Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades

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SUMMARY

This chapter provides an assessment of sulfur and mercury (Hg) status within the Everglades Protection Area (EPA), Holey Land and Rotenberger Wildlife Management Areas (WMAs) during Water Year 2013 (WY2013) (May 1, 2012–April 30, 2013). This report fulfills the requirements of the Everglades Forever Act (EFA) more specifically §373.4592(13) Florida Statue. The information provided in this chapter is an update to Chapter 3B of the *2013 South Florida Environmental Report* (SFER) – *Volume I*.

The analysis and summaries provide a synoptic view of Hg and sulfur in the EPA on a regional scale including the Arthur R. Marshall Loxahatchee National Wildlife Refuge [Refuge, or Water Conservation Area 1 (WCA-1)], Water Conservation Areas 2 and 3 (WCA-2 and WCA-3, respectively), and Everglades National Park (ENP or Park). This chapter updates the status of mercury and sulfur monitoring in the Everglades region and provides a summary of biota mercury concentrations; mercury atmospheric deposition; and surface water sulfate (SO_4^{2-}) concentrations, loads, and atmospheric deposition to the EPA.

- During WY2013, 339 largemouth bass (LMB; *Micropterus salmoides*) were collected from 13 locations within the EPA and 4 locations in the Everglades region outside the EPA. Non-EPA locations include Stormwater Treatment Area 1 West (STA-1W), Holey Land WMA, and Lake Tohopekaliga and East Lake Tohopekaliga in the Upper Kissimmee Basin. Across all sites, individual LMB total mercury (THg) ranged from 0.02 to 2.0 milligrams per kilogram (mg/kg), with a median concentration of 0.40 mg/kg.
- During WY2013, THg concentrations in mosquitofish (*Gambusia* spp.) from 12 monitoring sites ranged from 0.01 mg/kg at site WCA2F1 to 0.19 mg/kg at site WCA2U3, with a median concentration of 0.05 mg/kg.
- During WY2013, THg concentrations in the three trophic level 3 (TL3) sunfish species from 9 monitoring sites ranged from 0.10 mg/kg at WCA2F2 to 0.25 mg/kg

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at L67F1, which exceeded the federal methylmercury (MeHg) criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. THg concentrations in these species from all sites followed the period of record (POR) trend—highest in spotted sunfish (*Lepomis punctatus*; 0.35 mg/kg), intermediate in bluegill (*L. macrochirus*; 0.20 mg/kg), and lowest in redear sunfish (*L. microlophus*; 0.14 mg/kg).

- During the 2013 Florida legislative session, the statewide Total Maximum Daily Load (TMDL) for Hg was finalized and ratified.
- Wet deposition of Hg is the dominate source of Hg to the Everglades. During WY2012, wet deposition of THg accounted for 136.7 kilograms of Hg to the EPA. No statistically significant trend was apparent in annual Hg wet deposition; however, deposition was significantly different between the northern, central, and southern regions of the EPA. The complete dataset for WY2013 is under quality assurance review and is expected to be reported in the next SFER.
- During WY2013, annual mean inflow SO_4^{2-} concentrations ranged from 50.9 milligrams per liter (mg/L) for the Refuge to 3.5 mg/L for ENP. The annual mean SO_4^{2-} concentrations at interior marsh regions ranged from 37.9 mg/L for WCA-2 to 4.7 mg/L for ENP.
- SO_4^{2-} loads from surface sources, including internal transfers to the EPA totaled approximately 96,263 metric tons (mt), with a flow-weighted mean concentration of 20.0 mg/L. Another 8,655 mt of SO_4^{2-} are estimated to have entered the EPA through atmospheric deposition (wet + dry deposition). The 96,263 mt SO_4^{2-} load in the surface inflows to the EPA represents an increase of approximately 80 percent compared to the previous year (53,545 mt in WY2012).
- Wet deposition of SO_4^{2-} to the Everglades ecosystem (i.e., EPA) is a small contribution of SO_4^{2-} to the overall system relative to surface water inflows. Contributions for WY2012 range from 4.8 to 31.6 percent of the total SO_4^{2-} load to the EPA. During WY2012, wet deposition of SO_4^{2-} accounted for 7,375 mt to the EPA. The complete dataset for WY2013 is under quality assurance review and expected to be reported in the next SFER.
- Sulfur research within the Everglades Agricultural Area (EAA) has determined that there is a strong relationship for sugarcane between sucrose yield and soil pH, with yield being reduced at pH $\geq$ 7.2. Research is continuing to determine if other soil factors, such as extractable calcium or manganese, will improve the prediction of yield response to elemental sulfur. This research will aid in determining the effectiveness of sulfur application and potentially lead into development and employment of alternative fertilizer treatments.
- Through a cooperative agreement between the South Florida Water Management District (SFWMD or District) and Florida Department of Environmental Protection (FDEP), the FDEP has authorized a study to evaluate factors influencing mercury methylation in South Florida marshes. An abridged interim report for this study is presented in Appendix 3B-1 of this volume. So far, this study has suggested that in situ sources of SO_4^{2-} (i.e., rainfall, groundwater, and internal recycling of reduced sulfur species) in the Everglades may be adequate to support environmentally detrimental levels of methylation by sulfate-reducing bacteria (SRB), as SO_4^{2-} levels as low as 0.3 mg/L without added inorganic mercury (Hg^{2+}) supported modest MeHg accumulation in the laboratory incubation. Furthermore, the addition of bioavailable Hg markedly enhanced methylation, even in vessels containing only native SO_4^{2-} concentrations.

AREA OF INTEREST

The Greater Everglades is a vast mixed wetland ecosystem that stretches from Lake Okeechobee to Florida Bay and the Gulf of Mexico (DeAngelis et al., 1998). The EPA, Holey Land and Rotenberger WMAs, and ENP are situated within this immense ecosystem. The EPA is a complex system of marsh areas, canals, levees, and inflow and outflow water control structures that covers almost 2.5 million acres (1 acre = 0.405 hectare) of former Everglades marsh and currently is divided into separate distinct shallow impoundments, or Water Conservation Areas (WCAs; Bancroft et al., 1992). In addition to rainfall inputs, surface water inflows regulated by water control structures from agricultural tributaries, such as the EAA to the north and the C-139 basin to the west, feed the EPA. The EPA also receives surface water inflows originating from Lake Okeechobee to the north and from predominantly urbanized areas to the east. The timing and distribution of the surface inflows from the tributaries to the EPA are based on a complex set of operational decisions that account for natural and environmental system requirements, water supply for urbanized and natural areas, aquifer recharge, and flood control. Holey Land and Rotenberger WMAs are located just north of the EPA, have a combined span 64 thousand acres, and consist of remnant Everglades' marsh with scattered small tree islands (Newman et al., 1998). The major features of the EPA and surrounding area are illustrated in **Figure 3B-1** of this volume.

MERCURY IN EVERGLADES FISH AND WILDLIFE

LARGEMOUTH BASS

Ted Lange[3] and Binhe Gu

Introduction

Mercury (Hg) contamination of freshwater fish stocks has been recognized as a problem throughout the world for several decades (Lange et al., 1993). Within the Everglades ecosystem, elevated Hg concentrations were first observed within biota, including fish species collected within Everglades National Park (ENP or Park) during the early 1970s (Ogden et al., 1973). Further evidence of widespread elevated Hg concentrations within fish species was obtained during the late 1980s, which promoted a state fish consumption advisory for selected species and locations within the Greater Everglades (Rumbold et al., 2001). Elevated Hg concentrations in fish are of concern because of the direct health threat to humans and other piscivorous mammals and birds that consume Hg-laden fish (Wiener, 1987).

This section evaluates spatial and temporal total mercury (THg) concentrations within largemouth bass (LMB; *Micropterus salmoides*) of the Everglades. THg concentrations within LMB provide an integrated measure of exposure to a long-lived sport fish (on average three years), which can be used to assess potential human and wildlife exposure to THg.

Methods

To assess both spatial and temporal trends in THg concentrations, LMB were collected from stations within the Everglades Protection Area (EPA) as well as other locations within the Greater Everglades (**Figure 3B-1**). Largemouth bass were collected from the Water Conservation Areas (WCAs), Holey Land and Rotenberger Wildlife Management Areas (WMAs), and Stormwater Treatment Area 1 West (STA-1W) during October and November 2012 while sites within ENP and the Kissimmee Chain of Lakes were collected in February and March 2013 using direct-

current electro-fishing equipment. In the laboratory, LMB were weighed, measured, and sexed, and the sagittal otoliths removed for determination of age as described by Taubert and Tranquilli (1982). An entire skinless axial muscle fillet was removed and frozen for analysis. Assessment of Hg concentrations in LMB within the EPA began in 1988; however, a more comprehensive spatial and temporal assessment was initiated in the mid-1990s.

Mercury Analysis

THg concentrations of homogenized axial muscle tissue of LMB were analyzed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee using U.S. Environmental Protection Agency (USEPA) Method 245.6 (Mercury in Tissues by Cold Vapor Atomic Absorption Spectroscopy). The minimum detection limit (MDL) was 0.02 milligrams per kilogram (mg/kg). While THg concentrations in fish were analyzed in this study, more than 95 percent of the Hg found in top-level predatory fish such as LMB is in the form of methylmercury (MeHg) (Grieb et al., 1990; Bloom, 1992) and, as such, THg concentration are considered to be a reasonable approximation of MeHg concentrations. Because exposure to MeHg in humans occurs primarily through consumption of fish, distributions of LMB provide an assessment tool for human health risk assessment within the Everglades including the EPA. The USEPA-recommended MeHg criterion for the protection of human health (0.3 mg MeHg/kg in fish tissue) provides a baseline for these assessments (USEPA, 2001). All results are reported as THg on a wet-weight basis as mg/kg.

LMB THg concentrations were summarized by station, region, and water year using basic descriptive statistics. Analysis of variance (ANOVA) was used to determine the difference of THg concentrations between sites and regions of the EPA. THg concentration values were transformed using the natural logarithm to fit the assumptions of the statistical test.

Results and Discussion

During Water Year 2013 (WY2013) (May 1, 2012–April 30, 2013), 339 LMB were collected from 13 locations within the EPA and four locations in the Everglades region outside the EPA (**Table 3B-1**). Non-EPA locations include STA-1W [the longest continually monitored Stormwater Treatment Area (STA)], Holey Land WMA, and Lake Tohopekaliga and East Lake Tohopekaliga in the Upper Kissimmee Basin (**Figure 3B-1**). Across all sites, individual LMB THg ranged from 0.017 to 2.0 mg/kg, with a median concentration of 0.4 mg/kg during WY2013 (**Table 3B-1**).

Table 3B-1. Location and description of largemouth bass (LMB; *Micropterus salmoides*) collection sites sampled during Water Year 2013 (WY2013) (May 1, 2012–April 30, 2013). Grouping by region and sites located within the Everglades Protection Area (EPA) are identified. Annual collections of 20 LMB between 200 and 500 millimeters (mm) were attempted at each location. No LMB were collected from sites WCA2F1, CA33ALT, and ROTENC.

Region	Within EPA	Site Name	Description	WY2013 Total Mercury (milligram per kilogram)		
				N	Median	Range
KISS	NO	ETOH	East Lake Tohopekaliga	20	0.39	0.21 – 1.0
KISS	NO	TOHO	Lake Tohopekaliga	20	0.58	0.16 – 1.1
STA1W	NO	STA1W	Man-made marsh, Cell 3	20	0.05	0.02 – 0.36
LNWR	YES	L-7	Canal	20	0.27	0.08 – 0.83
LNWR	YES	LOXF4	Marsh	23	0.26	0.09 – 0.68
HOLYBC	NO	HOLYBC	Holey land WMA, North Borrow Canal	20	0.49	0.10 – 1.0
ROTENC	NO	ROTENC	Rotenberger WMA, East Borrow Canal	NS		
WCA2	YES	CA2NF	Marsh	20	0.18	0.06 – 0.49
WCA2	YES	WCA2F1	Marsh	NS		
WCA2	YES	WCA2U3	Marsh	16	0.5	0.27 – 1.2
WCA2	YES	L-35B	Canal	25	0.6	0.22 – 1.7
WCA3	YES	CA33ALT	Marsh	NS		
WCA3	YES	CA35ALT	Marsh	15	0.51	0.31 – 0.90
WCA3	YES	CA3F3	Marsh	20	0.28	0.17 – 0.44
WCA3	YES	L-67A	Canal	20	0.82	0.18 – 1.7
WCA3	YES	CA315	Marsh	20	0.55	0.27 – 1.8
WCA3	YES	CA3F2	Marsh	20	0.24	0.14 – 0.89
ENPSRS	YES	L67F1	Canal/Marsh	20	0.98	0.47 – 1.7
ENPSRS	YES	ENPNP	Estuarine Creek-North Prong	21	1.5	0.49 – 2.0
ENP	YES	ENPLOST	Estuarine Creek-Lostmans	19	0.4	0.24 – 0.76

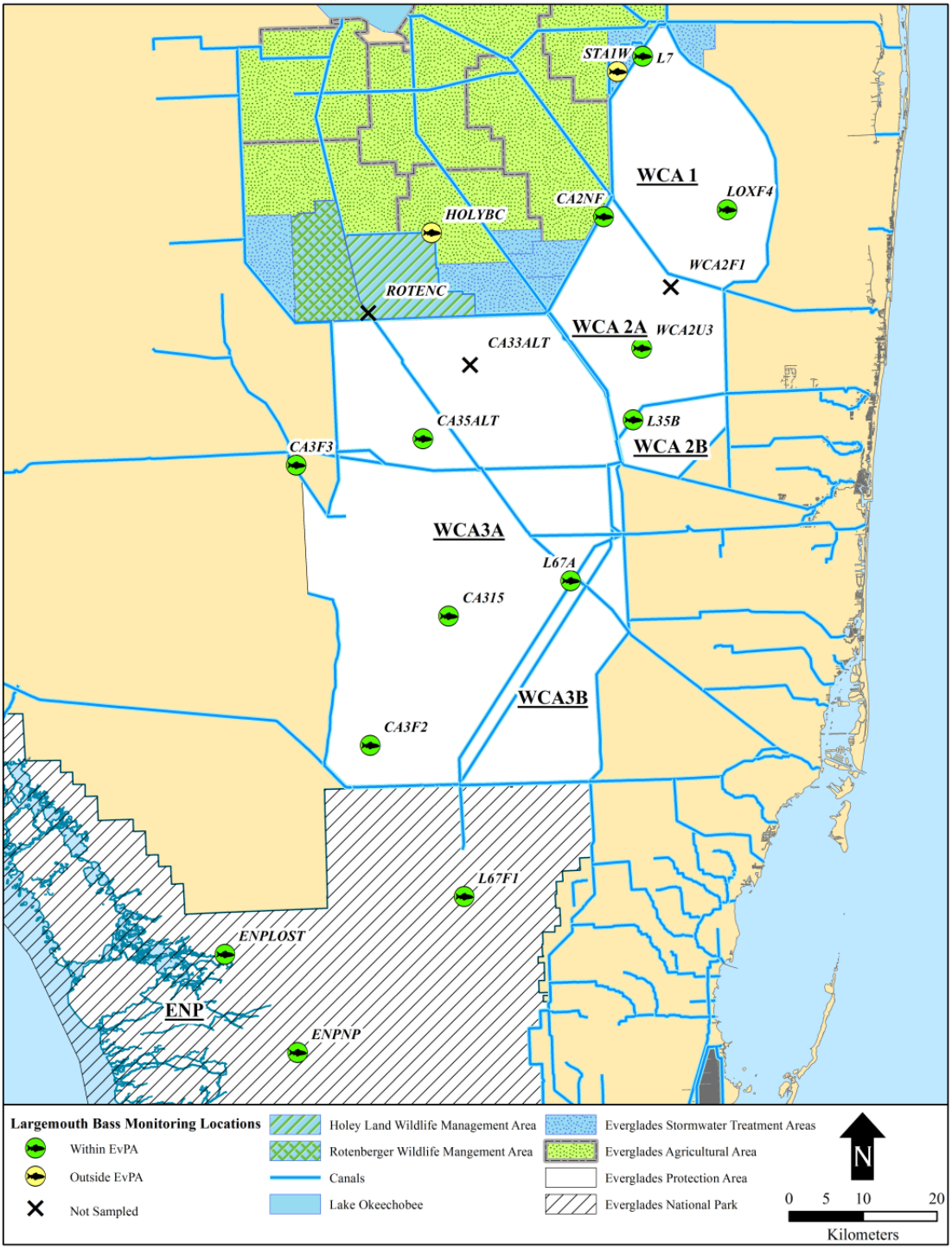

Figure 3B-1. Everglades fish long-term monitoring locations located within the Everglades Protection Area (EPA) and from other locations that were sampled during Water Year 2013 (WY2013; May 1, 2012–April 30, 2013). Lake Tohopekaliga (site TOHO) and East Lake Tohopekaliga (site ETOH) are located in the Upper Kissimmee Basin and are not shown. Largemouth bass (LMB; *Micropterus salmoides*) were not sampled from three locations during WY2013.

Temporal Trends in Bass Tissue Mercury Concentrations

Since 1988 (during WY1989), 4,734 LMB have been collected from the EPA at the sites described in **Table 3B-1**, as well as 39 other locations in the Arthur R. Marshall Loxahatchee National Wildlife Refuge [Refuge, or Water Conservation Area 1 (WCA-1)], Water Conservation Area 2 (WCA-2), Water Conservation Area 3 (WCA-3), and ENP (see Figure 3B-1 in Axelrad et al., 2013). THg concentrations in individual LMB ranged from 0.01 to 4.8 mg/kg, with a period of record (POR; WY1989–WY2013) median of 0.53 mg/kg. Over the POR, distinctly different trends in THg concentrations have been evident in LMB from the WCAs and Shark River Slough (SRS). The median THg concentration in the WCAs (including all sites in the Refuge, WCA-2, and WCA-3) declined from well in excess of 1 mg/kg in years prior to WY1994 to a median of 0.37 mg/kg in WY2013 (**Figure 3B-2**, top). This decline represents a 17 percent decrease from the previous year and a 79 percent decrease since WY1998. Virtually all the decline in LMB THg tissue concentrations occurred prior to WY2000, and there has been little change over the WY2000–WY2013 period, with medians varying between 0.30 and 0.55 mg/kg.

In SRS, annual collections of LMB from ENPSRS include those from sites L67F1 and ENPNP. For the POR, the median THg varied between 0.78 and 3.4 mg/kg and showed no significant temporal trend (**Figure 3B-2**, bottom). SRS receives surface flow from WCA-3 through the S-12 structures, which constitute the major source of freshwater flow exiting WCA-3 into ENP. LMB are well established in SRS due in part due to the deep water refugia to the north in the remnant L67 Extension canal (i.e., site L76F1) and to the south in numerous estuarine creeks (i.e., site ENPNP) where the populations survive periods of marsh drydown (Chick et al., 2004; Rehage and Loftus, 2007). Concurrent LMB collections were made from Lostmans Creek at site ENPLOST, which drains marsh north of SRS and where rainfall is the primary source of freshwater flow (**Figure 3B-1**). As a result, LMB growth and survival at ENPLOST are more limited and collections have been inconsistent. Moreover, the average size and age of LMB from ENPLOST have been smaller and younger than those from ENPNP. In spite of these differences in LMB populations, MeHg bioaccumulation at ENPLOST, which receives little or no surface flow from the WCAs, is greatly reduced relative to sites within SRS. Between WY1994 and WY2013, median THg concentrations at site ENPLOST varied between 0.31 and 1.1 mg/kg, with no evident temporal trends. For the POR, THg was on average 78 percent lower at ENPLOST than at ENPNP. The most recent median THg concentration at ENPLOST was 0.4 mg/kg, while ENPNP had a median THg concentration over three times higher at 1.5 mg/kg (**Table 3B-1**). Although site ENPLOST is not necessarily representative of MeHg bioavailability within ENP outside SRS drainage, these results do suggest that MeHg bioavailability is enhanced within SRS drainage. SRS has previously been identified as a MeHg hotspot within the EPA (USEPA, 1998; Rumbold et al., 2008; Krabbenhoft et. al, 2010) and MeHg continues to be a significant water quality concern in SRS.

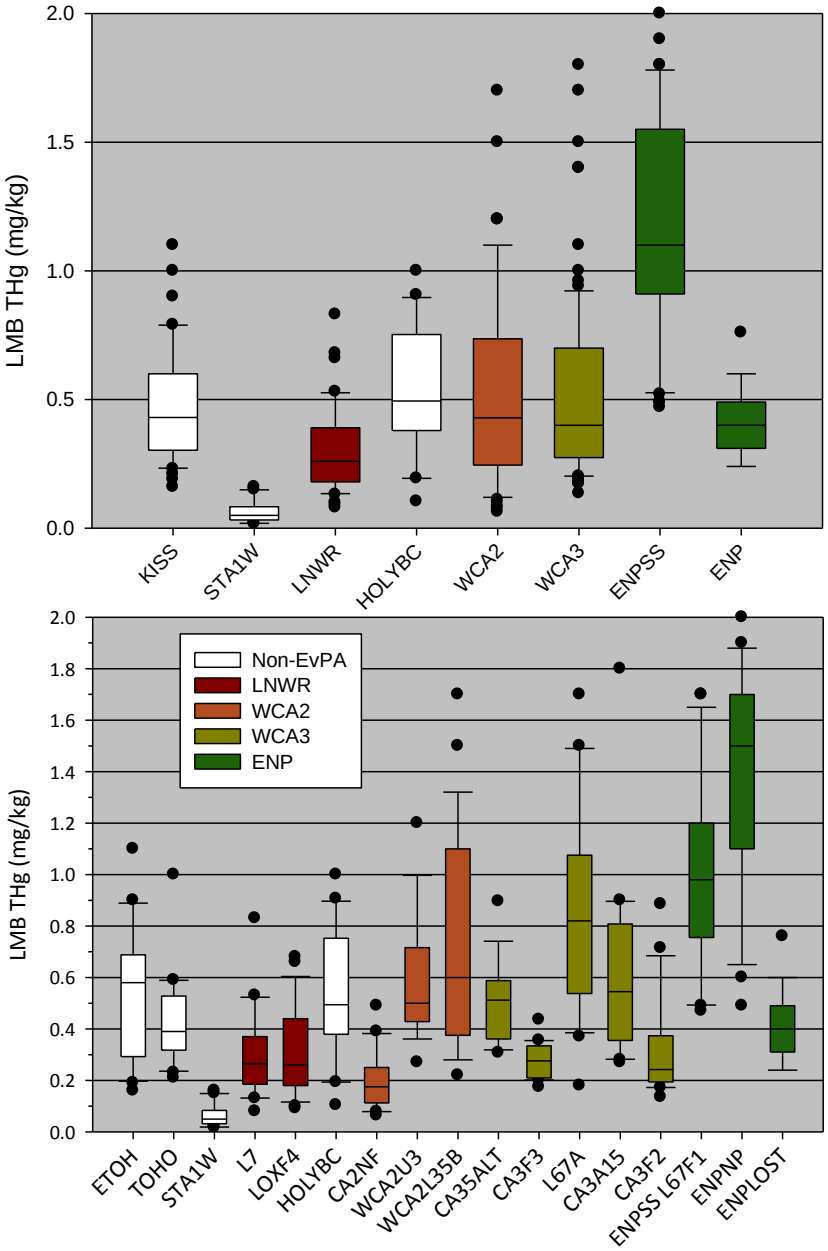

Figure 3B-2. Total mercury (THg) in muscle tissue in milligrams per kilogram (mg/kg) of 339 LMB collected from 13 locations within the EPA and 4 locations outside the EPA (no fill) during WY2013. *Top Panel:* THg summaries by regions indicated in **Table 3B-1**. *Bottom panel:* THg summaries by individual sample locations. Box plots represent the median and 25th and 75th percentiles, whiskers represent the 10th and 90th percentiles, and points are outliers. Sites are arranged from north to south. No LMB were collected from three sites (WCA2F1, CA33ALT, and RotenC) that are normally sampled annually.

Everglades Protection Area

Among EPA sites in WY2013, median THg ranged from a low of 0.175 mg/kg at site WCA2NF in the northern end of WCA-2 to 1.5 mg/kg at ENPNP in the estuarine portion of SRS (**Table 3B-1)**. Concentrations generally increased from north to south across the entire EPA (**Figure 3B-3**, top panel) and, when sites were grouped by region (identified in **Table 3B-1**), significant differences in THg concentration were observed with LNWR < WCA2 = WCA3 < ENPSS (df=3,236, F=40.8, P<0.001). Region ENP (represented by only one site; ENPLOST) was intermediate in THg and was statistically indistinguishable from the WCA3 region (P=0.99) and statistically higher than the LNWR and WCA2 regions (P<0.01) and lower than ENPSS (P<0.001) (**Figure 3B-3**, top panel).

It is evident that regional patterns in fish Hg concentrations are a direct result of MeHg production and bioavailability across the EPA. It has been suggested that factors contributing to LMB Hg declines prior to WY2000 likely include declines in sulfate (SO_4^{2-}) concentrations in the WCAs due to best management practices (USEPA, 2007) as well as reductions in local source Hg emissions (Atkeson et al., 2005). However, the current north to south gradient in fish THg cannot be explain solely by SO_4^{2+} dynamics. In addition to SO_4^{2+}, systemwide patterns of dissolved organic matter (DOM), which influence the bioavailability and transport of inorganic Hg (Hg^{2+}), and excess phosphorus, which can influence the character and quantity of DOM, play an important role in bioaccumulation of MeHg in LMB. Moreover, variations in LMB growth rate, trophic position, prey availability, and movement influence spatial and temporal patterns of LMB THg within the EPA. For example, similar to lake systems, LMB in EPA canals become predominantly piscivorous between 70–140 millimeter (mm) total length (TL) (Chew, 1974). However, LMB occupying marsh sites (e.g., CA315 and WCA2U3) within the EPA prey on decapod Crustacea (crayfish, *Procambarus* sp., and grass shrimp, *Palaemonetes paludosus*) to a much larger size than in canals, typically in the range of 200–300 mm (Florida Fish and Wildlife Conservation Commission unpublished data). Sampling efforts during the late 1990s, indicated that ontogentic shifts in diet were influential to MeHg bioaccumulation at site CA315 between 1996 and 2000, when LMB shifted from low MeHg crayfish to various species of sunfish (*Lepomis* spp.) with relatively high MeHg concentrations. This shift in diet occurred at approximately 300 mm TL, resulting in rapid increases in LMB THg concentrations to levels in excess of 2 mg/kg in larger LMB. The current distribution of LMB THg levels within the EPA are a function of a suite of biogeochemical factors that are not easily predicted by any single factor.

While across the EPA, regional trends were evident along a north-to-south gradient, variations existed among locations within individual WCAs (**Figure 3B-3**, bottom panel; **Table 3B-1)**. The largest gradient in median THg existed in the WCA2 region, where patterns were consistent with those observed in mosquitofish and sunfish. Median THg varied from 0.18 mg/kg at CA2NF to 0.50 mg/kg at WCA2U3 and 0.60 mg/kg at canal site WCA2L35 (**Table 3B-1**), a north to south increase in THg. Within the WCA3 region, median THg was maximal in the middle of the WCA at sites L67A and CA315 (**Table 3B-1**) while in region LNWR, no variations in LMB THg were evident. Clearly, patterns in SO_4^{2+}, DOM, nutrients, and fish population dynamics that influence systemwide patterns in fish MeHg are at work on a smaller scale within individual WCA impoundments.

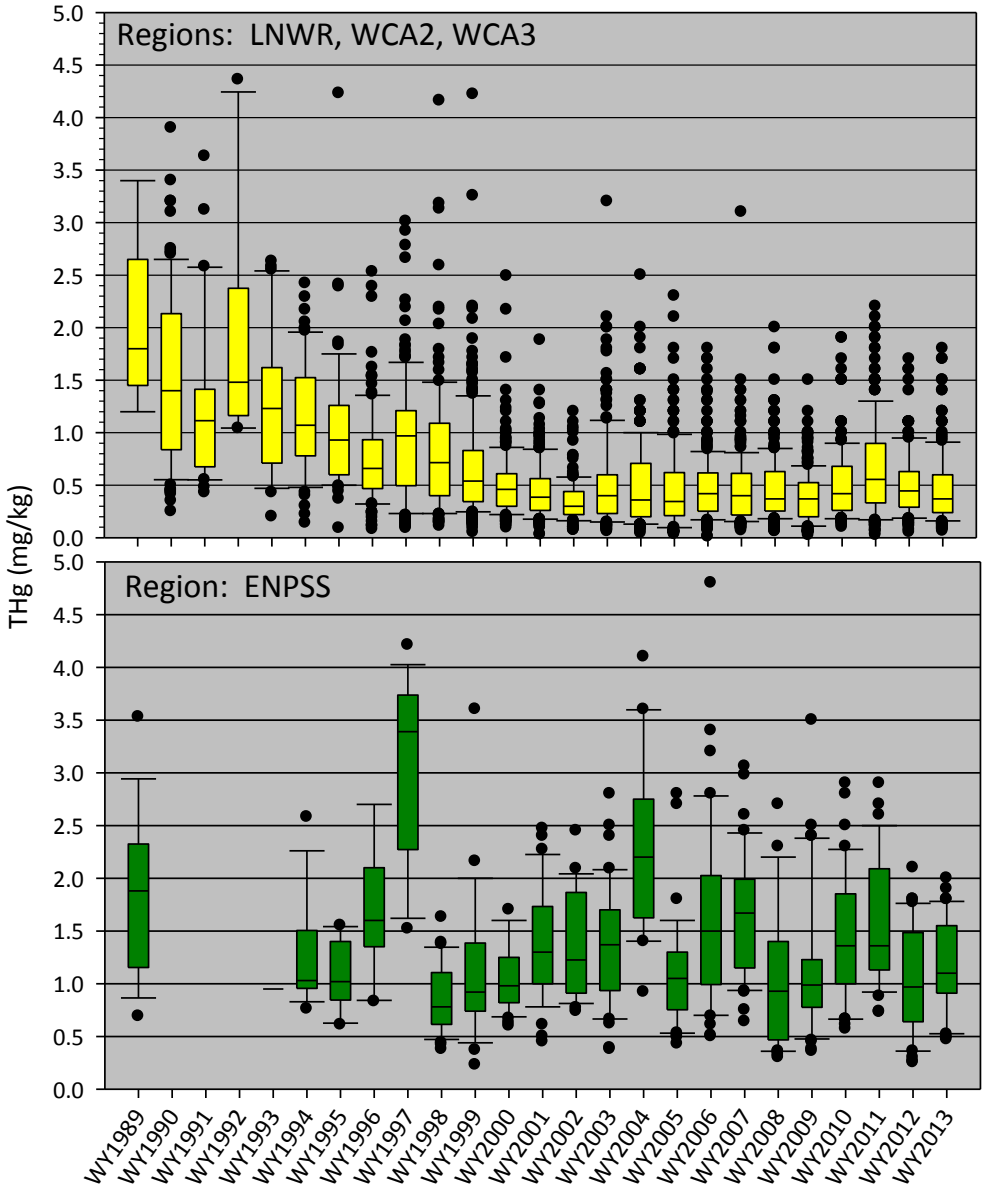

Figure 3B-3. THg in muscle tissue of 339 LMB collected from 13 locations within the EPA and 4 locations outside the EPA during WY2013. *Top Panel:* THg summaries by regions indicated in **Table 3B-1**. *Bottom panel:* THg summaries by individual sample locations. Box plots represent the median and 25th and 75th percentiles, whiskers represent the 10th and 90th percentiles, and points are outliers. Sites are arranged from north to south. No LMB were collected from three sites (WCA2F1, CA33ALT, and RotenC) that are normally sampled annually.

It has been suggested that SO_4^{2-} can enhance production of MeHg, the relationship is unimodal with peak production hypothesized to lie between 7 and 14 milligrams per liter (mg/L) SO_4^{2-} in WCA waters (Orem et al., 2011); however, shifts in this optimal range for production of MeHg shift across the EPA. Therefore, in spite of declines in SO_4^{2-} in WCA surface waters, areas of maximal MeHg production, commonly referred to as "hot spots", can shift in response to reductions or changes in SO_4^{2-} concentrations and biotic factors. For example, site CA315 in WCA3 was considered a MeHg "hot spot" due to high fish THg concentrations in the 1990s (USEPA, 1998; Kalla et al., 2010). Over the POR WY1993 to WY2013, THg in CA315 LMB decreased significantly (df=1,298, F=114, P<0.001) at a linear rate of 0.044 mg/kg per year. During the same POR, LMB THg showed no significant change (df=1,394, F=3.12, P=0.077) at site WCA2U3. The current median concentrations for CA315 and WCA2U3 are virtually the same at 0.55 and 0.50 mg/kg, respectively (**Table 3B-1**) while SO_4^{2-} concentrations at CA315 have reached concentrations below 1 mg/L while concentrations at U3 of greater than 10 mg/L have been observed. Trends in LMB THg have followed different trajectories over the past two decades and seem to not be controlled in any predictable manner by SO_4^{2-} concentrations alone. The relative importance of factors affecting temporal and spatial patterns of MeHg production and ultimately MeHg bioaccumulation in LMB vary across the EPA and even within individual WCAs.

Human Health Risks

Health risks associated with consumption of THg contaminated fish have resulted in fish consumption advisories recommending limited or even no consumption of certain species of fish from the Everglades region. Within the EPA, advisories for women of childbearing age and children suggest no consumption of LMB greater than 14 inches (356 mm) in length, except in the LNWR region (**Table 3B-1**) where only one meal per month is recommended. For LMB greater than 14 inches, advisories vary, but generally recommend 1 meal per month except in ENPSS where no consumption is recommended. Consumption recommendations within the EPA include nine additional freshwater and two estuarine species, with recommendations that range from two meals per week to no consumption (FDOH, 2013).

Within the EPA and the entire Everglades region, management of LMB fisheries allows anglers to select smaller LMB that are lower in THg for harvest. Size restrictions limit anglers to harvesting up to five LMB per day, only one of which may exceed 14 inches (356 mm) in length. Utilizing a reasonable size range of 10–14 inches (254–356 mm) for harvest in the WCAs, of 1,367 LMB collected since WY2000, 66 percent exceeded the USEPA MeHg criterion of 0.3 mg/kg. For the same period, 94 percent of 727 LMB longer than 14 inches exceed the criterion, while for smaller, less desirable (less than 10 inches) LMB, 57 percent exceeded the criterion. Within the WCA bass fishery, selecting smaller LMB for harvest, as recommended by Florida Department of Health fish consumption advisories, does lead to lower concentrations of THg in harvested fish. In contrast to the WCAs, all LMB collected from SRS have exceeded the USEPA MeHg criterion concentration.

The WCAs are an important fishery among urban Broward and Miami-Dade county anglers. Annual creel surveys in WCA-3 (December–May dry season) demonstrate this popularity where anglers expend an average of 25,000 angling hours per year toward LMB, which represents approximately 50 percent of the total angling effort for the area (FWC, 2013). The remaining fishing effort was divided between sunfish and catfish. Catch rates of LMB in the L67A canal are the highest in the state, with a long-term average near two LMB per angler hour; however, due to catch and release ethics, long-term harvested rates average less than 0.1 LMB per angler hour (FWC, 2012). Anglers catch and release LMB and choose to harvest species that are lower in Hg such as sunfish, catfish, exotic Mayan cichlids, and oscar, which have average harvest rates of 2.9, 1.3, 5.8, and 2.6 fish per angler hour, respectively. It has not been determined if the low

harvest rate for LMB is due to knowledge of Hg contamination or if it is related to the "catch-and-release" ethic that prevails among bass anglers.

Although Hg in fish remains a significant water quality issue within the EPA, human health criteria are commonly exceeded at other locations within the Greater Everglades system. In Holey Land WMA, site HOLYBC, THg in harvestable size LMB collected during WY2013 (n=17) exceeded the USEPA criterion (**Table 3B-1**). During WY2013, 88 and 81 percent of the harvestable size LMB collected from the Upper Kissimmee Basin lakes, sites TOHO and ETOH, respectively, exceeded the USEPA criterion. Median THg concentrations in each lake also exceeded the criterion (**Table 3B-1**), supporting the current advisories urging one meal per month for women and children. Similar advisories exist for LMB fisheries within other upper basin lakes as well as more liberal consumption advice for five other lower trophic level species of freshwater sport fish (FDOH, 2013).

Hg in fish, particularly in LMB, remains an important water quality issue in the EPA. However, fisheries management including fish consumption advisories, length and bag limits, and angler ethics can mitigate potential adverse health effects for anglers. Nonetheless, LMB continues to provide a means for monitoring spatial and temporal trends in ambient MeHg concentrations in an Everglades apex predator. In summary, it is evident from both single year and multiyear monitoring results that a north-to-south gradient in Hg bioaccumulation exists across the EPA, with maximal rates of bioaccumulation occurring in SRS in ENP. However, existing data indicate that other fresh waters in ENP have lower rates of Hg bioaccumulation. Moreover, conditions that lead to high rates of MeHg bioaccumulation are not unique to the EPA as high rates of bioaccumulation also occur in the Upper Kissimmee Basin lakes.

MOSQUITOFISH AND SUNFISH

Binhe Gu and Ted Lange[3]

Introduction

As stated previously, elevated Hg concentrations in fish and biota have been a concern for the Everglades regions since the 1970s. Accumulation of Hg in aquatic biota is of concern for both human health and wildlife. This concern is due to the ability of Hg to bioaccumulate and biomagnify in food webs to concentrations that may pose a potential health threat to wildlife and humans that consume fish (Hammerschmidt and Fitzgerald, 2006). Harmful health effects associated with high Hg concentrations have been observed in Everglades biota that have a semi-aquatic diet, including wading birds, alligators and Florida panthers (Cleckner et al., 1998).

This section provides an update to Hg fish tissue concentrations within mosquitofish (*Gambusia* spp.) and sunfish species (bluegill, *Lepomis macrochirus*; redear sunfish, *L. microlophus*; and spotted sunfish, *L. punctatus*). Hg data for warmouth sunfish (*L. gulosus*), which is positioned at approximately one trophic level in the food chain higher than that of the other three sunfish species, has been collected but are not reported. Mosquitofish provides an estimate of short-term exposure and represents a lower trophic level fish, which has the ability to shift its trophic level depending on age, habitat, and diet (Williams and Trexler, 2006). Alternatively, sunfish provide a longer-term environmental exposure estimate and represents a higher trophic level organism.

Methods

Fish Sampling Stations within the Greater Everglades Ecosystem

To assess THg concentrations and trends in fish, 12 monitoring stations have been established within the EPA and Holey Land and Rotenberger WMAs (**Figure 3B-4**). These stations are part of the long-term Hg monitoring projects of the South Florida Water Management District (SFWMD or District). Mosquitofish are selected as a representative indicator of short-term, localized changes in water quality because of their small size range, short life span, and widespread occurrence in the Everglades. Mosquitofish become sexually mature at approximately three weeks of age and have an average life span of only four to five months (though some individual females may live up to 1.5 years). Sunfish are thought to have an average life span of four to seven years in the wild. Sunfish are prevalent in the Everglades and are the preferred prey for several fish-eating species; therefore, this species was selected as an indicator of Hg exposure for wading birds and other fish-eating wildlife.

Fish collection was conducted once per water year in September and November using dip nets and boat mounted DC electrofishing equipment. At each station, one mosquitofish composite sample consisting of at least 100 individuals was collected using a dip net. Using electrofishing, up to 10 bluegill sunfish in the target size range of 102 to 178 mm (i.e., 4 to 7 inches) were collected at each station while the remaining sunfish were divided among the common species encountered at each site. A total of 20 sunfish were collected at each site. Species was identified, and TL and weight of each individual were measured at the laboratory. Each mosquitofish composite sample and each sunfish were homogenized respectively in laboratory for THg analysis.

Data Screening and Handling

The Hg data evaluated in this section of the chapter were retrieved from the District's DBHYDRO database. Similar t water quality analysis within this chapter and Chapter 3A of this volume, fish tissue data were screened based on laboratory qualifier codes. These qualifiers are consistent with the FDEP's Quality Assurance Rule [Chapter 62-160, Florida Administrative Code (F.A.C.)]. Any datum associated with a fatal qualifier (e.g., H, J, K, N, O, V, Q, Y, or Z) indicating a potential data quality problem was removed from the analysis (SFWMD, 2008). Fatal qualifiers are standard data qualifiers by both laboratories used for sample analysis and data users to indicate that the quality or accuracy of the data may not be suitable for statistical analysis.

Analysis

Fish tissue THg concentrations were summarized by station, region, and species using basic descriptive statistics for the current water year and the entire period of record (WY1999–WY2013). Spearman rank correlation analysis was applied to annual regional and stationwide fish tissue THg concentrations. Kruskal-Wallis analysis was used to test significant difference among three or more datasets.

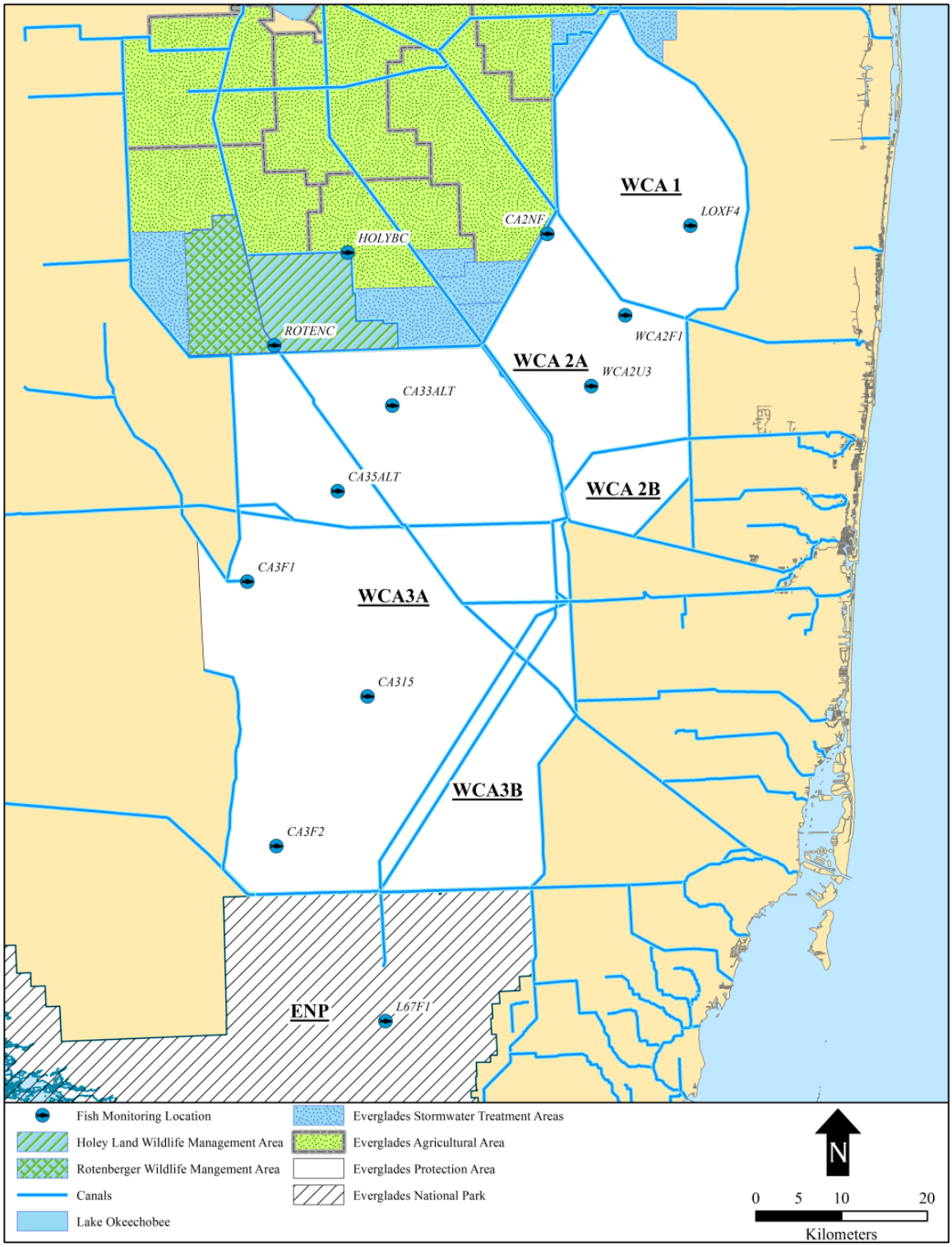

Figure 3B-4. Location of fish tissue monitoring locations within the EPA and Holey Land and Rotenberger Wildlife Management Areas (WMAs).

Results and Discussion

Mosquitofish

Mosquitofish composite samples from across the EPA have been collected for THg analysis since WY1999 (**Figure 3B-5**). During WY2013, THg concentrations in mosquitofish from 12 monitoring sites ranged from 0.01 mg/kg at site WCA2F1 to 0.19 mg/kg at site WCA2U3, with a median concentration of 0.05 mg/kg. In contrast to WY2012 where THg levels in mosquitofish were higher than the previous year at most sites, 10 of the 12 sites showed lower THg concentrations in WY2013 than in WY2012, representing on average an over 40 percent decline. There was no significant temporal trend of THg in mosquitofish over the POR for any site (Spearman Rank Order Correlation, all p>0.05). This is partly due to considerable interannual variations in THg concentrations within sites (**Figure 3B-6**). However, between 2000 and 2006 there was a significant drop and more or less leveling off or a slight increase thereafter in mosquitofish THg concentration (**Figure 3B-6**). Unlike sunfish and LMB, the highest THg concentrations in mosquitofish did not occur in ENP (**Figure 3B-5**).

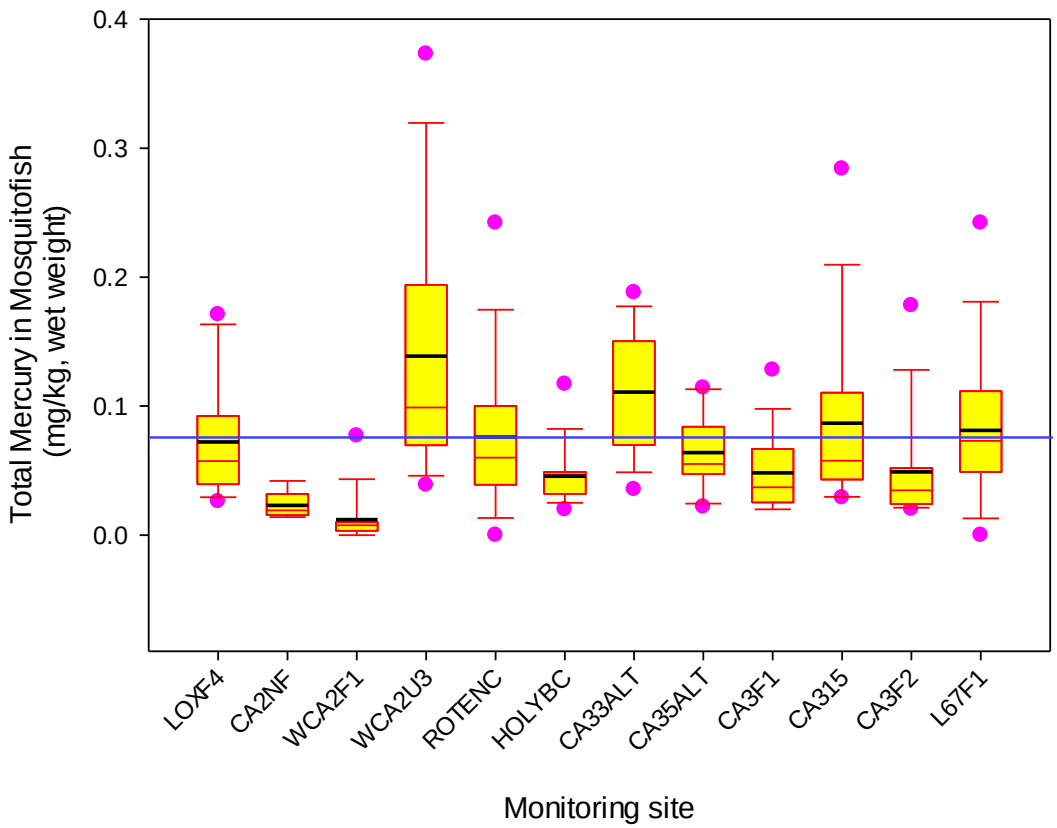

Figure 3B-5. Box plots of THg concentrations in mosquitofish at each monitoring site from WY1999–WY2013. Black and red lines within each box are annual average and median value, respectively. Blue line denotes the 0.077 mg/kg U.S. Environmental Protection Agency (USEPA) methylmercury (MeHg) criterion for trophic level 3 (TL3) fish for protection of wildlife.

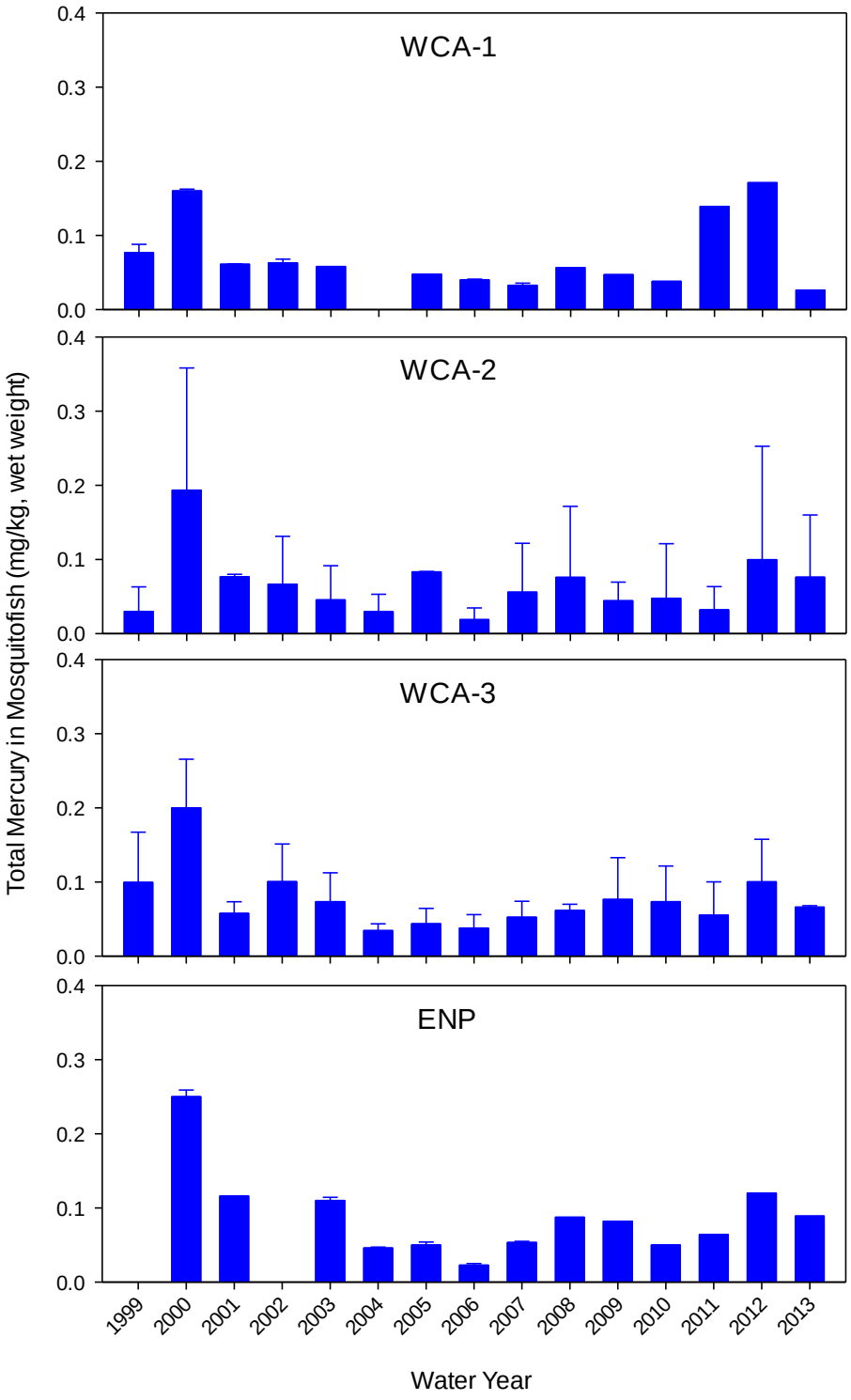

Figure 3B-6. Annual THg concentrations in mosquitofish composite samples at Water Conservation Areas 1, 2 and 3 (WCA-1, WCA-2, and WCA-3, respectively), and Everglades National Park (ENP or Park) from WY1999–WY2013. Error bars represent one standard deviation.

Since WY2006, when samples were collected from all 12 sites, the average percent change in mosquitofish THg within sites between two consecutive years was 60 percent. For example, THg concentration in the interior site of WCA-1 (LOXF4) changed from 0.17 mg/kg in WY2012 to 0.03 mg/kg in WY2013; THg concentration in the interior site (WCA2U3) of WCA-2 in WY2012 was highest (0.37 mg/kg) for the POR but decreased to 0.19 mg/kg in WY2013. It is not clear what factor(s) control the dramatic temporal variations in mosquitofish THg concentration within sites. However, significant interannual changes in precipitation, which affects prey availability and biogeochemistry [SO_4^{2-}, Hg^{2+}, dissolved organic carbon (DOC), and reduction-oxidation (redox)], might have played an important role on controlling THg concentration in mosquitofish.

In WY2013, THg concentrations in mosquitofish exceeded the federal criterion of 0.077 mg/kg MeHg for Trophic Level 3 (TL3) fish for protection of wildlife (USEPA, 1997) at 3 of the 12 monitoring sites. For the POR, 33 percent of the data exceeded the federal criterion. Site CA2NF near the L-6 Canal and site WCA2F1 near the Hillsborough Canal had no exceedance for the monitoring period. The site with the highest frequency of exceedance is WCA2U3, an interior site of WCA-2A, where over 70 percent of the mosquitofish composite samples exceeded federal criterion. Frequency of exceedances among sites fluctuated over time and no increasing or decreasing trend was found ($r=0.031$, $p=0.91$). It is noteworthy that CA2NF and WCA2F1 are located in the northern portion of WCA-2A near the Stormwater Treatment Area 2 (STA-2) outflow and within the heavily nutrient enriched areas of the marsh. On the other hand, WCA2U3 is located in the nutrient-poor area on the mid-southern end of the marsh.

Low THg concentrations (i.e., less than 0.077 mg/kg) in mosquitofish were found in wet years (WY2000, WY2002–2007, and WY2011), and THg concentrations greater than 0.077 mg/kg were typically associated with drought years. Drought conditions and dry out have been found to promote SO_4^{2-} production and Hg release from sediments and, consequently, high rates of Hg methylation in the Everglades (Gilmour et al., 2004; Rumbold and Fink, 2006). The annual median THg concentrations in mosquitofish in WCA-1 (0.06 mg/kg), WCA-2 (0.06 mg/kg) and WCA-3 (0.06 mg/kg) were less than THg concentrations at site L67F1 (0.07 mg/kg) in ENP SRS, but these differences are not statistically significant (Kruskal-Wallis analysis, $H=2.669$, $p=0.446$).

Sunfish

Three TL3 sunfish species—bluegill, redear sunfish, and spotted sunfish—have been sampled for THg analysis in the EPA since WY1999 (**Figure 3B-7**). The overall average sunfish whole-body concentration of THg for data pooled from all sites and years is 0.17 ± 0.17 mg/kg ($n=2469$). These values exceeded the USEPA MeHg criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. The average THg concentration for the POR was highest at the ENP site L67F1 (0.37 mg/kg for all sunfish) and lowest (0.04 mg/kg) at a WCA-2A site (WCA2F1) near the Hillsborough Canal (**Figure 3B-7**). This distribution pattern of THg concentrations in sunfish is consistent with that in mosquitofish. All interior sites in WCA-2 and WCA-3 displayed high long-term average THg concentrations (~0.200 mg/kg). The THg concentration in sunfish tended to increase from north to south (**Figure 3B-8**). There was no significant temporal trend of THg concentrations in all three sunfish species within each site (Spearman rank order correlation, all $p>0.05$). However, when only THg data from the target range (102–178 mm) of the dominant sunfish (bluegill) are used, three sites displayed significant trends over time, with increases in THg concentration in the interior sites of WCA-2 (U3) and WCA-3 (CA33ALT) and decrease in the Park (L67F1) (**Figure 3B-9**).

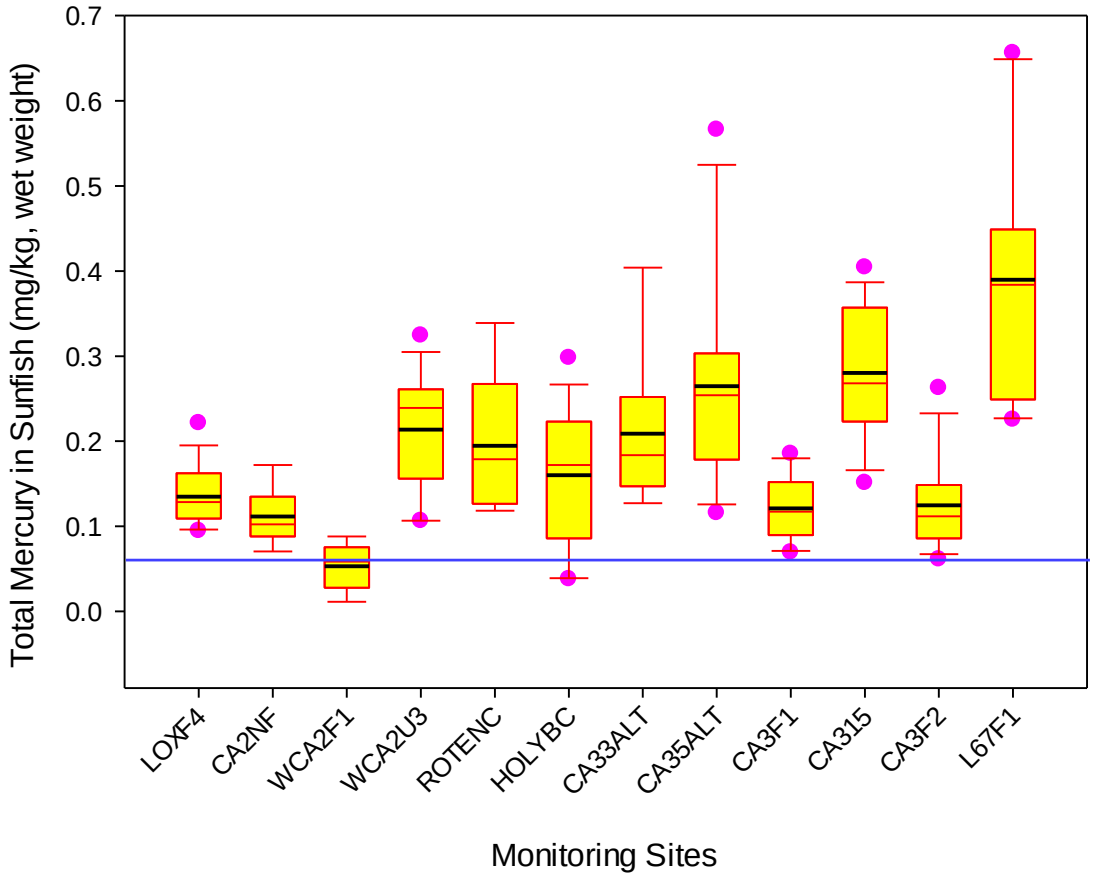

Figure 3B-7. Box plots of annual THg concentrations sunfish at each EPA monitoring site from WY1999–WY2013. Black and red lines within each box are annual average and median value, respectively. Blue line denotes the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of wildlife.

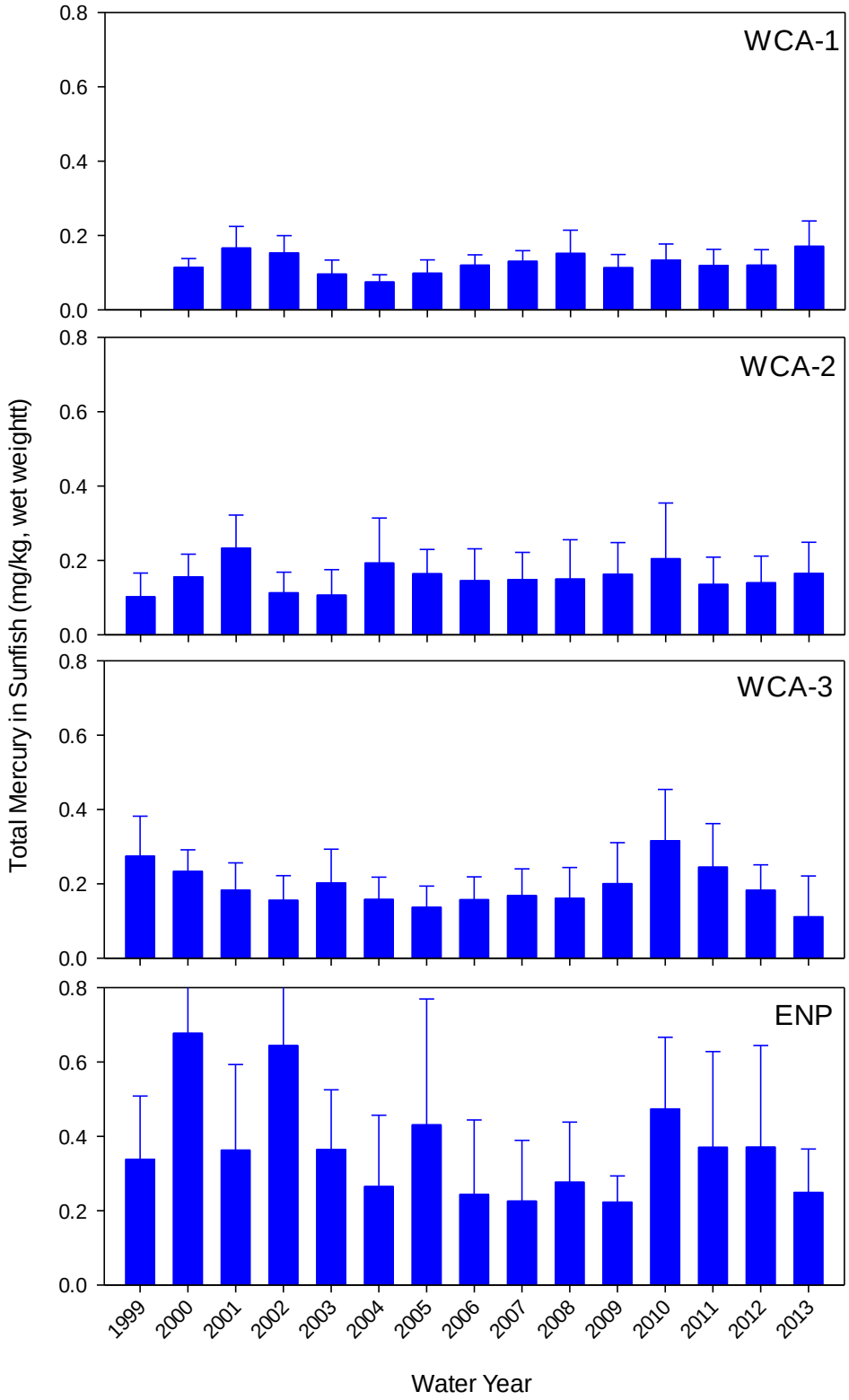

Figure 3B-8. THg concentrations TL3 sunfish at WCA-1, WCA-2, WCA-3, and ENP from WY1999–WY2013. Error bars represent one standard deviation.

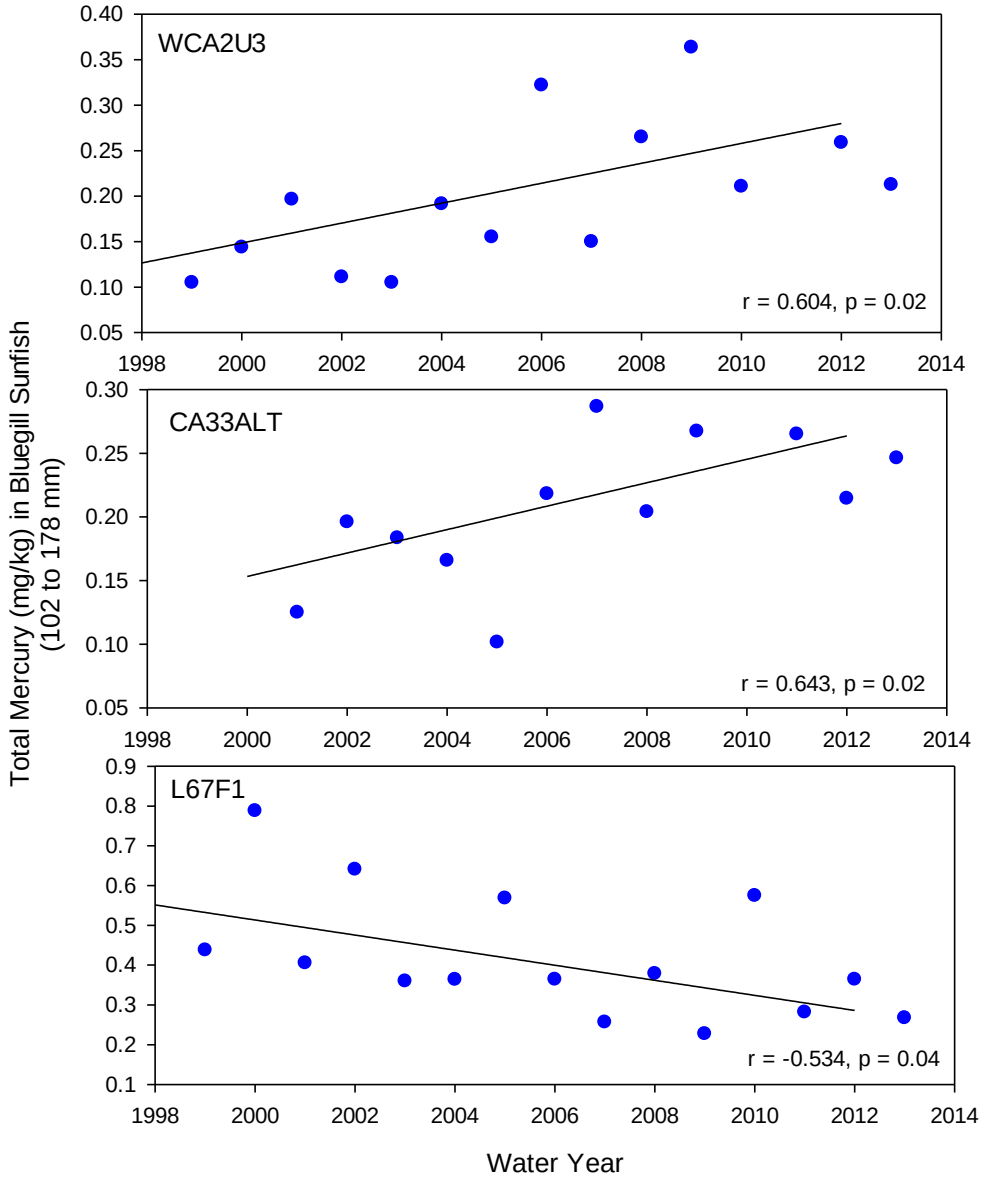

Figure 3B-9. Changes in THg concentrations of bluegill sunfish of the target range [102–178 millimeters (mm)] from WY1999–WY2013 at three EPA monitoring sites. There was a significant increase or decrease of THg concentration over time at these sites. Sites with no significant correlation are not shown.

During WY2013, the average THg concentration in the three TL3 sunfish species from 9 monitoring sites was 0.18 mg/kg, with a range from 0.10 mg/kg at WCA2F2 to 0.25 mg/kg at L67F1, which exceeded the federal MeHg criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. Compared to WY2012, THg concentrations in sunfish on average decreased by 0.02 mg/kg, with these reductions observed in 5 of the 9 sites. THg concentration in these species from all sites for the POR was highest in spotted sunfish (0.26 mg/kg), followed by bluegill (0.19 mg/kg), and redear sunfish (0.12 mg/kg), which could be due to feeding preferences between the three species (**Figure 3B-10**).

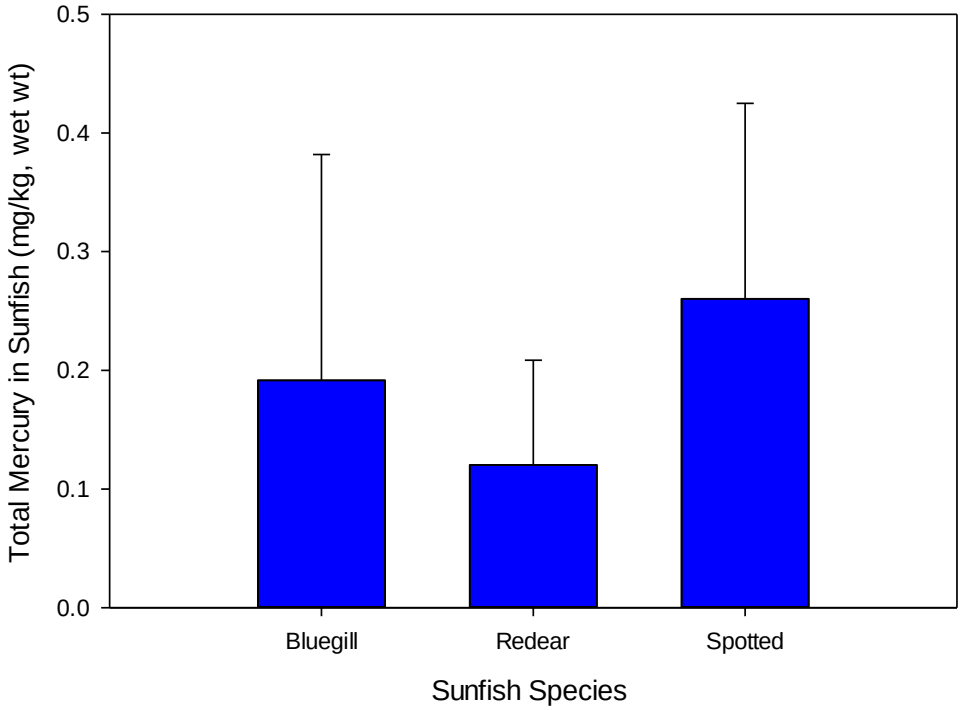

Figure 3B-10. Mean (± standard error) THg concentration for each sunfish species from WY1999–WY2013.

In summary, during WY2013, THg concentrations in mosquitofish and sunfish from the majority of the monitoring sites across the EPA exceeded the federal criterion for wildlife protection. Most sites did not exhibit an increasing trend in THg concentrations over the past 15 years. Mosquitofish THg concentrations in the southern portion of the EPA (WCA-3 and ENP) were generally higher than those in the central and northern WCAs. Similarly, there is a clear north-to-south trend of increasing THg concentrations in sunfish in the EPA, consistent with the distribution pattern of Hg concentrations in LMB (Gu et al., 2012).

MERCURY SOURCE TO THE EVERGLADES

STATEWIDE MERCURY TOTAL MAXIMUM DAILY LOAD UPDATE

Russ Frydenborg[2]

As discussed in Chapter 3B of the *South Florida Environmental Report (SFER) – Volume I* (Axelrad et al., 2013), the Statewide Mercury Total Maximum Daily Load (TMDL) Project involved gathering and assessing a complex suite of data (on Hg emissions, deposition, aquatic cycling and bioaccumulation) and conducting modeling to quantify the needed Hg reductions in order to address Hg-related impairment in surface waters. Elements of the Hg TMDL study included the following:

- Collecting comprehensive, highly temporally resolved measurements of wet and dry Hg deposition at four locations, along with a suite of tracers that may be used to link deposition with sources [Note: Sampling areas are referred to as "Supersites"]
- Identifying all significant sources of Hg (emissions inventory), whether fixed or mobile, in Florida
- Conducting atmospheric modeling (both dispersion and receptor models) to quantify Florida Hg sources versus those sources outside Florida that must be controlled to satisfy the TMDL
- Developing an empirical, probabilistic aquatic-cycling model to predict Hg levels in fish as a function of water quality parameters

In 2012, a draft of the Hg TMDL was published and revised based on public comment, and subsequently approved by the secretary of the FDEP. During the 2013 Florida legislative session, the Hg TMDL was ratified by the Florida legislature.

The statewide Hg TMDL requires an 86 percent reduction from all emission sources (local, regional, and global) and includes a waste load allocation of 23 kilograms per year. The TMDL, which includes an implicit margin of safety, is protective of the most sensitive components (children and women of childbearing age) and is applicable to all state waters (both fresh and marine). TMDL and supporting documentation used to develop the statewide Hg TMDL can be found at http://www.dep.state.fl.us/water/tmdl/draft_tmdl.htm#mercury.

ATMOSPHERIC MERCURY DEPOSITION TRENDS

Paul Julian II[1]

Introduction

The source of Hg^{2+} to the Everglades, as in most aquatic/semi-aquatic ecosystems, is through atmospheric deposition (Hammerschmidt and Fitzgerald, 2005; Liu et al., 2008). Due to amendments to the Clean Air Act (Public Law 101-549, Title IV), near-field (i.e., local) sources of Hg have been significantly reduced within the United States (FDEP, 2012). However, far-field (i.e., global) sources are still relatively unregulated and are the primary sources of Hg to the Everglades (Driscoll et al., in press). These sources are transported via the atmosphere, which is the principal transport pathway. Wet deposition of Hg from the atmosphere to the land/water surface is the result of scavenging of aerosol Hg and reactive gaseous forms of Hg (Guentzel et al., 2001). This section reports on the estimated Hg wet deposition flux and associated atmospheric load to the EPA using monitoring locations within the Mercury Deposition Network (MDN; **Figure 3B-11**).

Methods

Hg wet deposition data was retrieved from the National Atmospheric Deposition Program (NADP) MDN for the monitoring locations within the EPA (**Figure 3B-11**). The NADP is a cooperative effort among various groups—including federal, state, tribal, and local governmental agencies; educational institutions; private companies; and non-governmental agencies—to provide high quality atmospheric deposition data on various parameters. Similar to monitoring conducted for the NADP National Trend Network (NTN; discussed elsewhere in this chapter), rainfall is sampled in a specialized automated collector. Both laboratory and field data are rigorously checked according to quality assurance/quality control protocols approved by the USEPA.

There are three active MDN stations located within the EPA. Monitoring was discontinued at site FL04 during October 2006, at which time site FL97 began operation. To provide a regional assessment of Hg wet deposition, monitoring locations were assigned to different regions of the EPA. Monitoring stations FL34 was used to assess Hg deposition for the northern EPA (WCA-1 and WCA-2), FL97 and FL04 were used to assess Hg deposition within the central EPA (WCA-3), and FL11 was used to assess Hg deposition within the southern EPA (ENP).

Monthly Hg atmospheric deposition data was summarized by water year, which covers both the wet (May–October) and dry (November–April) seasons. The POR of this assessment includes WY1996–WY2012. For purposes of data analysis and summary statistics, data reported as less than the method detection limit (MDL) were assigned a value of one-half the MDL, unless otherwise noted. Annual precipitation weight mean (PWM) Hg concentrations were also calculated. Atmospheric loads were estimated by multiplying annual Hg atmospheric deposition values by the area of each region within the EPA. Regions were delineated latitudinally with the northern region accounting for WCA-1, central region for WCA-2 and WCA-3 combined and southern region for ENP. Water years with less than 12 months of data were not included in any statistical analysis. Trend analysis was performed on Hg deposition and PWM concentrations using the Kendall's τ correlation analysis. The Steel-Dwass multiple comparison test was used to compare Hg wet deposition and PWM concentrations among regions. All analysis was conducted using JMP® (Version 10.0.0, SAS, Cary, NC, USA) and the critical level of significance was set at $\alpha = 0.05$.

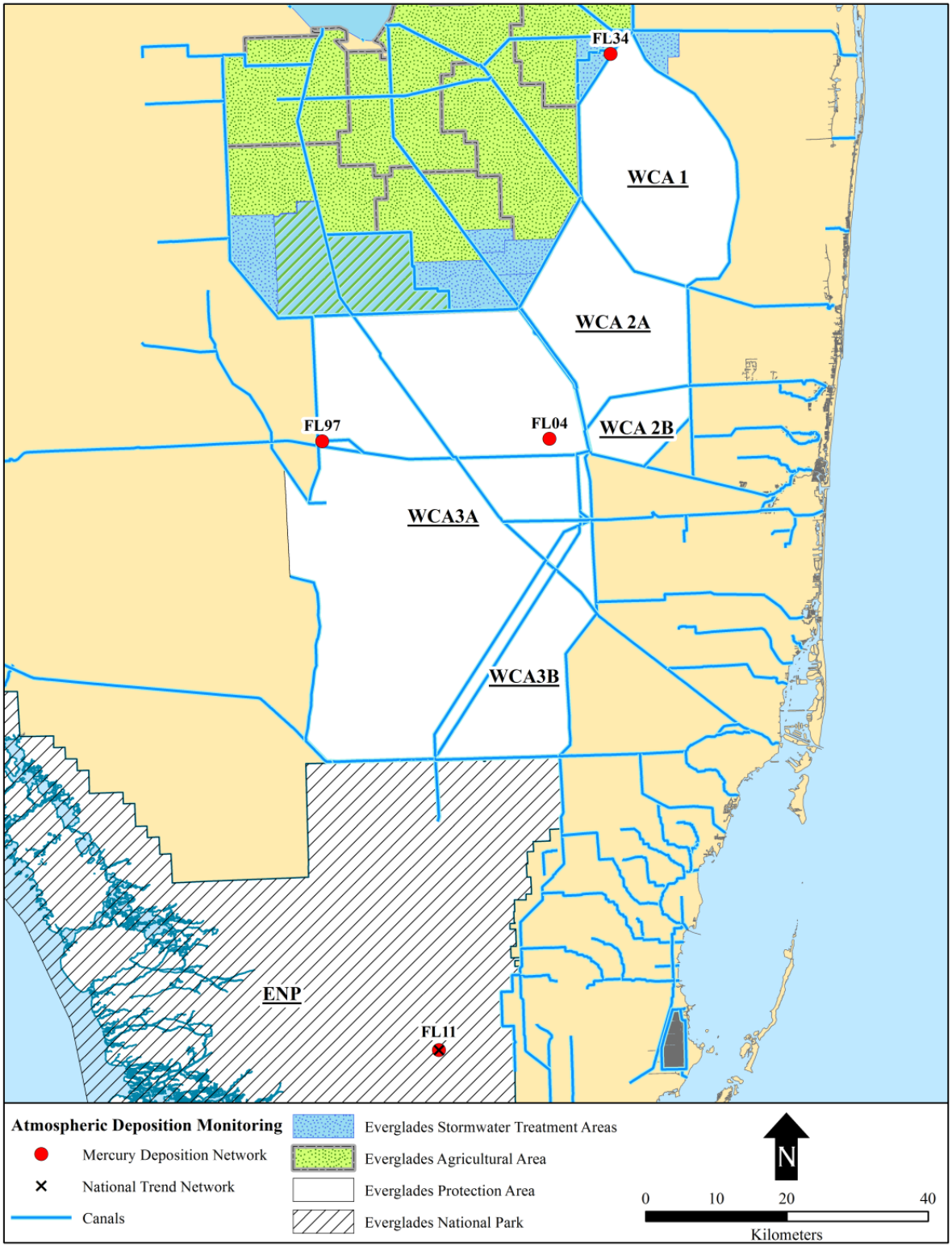

Figure 3B-11. Locations of atmospheric monitoring locations within the EPA (WCA-1, WCA-2, WCA-3, and ENP) and their associated monitoring networks.

Results and Discussion

Annual Hg wet deposition has remained relatively constant throughout the current POR for the northern, central, and southern EPA (**Table 3B-2**), with wet deposition values ranging from 7.7 micrograms per square meter (µg/m^2) to 26.1 µg/m^2 for all regions (**Figure 3B-12**). Wet deposition was significantly different between the southern and northern regions and the northern and central regions but not between the southern and central regions (**Table 3B-3**). Wet deposition seems to follow a south-to-north gradient, with the southern region exhibiting the highest POR mean (WY1996–WY2012) Hg wet deposition (19.7 ± 0.8 µg/m^2), followed by the central (18.3 ± 0.8 µg/m^2) and northern (14.6 ± 1.0 µg/m^2) regions. As the primary source of atmospheric Hg is international, the deposition patterns could potentially be driven by local weather patterns.

Similar to the wet deposition trend, Hg PWM concentrations remained relatively constant throughout the POR for the southern and central regions of the EPA, with the northern region experiencing slight fluctuations among years (**Table 3B-2**) and with PWM concentrations ranging from 6.9 to 17.2 nanograms per liter (ng/L) (**Figure 3B-12**). PWM Hg concentrations were significantly different between the northern and central regions, but not between the northern and southern, or central and southern regions (**Table 3B-3**).

Table 3B-2. Kendall's τ trend analysis results for both mercury (Hg) wet deposition and precipitation weight mean (PWM) concentrations for each region of the EPA.

Wet Deposition			
Region	**R**	**Kendall's τ**	**ρ value**
Northern	0.06	0.10	0.62
Central	-0.25	-0.19	0.35
Southern	-0.05	0.05	0.78
Precipitation Weight Mean Concentration			
Region	**R**	**Kendall's τ**	**ρ value**
Northern	0.25	0.15	0.48
Central	-0.06	-0.03	0.87
Southern	0.06	0.02	0.93

Table 3B-3. Steel-Dwass multiple comparison results for both Hg wet deposition and PWM concentrations comparing each region of the EPA. Significant ρ-values are bold and italicized.

Wet Deposition

		Northern	**Central**	**Southern**	
Northern	**ρ value**		-2.4	3.06	**Z Score**
Central		***<0.05***		1.48	
Southern		***<0.01***	0.30		

Precipitation Weight Mean Concentration

		Northern	**Central**	**Southern**	
Northern	**ρ value**		-2.41	1.43	**Z Score**
Central		***<0.05***		-1.56	
Southern		0.32	0.26		

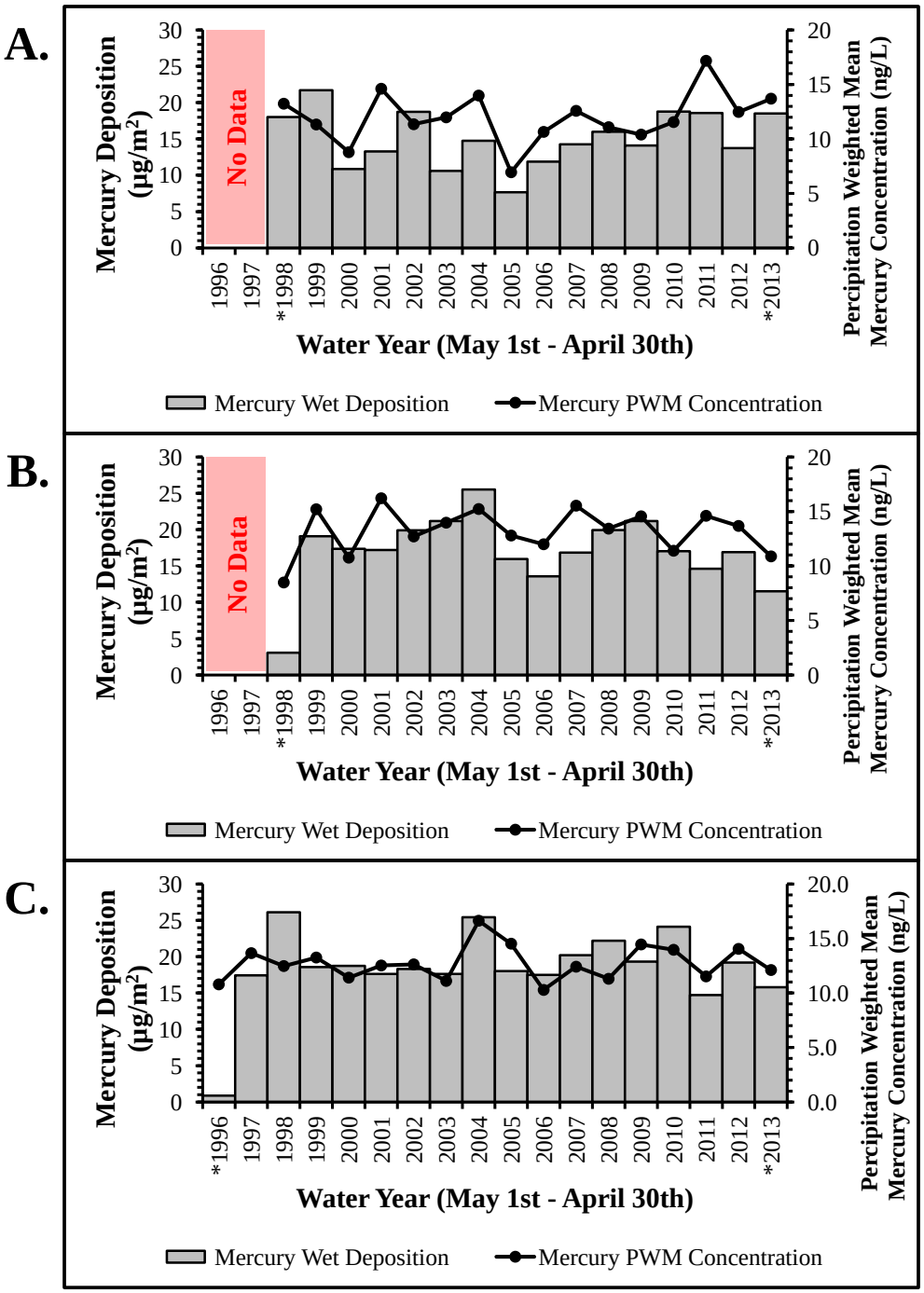

Figure 3B-12. Annual Hg deposition [in micrograms per square meter (µg/m^2)] and annual precipitation weight mean (PWM) [in nanograms per liter (ng/L)] Hg concentrations for the (A) northern, (B) central and (C) southern regions of the EPA for WY1996–WY2013. Stations with less than 12 months of data are identified with an asterisk (*).

Previously, it has been determined that the primary source of Hg to the Everglades is that of atmospheric deposition (Atkeson and Axelrad, 2004). During WY2012, atmospheric loading was highest within ENP between all regions of the EPA, followed by WCA-3, WCA-1, and WCA-2 (**Table 3B-4**). Furthermore, data presented within **Table 3B-4** supports the claim that the primary source of Hg to the Everglades is through atmospheric deposition with percent atmospheric contribution range from 96 to 99 percent throughout the EPA.

Annually both wet deposition and PWM trends were relatively consistent. A slight decline in both deposition and PWM concentrations have been observed in the recent water years for the central (WY2009–WY2012) and southern (WY2010–WY2012) EPA. However these values are well within the inter-annual variation throughout the POR. The northern EPA has experienced slight increases in both wet deposition and PWM trends in recent years (since WY2009). Qualitatively, it seems that there is a latitudinal gradient, with the southern and central regions receiving higher atmospheric deposition fluxes relative to the northern region. It should be noted that these values are derived from single stations within each region; therefore, these values should be used with caution. Additional analyses should be considered including error analysis associated with the use of these stations to estimate wet Hg deposition as well as exploratory Hg dry deposition analyses to quantify the dry Hg deposition quantities to the Everglades in an effort to refine atmospheric Hg deposition estimates.

Unfortunately, due to the data release schedules, this assessment only spans WY1996–WY2012. **Figure 3B-12** includes data for WY2013, but it should be noted that this dataset is currently incomplete. Therefore, values presented for WY2013 should be used with caution and are expected to be updated in the following SFER.

Table 3B-4. Atmospheric load of total mercury (THg) to each region of the EPA, including the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), Water Conservation Areas 2 and 3 (WCA-2, and WCA-3), and Everglades National Park (ENP), during WY2012 and mean (± standard error) surface water load amount during WY2001–WY2008.

Region	Atmospheric Load (kilograms)	WY2001–WY2008 Surface Water Inflow Load* (kilograms)	Percent Atmospheric Contribution
Refuge	10.5	0.27 ± 0.03	97
WCA-2	9.9	0.51 ± 0.06	95
WCA-3	40.4	1.89 ± 0.18	96
ENP	75.9	1.12 ± 0.21	99

* Load calculated using annual mean THg concentrations and flow data reported in Chapter 3A of this volume.

SULFUR SOURCES AND EFFECTS

SULFATE WITHIN THE EVERGLADES PROTECTION AREA

Paul Julian II[1]

Introduction

The primary source of Hg to the Everglades is through global transport and atmospheric deposition, as demonstrated within this chapter. Once deposited, Hg can be converted to MeHg, primarily by sulfate-reducing bacteria (SRB), which utilize SO_4^{2-} to metabolize organic matter under anaerobic conditions and to methylate THg (Gilmour and Henry, 1991; Gilmour et al., 1998). The exact quantitative role that SO_4^{2-} plays in the sulfur/Hg biogeochemical cycle is relatively unknown; biogeochemical cycling of Hg within the Everglades is complex and confounded by other variables. However, based on previous and ongoing research, SO_4^{2-} can potentially influence the Hg/MeHg cycle under some suite of ambient conditions. These complexities must be understood and quantified before an effective control or management strategy can be designed and implemented. Furthermore, various sources of SO_4^{2-} to the Everglades originate from both natural (oxidation of peat soil, groundwater, etc.) and anthropogenic sources (atmospheric deposition, fertilizer application, etc.). The purpose of this section is to provide an update to the SO_4^{2-} condition within the EPA, which was reported in Volume I, Chapter 3A, in previous SFERs.

Methods

A regional synoptic approach similar to that used for water quality evaluations in previous SFERs was applied to SO_4^{2-} data for WY2013 to provide an overview of SO_4^{2-} concentrations within the EPA. Consolidating regional water quality data provides the ability to analyze data over time but limits spatial analyses within each region. However, spatial analyses can be made among regions, because the majority of inflow and pollutants enter the northern third of the EPA and the net water flow is from north to south.

Water Quality Sampling Stations in the EPA

To efficiently assess annual and long-term water quality trends, a network of water quality sampling sites has been identified (Figures 3A-1 through 3A-4 of this volume). These sites are part of the District's long-term monitoring projects and are monitored for different purposes. These stations were carefully selected to be representative of either the EPA boundary conditions (i.e., inflow or outflow) or ambient marsh conditions (interior). Sampling locations throughout the WCAs and ENP were categorized as inflow, interior, or outflow stations within each region based on their location and function. Furthermore, an effort has been made to utilize a consistent group of stations among previous annual reports to ensure consistent and comparable results. Every attempt is made to maintain the same sampling frequency for the network of monitoring sites to ensure a consistent number of samples across years. The data available for each year undergo the same careful quality assurance/quality control screening to assure accuracy. The current District monitoring programs were described by Germain (1998). An overview of the water quality monitoring projects, including project descriptions and objectives with limited site-specific information, is available on the District's website at www.sfwmd.gov/environmentalmonitoring. The majority of the water quality data evaluated in this chapter were retrieved from the District's DBHYDRO database. Additionally, water quality data from the nutrient gradient sampling stations monitored by the District were obtained from the District's Water Resources Division database.

Analysis Periods

The primary focus of this section is to summarize SO_4^{2-} concentrations within the EPA during WY2013 and describe trends or changes in these concentrations over time. To accomplish this objective, comparisons are made across discrete periods that correspond to major restoration activities occurring within the EPA. The four periods are the (1) Baseline period including WY1979–WY1993, (2) intermediate period, or Phase I, includes WY1994–WY2004, (3) Phase II Best Management Practices (BMP)/STA implementation period after WY2004 (WY2005–WY2012), and (4) the current water year (WY2013).

The Baseline period corresponds to the timeframe prior to implementation of the Everglades Agricultural Area (EAA) BMP Program and the Everglades Construction Project, i.e., Everglades STAs. Phase I represents the period in which implementation of the EAA BMP Program was increasing, and all the initial STAs were constructed and became operational. The Phase II BMP/STA implementation period corresponds to when the performance of the BMPs and STAs were being optimized and enhanced. Additionally, during this period, various restoration projects were being implemented under the Long-Term Plan for Achieving Water Quality Goals in the EPA and Comprehensive Everglades Restoration Plan (CERP). Because optimization, enhancement, and other restoration activities are expected to continue for years, the Phase II period will continue to expand in future SFERs to incorporate additional years of sampling. In addition, data for the current water year (in this case, WY2013) will be used to make comparisons with the historical periods and will be analyzed independently as the fourth period.

Data Screening and Handling

Water quality data were screened based on laboratory qualifier codes, consistent with the FDEP's Quality Assurance Rule (Chapter 62-160, F.A.C.). Any datum associated with a fatal qualifier (e.g., H, J, K, N, O, V, Q, Y, or Z) indicating a potential data quality problem was removed from the analysis (SFWMD, 2008). Fatal qualifiers are standard data qualifiers used by both laboratories and field samplers to indicate that the quality or accuracy of the data may not be suitable for statistical analysis. As such data qualifiers can be used to indicate that a sample was not properly preserved (qualifier Y), sample was not analyzed within the acceptable window (qualifier Q), the analytical analysis was flawed (qualifier J, K, N, O, V, and ?), or data was estimated with a lower accuracy method (qualifier H). Multiple samples collected at the same location on the same day were considered as one sample, with the arithmetic mean used to represent the sampling period. Additional considerations in the handling of water quality data are the accuracy and sensitivity of the laboratory method used. For purposes of summary statistics presented in this section, data reported as less than the MDL were assigned a value of one-half the MDL unless otherwise noted. All data in this chapter, including historical results, were handled consistently with regard to screening and MDL replacement.

Analysis

Surface water SO_4^{2-} concentrations were summarized for each period, region, and classification using basic descriptive statistics including arithmetic mean, standard deviation, sample size, minimum, maximum, and median. Typically, geometric mean concentrations were employed when reporting concentrations at a given sampling location. Due to low sample size at each station, arithmetic mean concentrations were also employed for monitoring locations. Annual flow-weighted mean (FWM) SO_4^{2-} concentrations for WY2013 were estimated using flow and load values calculated from the Java-based District nutrient load program. Kendall's τ correlation statistic was applied to annual mean SO_4^{2-} concentrations of inflow and interior portions of each region of the EPA to determine trend direction and significance. ANOVA was used to determine if SO_4^{2-} loads were different between the analysis periods; for this analysis, the

current water year (WY2013) was included in the Phase II period. To detect difference among means, the Tukey-Kramer honestly significant difference test was used. Annual SO_4^{2-} load values for each region of the EPA were log-transformed to fit the assumptions of the statistical test and tested for normality using the Sharpiro-Wilk's W test. All statistical operations were performed with JMP® (Version 10.0.0, SAS, Cary, NC, USA). The critical level of significance was set at $\alpha = 0.05$.

Results and Discussion

Sulfate Concentrations

Sulfur is an essential plant macro-nutrient (Bellinger and Van Mooy, 2012) and enters the Everglades ecosystem primarily as SO_4^{2-} (Orem et al., 2011), but the role of organic sulfur in the total mass of sulfur entering the region remains undetermined. As stated above, SO_4^{2-} is of concern due to its ability to influence biogeochemical processes through microbial pathways that lead to Hg methylation and support the production of reduced sulfur compounds under anaerobic conditions. SO_4^{2-} monitoring results are presented in this section to provide an overview of current concentrations and evaluate temporal and spatial patterns. SO_4^{2-} summary statistics relative to the Baseline, Phase I, Phase II, and current year (WY2013) are shown in **Table 3B-5**.

Similar to other water quality parameters within the EPA, SO_4^{2-} follows a general north-to-south concentration gradient (**Figure 3B-13**). This gradient is apparent for inflow regions within the EPA for WY2013, with the highest mean SO_4^{2-} concentrations observed in the Refuge peripheral canals (50.9 mg/L), followed by WCA-2 (34.1 mg/L), WCA-3 (21.5 mg/L), and ENP (3.5 mg/L) inflows. Inflows into the Refuge, WCA-2, and ENP experienced a slight decrease in annual mean (arithmetic and geometric) and median SO_4^{2-} concentrations relative to the Phase II period. Meanwhile, annual mean (arithmetic and geometric) and median inflow SO_4^{2-} concentrations into WCA-3 were elevated relative to the Phase II period. The slight increase in the annual SO_4^{2-} concentrations in WCA-3 could be due to increased surface water flow into the EPA, more specifically WCA-3. WCA-3 experienced a 43 percent increase in surface water inflow volume from the previous water year (see Chapter 3A of this volume), which could provide an increase in SO_4^{2-} load.

Even though WCA-3 experienced a slight increase of SO_4^{2-} concentrations relative to the Phase II period, all regions experienced a significant decreasing trend in annual mean SO_4^{2-} concentrations as indicated by the Kendall's τ analysis (**Table 3B-6**). However, some trends are more pronounced than others, as shown in **Figure 3B-14**, with the Refuge trend being less apparent than all other areas. This could be due to the natural conditions that exist in the eastern portion of the EAA and EPA. Historically, water quality within the surficial aquifer in this region is affected by saltwater intrusion and highly mineralized groundwater. Highly mineralized ground in this region is typically associated with ancient connate seawater, which was the result of the interglacial seas that inundated the area during the Pleistocene Epoch (Miller, 1988). As noted in the previous SFER (Axelrad et al., 2013), connate seawater could potentially be a large source of SO_4^{2-}, chloride, and dissolved solids (i.e., other minerals) to the EPA, more specifically the Refuge.

Table 3B-5. Summary statistics of sulfate (SO_4^{2-}) concentrations in milligrams per liter (mg/L) for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), Phase II (WY2005–WY2012), and WY2013 periods.

Region	Class	Period	Sample Size	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Standard Deviation	Median	Min.	Max.
Refuge	Inflow	1979-1993	1554	71.9	53.1	59.5	5.9	59.8	8.3	435.7
		1994-2004	1152	54.5	34.0	47.2	5.6	50.5	1.0	460.7
		2005-2012	1306	54.5	22.8	49.3	5.5	51.5	2.4	172.0
		2013	168	50.9	17.4	47.0	5.4	52.1	6.2	89.5
	Interior	1979-1993	500	16.6	21.5	10.3	4.9	10.0	2.5	220.2
		1994-2004	1219	5.5	20.9	1.0	5.9	1.0	< 1.0	610.0
		2005-2012	1631	5.7	12.7	0.7	8.6	0.8	< 1.0	95.1
		2013	226	1.2	3.3	0.2	4.3	0.1	< 1.0	28.9
	Outflow	1979-1993	627	53.7	58.6	40.3	5.7	41.3	7.3	571.0
		1994-2004	707	44.9	32.5	37.5	5.5	41.1	1.4	418.9
		2005-2012	445	35.2	22.1	26.5	5.7	32.9	2.3	95.0
		2013	78	18.1	13.0	13.2	5.0	14.7	1.4	52.0
	Rim	1979-1993	96	42.2	37.1	25.2	6.5	34.4	2.5	139.8
		1994-2004	341	56.9	26.9	50.7	5.6	49.4	1.6	210.0
		2005-2012	122	52.8	28.3	44.0	5.8	48.2	3.5	185.0
		2013	16	37.1	14.4	34.5	5.0	36.4	14.3	61.7
WCA-2	Inflow	1979-1993	791	61.4	64.2	49.5	5.8	51.5	7.3	644.5
		1994-2004	728	49.1	29.4	43.5	5.4	46.9	6.2	418.9
		2005-2012	711	45.3	19.4	39.3	5.6	45.0	< 1.0	106.0
		2013	136	34.1	16.4	28.3	5.4	36.3	1.4	70.3
	Interior	1979-1993	1484	42.1	35.8	32.7	5.6	36.8	2.5	344.3
		1994-2004	1640	46.3	93.2	35.3	5.7	41.0	< 1.0	3230.0
		2005-2012	1066	42.7	20.4	35.9	5.6	45.1	1.8	128.0
		2013	188	37.9	15.7	33.1	5.4	39.6	4.0	69.6
	Outflow	1979-1993	906	42.0	32.1	34.3	5.4	35.9	2.5	224.4
		1994-2004	701	29.2	13.4	25.7	5.0	27.8	2.3	72.9
		2005-2012	530	30.2	17.8	24.2	5.3	28.9	2.3	86.1
		2013	85	23.8	15.9	17.8	5.2	25.4	3.2	68.8
WCA-3	Inflow	1979-1993	2116	31.2	31.4	20.6	5.6	21.1	1.0	286.0
		1994-2004	1832	20.4	14.6	14.7	5.2	18.0	< 1.0	72.9
		2005-2012	1641	19.6	21.2	8.6	7.1	10.7	< 1.0	224.0
		2013	201	21.5	17.9	10.2	7.4	18.7	< 1.0	68.8
	Interior	1979-1993	611	14.9	17.3	10.5	4.6	10.7	2.0	261.5
		1994-2004	1645	11.7	45.3	3.7	6.8	4.4	< 1.0	1300.0
		2005-2012	972	13.4	16.2	3.5	9.9	4.9	< 1.0	126.0
		2013	87	10.6	13.0	2.1	11.7	4.0	< 1.0	49.4
	Outflow	1979-1993	1746	17.8	19.0	11.5	5.1	12.7	1.0	113.2
		1994-2004	1726	7.0	9.3	1.8	8.7	2.7	< 1.0	47.7
		2005-2012	1238	9.5	13.4	1.4	12.2	1.9	< 1.0	58.2
		2013	186	7.1	11.9	0.6	13.5	0.4	< 1.0	41.3
ENP	Inflow	1979-1993	2121	17.4	19.1	11.3	5.0	12.2	1.0	113.2
		1994-2004	1999	5.1	6.2	1.8	6.9	2.6	< 1.0	36.5
		2005-2012	1499	5.6	7.5	1.4	8.3	1.9	< 1.0	35.8
		2013	244	3.5	5.4	0.7	8.2	0.8	< 1.0	18.9
	Interior	1979-1993	572	9.0	19.5	4.3	4.4	4.3	< 1.0	205.5
		1994-2004	1044	5.5	17.7	2.1	4.9	2.6	< 1.0	403.0
		2005-2012	533	6.5	22.4	1.3	6.6	1.7	< 1.0	242.0
		2013	80	4.7	26.3	0.6	6.1	0.6	< 1.0	236.0

Table 3B-6. Kendall's τ annual arithmetic mean SO_4^{2-} concentration trend analysis results for each region's inflow and interior classification within the EPA between WY1979 and WY2013. Statistically significant ρ-values are italicized.

Area	Class	Kendall τ	ρ
Refuge	Inflow	-0.24	*<0.05*
	Interior	-0.49	*<0.01*
WCA-2	Inflow	-0.26	*<0.05*
	Interior	0.10	0.42
WCA-3	Inflow	-0.33	*<0.01*
	Interior	-0.13	0.35
ENP	Inflow	-0.51	*<0.01*
	Interior	-0.15	0.28

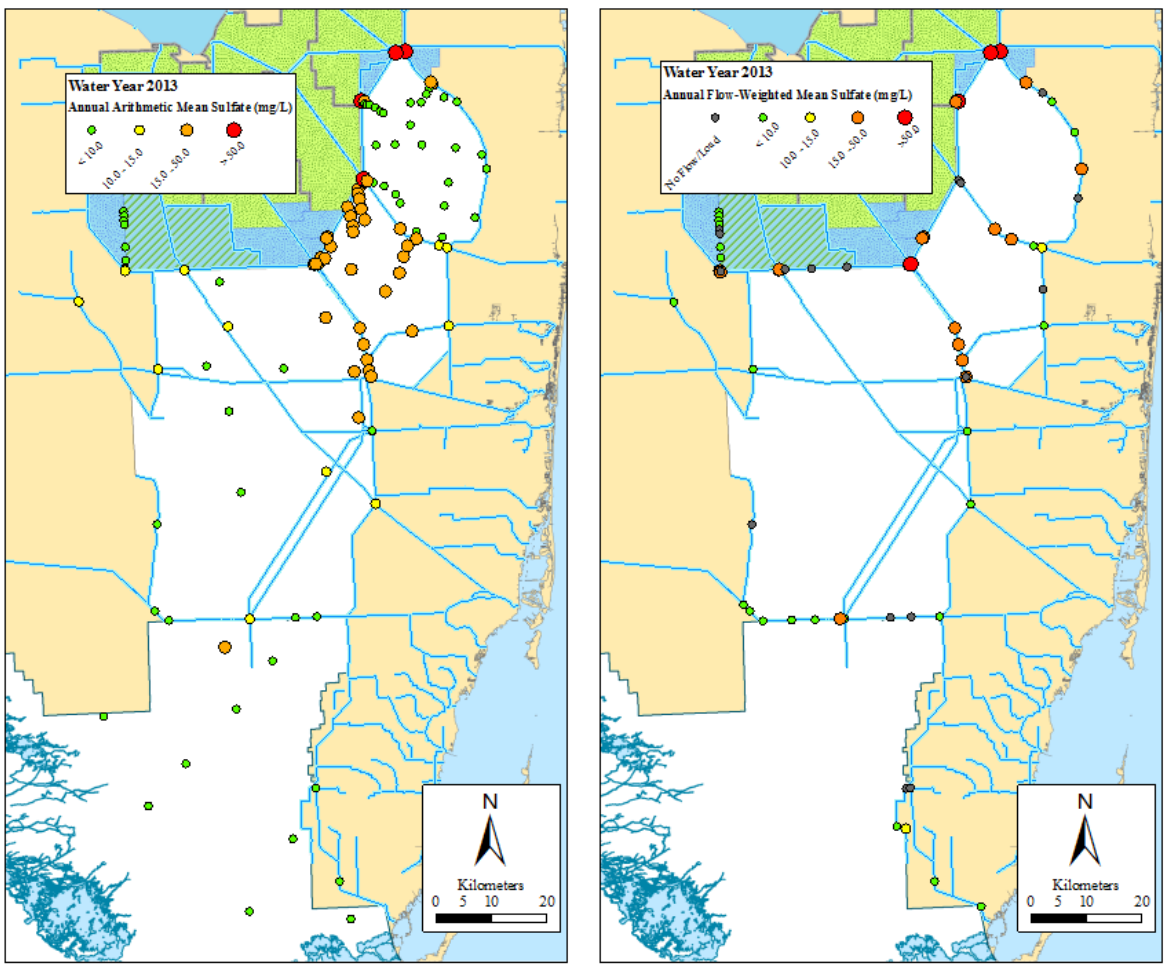

Figure 3B-13. Annual arithmetic mean sulfate (SO_4^{2-}) concentrations (milligrams per liter, or mg/L) for all classifications (left panel) and annual flow-weighted mean SO_4^{2-} concentrations at water control structures (right panel) for WY2013 at stations across the EPA.

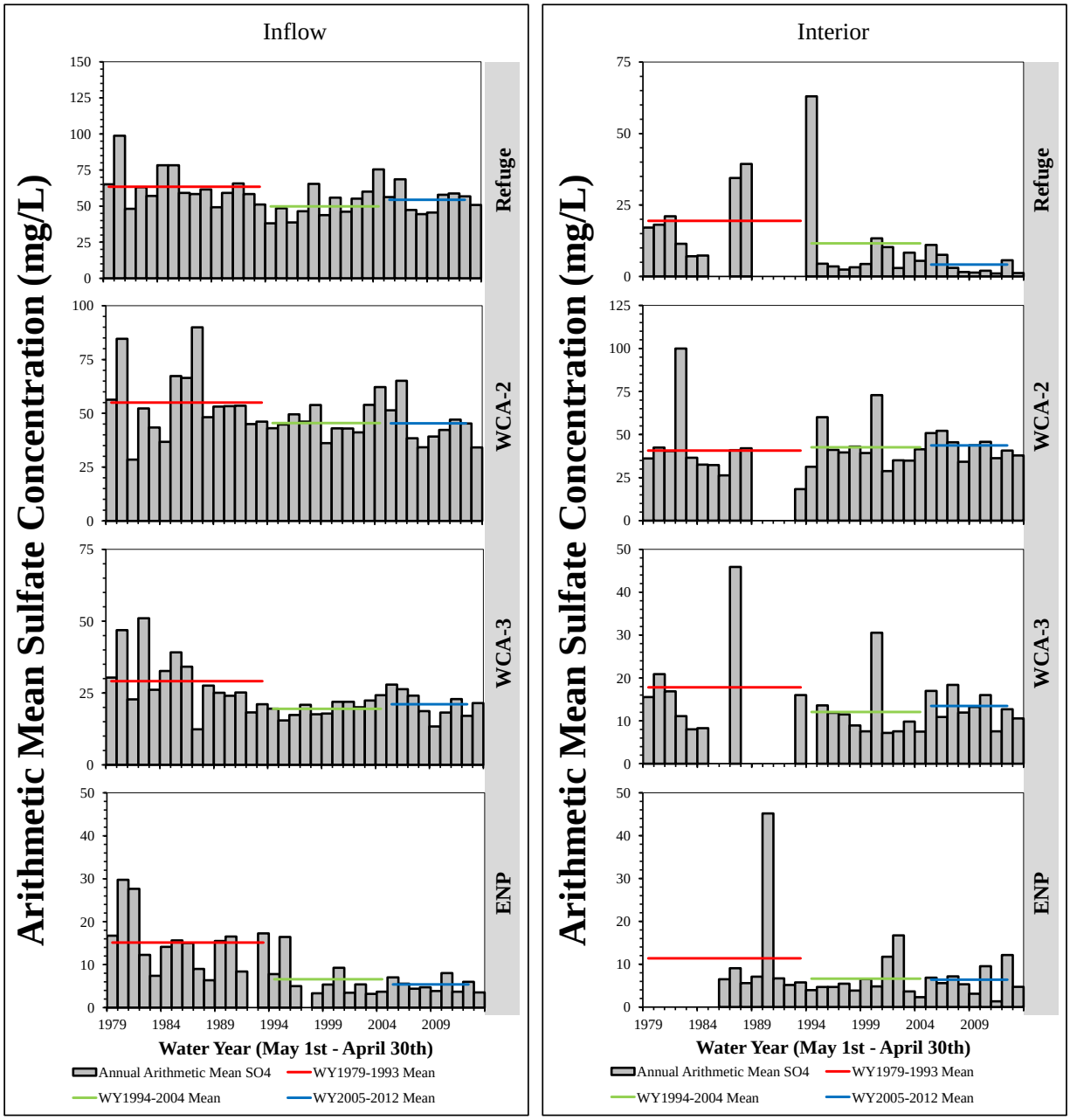

Figure 3B-14. Annual arithmetic mean SO_4^{2-} concentrations (mg/L) for inflow (left panel) and interior (right panel) areas of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), WCA-2, WCA-3, and ENP from WY1978–WY2013. The horizontal lines indicate the mean annual geometric mean SO_4^{2-} concentrations for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), and Phase II (WY2005–WY2012) periods. [Note: Area with no bars indicates data gaps.]

The typical north-to-south gradient was not evident at interior monitoring stations of the EPA. During WY2013, WCA-2 had the highest annual mean SO_4^{2-} concentration of 37.9 mg/L, followed by WCA-3 (10.6 mg/L), ENP (4.7 mg/L), and the Refuge (1.2 mg/L). Furthermore, the only region with a significant decreasing annual mean SO_4^{2-} concentration was the Refuge, with all other areas experiencing non-significant trends (**Table 3B-6**). SO_4^{2-} concentrations within the Refuge significantly decreased during the Phase II period (**Figure 3B-14**), which could possibly be due to the construction and operation of STA-1W and Stormwater Treatment Area 1 East (STA-1E) in combination with the rainfall-driven hydrology. However, it has been suggested that the Everglades STAs reduce surface water SO_4^{2-} concentrations and loads by a small portion, approximately 10 percent of the SO_4^{2-} from the water column (SFWMD, unpublished data). Another factor influencing this trend of decreasing SO_4^{2-} concentrations with time could be changes in water management or establishing and managing BMPs within the EAA. It is also important to note that SO_4^{2-} concentrations within the Refuge spiked after extended periods of dry conditions as observed between WY1985–WY1994. This was not just isolated to water column SO_4^{2-}, but phosphorus and nitrogen also spiked during these periods. The very low SO_4^{2-} concentrations observed for the interior portion of the Refuge indicate that assimilation of SO_4^{2-} is occurring and potentially could be limiting due to its low availability (Bellinger and Van Mooy, 2012).

Annual mean SO_4^{2-} concentrations within WCA-2 are approximately twice that of other regions with the EPA. This could potentially be due to historical EAA runoff containing both local and regional inputs of SO_4^{2-}. The hydrology of WCA-2A spreads the canal inflow broadly, which has resulted in a very large area of impacted wetlands (Payne et al., 2000). However, since WY2001, water does not directly enter the L-39 canal due to construction and operations of STA-2 and the G-338 structure. Due to this extended period of discharge that resulted in impacted regions of the marsh, WCA-2 soils have relatively high concentrations of sulfur. Yet, it should also be noted that there are many complicating factors which influence the delivery, fixation, and retention of sulfur in sediments (Bates et al., 1998). A brief assessment based on samples collected between 2003 and 2004 at limited locations within each region indicates that WCA-2A soils had the greatest concentration of sulfur (14,025 ± 1,173 mg/kg; mean ± standard error), followed by WCA-3A (9,100 ± 576 mg/kg) and the Refuge (8825 ± 1,019 mg/kg; data source: District's DBHYDRO database). This assessment did not take into account soil types or bulk density and was only limited to two sampling locations per area; therefore, statistics could not be applied. Regardless, it is apparent qualitatively that soils within WCA-2 have excessive sulfur content. This high concentration of sulfur within the soils could result in excessive internal loading, which explains why interior mean concentrations are higher than inflow mean concentrations. Due to this relatively high marsh concentration within WCA-2, it is reasonable to suggest that growth of macrophytic biota within this region of the EPA is not sulfur/SO_4^{2-}-limited, corresponding to results presented by Bellinger and Van Mooy (2013).

Previous peer-reviewers of this portion of the report, previously reported in Chapter 3A of this volume, as well as a peer-reviewed journal article (Corrales et al., 2011) have suggested the development of a site-specific SO_4^{2-} water quality standard. As stated above, the sulfur/Hg biogeochemical cycle proves very complex and provides little predictive power to link water column concentrations to environmental Hg levels. Also, the EPA received a highly variable rate of SO_4^{2-} load, fluctuating widely from year to year, as discussed below. Therefore, these combined factors complicate the development of a site-specific criterion. Furthermore, it is uncertain based on the best available data at this time if reduction of sulfur will reduce Hg methylation or shift methylation hot spots, or if it is even feasible to reduce sulfur/SO_4^{2-} entering the EPA.

Currently, the FDEP is funding research to investigate Hg methylation potential at low concentrations of SO_4^{2-} in surface water in an effort to assess if reduction of sulfur/SO_4^{2-} will cause a positive or negative ecological response. Additionally, the commonly referenced CERP performance measure for SO_4^{2-} that recommended 1 mg/L as a goal for Greater Everglades wetlands (RECOVER, 2007) was developed to indicate background marsh concentrations. However this limit was developed without detailed technical support. While concerns have been raised that concentrations above this level could stimulate significant Hg methylation, the 1 mg/L SO_4^{2-} goal is not consistently associated with any particular level of Hg in the Everglades (see discussion below). The 1 mg/L goal should not be propagated, at this point in time, due to the lack of empirical evidence suggesting that 1 mg/L is protective or that higher levels are consistently associated with harm. Furthermore, to date, no studies have been documented to justify either a numeric SO_4^{2-} criterion of 1 mg/L, or a site-specific alternative criterion that incorporates other potential factors in the methylation process, for the protection of fish and wildlife in the EPA.

Sulfate Loads

Each year, the EPA receives variable amounts of surface water inflows. These inflows contribute to loading of surface water constituents, including SO_4^{2-} to the EPA system. **Table 3B-7** provides estimates of the inflow SO_4^{2-} load to each portion of the EPA for WY2013. Flows and SO_4^{2-} loads are also provided for the Baseline, Phase I and Phase II periods for comparison. Major sources of surface SO_4^{2-} loads to EPA include runoffs from EAA and Lake Okeechobee discharge (James and McCormick, 2012).

Table 3B-7. Mean flow-weighted mean (FWM) SO_4^{2-} concentrations (mg/L) and SO_4^{2-} loads (metric tons, or mt) to the EPA for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), Phase II (WY2005–WY2012), and WY2013 periods.

		Period			
	Area	Baseline 1979-1993	Phase I 1994-2004	Phase II 2005-2012	Current 2013
Mean Annual Sulfate Load (mt)[1]	Refuge	53,419	54,924	19,608	17,553
	WCA-2	41,773	45,319	47,278	54,039
	WCA-3	14,433	13,409	12,069	11,567
	ENP	16,035	15,979	11,550	13,104
Mean Annual Sulfate FWM (mg/L)	Refuge	86.1	69.5	56.9	39.0
	WCA-2	60.1	52.3	50.8	41.0
	WCA-3	10.1	7.3	7.5	6.9
	ENP	14.6	8.0	10.7	9.6

[1] Mean (Range)

In addition to surface water, atmospheric deposition contributes to the SO_4^{2-} loading into the EPA (see below). Atmospheric deposition is an important source of nutrients to oligotrophic ecosystems; however, Alewell et al. (2000) states that increased atmospheric deposition of SO_4^{2-} has resulted in a significant addition of SO_4^{2-} loads to sediments, soils, and surface waters. Atmospheric deposition rates of SO_4^{2-}, much like other mineral and nutrient constituents, can be highly variable. Based on data presented within this chapter, wet deposition rates of SO_4^{2-} to the EPA can range from 610.7 milligrams per square meter per year (mg m^{-2} yr^{-1}) to 1,507.0 mg m^{-2} yr^{-1}. Using these deposition rates, the EPA received approximately 7,836 ± 51 metric tons (mt; mean ± SE) of SO_4^{2-} through wet deposition. Based on the limited data available from the USEPA (CASTNET, www.epa.gov/CASTNET), a preliminary assessment determined that SO_4^{2-} dry deposition rates ranged from 91.0 mg m^{-2} yr^{-1} to 127.6 mg m^{-2} yr^{-1}. Again, using these deposition rates, the EPA receives approximately 819 ± 37 mt of SO_4^{2-} through dry deposition. Based on these estimates, the EPA can potentially receive between 8,565 and 8,744 mt of SO_4^{2-} from atmospheric deposition.

Annual SO_4^{2-} load from surface water sources, including internal transfers to the northern portion of the EPA (Refuge, WCA-2, and WCA-3) was 83,158 mt, with a FWM SO_4^{2-} concentration of 24.06 mg/L. This represents an 85 percent increase in SO_4^{2-} load relative to the previous year (WY2012: 45,048 mt); however, due to lower flow during WY2012, the FWM concentration (24.1 mg/L) remained relatively constant between years. Discharges from the EPA accounted for 53,729 mt of SO_4^{2-}, with a FWM concentration of 18.4 mg/L during WY2013. The difference between inflow and outflow loads, 29,429 mt, indicates that plant and microbial uptake, burial, and gaseous sulfur emissions (i.e., hydrogen sulfide, dimethyl sulfide, etc.) after anaerobic reduction by SRB are occurring within the natural communities of the EPA. Annual SO_4^{2-} load from surface waters to ENP was 13,105 mt, with a FWM concentration of 9.6 mg/L. This corresponds to a 54 percent increase in SO_4^{2-} load from the previous year (WY2012: 8,498 mt), most likely due to an increase in surface water flow.

Flows and loads to the EPA during Phase II and the current water year have been highly influenced by climatic extremes in the region, which has experienced extended drought conditions as well as extended periods of heavy rainfall. The annual SO_4^{2-} load to the Refuge was 17,553 mt during WY2013, representing a 59 percent increase in load from the previous year (WY2012: 11,049 mt). The annual SO_4^{2-} load to WCA-2 also had an increase with 54,039 kilotons (kt) of SO_4^{2-} entering WCA-2 during WY2013, representing a 104 percent increase in load from the previous year (WY2012: 26,430 mt). WCA-3 also experienced an increase in SO_4^{2-} load with 11,567 kt of SO_4^{2-} entering WCA-3, corresponding to a 53 percent increase from the prior year (WY2012: 7,568 mt).

Annual SO_4^{2-} loads were only significant between periods for the Refuge (df=2, F=14.6, $\rho<0.01$), with loads being significantly reduced during the Phase II period relative to the Baseline and Phase I periods. Even though SO_4^{2-} loads spiked throughout the EPA during WY1993 and WY1995 most likely due to drought and flood cycles, the Refuge experienced significant load decreases. This potentially could be due to the reduction of SO_4^{2-} loads and concentrations by the STAs, even though as stated above they only remove approximately 10 percent of the SO_4^{2-} entering the STAs. Other possibilities include changes in agricultural practices, water management, and improvements to BMPs within upstream basins. Furthermore, a drastic difference is apparent between Phase I and Phase II within the Refuge (**Table 3B-7** and **Figure 3B-15**). Meanwhile, annual SO_4^{2-} loads were not significantly different between the period for WCA-2 (df=2, F=0.55, ρ= 0.58), WCA-3 (df=2, F=0.41, ρ=0.67), and ENP (df=2, F=0.33, ρ=0.72).

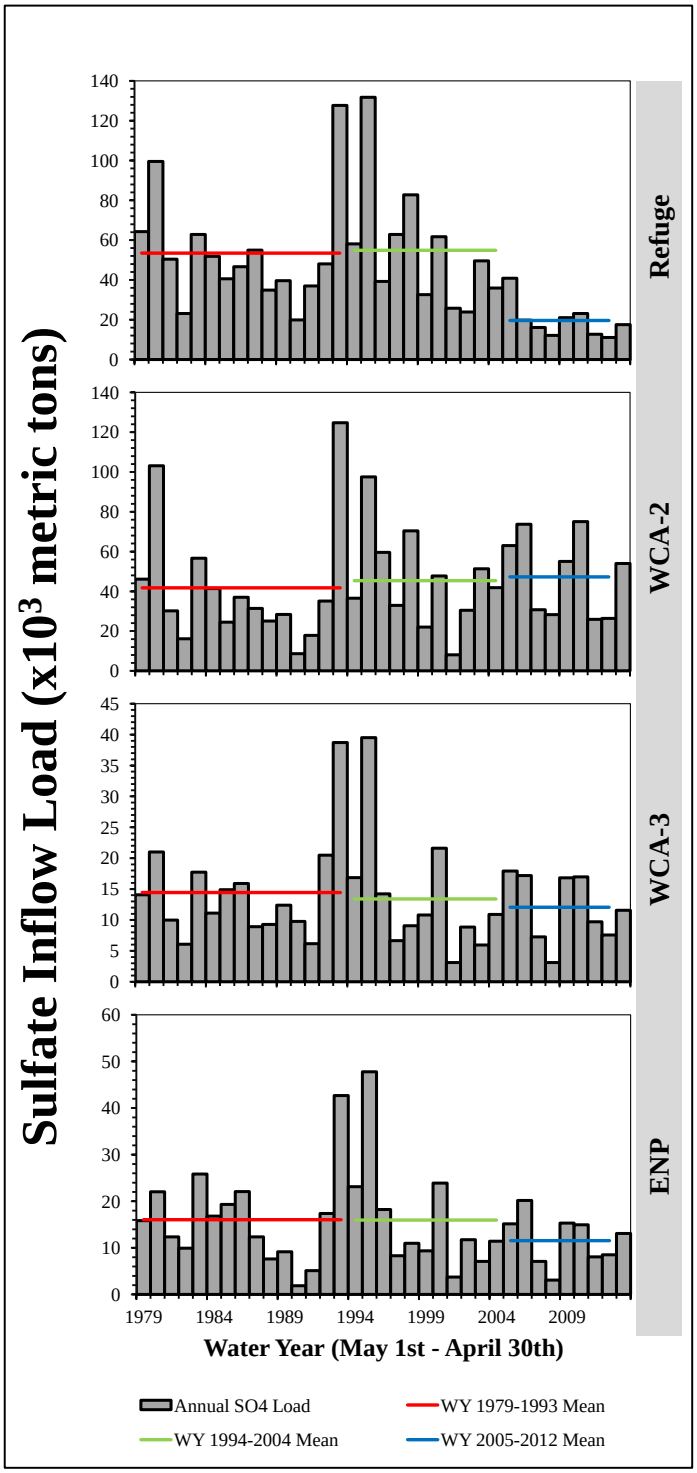

Figure 3B-15. Annual inflow SO_4^{2-} load for the Refuge, WCA-2, WCA-3, and ENP from WY1979–WY2013. Horizontal lines indicate the mean annual loads and flows for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), and Phase II (WY2005–WY2012) periods.

While the EAA and Lake Okeechobee contributes significant SO_4^{2-} loads to the EPA, they are not the sole source of surface water SO_4^{2-}. Drainage districts and other basins to the east as well as agricultural lands from the west also contribute SO_4^{2-} to the EPA. A large range of values have been published in the peer-review and technical literature regarding EAA outflow SO_4^{2-} loads (**Table 3B-8**), ranging from 31.7 kt (James and McCormick, 2012) to 116.4 kt (Corrales et al., 2011) of SO_4^{2-} discharging from the EAA. These values may represent total outflow load, which could include historical back pumping from the EAA back into Lake Okeechobee (James and McCormick, 2012).

Table 3B-8. Estimates of annual Everglades Agricultural Area (EAA) SO_4^{2-} outflow load from peer-reviewed and technical literature in relation to EPA inflow. Note that EPA inflow SO_4^{2-} load was converted from metric tons per year (mt/yr) to kilotons per year (kton/yr), with conversion factor provided.

		Schueneman, 2001; Wright et al., 2008	Gabriel et al., 2010[1]	Corrales et al., 2011	James and McCormick, 2012	Reported in this Chapter[2]
EAA Outflow	Flow Volume (1,000 ac-ft)	---	---	2,325	515.7	---
	SO_4^{2-} Load (1 kton/yr)[3]	61.7	48.7 (43.7 - 55.4)	116.4	31.7	---
	SO_4^{2-} FWM (mg/L)	---	---	40.6	49.9	---
EPA Inflow	Flow Volume (1,000 ac-ft)	---	---	---	---	2,439 ± 9,879
	SO_4^{2-} Load (1 kton/yr)[3]	---	---	---	---	113.0 ± 11.1
	SO_4^{2-} FWM (mg/L)	---	---	---	---	34.2 ± 1.9

[1] Mean (Range)
[2] Mean ± standard error of the entire period of record (WY1979–WY2013)
[3] 1 kiloton = 906 metric tons
acre-feet (ac-ft)

ATMOSPHERIC SULFATE DEPOSITION TRENDS

Paul Julian II[1]

Introduction

Acid precipitation and its associated acid anions deposition have become widely recognized as a potential environmental issue in the United States and abroad since the mid-1970s (Dochinger and Seliga, 1976). Since that time, several atmospheric deposition monitoring networks have been established, which has helped guide lawmakers in developing environmental policy and law to reduce main anthropogenic causes of acid precipitation. Assessment of the data generated from the atmospheric deposition monitoring network allowed the U.S. Congress to amend the Clean Air Act in 1990 (P.L. 101-549, Title IV), which was designed to reduce the adverse effects of acid precipitation in the United States through phased reductions in emissions (Lynch et al., 2000).

Elevated atmospheric SO_4^{2-} deposition has resulted in SO_4^{2-} accumulation in soils and increased loading to surface waters (Alewell et al., 2000). This SO_4^{2-} accumulation within ecosystem such as the Everglades is significant especially as SO_4^{2-} is an integral factor in the biogeochemical cycle resulting in the conversion of Hg to the more toxic MeHg (Gilmour et al., 1992). Very few studies have focused on the quantity and timing of atmospheric SO_4^{2-} deposition. Those studies that have investigated wet SO_4^{2-} deposition reported rainwater SO_4^{2-} concentrations ranging from 0.5-2.5 mg/L (Orem et al., 2011). Orem et al. (2011) concludes that rainwater may be an important source of SO_4^{2-} to unenriched areas, but it cannot account for the high SO_4^{2-} loads and concentrations in canals or SO_4^{2-}-enriched marshes.

This section reports on the estimated SO_4^{2-} wet deposition flux and associated atmospheric load to the EPA by using data collected from the ENP atmospheric deposition monitoring location (**Figure 3B-11**).

Methods

Atmospheric deposition data was retrieved from the NADP NTN for ENP monitoring location (FL11; **Figure 3B-11**). As previously noted, the NADP is a cooperative effort between many different groups and stakeholders to provide high quality atmospheric deposition data on various parameters. The NADP, and its associated laboratory as part of the NTN, measures free acidity (H^+ as pH), conductance, calcium, magnesium, sodium, potassium, SO_4^{2-}, nitrate, chloride, and ammonium. Both laboratory and field data are rigorously checked according to quality assurance/quality control protocols approved by the USEPA.

Monthly SO_4^{2-} atmospheric deposition data was summarized according to water year, including both wet and dry seasons. The POR of this assessment includes WY1981–WY2012. For purposes of data analysis and summary statistics, data reported as less than the MDL were assigned a value of one-half the MDL, unless otherwise noted. Annual PWM SO_4^{2-} concentrations were also calculated. Atmospheric loads were estimated by multiplying annual SO_4^{2-} atmospheric deposition values by the area of each region of the EPA (i.e., WCA-1, WCA-2, WCA-3 and ENP). Water years with less than 12 months of data were not included in the trend analysis. Trend analysis was performed on SO_4^{2-} deposition and PWM concentrations using the Kendall's τ correlation analysis. All analysis was conducted using JMP® (Version 10.0.0, SAS, Cary, NC, USA) and the critical level of significance was set at $\alpha = 0.05$.

Results and Discussion

Annual SO_4^{2-} wet deposition has remained relatively constant throughout the current POR (τ=0.09, ρ=0.48) with values ranging between 348.8 milligram per square meter (mg/m^2) and 1,507.0 mg/m^2 (**Figure 3B-16**). Based on surface water inflow loads into each respective region (presented elsewhere within this chapter), atmospheric wet deposition of SO_4^{2-} is a relatively low contributor of SO_4^{2-} to each region of the EPA. During WY2012, atmospheric loading accounted for 4.8, 2.0, 7.2, and 31.6 percent of the total load into WCA-1, WCA-2, WCA-3, and ENP, respectively (**Table 3B-9**). However, these values should be used with caution as only one monitoring station was used to determine wet atmospheric loads. Furthermore, there may be a latitudinal gradient of SO_4^{2-} deposition that spans the EPA. Therefore, these atmospheric load estimates may overestimate some areas and underestimate others.

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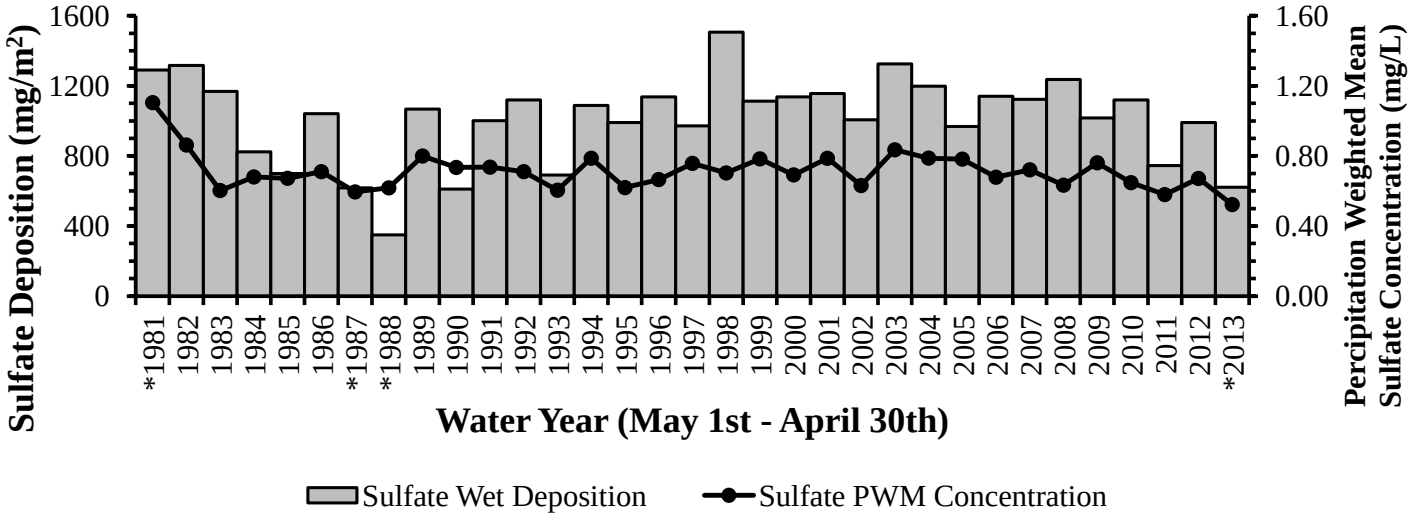

Figure 3B-16. Annual SO_4^{2-} deposition in milligrams per square meter (mg/m^2) and annual PWM SO_4^{2-} concentration at FL11 for WY1981–WY2013. Stations with less than 12 months of data are identified with an asterisk (*).

Table 3B-9. Atmospheric SO_4^{2-} load from wet deposition and surface water inflow load to each region of the EPA for WY2012.

	Atmospheric Load (mt)	Surface Water Inflow Load (mt)	Percent Atmospheric Contribution
WCA-1	560	11,049	4.8
WCA-2	531	26,431	2.0
WCA-3	2,368	7,569	23.8
ENP	3,916	8,499	31.6

Similar to the wet deposition trend, PWM SO_4^{2-} concentrations remained relatively constant throughout the period of record (τ=-0.05, ρ=0.67). PWM concentrations ranged between 0.58 mg/L and 1.10 mg/L (**Figure 3B-16**). The range of annual PWM SO_4^{2-} concentrations within this assessment is consistent with values presented by Orem et al. (2011). Even though both wet deposition and PWM trends were not significant, a steady decline in both deposition and PWM concentrations have been observed in recent water years. Unfortunately, due to the data release schedules, this assessment only spans WY1981–WY2012. **Figure 3B-16** includes data for WY2013, but this data is incomplete. Therefore, values presented for WY2013 should be used with caution and will be updated in the following SFER. Even though data on dry deposition of SO_4^{2-} in South Florida are not readily available, data from other areas of North America shows that dry deposition is unlikely to be a major contributor to the total SO_4^{2-} flux to the Everglades. Therefore, an exploratory analysis of dry SO_4^{2} deposition should be undertaken to quantify the dry deposition quantities to the Everglades.

SULFUR RESEARCH IN THE EVERGLADES AGRICULTURAL AREA

Alan L. Wright[4] and J. Mabry McCray[4]

Surface water is a major transport mechanism for sulfur discharged from the EAA. Research has not conclusively demonstrated the relative contribution of different potential sulfur sources to the Everglades sulfur load, which may include sulfur fertilizers, sulfur released by soil oxidation, groundwater sulfur, rainfall, etc. (Bates et al., 2002). Bates et al. (2002) conducted sulfur isotopic ratio (δ^{34}) studies to further determine the potential sources. The results of their investigation indicated that fertilizers applied in the EAA are a significant contributor of sulfur to EAA canal waters and subsequently the Everglades. However, this source may include both current and legacy sulfur applications made decades in the past. Sulfur fertilizers and fungicides have historically been applied in the EAA to reduce soil pH and increase micronutrient availability to crops (Ye et al., 2010).

Sugarcane (*Saccharum* spp. L.) is the primary crop cultivated in the EAA and sulfur is applied periodically when soil pH exceeds 6.6 to enhance micronutrient availability (Schueneman, 2001). Grower surveys have indicated that sulfur applications are generally less than the amounts suggested because the recommendations are not considered cost-effective (Schueneman, 2001). In a survey of sugarcane fields in 2004–2006, 54 percent of fields sampled on organic soil had pH > 6.6, or approximately 70,000 hectares within the EAA. The survey also indicated that 36 percent of fields on organic soil were limited in production by insufficient manganese, with 10 percent of fields estimated to have greater than 25 percent yield limitation.

The lack of grower confidence in the sulfur recommendations and the substantial amount of yield limitation due to micronutrient deficiency emphasizes the need for improved elemental sulfur recommendations for high pH organic soils. This study has the objective of revising elemental sulfur recommendations for sugarcane grown on organic soils in Florida. In a field study at two locations, there was a strong relationship between sucrose yield and soil pH, with yield being reduced at pH $\geq$ 7.2 (McCray and Rice, in press). Substantial yield reductions were determined at pH $\geq$ 7.5, with reduced sugarcane yields associated with leaf manganese deficiency occurring at high pH. Research is continuing to determine if other soil factors, such as extractable calcium or manganese, will improve the prediction of yield response to elemental sulfur.

A comprehensive extension program is used to keep sugarcane and vegetable growers informed of the progress of research projects and to allow for feedback from growers. Based on the estimated percentage of organic soils in the EAA with pH > 6.6, approximately 45 percent of the current sugarcane acreage in Florida could be affected by alternatives to the current University of Florida Institute of Food and Agricultural Sciences elemental sulfur recommendation for organic soils. Effectiveness of alternative fertilizer treatments are presented at field days, and information about sulfur use, alternative treatments, and environmental concerns are presented to growers and managers at BMP workshops.

FACTORS INFLUENCING MERCURY METHYLATION IN THE EVERGLADES

Paul Julian II[1] and Binhe Gu

THE "GOLDILOCKS" THEORY

In the past SFER Chapter 3B, the "Goldilocks" theory or window was a common theme of the chapter and played a dominate role in the agencies thinking for a long period of time. The term "Goldilocks" refers to a posited unimodal relationship between sulfur and methyl Hg production that strikes a balance between SO_4^{2-} limiting and sulfide inhibiting Hg methylation. Gilmour (2011) provides a thorough review of the role played by SO_4^{2-} in methylation rates in sediments across a wide range of ecosystem types. Gilmour (2011) documents the sulfur-Hg relationship from numerous studies and highlights the responses to SO_4^{2-} additions as well as the enormous variability of MeHg within sediments. Unfortunately, not discussed is the variability inherent in translocating MeHg into the water column or transferring through constantly changing trophic structures in wetlands. Therefore, based on the preliminary analysis presented below, it is not surprising that ecosystem-level Hg accumulation is not predictable from SO_4^{2-} concentrations in surface water of marshes like the Everglades.

It should be noted that the hypothetical sulfur-Hg unimodal relationship as a conceptual model is based largely on the theoretical relationship between $SO_4^{2-}$and Hg methylation (Gilmour and Henry, 1991; Gilmour, 2011). Gilmour and Henry (1991) hypothesized that freshwater sediments impacted by SO_4^{2-}-deposition may be prime locations for microbial methylation of Hg (**Figure 3B-17**). This hypothesis partially explained the elevated concentrations of Hg in fish from acid-impacted lakes, while the exact influence of SO_4^{2-} on lacustrine methylation remains unresolved (Gilmour and Henry, 1991).

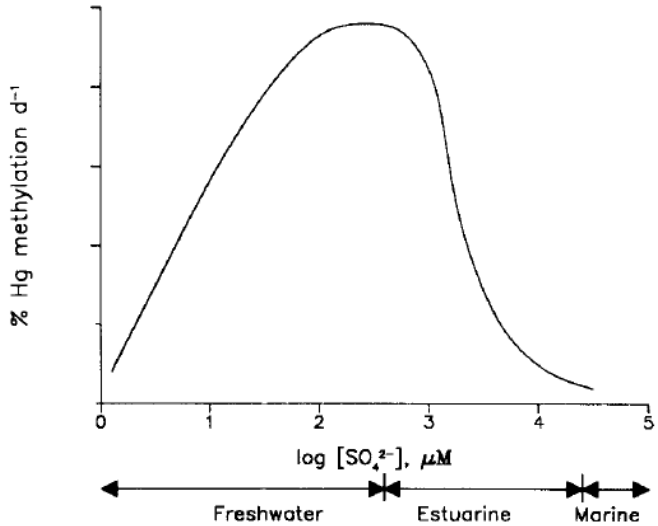

Figure 3B-17. Theortical relationship between water column SO_4^{2-} concentrations and sediment Hg methylation rate (Gilmour and Henry, 1991).

Since the publication of Gilmour and Henry (1991), other early Hg/SO_4^{2-} studies and several large-scale biogeochemical surveys (Gilmour et al., 1998; Benoit et al., 1999; Gilmour, 2011; DB Environmental, 2012; Hsu-Kim et al., 2013) our understanding of the role that sulfur plays has evolved. Generally, it is accepted that sulfur plays a role in the sulfur-Hg biogeochemical cycle; however, the exact role and the influences from other environmental variables are still not fully understood. Biogeochemical cycling of Hg within the Everglades is complex and confounded by many other non-chemical variables including the types and abundance of bacteria present (King et al., 2000; Kerin et al., 2006; Shao et al., 2012), dynamics of food web structure and the hydrology (DB Environmental, 2012; Julian, 2013a) of a particular site. Chemical factors such as the availability of dissolved Hg^{2+}, concentrations of dissolved organic carbon, pH, chloride, and dissolved oxygen also play a critical role in the Hg methylation process (Gu et al., 2011; Hsu-Kim et al., 2013). Hg methylation is controlled not only by SO_4^{2-}, but a combination of many environmental factors as demonstrated in **Figure 3B-18**. Due to this complexity and variability, the SO_4^{2-}-Hg unimodal relationship is not spatially or temporally consistent within the Everglades. Very few studies have been able to determine a significant SO_4^{2-}-Hg unimodal relationship under conditions found in natural freshwater marshes. The proof of an ecological concept lies in its predictive capability in nature. An analysis of the plethora of ambient monitoring data from the Everglades does not support the theory of a unimodal relationship between SO_4^{2-} and Hg.

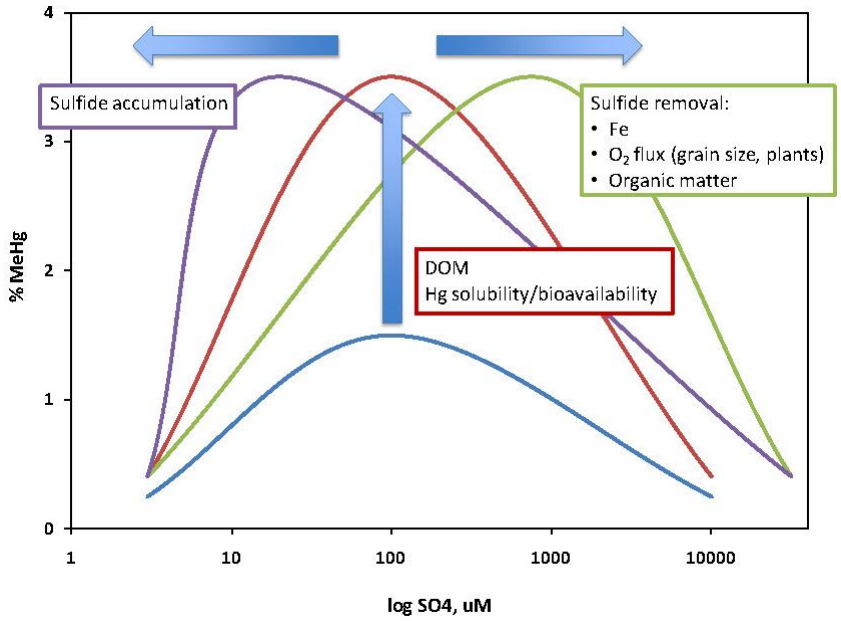

Figure 3B-18. A conceptual diagram of the relationship between SO_4^{2-} concentration and MeHg accumulation indicating the influences of the curve as it relates to SO_4^{2-} /sulfide [S^{2-}] dynamics [horizontal arrows] as well as dissolved organic matter [vertical arrow; Gilmour (2011)]. [Note: µM - micromolar; Fe - iron; O_2 - dioxide; DOM - dissolved organic matter.]

SULFATE–METHYLMERCURY RELATIONSHIP

The analysis presented within this section illustrates the poor predictive capability of field data as it relates to the theoretical S-Hg relationship in the EPA. It is not possible to explain all variables associated with the disparity between the theoretical relationship and actual field data. The section does attempt to summarize key data from Everglades marshes that demonstrate the disparity. A very commonly used dataset collected within the EPA is the USEPA Regional Environmental Monitoring and Environmental Assessment Program (R-EMAP). This program monitors and assesses areas of the Everglades including the EPA by using a probabilistic sampling design (Stober et al., 2001). Monitoring events associated with R-EMAP have occurred three times over the past 18 years, these monitoring events have been termed phases. Monitoring under the first phase (Phase I) occurred during calendar year 1995 (CY1995) and CY1996, Phase II during CY2000 (Stober et al., 2001) and Phase III during CY2005 (Scheidt and Kalla, 2007).

Each Phase of R-EMAP sampling represents unique hydrologic conditions. For instance, Phase I sampling was in a very wet period with several tropical storm systems in South Florida resulting in record rainfall totals and elevated stages in the majority of the Everglades. Phase II sampling was conducted in a very dry period in which very little rainfall entered the Everglades, while Phase III sampling occurred during a relatively normal hydrologic period. These changes in hydrologic conditions can have profound effects on biogeochemical cycles as discussed above. Also noteworthy within the R-EMAP dataset is the fact that the minimum detection limit for the methods used for analyzing SO_4^{2-} was significantly higher for Phase I sampling than both Phase II and III. This change can be seen in **Figure 3B-19** and more so in **Figure 3B-20** and explains the relative truncation of the left side (lower limit) of the Phase I data distribution.

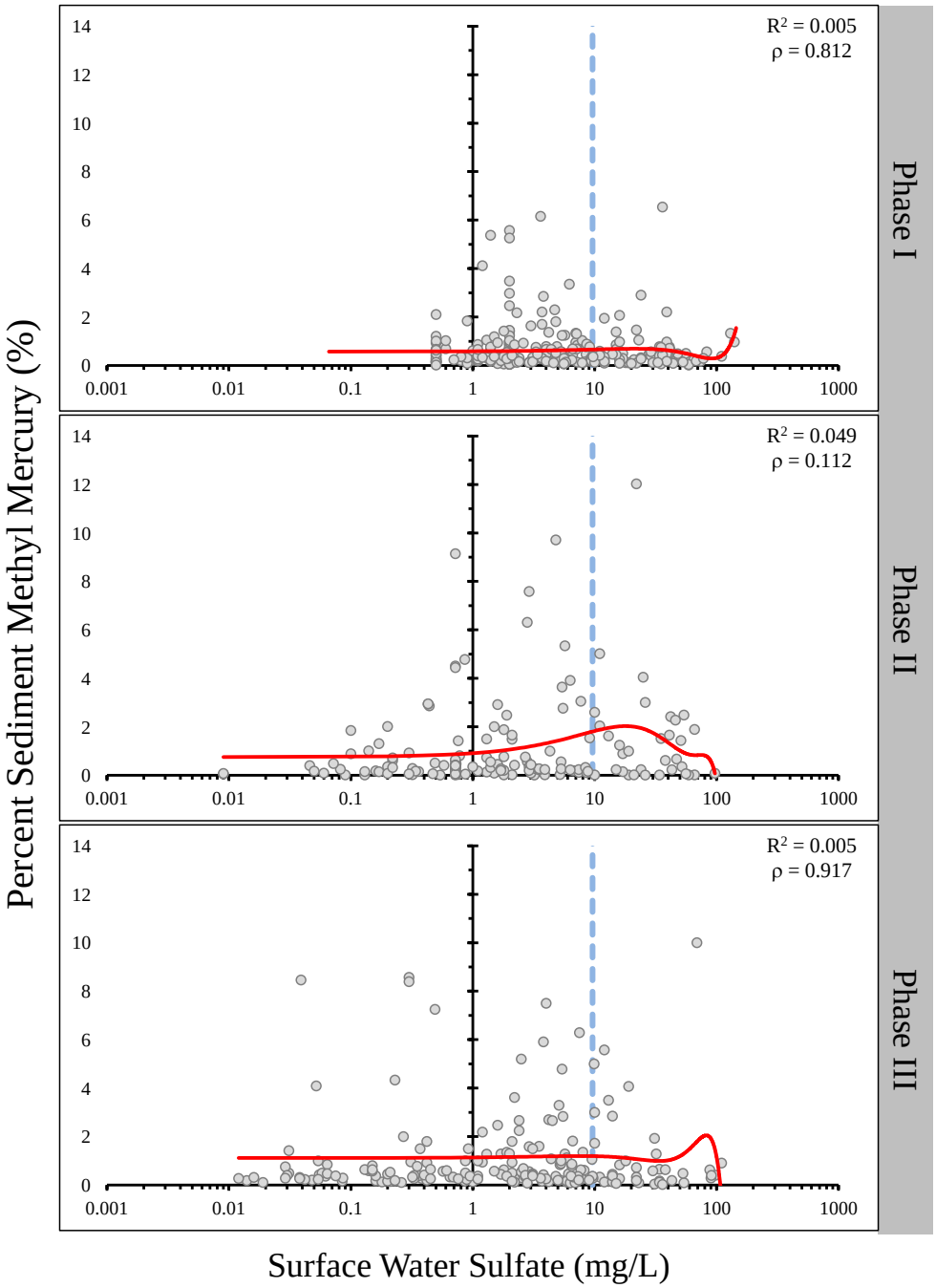

Figure 3B-19. The relationship between surface water SO_4^{2-} concentrations and sediment percent MeHg using Regional Environmental Monitoring and Environmental Assessment Program (R-EMAP) data. Data was collected during each phase of the R-EMAP monitoring program to date from each portion of the EPA (i.e., WCA-1, WCA-2, WCA-3, and ENP). Red line indicates a quartic (4-order) regression curve through the data, blue dashed vertical line corresponds to the 100 μM SO_4^{2-} (9.6 mg/L) optimum referenced by Gilmour (2011). X-axis is on a log scale.

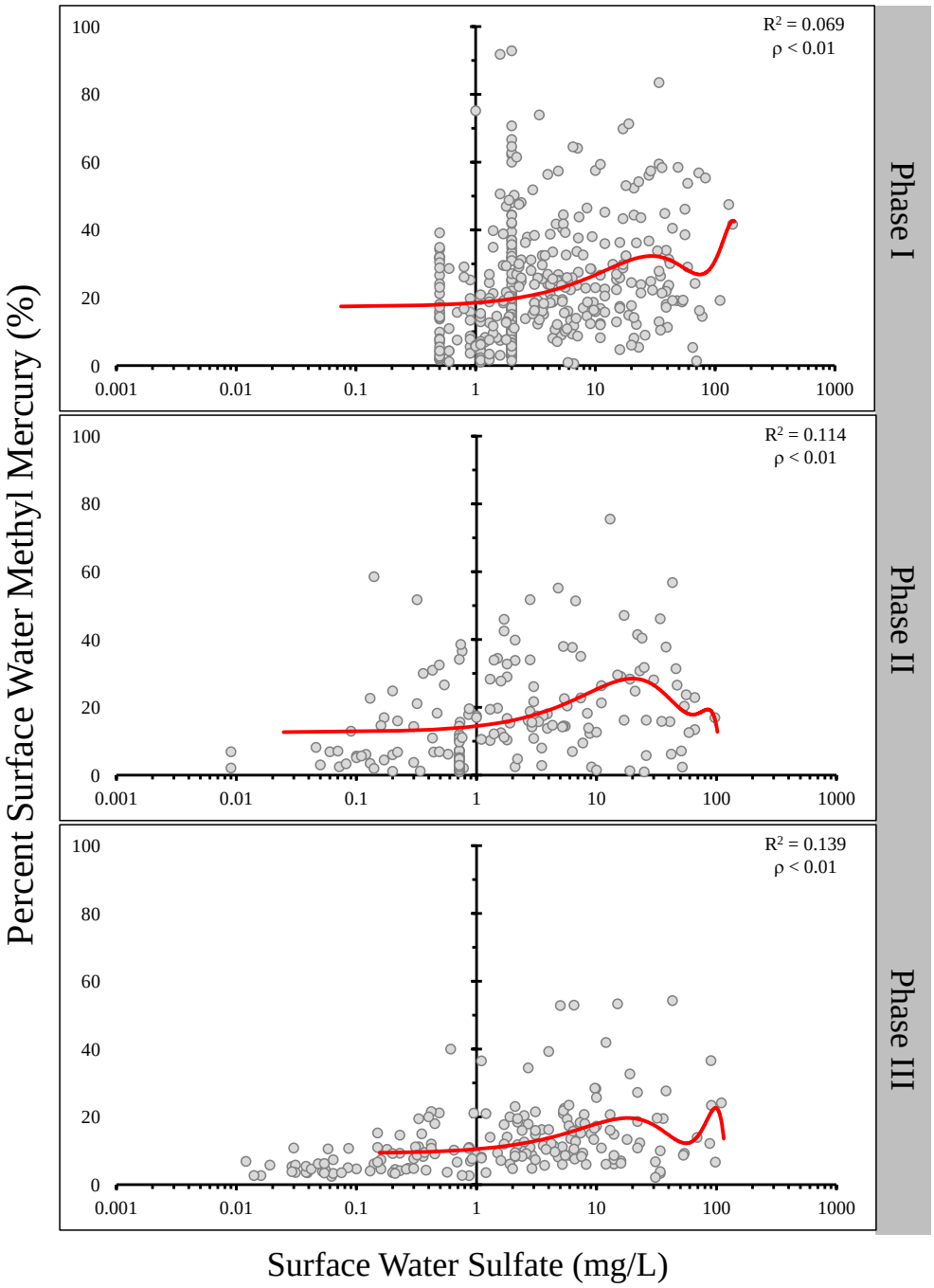

Figure 3B-20. The relationship between surface water SO_4^{2-} concentrations and surface water percent MeHg using R-EMAP data. Data was collected during each Phase of the R-EMAP monitoring program to date from each portion of the EPA (i.e., WCA-1, WCA-2, WCA-3, and ENP). Red line indicates a quartric regression curve through the data. X-axis is on a log scale.

There is a high level of variability between the S-Hg unimodal relationship during each monitoring phase. Qualitatively, some of the data seem to conform to a unimodal distribution with what appears to be peaks at key locations. However, based on a quartic regression, these relationships are not statistically significant ($\rho>0.05$; **Figure 3B-19**) and explain very little of the variation in the proportion of MeHg. It should be noted that when using MeHg soil/sediment concentrations-based approach utilizing both concentrations based on weight (mg/kg) and volume [milligrams per cubic centimeters (mg/cm^3)], the relationship with sulfur is also not significant (figures not shown). These data do not support the theoretical unimodal relationship across the Everglades. Previous assertions of this unimodal relationship have either been conducted at a single site or a very isolated section of the Everglades (Gilmour et al., 2000; Gilmour, 2011; Axelrad et al., 2013). Unfortunately, these cases lacked any statistical quantification, therefore it is not known if this relationship is true or just an artifact of the data distribution. Currently, scientists with the FDEP and District are conducting analyses investigating statistical methods that can be applied to determine the significance of this relationship. This analysis will be presented in a forthcoming manuscript and the results of this study are expected to be presented in next year's SFER.

MINIMUM AND OPTIMAL CONCENTRATIONS OF SULFATE FOR MERCURY METHYLATION

Gilmour (2011) reviewed results of several sulfur amendment mesocosm studies from a large array of locations and experimental designs, including three (out of 15) studies centered within the Everglades (Taylor Slough in ENP, WCA-1, and WCA-2). Most of the 15 studies demonstrated that net MeHg production was favored under biogeochemical condition "where SO_4^{2-} is sufficient to support rates of microbial SO_4^{2-} reduction, without the accumulation of aqueous sulfide." Across these studies, the SO_4^{2-} concentration at which MeHg production was highest seemed to occur at approximately 100 micromolar (µM; ~9.6 mg/L). However, a closer look at the Everglades studies finds that SO_4^{2-} concentration from two out of the three studies occurred within the 100 µM "optimal MeHg production" SO_4^{2-}concentration. Like most mesocosm studies, extrapolating this information into actual ecosystem dynamics is laden with assumptions and often times not scalable. Their findings are not consistent with **Figure 3B-19** where there is no notable or consistent change in the percentage of MeHg at a SO_4^{2-} concentration of 9.6 mg/L (blue line). Gilmour (2011) recognizes that any apparent SO_4^{2-} optimum in nature is a reflection of the complex underlying biogeochemical condition including the availability of Hg and the presence of methylating bacteria.

Corrales et al. (2011) have suggested that SO_4^{2-} concentrations above 1 mg/L exhibited elevated MeHg concentrations within surface water. They used a combined dataset from ENP to indicate that after 1 mg/L of SO_4^{2-}, MeHg concentrations within surface water increased dramatically, this in spite of the fact that a large portion of the MeHg data did not respond to the increases in SO_4^{2-} concentration (Figure 7 in Corrales et al., 2011). It is also not clear if elevated MeHg at higher SO_4^{2-} concentrations are controlled by SO_4^{2-} alone or by other limiting variables such as Hg^{2+}, DOC, pH and redox. Furthermore, there is insufficient information provided in the publication to determine the representativeness of these data and to allow rigorous objective interpretation of the suggested pattern. Corrales et al. (2011) went on to suggest that the State of Florida should adopt this threshold as a water quality standard (discussed earlier in this chapter). As is the case with other SO_4^{2-}/MeHg data analyses, very little emphasis has been placed on statistics or rigorous analysis of conditions reflected in the dataset. The data presented within Corrales et al. (2011) and the R-EMAP dataset do not support the development of a 1 mg/L SO_4^{2-} limit (**Figure 3B-20**). The red line running through the data within **Figure 3B-20** is a quartic regression line; while significant from a statistical viewpoint, it has little utility for environmental decision-making due to the very low R^2 values. Further analysis of the R-EMAP dataset suggests

that this relationship is not consistent between monitoring periods and that SO_4^{2-} concentrations have little influence on MeHg concentrations (**Figure 3B-21**). This could be due to many different factors including THg and MeHg flux from sediment as well as demethylation processes occurring within the water column.

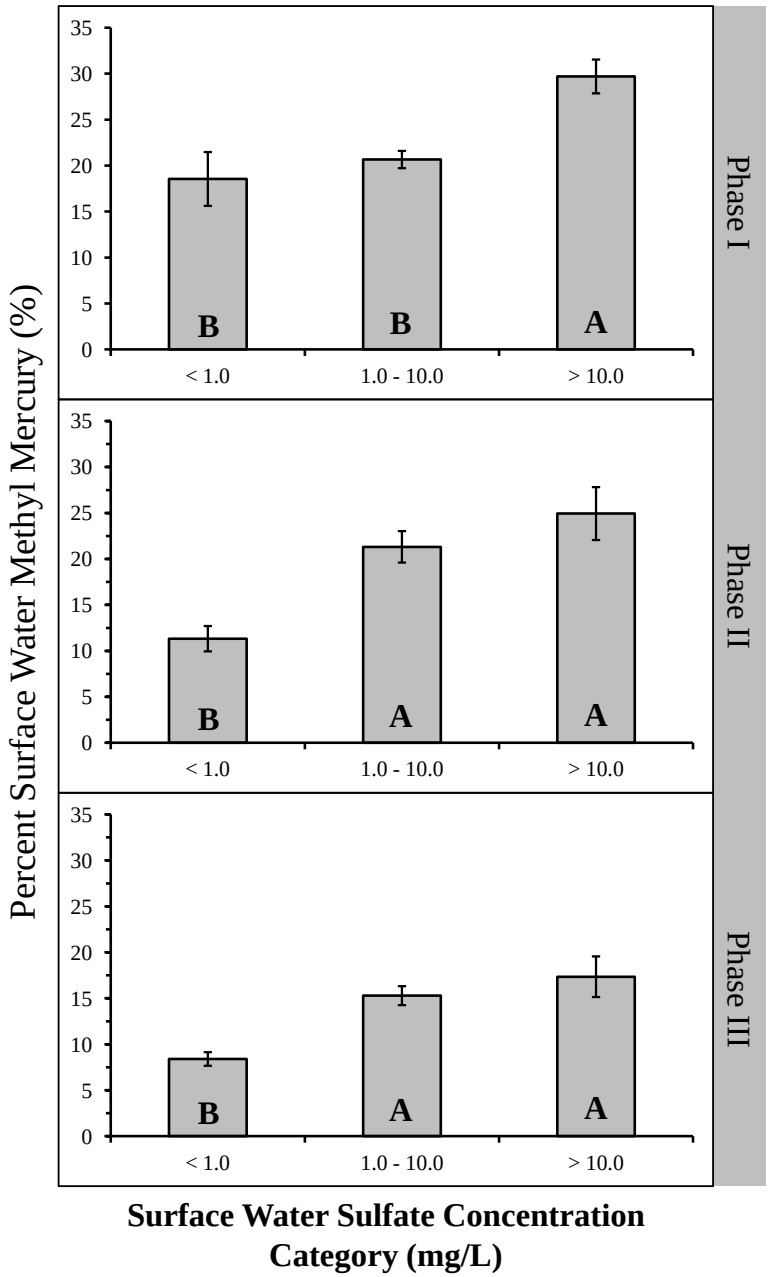

Figure 3B-21. Mean (± standard error) percent MeHg for each surface water SO_4^{2-} concentration category using R-EMAP data. These categories are separated into less than 1.0 mg/L, 1.0-10 mg/L, and greater than 10.0 mg/L of $SO4^{2-}$. Letters inside the base of the bars indicate statistical similarities based on the Steel-Dwass non-parametric multiple comparison test.

The SO_4^{2-} manipulation studies centered within the Everglades reviewed by Gilmour (2011) and others reviewed by DB Environmental (2012) all involved the addition of SO_4^{2-}. None of these studies investigated the usefulness of reducing SO_4^{2-} loading to areas currently impacted with anthropogenic SO_4^{2-}. This is of interest to both the FDEP and District due to the hypothetical situation that internal sulfur loading could potentially maintain sulfur cycling for a prolonged period of time post reduction of inputs. Due to this data gap, the FDEP, through a cooperative agreement with the District, has authorized a study to evaluate factors influencing Hg methylation, particularly at very low SO_4^{2-} concentrations. An interim report on this study can be found within Appendix 3B-1 of this chapter. This study has shown that bio-available Hg (as Hg^{2+}) enhanced bio-methylation, even in vessels containing very low (native) concentrations of SO_4^{2-} (0.3 mg/L). However, it is not known at this time if this response was due to the activity of reducing bacteria (i.e., SRB, iron reducing bacteria, methanogens, etc.) or an unknown bio-methylating bacterium. Low concentration SO_4^{2-} amendments (0.5–1.0 mg/L) increased MeHg accumulation further in the presence of bioavailable Hg. The enhancement of MeHg accumulation in response to SO_4^{2-} with bioavailable Hg amendments exhibited a plateau at higher SO_4^{2-} concentrations (10–20 mg/L). These results suggest that in-situ sources of SO_4^{2-} in the Everglades may have the ability to support Hg methylation by reducing bacteria. This dynamic has also been documented in other wetlands including peatlands located in northwestern Ontario and northern Minnesota. For these peatlands, Mitchell et al. (2008) reported that most MeHg hotspots (defined as %MeHg exceeding the 90th percentile of the dataset or > 22 percent of THg as MeHg) occurred at average SO_4^{2-} concentrations of only 0.1 to 0.6 mg/L. Preliminary results suggest that bioavailable Hg could be the limiting factor in the Hg methylation equation. This is supported by observations of elevated fish THg concentration at a long-term monitoring site (CA315) in WCA-3A, which exceeded USEPA trophic level 3 and 4 tissue Hg concentration limits that occurred under background SO_4^{2-} concentrations (< 1 mg/L SO_4^{2-}).

While generally the hypothetical S-Hg unimodal relationship may be present within some ecosystems, within the Everglades ecosystem (i.e., EPA) this relationship may not be as pronounced and is highly variable in space and time. There is a high degree of variability between SO_4^{2-} and MeHg production that is confounded by other chemical and physical factors present within the ecosystem (discussed above). Marsh ecosystems tend to be more dynamic than lake ecosystems with respect to hydrology and biogeochemical cycles. Due to this high degree of variability and poor quantitative relationships in South Florida, development of a sulfur or SO_4^{2-} criterion is not feasible scientifically. Any water quality criterion must be supported by strong and consistent field relationships; the sulfur and MeHg linkage is not directly quantifiable or reasonably predictable. Furthermore the minimal and optimal SO_4^{2-} concentrations that support Hg methylation in sediments is still not known. Preliminary results indicate that Hg methylation still occurs at ambient SO_4^{2-} concentrations and that Hg is the limiting factor. Moreover, within recent years regional atmospheric wet deposition of Hg has remained relatively constant (see above, *Atmospheric Mercury Deposition Trends* section). Therefore, based on the current information available, controlling SO_4^{2-} loads and concentrations may not significantly reduce MeHg production and accumulation.

MERCURY ACCUMULATION IN AQUATIC CONSUMERS

Several studies have attempted to extract the hypothetical S-MeHg unimodal relationship and apply it to surface water SO_4^{2-} and biota MeHg in an effort to establish that SO_4^{2-} above background concentrations is the primary control for MeHg production. To evaluate MeHg production, fish THg concentrations are often times used as a surrogate for MeHg in water. However, since THg concentrations within fish tissue are also affected by other factors, which are not related to Hg methylation, the use of THg fish tissue concentration is weakened by the complexity of not only MeHg production but also bioaccumulation.

In Axelrad et al. (2013) and other previous SFERs, the distinction between MeHg formation and Hg accumulation was subtle. While Hg accumulation in aquatic species is often times used as a proxy for formation/conversion of bioavailable Hg, it does not necessarily indicate the formation of MeHg due to the biological mechanisms of absorption. Hg methylation can occur through several different pathways, the most common pathway is through bacteria-mediated methylation via SRB, iron reducing bacteria or methanogenic bacteria (Li and Cai, 2013). As discussed in this chapter, previous SFERs, and peer-reviewed literature, many different factors can influence the rate of Hg methylation and accumulation through trophic transfer. However, the Hg accumulation pathway least discussed is accumulation via direct uptake, which has the ability to significantly influence Hg accumulation dynamics in aquatic consumers (Pickhardt et al., 2006; Liu et al., 2012).

Studies in the literature tend to downplay the importance of Hg accumulation through direct aqueous uptake by fish. This is primarily due to the fact that fish bio-accumulate a large proportion of Hg via food web trophic transfer (Liu et al., 2012). However as seen by Pickhardt et al., (2006), subtle differences in uptake rates for Hg by fish combined with the temporal variability in dissolved Hg in most freshwater systems can alter fish Hg burdens with no change in methylation. Similarly for larger, predatory fish when prey availability is low or there is an increase in competition due to high predatory fish abundance, a greater proportion of total tissue Hg originates from direct aqueous uptake (Pickhardt et al., 2006). Direct aqueous uptake is done through passive diffusion or active uptake mechanisms, therefore the skin and gills can be important sites of accumulation of aqueous Hg. The rate and magnitude of direct Hg uptake is dependent on the chemical form of Hg.

Water quality conditions within each region of the EPA are unique, primarily due to differences in water quality conditions of surface water inflow (Julian et al., 2013). To provide an estimate of water quality effects on fish tissue Hg concentrations, a combination of monitoring data from fish collection sites identified in **Figure 3B-4** and co-located or paired water quality sites were used for a preliminary analysis presented in **Figures 3B-22** and **3B-23** which demonstrate the influence of SO_4^{2-} on fish tissue Hg concentrations. Currently, scientists with the FDEP and District are conducting analyses investigating other water quality parameters that could potentially influence tissue Hg concentrations. Based on a preliminary analysis of surface water quality and tissue Hg, the relationship between surface water quality and tissue Hg concentration for the three major fish species support a hypothesis that water quality parameters other than SO_4^{2-} potentially influence tissue Hg concentrations and help to explain ecosystem variability in Hg accumulation.

Areas within the EPA with low to moderate SO_4^{2-} concentrations appear to have a highly variable concentration of fish tissue Hg within the three species of fish typically assessed within the EPA. This trend is consistent with trends present within the R-EMAP dataset associated with mosquitofish Hg concentrations as presented by Julian (2013b). Significant emphasis has been placed on the potential role that SO_4^{2-} plays in the formation of MeHg, however it is an indirect highly variable measure of Hg accumulation as seen in **Figures 3B-22** and **3B-23**. While the general quartic regressions are significant, the R^2 values are very low, indicating that the trend is highly variable and has low predictive power (i.e., regression accounts for 12–38 percent depending on species). Interestingly, the trend lines exhibit a bimodal relationship, the first hump occurring at approximately 10 mg/L and is very pronounced for LMB, less pronounced for sunfish and non-existent for mosquitofish. The second hump, lower in intensity, occurs at higher SO_4^{2-} concentrations for LMB and sunfish but not mosquitofish. This second hump could potentially be an artifact of the regression, the dataset or a combination of the two. Another interesting result of this analysis is that it seems that tissue Hg concentrations with mosquitofish potentially drop after 10 mg/L. Even though the quadratic regression for the LMB and sunfish

datasets exhibit a degree of modality (either bi- or uni-modal), it is not certain if this modality is significant (i.e., line may be significant but the "hump" may not).

If SO_4^{2-} concentrations are grouped together similar to the surface water MeHg analysis above (**Figure 3B-21**) it is apparent that tissue Hg concentrations for LMB and sunfish are significantly higher when SO_4^{2-} conditions are between 1.0 and 10.0 mg/L and lower at very low and very high SO_4^{2-} concentrations (**Figure 3B-23**). This relationship supports the quadratic regression results. Additionally, mosquitofish tissue Hg concentrations are significantly lower at relatively high SO_4^{2-} concentrations, consistent with the quadratic regression (**Figure 3B-22**). These changes in all fish species could potentially indicate a change in trophic position (i.e., feeding behavior), fish biochemistry, water and/or soil quality or other system conditions. Further investigation is warranted.

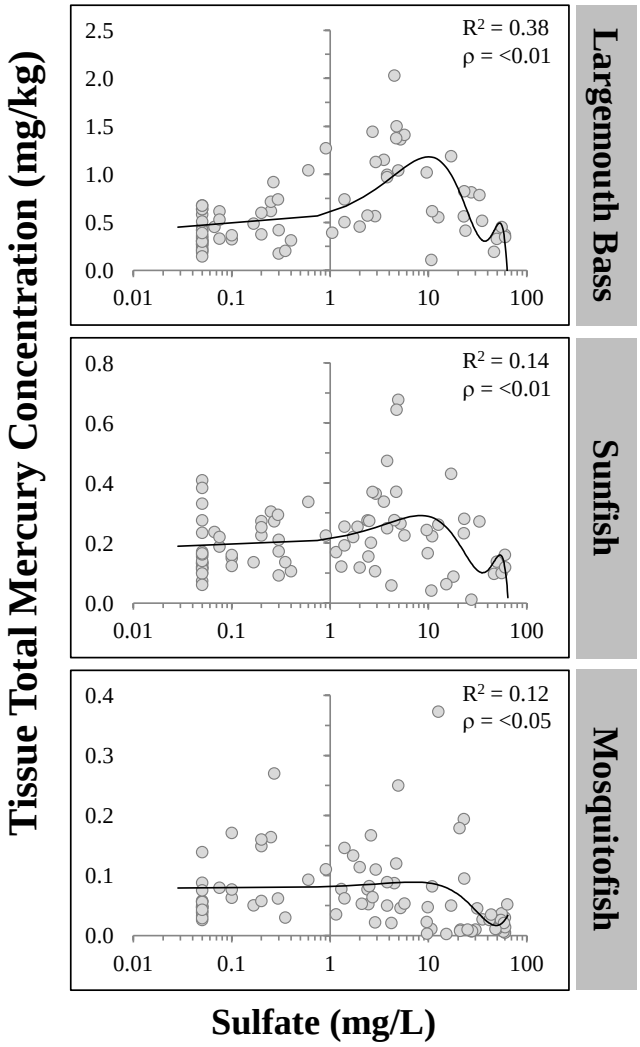

Figure 3B-22. Scatter plot of surface water SO_4^{2-} and tissue THg concentration for LMB, sunfish and mosquitofish collected throughout the EPA between WY1999–WY2013 (May 1, 1998–April 30, 2013). The black line that transverses the data is a quadratic (polynomial) regression line, R^2 and ρ values for the trend line are present within each panel. X-axis is on a log scale.

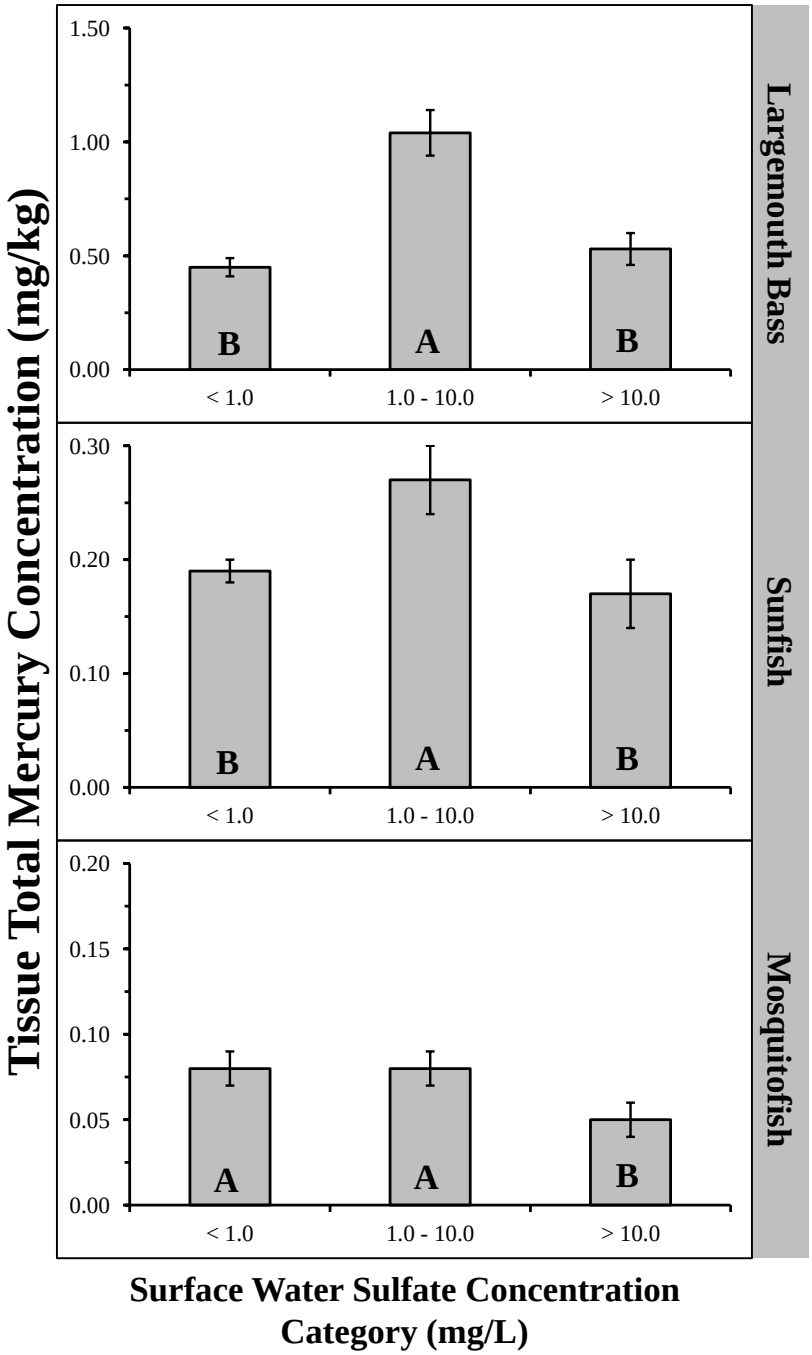

Figure 3B-23. Mean (± standard error) tissue Hg concentration for each surface water SO_4^{2-} concentration category and fish species. These categories are separated into less than 1.0 mg/L, 1.0-10 mg/L and greater than 10.0 mg/L of SO_4^{2-}. Letters inside the base of the bars indicate statistical similarities based on the Steel-Dwass non-parametric multiple comparison test.

Based on the available data, the hypothetical S-MeHg unimodal relationship does not necessarily extend to or explain fish tissue Hg concentrations. This relationship is very dynamic and is potentially influenced by other water quality parameters, especially those parameters that influence aqueous Hg uptake from the water, changes in trophic position or a combination of these factors. While SO_4^{2-} is an important water quality parameter, it is not the sole parameter that should be focused on with regards to fish tissue Hg concentrations. This is even more apparent in **Figure 3B-24** which depicts LMB THg concentrations and mean SO_4^{2-} indicating that SO_4^{2-} concentrations at CA315 have reached concentrations below 1 mg/L and concentrations greater than 10 mg/L have been observed at WCA2U3. Trends in LMB THg have followed different trajectories over the past two decades and do not seem to be controlled by SO_4^{2-} concentrations alone. A better understanding of factors that influence direct uptake of Hg, environmental factors affecting fish physiological conditions, and fish trophic position is needed.

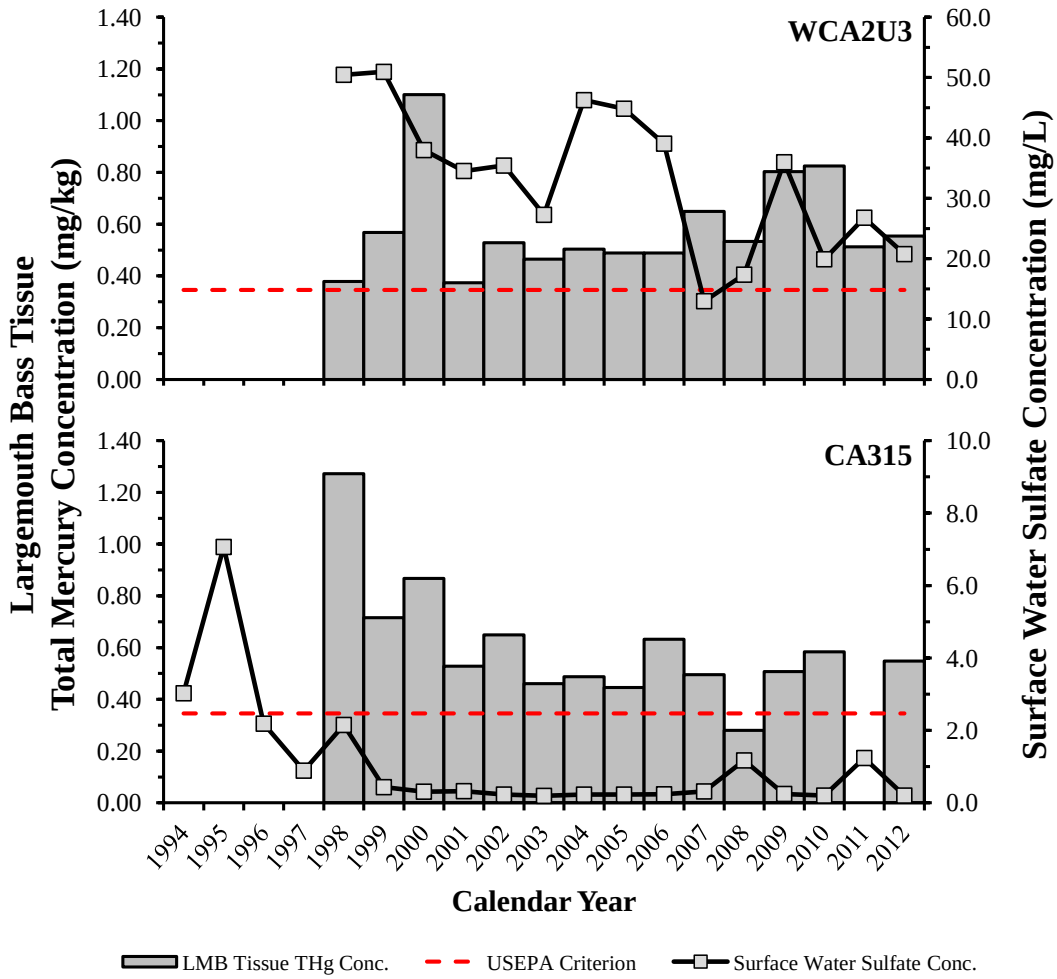

Figure 3B-24. Calendar year mean SO_4^{2-} and LMB tissue THg concentrations for sites WCA2U3 located within WCA-2 and CA315 located within WCA-3 relative to the USEPA MeHg criterion.

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