury deposition to the Everglades originated from sources within South Florida.
- Presently, anthropogenic point source emissions of mercury from South Florida are calculated to be a small fraction (about 10 percent) of peak historical levels (ca. 1990); however, South Florida mercury sources remain poorly quantified.
- There was no significant trend during 1994–2005 in mercury wet deposition in South Florida.

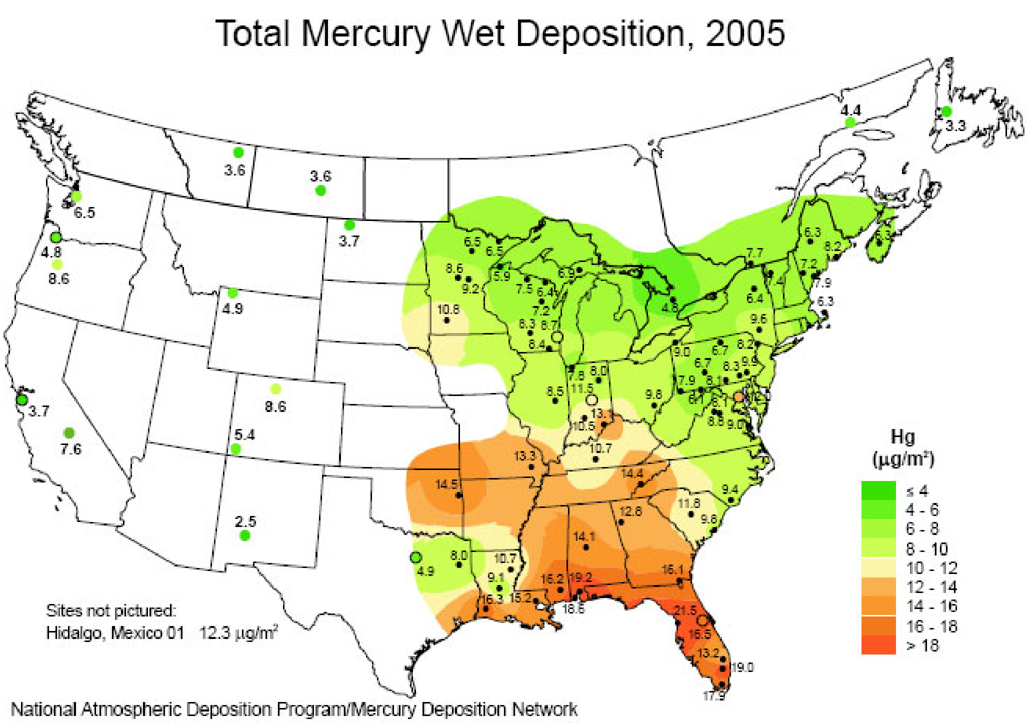

Figure 3B-19. Wet deposition of total mercury (micrograms/m^2) in 2005. Data from National Atmospheric Deposition Program's Mercury Deposition Network (NADP, 2006)

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 appears to be determined by the balance between sulfate and sulfide; methylation is generally highest at ca. 2–20 mg/L sulfate in Everglades surface waters (Gilmour et al., 2007a) where porewater sulfide concentrations are moderate (5–150 ppb or µg/L) (Gilmour et al. 1998; Benoit et al., 2003).

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, 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).

Freshwater wetlands typically have low sulfate concentrations; concentrations in the Everglades, however, are relatively high due to major inputs of sulfate to the ecosystem (Orem, 2004). Surface water sulfate concentrations in northern Everglades marshes can reach ca. 100 times historical (Everglades background) levels, averaging about 40-70 mg/l in WCA-2 compared to <1 mg/l in parts of the ecosystem further south and away from canal discharges (Bates et al., 2002; Gilmour et al., 2007b; Weaver et al., 2007; **Figure 3B-20)**.

Highest surface water sulfate concentrations (excluding marine-influenced sites) were observed in Everglades Agricultural Area (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. 2007; Orem et al., In Press). Sulfate concentrations elevated above background levels (1 mg/l) are evident in about 60 percent of freshwater Everglades marshes (**Figures 3B-21** and **3B-22**).

The extent of sulfate enrichment was first documented by Orem et al. (1997), and later confirmed by Bates et al., 2002 and Stober et al., 2001. Sulfate, similar to several other water quality parameters entering the Everglades, including for example conductivity and phosphate, generally shows a north to south concentration gradient in surface waters (McCormick et al., 2000), with higher concentrations in the north (excluding e.g. WCA-1) (**Figure 3B-23**).

As regards phosphate, research has demonstrated that fertilizer washed from EAA soils during rain events, is transported to canals, and eventually discharged into the Everglades (Payne et al., 2003). Agricultural sulfur (comprising ca. 98 percent elemental sulfur) is used as a soil amendment in the EAA to solubilize micronutrients (Schueneman, 2000) and enhance uptake of phosphorus by crop plants (Bottcher and Izuno, 1994; Rice et al., 2006). Oxidation of agricultural sulfur in the aerobic soils of the EAA produces sulfate, which is highly water-soluble and may wash off fields into canals during rain events. As well, sulfate is used as a counter-ion (e.g., potassium sulfate) or as filler (e.g., gypsum) in some fertilizer formulations. This sulfate could then be delivered to the Everglades in the same manner as phosphate (Bates et al., 2002).

Based on sulfate concentration data, it can be concluded that Everglades sulfate sources originate, and have done so for a number of years, in canals draining the EAA (**Figure 3B-24**). Everglades sulfate concentrations are lowest in marsh areas in the south, gradually increase in marsh areas towards the north, reach peak concentrations in canals within and just downstream of the EAA, then drop at Lake Okeechobee and rivers to the north of the Lake (**Figure 3B-25**). Sites in the generally pristine freshwater marshes in the south with elevated sulfate concentrations are invariably located close to canal discharge or breaks in canal levees (Bates et al., 2002).

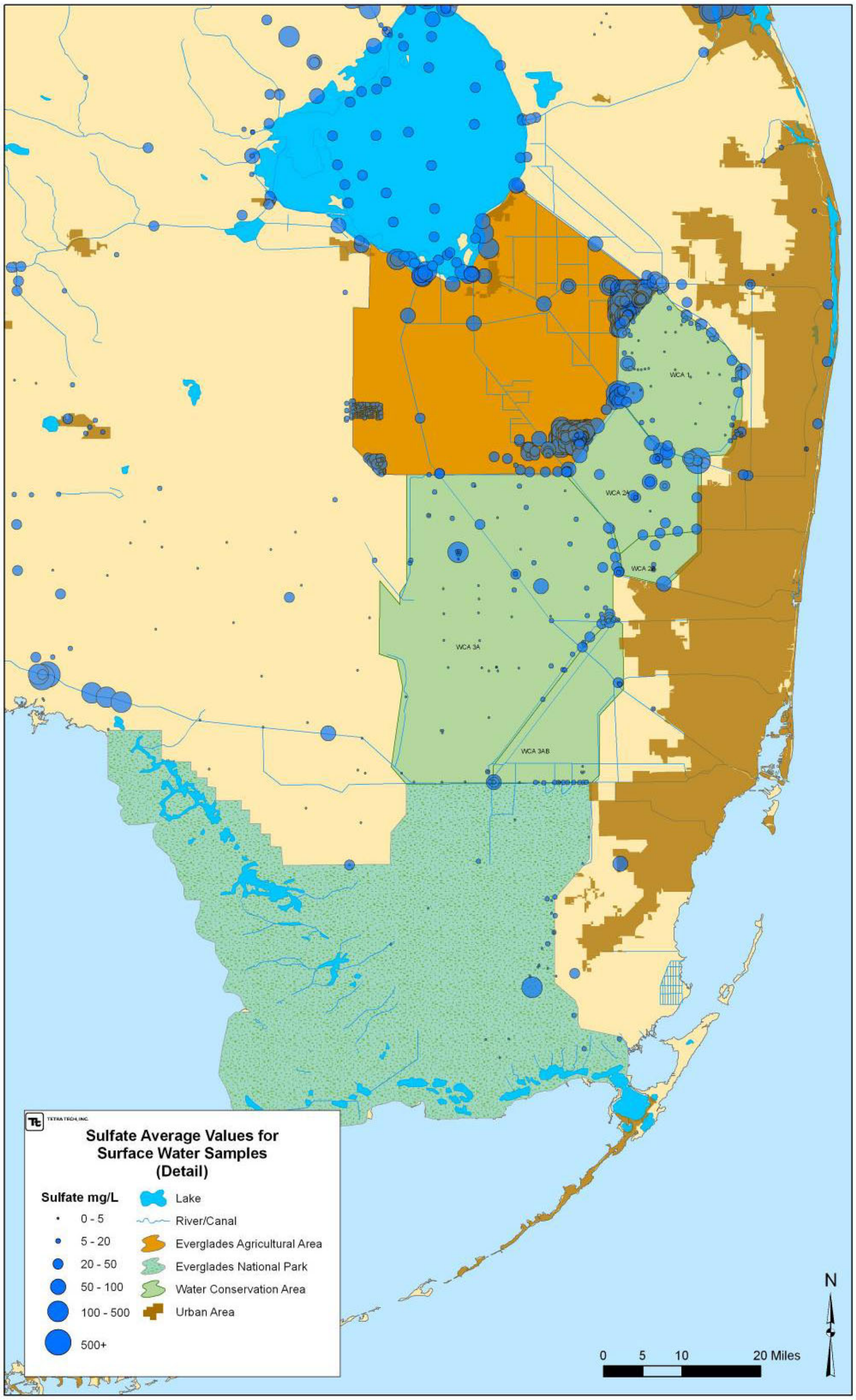

Figure 3B-20. Average surface water sulfate concentrations from the combined SFWMD/ACME dataset.

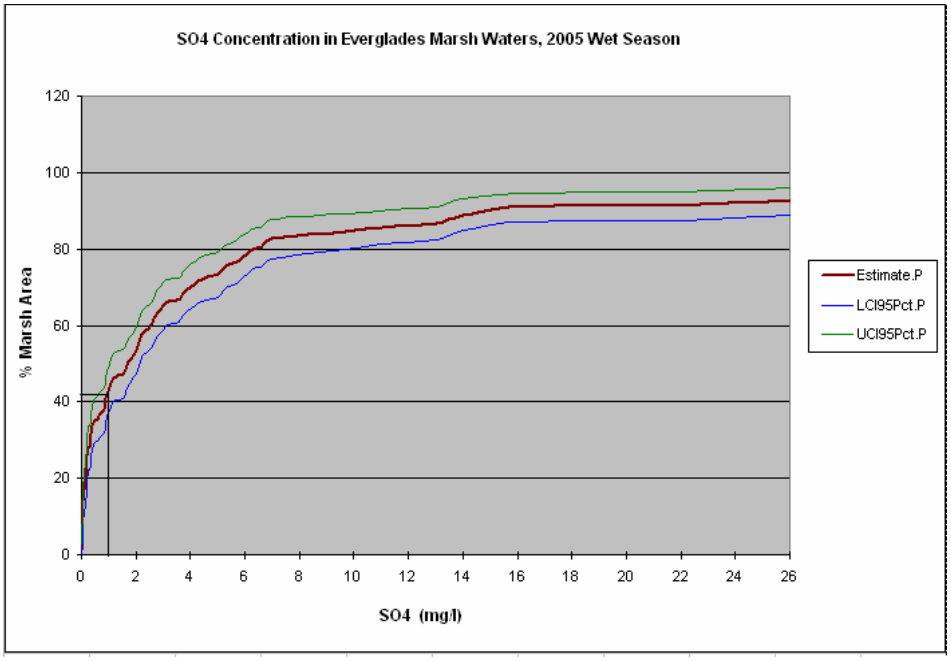

Figure 3B-21. Cumulative distribution function for sulfate in Everglades marsh surface waters, 2005 wet season, with 95% lower and upper confidence intervals (LCI95Pct.P and UCI95Pct.P), USEPA REMAP sampling.

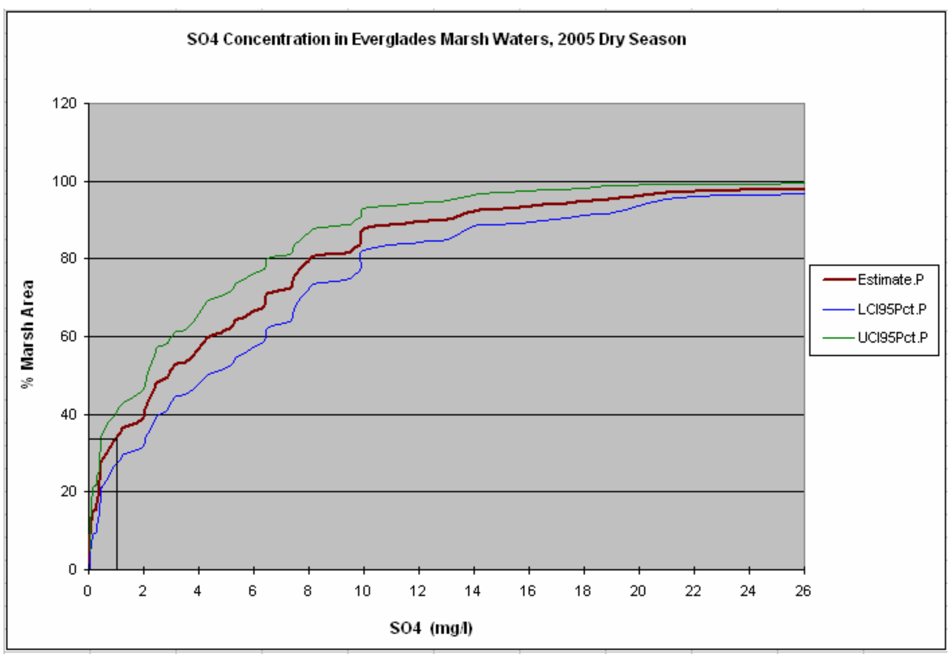

Figure 3B-22. Cumulative distribution function for sulfate in Everglades marsh surface waters, 2005 dry season, with 95% lower and upper confidence intervals (LCI95Pct.P and UCI95Pct.P), USEPA REMAP sampling (marine-influenced station excluded).

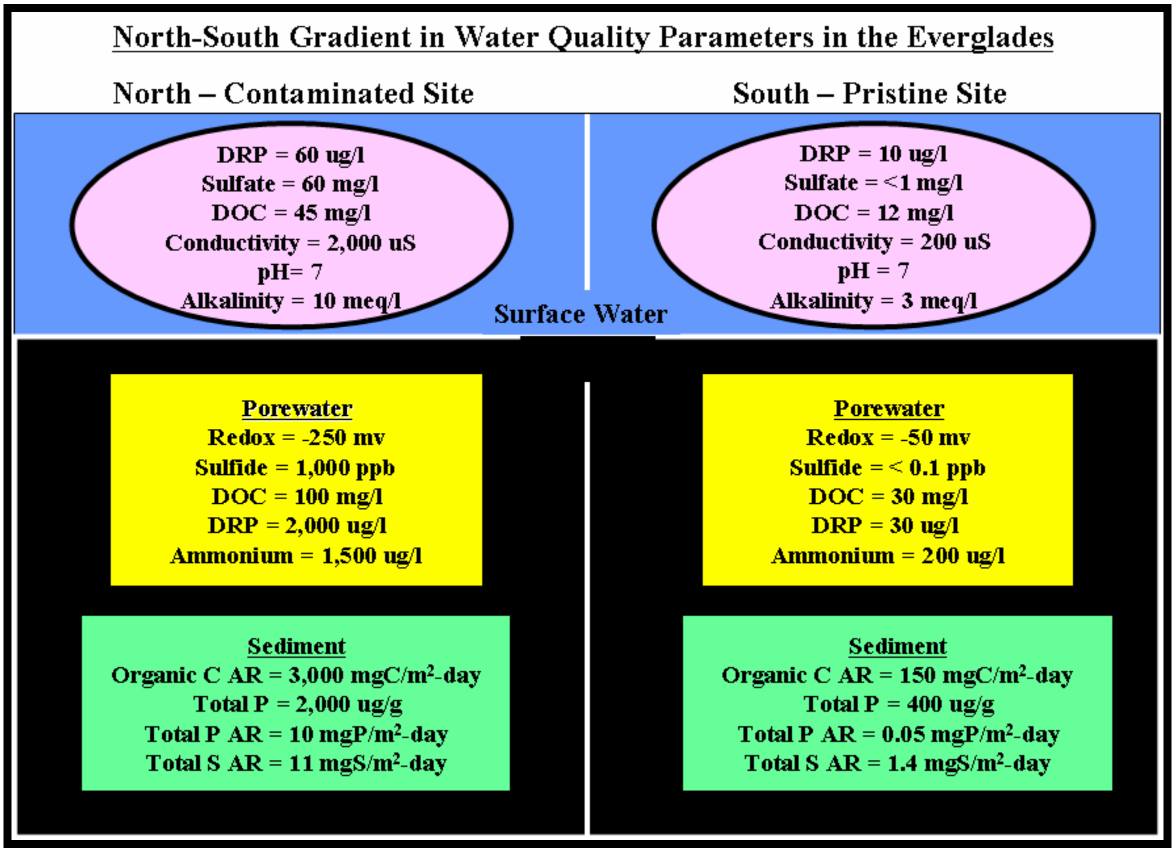

Figure 3B-23. Synopsis of the North-South gradient in chemical parameters observed in surface water, porewater, and sediments in the Everglades. Figure compiled from USGS data collected from 1994-2006. DRP = dissolved reactive phosphorus, DOC = dissolved organic carbon, and AR = accumulation rate.

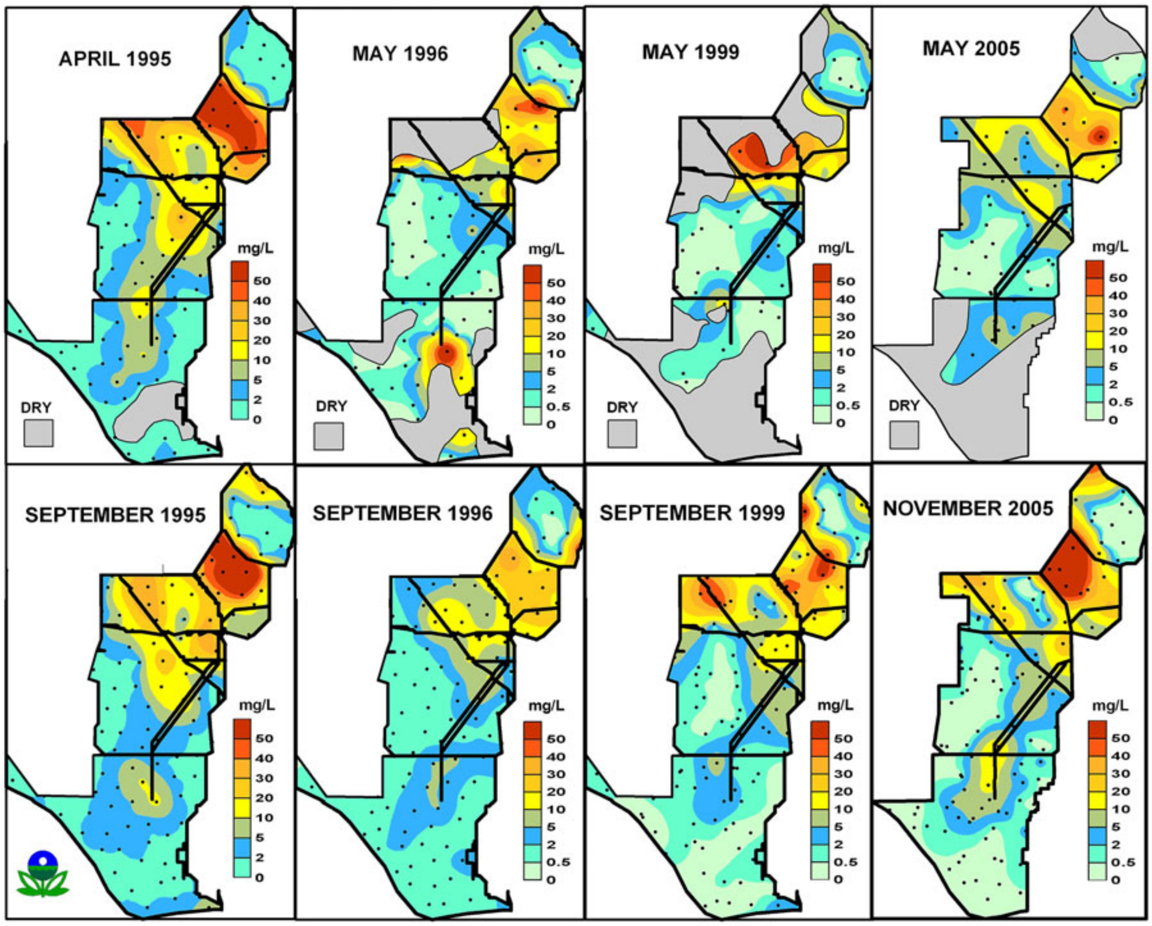

Figure 3B-24. Sulfate in Everglades surface waters, USEPA REMAP sampling 1995, 1996, 1999, and 2005 dry (April/May) and wet (September/November) seasons.

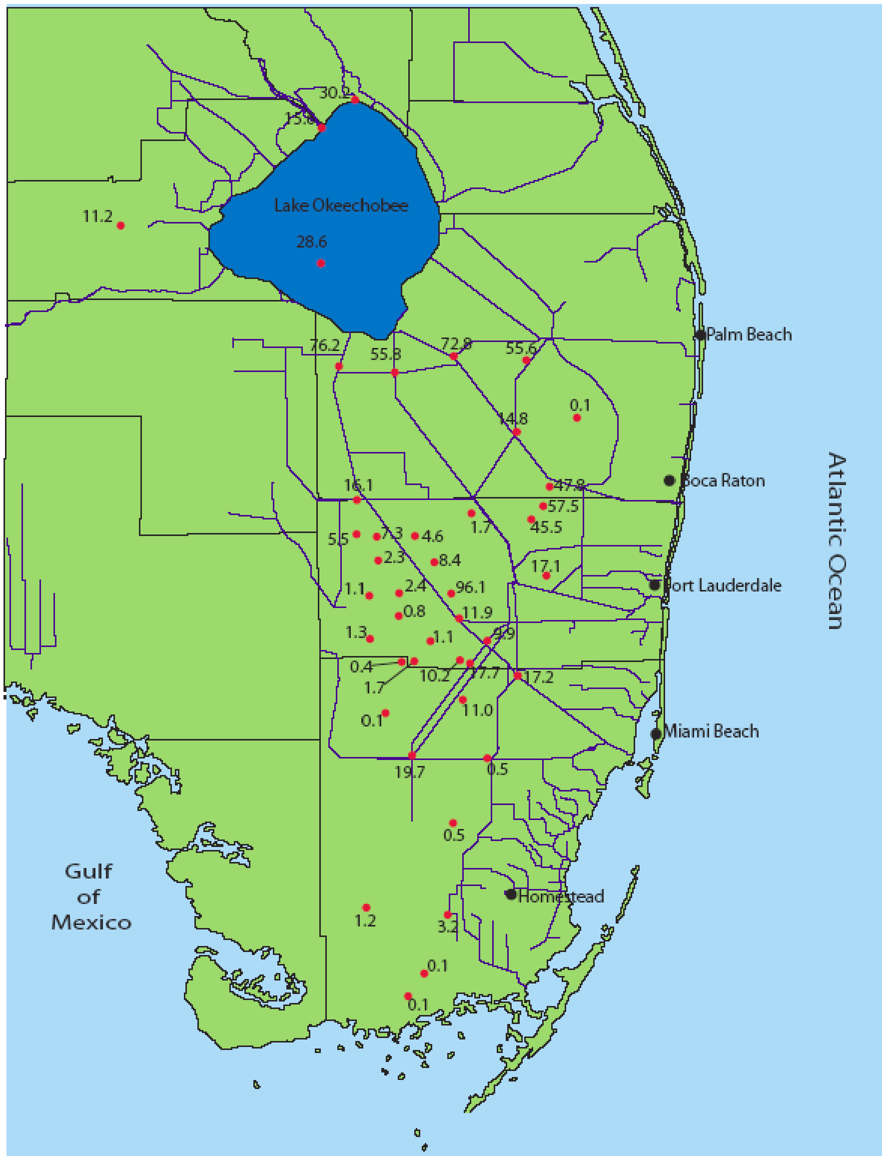

Figure 3B-25. Average sulfate concentrations (mg/l = ppm) in surface water in the South Florida ecosystem, including Lake Okeechobee and its drainage, EAA canals, and the freshwater Everglades, from USGS sampling 1994–2000 (Orem et al., In Press).

In essence, in locations where rainfall has a much greater influence than canal water transport on interior marsh water quality, sulfate concentrations, and conductivity are low; moreover, sulfate and conductivity gradients always decrease away from the areas of canal overflow and points of canal discharge.

Evaluation of sulfate sources was conducted at marsh site F1, located ca. 2 km southwest of the S10C discharge structure of the Hillsboro Canal. Site F1 is representative of sites in the northern Everglades with high conductivity and containing elevated concentrations of phosphate and sulfate (Bates et al., 2002). Data indicated that EAA canal water was the source of the sulfate to this site (Bates et al., 2002; Gilmour et al., 2007b):

(1) Rainwater had sulfate concentrations too low to account for the levels in the marsh surface water, and sulfur isotopic composition different from that of the marsh surface water (Waller and Earl, 1975; Bates et al., 2001, 2002).

(2) Shallow groundwater (<9 m depth) had sulfate concentrations too low to account for the sulfate concentrations observed in the marsh surface water (Bates et al., 2001, 2002).

(3) Deep groundwater (>9 m depth) at this site had high sulfate concentrations, but a sulfur isotopic composition and a sulfate/chloride ratio different from that in the marsh surface water (Bates et al., 2001, 2002; Orem, 2004).

(4) Nearby canal discharge water had a sulfate concentration and sulfur isotopic composition nearly identical to that of the marsh surface water (Bates et al., 2001, 2002) (**Figure 3B-26**).

From these findings, it is clear that EAA canal water is the source of sulfate to this marsh site.

The potential sources of the excess sulfate in EAA canals include agricultural application of elemental sulfur and sulfur compounds, rainfall, shallow groundwater, upwelling of deep groundwater (connate seawater), and Lake Okeechobee.

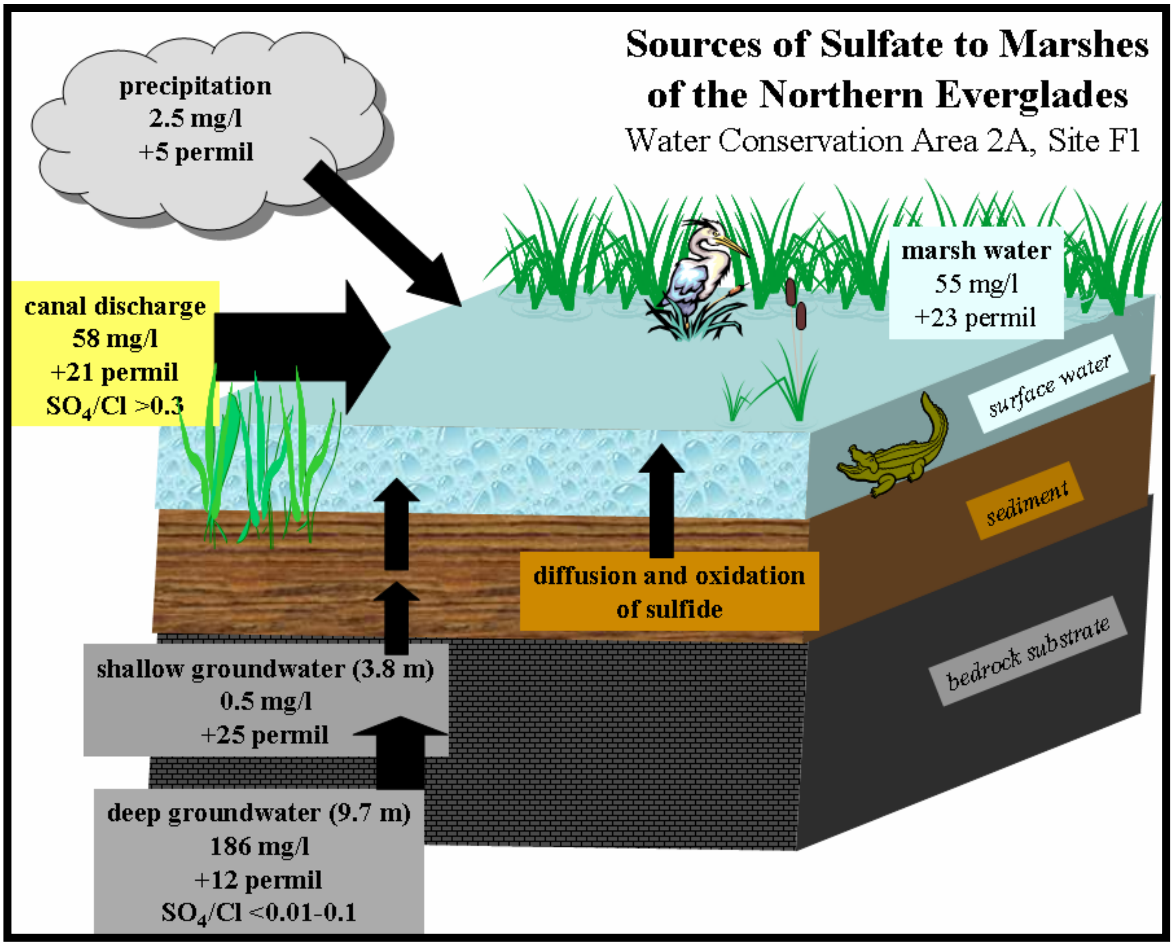

Figure 3B-26. Sulfur balance at a heavily sulfate enriched site (F1) in WCA-2A. Sulfate concentration, sulfate to chloride ratios and/or sulfur isotope (δ34S, permil) data indicate that EAA canal water discharge is the principal source of sulfur to the Everglades (Orem, 2004).

Considering the potential sources of the excess sulfate in EAA canals, the data (from the EAA, STA-1W, and Site F1) are consistent with agricultural sulfur applied as a soil amendment in the EAA, as most likely being the principal — but not the only — sulfate source (Bates et al., 2002; Gilmour et al., 2007b):

(1) Isotopic composition of EAA canal water sulfate was similar to that for agricultural sulfur as used in the EAA (Bates et al., 2002);

(2) Sulfur released from mineralization of EAA soils (Schueneman, 2000) plausibly was sourced in part from previously applied agricultural sulfur (Axelrad et al., 2006); EAA soil had sulfur isotopic composition similar to that of agricultural sulfur, but different from the isotopic composition of Everglades soil (Bates et al., 1998, 2002).

(3) In EAA canals where the highest sulfate concentrations occur, variation in sulfur isotopic composition declines markedly compared to that at sites with low sulfate, indicating that in EAA canals with high sulfate levels, a single source of sulfate becomes dominant (Bates et al., 2002). Sulfur isotopic composition in high sulfate EAA canal water approaches a value similar to that measured in agricultural sulfur and in sulfate extracted from shallow EAA soils (Bates et al., 2002).

(4) Groundwater, another possible source of sulfate to EAA canals, has a different sulfate concentration, isotopic composition and/or a different ionic composition (sulfate/chloride ratio) than canal water (Bates et al., 2002; Orem, 2004; Orem et al., In Press).

(5) Lake Okeechobee, which has elevated sulfate concentrations from rivers entering the Lake from the north that drain urban and agricultural lands (Zielinski et al., 2006), contributes sulfate to EAA canals. However the Lake, which has annual average sulfate concentrations less than half of those in EAA canals (ca. 30 mg/l versus ca. 70mg/l) (Bates et al., 2002), is also elevated in sulfate from EAA sources through backpumping and leakage from the heavily sulfate-contaminated rim canal.

(6) Additionally, Lake Okeechobee during times of normal rainfall has low sulfate concentrations compared to EAA canals, while during for example the 1998 "La Nina" drought, sulfate concentrations in EAA canal water dropped dramatically, to only slightly higher than concentrations in the Lake (Bates et al., 2002). It is probable that during prolonged dry periods, most water and sulfate in the EAA canals comes from Lake Okeechobee (Bottcher and Izuno, 1994), while during times of normal rainfall, EAA canal sulfate concentrations increase due to runoff from the EAA (Bates et al., 2002). At the same time, EAA canal flow rates increase delivering more water and sulfate to the EPA. These data suggest that the EAA, not Lake Okeechobee, is probably the principal sulfate source to EAA canals and Everglades marshes.

While existing data support the hypothesis that EAA canals are the principal source of sulfate to the Everglades, and sulfur used in EAA agriculture (new sulfur soil amendments and both legacy agricultural sulfur and natural sulfur released via mineralization of EAA soils) is the principal source — but not the only significant source — of sulfate to EAA canals, additional investigation of the sources of sulfate to EAA canals is necessary to further test this hypothesis.

Much of the ENP has surface water sulfate concentrations <1 mg/l **(Figures 3B-24** and **3B-25)**, a concentration that does not support high rates of mercury methylation (Gilmour et al. 2007a). There are however mercury hotspots for mosquitofish, sunfish and largemouth bass in the ENP, suggesting that sulfate is available at some sites in the ENP to allow sulfate-reducing bacteria to methylate mercury. Sulfate concentrations are shown to be higher than ENP background sulfate levels around the L-67 Extension canal in **Figure 3B-24.** As well, **Figure 3B-27** shows approximate correspondence between elevated levels of total mercury in Gambusia, and sulfate and conductivity around the L-67 Extension canal, suggesting that the canal may be a source of sulfate to the ENP. Additionally, data from L-67 Extension canal sampling 1993–1995 (Scheidt et al., 2000) and Gilmour et al. (2007a) show elevated sulfate in the canal. There is a need to conduct further monitoring to determine the sulfate sources to the ENP.

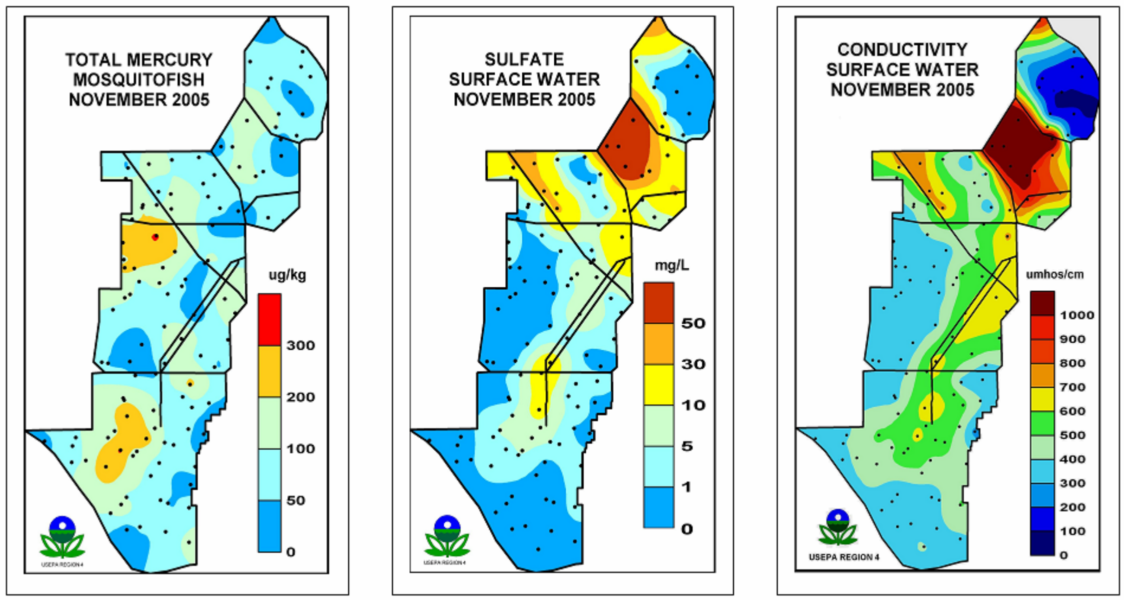

Figure 3B-27. Total mercury in Gambusia (mosquitofish), sulfate concentrations, and conductivity in the ENP, November (wet season) 2005 (USEPA REMAP data).

EFFECTS OF SULFUR

In addition to promoting methylation of mercury, sulfur can have other negative environmental consequences. Sulfide, which as hydrogen sulfide ("rotten-egg gas") is toxic, is a byproduct of sulfate reduction by SRB, and surface water sulfate concentrations in northern Everglades marshes can reach ca. 100 times historical levels (Bates et al., 2002; Gilmour et al., 2007b; Weaver et al., 2007). Northern Everglades sediment porewater sulfide concentrations show the effects of these sulfate inputs, with sulfide ranging from hundreds to thousands of ppb, while porewater sulfide concentrations at sites distant from canal discharge but receiving some excess sulfate, range from one to hundreds of ppb, and pristine Everglades sites in the south have porewater sulfide values usually <0.1 ppb. Everglades sediment porewaters are enriched in sulfide by a factor of ca. 10,000–100,000 due to sulfate loading from the EAA (Orem, 2004).

Sulfide can be directly toxic to plants and animals, but it can also indirectly impact plants by binding iron (Smolders et al., 2006), thus making this essential micronutrient unavailable, and by increasing soil reduction-intensity and thereby increasing oxygen deficiency stress (Koch et al., 1990). Although most wetland plants can detoxify hydrogen sulfide (H_2S) in the oxic rhizosphere surrounding the roots, the extent of detoxification does differ with the plant species. It has been clearly demonstrated that cattail (*Typha domingensis*) has a significantly greater ability to transport oxygen to its roots and so produce a more extensive oxidized rhizosphere than sawgrass *(Cladium jamaicense*). Hence, sawgrass may be more sensitive to H_2S production than cattail.

It has been widely accepted, and documented in past SFERs, that long term phosphorus loading from agricultural runoff into the northern Everglades has converted thousands of hectares of historically oligotrophic areas, characterized by open sloughs and sawgrass, into eutrophic areas characterized by monotypic stands of cattail (Sklar et al., 2007).

The realized niche of cattail in the Everglades is high nutrient, high organic-content, low Eh, high sulfide soils, whereas sawgrass commonly occurs in shallower water, lower nutrient, lower organic-content, higher Eh, lower sulfide soils. This leads to the hypothesis that in addition to high phosphorus levels selecting for cattail, one or several of these co-occurring conditions may contribute to replacement of sawgrass by cattail (**Figure 3B-23**).

For example, Pezeshki, et al. (1996) have demonstrated that cattail has a greater tolerance to low Eh than sawgrass. As well, a number of researchers have demonstrated that sulfide may inhibit wetland plant growth and alter species distribution, (Mendelssohn et al., 1981; Mendelssohn and McKee, 1988; McKee et al., 1988; McKee and Mendelssohn, 1989; Koch and Mendelssohn, 1989; Bradley and Morris, 1990; Koch et al., 1990; McKee et al., 1990; Mendelssohn and Morris, 2000). As such, it is a reasonable hypothesis that factors in addition to soil phosphorus, such as soil sulfide, Eh and oxygen levels affect cattail and sawgrass distribution in the Everglades.

Research on sulfur was initiated to determine the extent to which sulfate loading to the freshwater Everglades — which results in increased sulfide levels in sediments — affects the growth and photosynthetic responses of cattail and sawgrass; if these responses differ in the two species; and, if this offers an additional explanation for the expansion of cattail into areas previously occupied by the historically dominant sawgrass (Gilmour et al., 2007b).

The effects of sulfate loading on growth and photosynthesis of cattail and sawgrass were quantified in a field manipulative experiment conducted in WCA-3A, site 3A-15, in the central Everglades from November 2003 through March 2006.

It was hypothesized that higher sulfate loading could result in greater sulfate reduction and consequently higher interstitial concentrations of sulfide, which would limit plant growth. Both cattail and sawgrass were exposed in field mesocosms (1-m diameter plastic rings) to four sulfate treatment-levels: (1) control (0 mg L^{-1}), (2) low (20 mg L^{-1}), (3) medium (50 mg L^{-1}), and (4) high (100 mg L^{-1}); an ambient treatment-level with no added sulfate and no mesocosm served as a control for any potential effect of the mesocosm, per se.

Growth-related processes, including photosynthetic capacity, maximum quantum efficiency of Photosystem II reaction centers, shoot elongation rate and shoot turnover rate, were measured as response variables for cattail and sawgrass.

Sulfate loading in the experimental mesocosms did not result in interstitial sulfide concentrations high enough to affect the growth or photosynthetic responses of either species, possibly because of drought, inability to dose mesocosms as a result of hurricane-related field work delays, and/or lower sulfide production than expected for the sulfate treatment dosing regimes.

To determine if sawgrass is potentially more sensitive to sulfide than is cattail, a short-term (7-day) hydroponic experiment in which both species were treated with a range of porewater sulfide concentrations from 0 to 1 mM was conducted. The growth and photosynthetic responses of sawgrass were impacted at a lower sulfide concentration than for cattail (**Figures 3B-28** and **3B-29**). Thus, sawgrass is more likely to be negatively affected by sulfide accumulation resulting from elevated sulfate concentrations than is cattail.

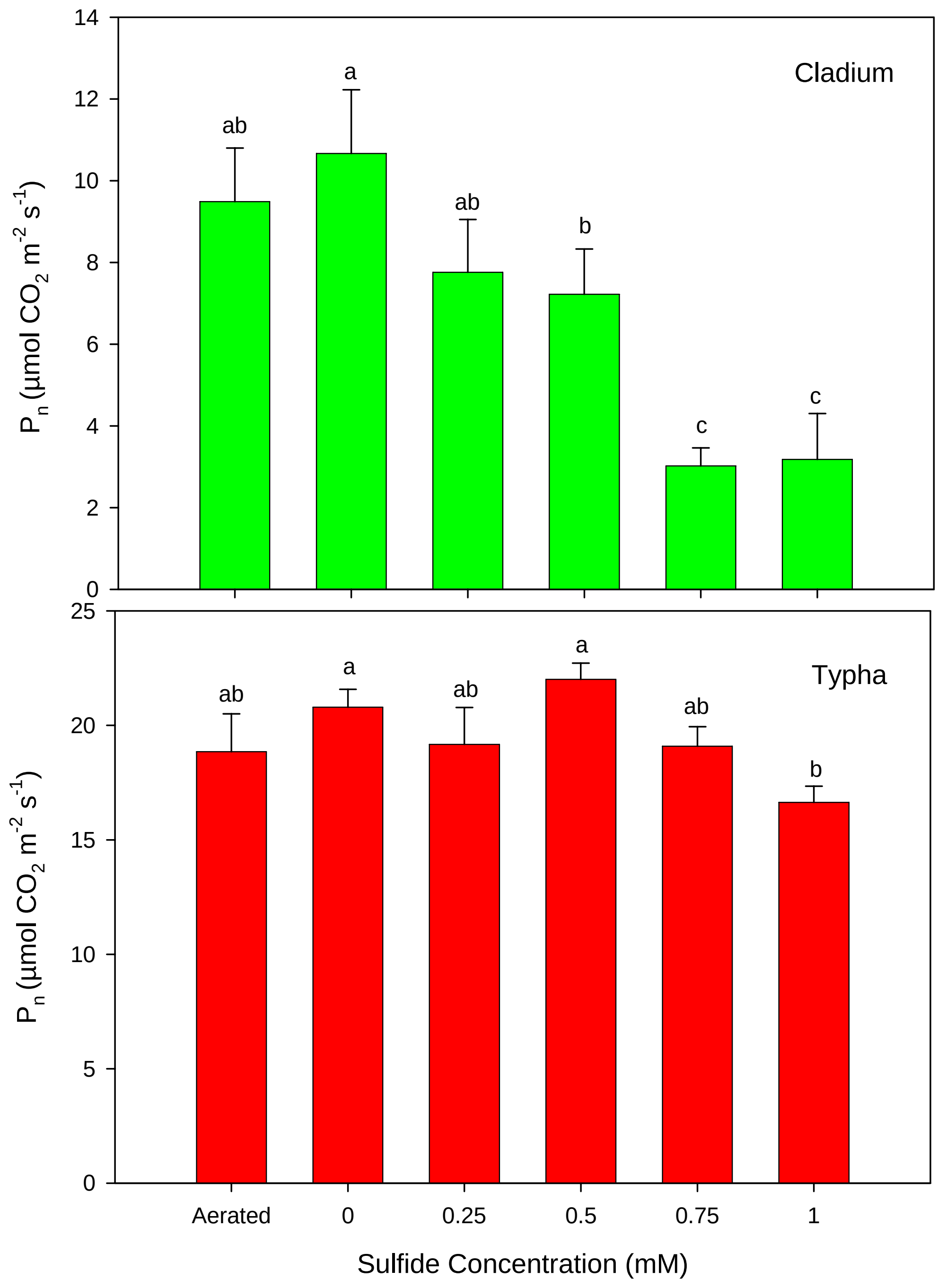

Figure 3B-28. Net photosynthesis rate for *Cladium jamaicense* (sawgrass) and *Typha domingensis* (cattail) in response to six treatments-levels (aerated, hypoxic with 0 mM sulfide, and hypoxic with sulfide concentrations of 0.25, 0.5, 0.75, and 1mM). Each value is the mean ± SE. Different letters indicate significant differences across treatments within each species identified with Fisher's protected LSD test.

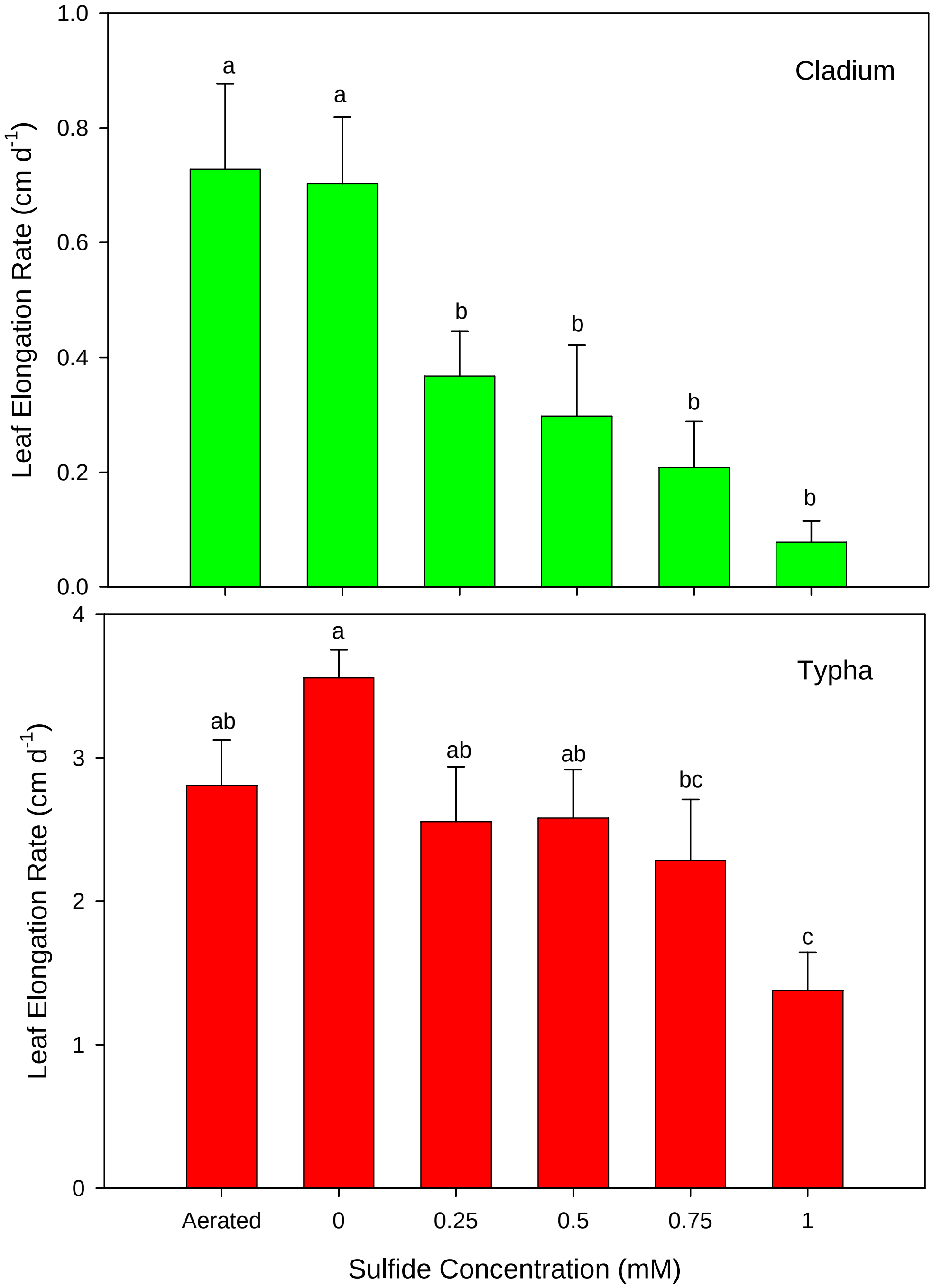

Figure 3B-29. Leaf elongation rate for *Cladium jamaicense* and *Typha domingensis* in response to six treatments-levels (aerated, hypoxic with 0 mM sulfide, and hypoxic with sulfide concentrations of 0.25, 0.5, 0.75, and 1mM). Each value is the mean ± SE. Different letters indicate significant differences across treatments within each species identified with Fisher's protected LSD test.

Sawgrass response was negatively affected at porewater sulfide concentrations from 0.25 to 0.5 mM (8–16 mg/L) (**Figures 3B-28** and **3B-29**). After titration-standardization of the sulfide standards, these growth-limiting values range from 0.22 to 0.46 mM (7–15 mg/L). Porewater sulfide in the field mesocosms never reached these growth-limiting concentrations. Hence, the absence of response in the field mesocosm experiment was likely due to inadequate sulfide accumulation. However, porewater sulfide levels surpassing these have been documented in WCA-2A (Orem, personal communication). Thus, excess sulfide may be growth-limiting to sawgrass in some areas of the Everglades. In contrast, sulfide concentrations high enough to affect the growth of cattail have not been measured, as far as is know, in the freshwater sections of the Everglades.

In conclusion, sulfate loading in the experimental field mesocosms did not result in interstitial sulfide concentrations high enough to affect the growth or photosynthetic responses of sawgrass or cattail. However, based on the controlled hydroponic (greenhouse) experiment, sawgrass is more likely to be affected than cattail by elevated interstitial sulfide concentrations. Additional research on this issue is planned.

Although further research is needed to determine if sulfide is important in causing cattail to replace sawgrass, phosphate, a contaminant in the Everglades that — like sulfate — originates in the EAA, is widely regarded as implicated in the replacement of historically dominant sawgrass by invasive cattail. Sulfate could add to the Everglades phosphate problem in that sulfate has been demonstrated to cause phosphate release from sediments in lakes and wetlands.

Lamers et al. (1998) and Smolders et al. (2006) described the phenomenon of "internal eutrophication," whereby increased sulfate loading considerably increased phosphate concentrations in the interstitial water of soils of a freshwater wetland (via sulfate stimulation of the decomposition of organic matter), and thus concluded that reduction in phosphate input to a wetland alone may not be sufficient to restore the ecosystem. It has also long been known that sulfide binds with iron, decreasing the abundance of iron forms that can bind with phosphate in sediment, and resulting in release of phosphorus from sediments (Hasler and Einsele, 1948).

To test whether sulfate induced phosphate release from Everglades sediments, sulfate was added to mesocosms at 3A-15 in WCA-3, to produce three dose levels, low (20 mg/L), medium (50 mg/L), and high (100 mg/L).

Initial findings are that sulfate does induce phosphate release from Everglades sediments (**Figure 3B-30**). Further information on this research is available in Gilmour et al. (2007b) and additional research on this issue is planned.

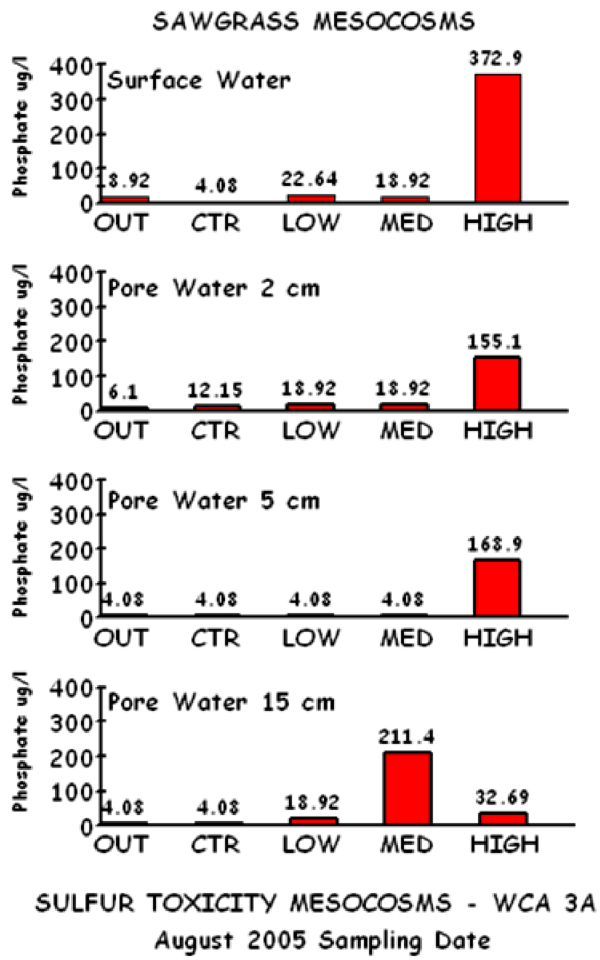

Figure 3B-30. Phosphate in surface water (top graph) and in porewater at 2 cm, 5 cm and 15 cm sediment depth for sulfate addition mesocosm treatments, low (20 mg L^{-1}), medium (50 mg L^{-1}), and high (100 mg L^{-1}) at 3A-15, WCA-3. (CTR = control, no sulfate addition; “OUT” = outside the mesocosm.)

To summarize sulfur effects on the Everglades:

(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. Broad areas of the Everglades currently exhibit sulfate concentrations at which increased sulfate levels would enhance, and decreased sulfate concentrations would reduce, MeHg production.

(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 porewaters 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.

(3) **Increased Phosphate Release and Eutrophication**: Excess sulfate may release phosphate from soil to the overlying water column, increasing the degree of eutrophication and slowing the rate of recovery of the ecosystem.

The mercury and sulfur connection has been discussed in the mercury chapter of every SFWMD Everglades “consolidated” report from 1999 to the present (SFWMD, 1999–2006). In recent years, other effects of sulfur on the Everglades have been discussed. A sampling of findings, revealing the incremental improvements in our understanding of the relationship between MeHg and sulfate, sulfate and toxic sulfide, and sulfate and phosphate release, follows.

> From SFWMD, 1999: “Sulfur can govern the rate of methylmercury production; too little sulfate starves the production process, while too much sulfide poisons it.” (Redfield, 1999)

> From SFWMD, 2000: “The excess sulfate in the northern and central Everglades can be traced to the EAA, but there are still some uncertainties regarding the relative contributions of natural and cultural sources and historical and present-day cultural practices.” (Fink and Rawlik, 2000)

> From SFWMD, 2001: “Information developed by the USEPA Region 4 Regional Environmental Monitoring and Assessment Program (REMAP) and USGS Aquatic Cycling of Mercury in the Everglades (ACME) projects indicates that agricultural practices in the Everglades Agricultural Area result in significant export of sulfate into the Everglades Protection Area. The Stormwater Treatment Areas (STAs) and Everglades marshes only attenuate sulfate weakly; therefore, a sulfate gradient extends south through the Water Conservation Areas to Everglades National Park.” (Atkeson and Parks, 2001)

> From SFWMD, 2002: "Because mercury emissions to the atmosphere are the first step in creating the mercury problem, the Department's primary strategy for control is emissions reduction. In the event emissions controls are insufficient, control of sulfate in EAA runoff is a potential candidate for further investigation." (Atkeson and Parks, 2002)

> From SFWMD, 2003: "Sulfur follows inorganic mercury deposition rate in order of importance regarding factors controlling methylmercury production and bioaccumulation." (Atkeson and Axelrad, 2003)

> From SFWMD, 2004: "Sulfate entering the Everglades in canal discharge, in combination with the "new" mercury entering the ecosystem predominantly from atmospheric deposition, controls the magnitude and distribution of methylmercury production in the Everglades." "Sulfate contamination originating from the EAA plays a key role in regulating the concentration and distribution of methylmercury in Everglades sediments and fish." (Atkeson and Axelrad, 2004)

> From SFWMD, 2005: "Recent mercury and sulfate data suggests that sulfate control has efficacy for MeHg production control in the Everglades now that local mercury emission sources to the atmosphere have been reduced,…" (Axelrad et al., 2005) "Sulfate contamination affects as much as one-third of the freshwater Everglades, and sulfate concentrations are 60–100 times historical levels in heavily affected areas." "Implementation of BMPs for sulfur use in the EAA could significantly reduce the amount of sulfate entering the Everglades. BMPs for sulfur could include (1) reducing the amounts of agricultural sulfur used, (2) replacing agricultural sulfur with another soil amendment that would enhance phosphorus uptake by plants, and (3) using chloride instead of sulfate as the counter-ion in many fertilizers and other agricultural products." (Orem, 2005)

> From SFWMD, 2006: "There is a need to investigate Everglades sulfur biogeochemistry other than as regards mercury methylation. Sulfur as a biologically very active element has forms that are highly toxic (sulfide), and others (sulfate) which will promote eutrophication of the Everglades via liberation of phosphorus from sediments."… "Results from Bates et al. (2002) implicate agricultural fertilizer as a major contributor of sulfate contamination of the Everglades."… "High sulfide levels in sediments (resulting from sulfate inputs) are not desirable even though they may reduce MeHg production. Sulfide, as undissociated hydrogen sulfide, is water soluble and highly toxic." (Axelrad et al., 2006)

There is now a need to construct an Everglades sulfur mass balance to quantify sources and sinks, and 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.

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 appear problematic too, from the standpoint of stimulating mercury methylation, as regards potential sulfide toxicity to plants and animals, and with regards to sulfate-induced liberation of phosphate from Everglades soils, possibly counteracting Everglades restoration efforts.

The declines in mercury levels in fish and fish-eating birds ca. 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 peak historical levels (ca. 1990), and despite this, mercury deposition to the Everglades remains high compared to other sites in the U.S.

If in fact local atmospheric mercury emissions have been reduced by 90 percent from levels of ca. 1990, that would leave little scope for source reductions through regulation in Florida or the U.S. 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 to identify and develop opportunities for reducing mercury deposition to the Everglades. As well, there remains a need to determine the relative importance of local, regional, and global, wet and dry atmospheric mercury deposition sources.

Similarly, a sulfur mass balance for the Everglades would allow for identification of sulfate sources amenable to controls (through BMPs, rerouting of water flow, or other means) for reducing mercury methylation rates and reducing other negative ecological effects of sulfate. As well, 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.

It is of note that a new coal-fired power plant is proposed in the vicinity of Lake Okeechobee. The Everglades, with its efficient rate of producing methylmercury from inorganic mercury, is very sensitive to atmospheric deposition of mercury, and so plans for this power plant (location, mercury emissions rate) ought to take that into account.

RESEARCH PROGRESS

The following research needs were identified in comments regarding Everglades Consolidated Reports (ECR) 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).**

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

While this information collectively is suggestive of a role for mercury contamination in fluctuations in breeding success and size of breeding population in the Everglades, the evidence remains largely associative.

As such, 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 LOAEL for effects of MeHg on development and reproduction in these animals. The approach in this study is to raise White Ibises (*Eudocimus albus*) in captivity on controlled diets containing different levels of methylmercury, and to examine these birds for treatment effects on health, survival, appetite, behavior, and endocrine function.

The global hypothesis examined with this project 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.

During spring 2005, a 1,233 m^2 (13,000 ft^2) aviary was constructed in Gainesville Florida and populated it with 200 young White Ibis, collected predominately from a large colony in the Everglades, supplemented with 20 female birds from a colony near White Springs, Florida.

Beginning in March 2006, courtship, nest building, egg laying and successful hatching of young, were observed fully a year before expected. The control group began breeding nearly two weeks prior to the other two groups, and had, by the end of the season, 37 percent more nesting attempts (Frederick and Adams, 2006).

The high dose group had the latest laying date of any treatment, although the number of nests initiated was about the same as the medium and low dose groups. These first-time breeders and perhaps juvenile breeders showed poor nest success, poor parental care, and apparently maladaptive behaviors like homosexual pairings, cannibalism of eggs, and aggression towards their own offspring.

Females in the control group had significantly lower incidences of homosexual pairings than any of the mercury treatment groups. Males also had lower incidences but these were not significantly different among groups.

The control group as a whole had 37 percent more nest initiations, 27 percent more eggs laid, and a 56 percent higher proportion of nest attempts that resulted in eggs than did the highest scoring of the mercury dose groups. Egg failure could not be distinguished from embryonic death or infertility because of confounding evidence, largely stemming from poor parenting behavior. The largest source of egg failure was cannibalism or scavenging of eggs by adults. Survival of hatching young was very poor (approximately 25 percent) in all cages except for the low dose group (67 percent); the differences did not appear to be due to mercury dosing, and were apparently the result of inattention by parents, and aggression directed towards young.

The results of this year's breeding season suggest that there may be some effects of mercury on reproduction, but the confounding effects of poor parenting abilities and juvenile behaviors clouded the picture considerably. This multigenerational effects study is planned to continue for a further three years.

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

Over the past five years, FDEP, the USEPA National Exposure Research Laboratory, and the Broward County Environmental Protection Department have collaborated in the operation of mercury monitoring super sites at Coral Springs and downtown Ft. Lauderdale. Our efforts there were to develop and vet technologies and procedures to address questions of source apportionment among the natural and anthropogenic the sources in an airshed, as well as address larger-scale transport and fate issues. A major portion of this effort was in support of the thorough field vetting of the Tekran mercury speciation instrument suite; a key tool needed for advanced atmospheric mercury studies. FDEP and USEPA have supported extensive technology development and testing of advanced field equipment for use in future field studies.

The 2007 goal is for FDEP and its collaborators to implement a multi-site 3rd phase[15] atmospheric mercury study in peninsular Florida, with candidate sites at the ENP Research Station, Miami area, Fort Lauderdale, or perhaps Tampa. These sites will employ trace-element grade automated daily event rain sampling using the University of Michigan Automated Sequential Precipitation Sampler, which allows for the economy of only weekly servicing of the field equipment.

Sites will be operated in accordance with current recent trace element apportionment techniques in accordance with current best state-of-the-art multi-element tracer techniques (Keeler et al, 2006) to improve the ability to parse out the local versus larger scale transport and fate of mercury to the Everglades in the past year.

Previous work indicated that the local contributions in 2000 were approximately 8 percent of the total (Pollman et al., 2005a). These results are consistent with that of Seigneur et al. (2003), who estimated that that only 17 percent of the total mercury deposition in the Everglades during 1998 originated from within North America. (There was no further delineation to identify the magnitude of local sources).

The Dvonch et al. (1999) and Graney et al. (2004) estimated that local sources contributed 70–80 percent of the wet deposition flux at the interface between the South Florida urban fringe and the Everglades between June 1995 and June 1996. This is to be contrasted with the box model estimates of Guentzel et al. (2001), who estimated that 30–46 percent of the mercury deposited in wet deposition during the summer was derived from local sources for 1995–1996. For the same period, Pollman et al. (2005a) estimated that local sources contributed about 21 percent based on measured changes in wet deposition and the background total gaseous mercury signal.

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

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[15] The earlier *Florida Atmospheric Mercury Study* (FAMS) and *South Florida Mercury Monitoring Pilot Study (SoFAMMS)* projects of mid-nineties.

Most recently:

For 2007, the FDEP will retain the existing Speciated Atmospheric Mercury Study (SAMS) site at Coral Springs and move our second Tekran mercury speciation system to another location, likely Tampa or the ENP. This new alignment is a step toward our desire to have three full mercury speciation supersites in peninsular Florida as a part of the third-generation mercury study (EgHgIII) to come. SAMS collects highly time-resolved measurements of all known forms of atmospheric mercury and associated tracer species. It is expected that this measurement and modeling project will continue through 2008.

As a prelude to this third-generation mercury study, the USEPA has established mercury supersites in Ohio and Hawaii to assess and contrast the impacts of the emissions and transport among the handful of intensive mercury-monitoring sites worldwide.

This joint study by the USEPA and the FDEP envisioned for 2007–2010 will add monitoring sites at ENP and Tampa, Florida as part of a nascent, global network. Coordinated analyses among these sites will provide improved data, tools, and understanding in the effort to resolve the question of the importance of long-distance transport of mercury into Florida.

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

No modifications to the simplified sulfate mass balance model incorporated into the Mercury Cycling Model (MCM) have been made since the module was first built into the model several years ago. There remain two needs:

- The basic sulfate mass balance model needs to be applied across the entire spatial domain of the Everglades to further refine the parameterization and calibration of the model and tie it to phosphorus uptake or productivity dynamics. (There is a need to establish a sulfur mass balance for the Everglades.)
- Construction of a diagenetic model for mercury methylation (in progress) that will specifically code the dependence of methylation on microbial activity and soil geochemistry, to run in parallel with the larger-scale modeling efforts Everglades-MCM (E-MCM).

E-MCM development and application remains a SFMSP goal to continue to develop the model as a tool to assess systemwide responses to mercury sources, water quality and especially sulfur, and management scenarios being evaluated by CERP.

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

The FDEP continues to support a series of studies with the USGS and the Smithsonian Institution. Field mesocosm experiments using stable-isotope and other tracer techniques have been used to examine the interactions between mercury, sulfur, and DOC, and methylation rates of old versus new mercury. Field work began with deployment of mesocosms in spring 2001; field experiments are presently scheduled through 2006. Results to date are included in Volume I Appendix 3B-2 of this 2007 SFER, and include:

- Broad areas of the Everglades Protection Area (the WCAs and the ENP) 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.

- At multiple locations across the ecosystem, net mercury methylation and bioaccumulation responded linearly to single-dose mercury loads up to twice the annual mercury wet deposition rates.
- The slope of the methylation response to mercury loads varied substantially across the Everglades, reflecting differences in biogeochemistry.
- Net MeHg produced from mercury spikes was maximal within days to weeks after the spike, and declined thereafter. The timing of the response varied among sites. Bioaccumulation of spike mercury into mosquitofish followed the same pattern, with a longer delay.
- Sulfate and DOC additions to mesocosms in central WCA-3A stimulated net mercury methylation and bioaccumulation over periods of weeks.
- Sulfate and DOC had stronger impacts on the methylation of new mercury spikes than of mercury stored in soils.

5. Determine sulfur sources to and effects on the Everglades (2006 SFER).

The Everglades is contaminated by sulfate originating in the EAA, and there remains a need to derive a sulfur mass balance. Sulfur is a biologically very active element, and sulfate is essential for the dominant Everglades producer of MeHg — that is sulfate-reducing bacteria. Broad areas of the Everglades Protection Area 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 fish, birds and mammals, and human exposure to mercury resulting 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. These results are discussed in the sulfur section of this Chapter and in more detail in Appendix 3B-3 in this volume.

MERCURY PROGRAM FUTURE ACTIVITIES

In 2007, FDEP, in collaboration with USEPA, proposes to initiate substantial efforts to improve our understanding of the impact of atmospheric sources of mercury — whether near or far — on Florida's watersheds and water bodies. Atmospheric deposition continues to be viewed as a primary driver of mercury load, methylation, bioaccumulation, and risk in Florida waters, with particular emphasis on the interaction between mercury methylation and sulfur chemistry. Anticipated projects are described below.

Third-Phase Analysis of Mercury Transport and Fate

A large state-sponsored effort in 2007 will be the initiation of a three-year[16] study entitled EgHgIII (Everglades Mercury Phase III). This project represents a renewed focus on developing a better understanding of the relative importance of the local, regional, and global scales of mercury influence on Florida waters with respect to their impairment by mercury.

[16] Two years of field monitoring, one year of data analysis and modeling.

Previous efforts proved limited by available measurement techniques and technology; issues that have been substantially surmounted following earlier projects listed below: Our partners will be:

- USEPA Office of Research and Development (USEPA ORD)
- Broward County Environmental Protection Department (Broward EPD)
- Everglades National Park (ENP)
- University of Michigan Air Quality Laboratory
- University of South Florida College of Public Health

Our plan is to conduct a two-year field study to examine mercury transport, fate and deposition in South Florida to resolve significant uncertainties in earlier studies; a third year is reserved for data analysis, modeling and reporting.

Monitoring is planned at two sites, each employing an Automated Sequential Precipitation Sampler, i.e. at a background site (ENP), at in a more industrialized area in southern Florida.

The goal is to measure ambient concentrations of mercury and extensive trace element constituents. We will use automation where possible to economize on this field study itself.

The intent is to build on earlier efforts such as the SoFAMMS study[17] . improvements in monitoring and modeling technologies the earlier FAMS[18] South Florida Monitoring and Modeling Pilot Study (SoFAMMS) study of 1995–1996, return to the field in 2007/10 for a three-year multi-site field study in South Florida.

A coordinated effort among the participating agencies is proposed, that will incorporate sites that allow gauging the influence of local and regional sources on all of Florida and much of the Gulf of Mexico. The SFWMD provides monitoring support for this effort by its continuing sponsorship of the three MDN sites, which record annual atmospheric mercury deposition load across southern Florida. The intent is to:

1. Redeploy equipment from the Speciated Atmospheric Mercury super site (SAMS) at Coral Springs where it was used to vet the Tekran speciation instruments under field conditions, in preparation to support atmospheric mercury studies relevant to the mercury transport and fate in an area impacted by mercury deposition.

2. Sponsor high-frequency direct measurements of the transport of mercury species and related tracers into Florida from within and without Florida

3. Describe and quantify the atmospheric concentrations and dispersion of mercury that facilitate deposition, relying on existing emissions inventories and available meteorology.

4. Employ the NOAA/USEPA Community Model for air quality (CMAQ), a well characterized, public domain photochemical grid model, to project deposition fields across Florida for the benefit TMDL basin managers.

[17] South Florida Mercury Monitoring and Modeling Pilot Study (SoFAMMS) 1995-1996

[18] Florida Atmospheric Mercury Study (FAMS) 1992-1996

The Speciated Atmospheric Mercury Study (SAMS) operated in conjunction with Broward County Air Quality Division will be re-deployed to the Miami area; and one of the two sites there will be relocated to the ENP, where it will serve as a marine background site for the other sites to be emplaced in the coming years.

EgHgIII will continue to focus on the paramount importance of determination of the speciation of mercury in the atmosphere as a controlling factor in its atmospheric transport, deposition, and fate. The project will focus on making highly time-resolved measurements of all known forms of mercury in the atmosphere along with extensive associated tracer species. It is expected that this measurement and modeling project will begin operation in 2007, operate in the field for two years, followed by a year for analysis and reporting. As a prelude to EgHgIII, the USEPA has established mercury super sites in Ohio and Hawaii to assess and contrast the impacts of the emissions and transport among the handful of intensive mercury monitoring sites worldwide. This joint study by the USEPA and FDEP envisioned for 2007 through 2009 will add establish an automated event precipitation at the ENP and Tampa, Florida as part of a nascent, global network. Coordinated analyses among these sites will provide improved data, tools, and understanding in the effort to resolve the question of the importance of long-distance transport of mercury into Florida.

TMDL Program Support

By 2012, the FDEP will require specific information on atmospheric deposition for those impaired waters significantly influenced by atmospheric deposition (i.e., mercury, fixed nitrogen, and perhaps phosphorus). The department is beginning to develop plans for a statewide analysis of these substances that will require both a field and modeling component. The plan is to organize this effort in the coming year and begin field measurements in 2007, continuing through 2009.

Mercury in Coastal Waters

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

Dry Deposition Processes

In addition to the projects described above, the USEPA has awarded the FDEP a two-year Regionally Applied Research (RARE) grant from USEPA Region 4 that will focus on the processes that govern the dry deposition of mercury from the atmosphere, a substantial, likely dominant but poorly quantified, portion of the total mercury deposition load. Dry deposition studies in general have trailed other aspects of this science because of the minuscule concentrations and fluxes of mercury species to the earth's surface. Despite the subtlety of dry of deposition, gaseous and particulate dry deposition occurs continuously, night & day, wet or dry, whereas rainfall at any point scrubs the air column for only a few hundred hours per year. Thus the net of dry deposition is thought to exceed the rainfall load, perhaps by several-fold. The potential importance of dry deposition as a contributor to ecosystem load has been apparent for decades, but has defied quantification because of technical limitations.

The FDEP and USEPA have sponsored two previous field studies, but rapidly evolving measurement technology and modeling techniques should allow for higher resolution analyses since our earlier efforts FEDDS dry deposition study of 2000–2001. The capabilities of sampling and analytical instrumentation and computing power have advanced rapidly over the past decade, allowing for more sensitive and specific techniques. This yields higher temporal resolution data, which in turn can support more higher-resolution modeling analyses. It was only a few years ago that 24-hour samples were the norm; today, semi-continuous or continuous data can be obtained, and in many instances data capture cycles of an hour or less can be achieved.

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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