

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

Edited by Paul Julian II<sup>1</sup>, Binhe Gu, Garth Redfield, Ken Weaver<sup>2</sup>

Contributions by Forrest E. Dierberg<sup>3</sup>, Mike Jerauld<sup>3</sup>, Thomas A. DeBusk<sup>3</sup>,  
Michelle D. Kharbanda<sup>3</sup>, Janelle A. Potts<sup>3</sup> and Nichole R. Larson<sup>3,4</sup>

---

## SUMMARY

---

This chapter provides an assessment of sulfur (S) and mercury (Hg) status within the Everglades Protection Area (EPA), Holey Land and Rotenberger Wildlife Management Areas (WMAs) during the Water Year 2015 (WY2015) (May 1, 2014–April 30, 2015) reporting period. The report fulfills the requirements of the Everglades Forever Act (EFA), Subparagraph 373.4592(4)(d)13, Florida Statutes. The information provided in this chapter is an update to Chapter 3B of the *2015 South Florida Environmental Report (SFER) – Volume I*.

The analysis and summaries provide a synoptic view of Hg and S in the EPA and surrounding areas on a regional scale and include the Arthur R. Marshall Loxahatchee National Wildlife Refuge [LNWR, or Water Conservation Area (WCA-) 1], WCA-2, WCA-3, and Everglades National Park (ENP). This chapter updates the status of Hg and S monitoring in the Everglades region and summarizes Hg concentrations in biota; Hg atmospheric deposition; and surface water sulfate ( $\text{SO}_4^{2-}$ ) concentrations, loads, and atmospheric deposition to the EPA. Analytical data is reported for the following timeframes: WY2015 for wildlife [mercury in fish tissue for largemouth bass (LMB; *Micropterus salmoides* Lacepède), sunfish (*Lepomis* spp.), and mosquitofish (*Gambusia* spp.)] and for surface water  $\text{SO}_4^{2-}$ ; and WY2014 for atmospheric deposition of  $\text{SO}_4^{2-}$  (wet + dry) and Hg (wet).

Key highlights for this year's reporting period are as follows:

- WY2015 total mercury (THg) concentrations in mosquitofish from 13 monitoring sites ranged from 0.012 milligrams per kilogram (mg/kg) at site CA33ALT to 0.099 mg/kg at site CA35ALT, with a median concentration of 0.040 mg/kg, which is 13 percent lower than the reported median value of WY2014. Mosquitofish THg concentrations during WY2015 exceeded the United States Environmental Protection Agency (USEPA) trophic level 3 (TL3) criterion (0.077 mg/kg) for protection of piscivorous wildlife at two of the 13 sites (ST1ELX and CA35ALT).

---

<sup>1</sup>Florida Department of Environmental Protection, Office of Ecosystems Projects, Ft. Myers, FL

<sup>2</sup>Florida Department of Environmental Protection, Division of Ecosystem Assessment and Restoration, Tallahassee, FL

<sup>3</sup>DB Environmental, Rockledge, FL

<sup>4</sup>The authors acknowledge Julianne LaRock, Garth Redfield (SFWMD), and Frank Powell and Edward Smith (FDEP) for providing valuable comments and suggestions to this document.

- In WY2015, THg concentrations in TL3 sunfish from 13 monitoring sites ranged from 0.06 mg/kg at HOLYSC to 0.379 mg/kg at CA35ALT. During WY2015, 11 stations were sampled for sunfish species, of the 11 stations mean sunfish THg concentrations exceeded the USEPA protection of wildlife criterion at nine stations. THg concentrations in these species from all sites followed the period of record trend—highest in spotted sunfish (*Lepomis punctatus* Valenciennes; 0.265 mg/kg), intermediate in bluegill (*L. macrochirus* Rafinesque; 0.207 mg/kg), and lowest in redear sunfish (*L. microlophus* Günther; 0.130 mg/kg).
- During WY2015, THg concentrations in largemouth bass were collected from nine of the 13 locations within the EPA. THg concentration from EPA sites ranged from 0.141 mg/kg (CA3F2) to 1.660 (L67F1) mg/kg, with a median value of 0.433 mg/kg. During WY2015, six locations exceeded the USEPA recommended criterion for the protection of human health (0.350 mg/kg).
- Wet deposition is the dominant Hg source to the Everglades. During WY2014, wet deposition of THg accounted for 119.8 kg Hg to the EPA<sup>5</sup>. No statistically significant trend was apparent in annual Hg wet deposition.
- During WY2015, annual mean inflow SO<sub>4</sub><sup>2-</sup> concentrations ranged from 8.8 milligrams per liter (mg/L) for ENP to 60.1 mg/L for LNWR. The annual mean SO<sub>4</sub><sup>2-</sup> concentrations at interior marsh regions ranged from 4.4 mg/L for ENP to 42.2 mg/L for WCA-2.
- In WY2014, total SO<sub>4</sub><sup>2-</sup> deposition (wet + dry) accounted for 7911.1 kg Hg to the EPA. Statistically significant decreasing trends were observed for both wet and dry atmospheric deposition throughout the entire period of record (WY1995–WY2014).
- Under a cooperative agreement between the South Florida Water Management District (SFWMD or District) and Florida Department of Environmental Protection (FDEP), ongoing studies are being conducted to evaluate factors influencing mercury methylation in South Florida marshes. Initial data suggests that food web dynamics and habitat influences mosquitofish THg concentrations.
- An analysis of synoptic mercury data collected within the EPA was completed, while the data set was spatially and temporally limited, this analysis suggests that several parameters have the ability influences the availability of Hg for methylation including sediment calcium, dissolved organic matter, and iron (see Appendix 3B-1 of this volume).

## 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 and Holey Land and Rotenberger Wildlife Management Areas (WMAs) 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 WCAs (Bancroft et al. 1992). In addition to rainfall inputs, surface water inflows regulated by water control structures from agricultural tributaries, such as the Everglades Agricultural Area (EAA) to the north and the C-139 basin to the west, feed the EPA. The EPA also receives surface water inflows

---

<sup>5</sup> The complete data set for WY2015 is under quality assurance review and is expected to be reported in the 2017 SFER.

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. The Holey Land and Rotenberger WMAs are located just north of the EPA, and together span 64,000 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 1-1 of this volume.

---

## METHYL MERCURY FORMATION IN THE EVERGLADES

---

Over the past several decades, multiple research studies have been done regarding the factors that influence the formation of methyl Hg (MeHg) in the aquatic and semi-aquatic environments, particularly within the Everglades ecosystem. As a result, a suite of peer reviewed and technical publications have been produced exploring the underlying biogeochemical regulation of MeHg production within natural systems. The majority of these with relevance to South Florida focus on the hypothetical unimodal relationship of S/SO<sub>4</sub><sup>2-</sup> and MeHg production (Axelrad et al., 2013, 2008; Benoit et al., 2003, 1999a, 1999b; Gilmour et al., 1992; Orem et al., 2011). Since the development of the theoretical relationship between SO<sub>4</sub><sup>2-</sup> and MeHg production, early S/Hg studies and large-scale biogeochemical surveys have informed our understanding of S and the role it plays in wetland biogeochemistry. However at the landscape scale, Hg methylation is subject to large unexplained variations and appears to be controlled not only by SO<sub>4</sub><sup>2-</sup> but a combination of many environmental factors (Gilmour 2011, Julian et al. 2014). Due to this complexity and variability, the SO<sub>4</sub><sup>2-</sup>-Hg unimodal relationship is not spatially or temporally consistent within the Everglades (Julian et al. 2015b, 2014). The proof of an ecological concept lies in its predictive capability in nature and direct evidence of the SO<sub>4</sub><sup>2-</sup> and MeHg linkage has proven elusive. Rigorous analysis of the plethora of ambient monitoring data from the Everglades in combination with decades of research have yet to yield satisfactory models to develop a scientifically rigorous relationships to explain MeHg formation and dynamics in a predictable manner.

---

## MERCURY IN EVERGLADES FISH AND WILDLIFE

---

Elevated Hg concentrations in fish and biota have been a concern for the Everglades regions since the 1970s (Ogden et al. 1973). Subsequently, elevated Hg levels were reported in other wildlife species including American alligators (*Alligator mississippiensis* Daudin), blue crayfish (*Procambarus alleni* Faxon), Florida softshell turtles (*Apalone ferox* Schneider), pig frogs (*Rana grylio* Stejneger), mottled ducks (*Anas fulvigula* Ridgway), white-tailed deer (*Odocoileus virginianus* Zimmermann), and the endangered Florida panther (*Puma concolor coryi* Bangs) (Ware et al. 1991). More detailed synoptic monitoring programs identified elevated and variable Hg concentrations in piscivorous wildlife within the EPA including raccoons (*Procyon lotor* L.), alligators, wading birds, and Florida panthers (Porcella et al. 2004, Roelke et al. 1991, Rumbold et al. 2002, Spalding et al. 2000).

Because of its large size, extensive wetlands, and relatively high rates of Hg deposition, the Everglades is considered sensitive to Hg methylation and subsequent bioaccumulation into piscivorous wildlife (Wiener et al. 2003). Methylation of inorganic Hg in Everglades wetlands leads to the formation of MeHg, a potent neurotoxin. MeHg in aquatic biota is of human health and ecological concern due to its ability to bioaccumulate and biomagnify in food webs to concentrations that may pose a potential health threat to wildlife and humans that consume fish (Frederick et al., 2004; Hammerschmidt and Fitzgerald, 2006; Lange et al., 1993; Rumbold et al., 2001). Because fish are the main MeHg exposure pathway to both human and wildlife consumers

(Sunderland 2007), monitoring is necessary to understand the ecological significance of the spatial and temporal patterns in THg bioaccumulation in the Everglades. This section summarizes the research on the status and trends of mercury in native fish and wading birds from the Everglades region.

## **SPATIAL AND TEMPORAL TRENDS IN MERCURY LEVELS IN EVERGLADES FISH**

Binhe Gu and Paul Julian<sup>1</sup>

As discussed above, the Everglades ecosystem continues to experience elevated concentrations of Hg in various wildlife species. For the majority of these wildlife species, fish are an integral part of their diet either directly or indirectly. As such, biological monitoring of fish species are very important in the Everglades system. Fish can be useful indicators of the relative condition of aquatic ecosystems, as various fish species exhibit different ecological characteristics and they have the ability to integrate ecological processes of the system across both temporal and spatial scales (Joy and Death 2002).

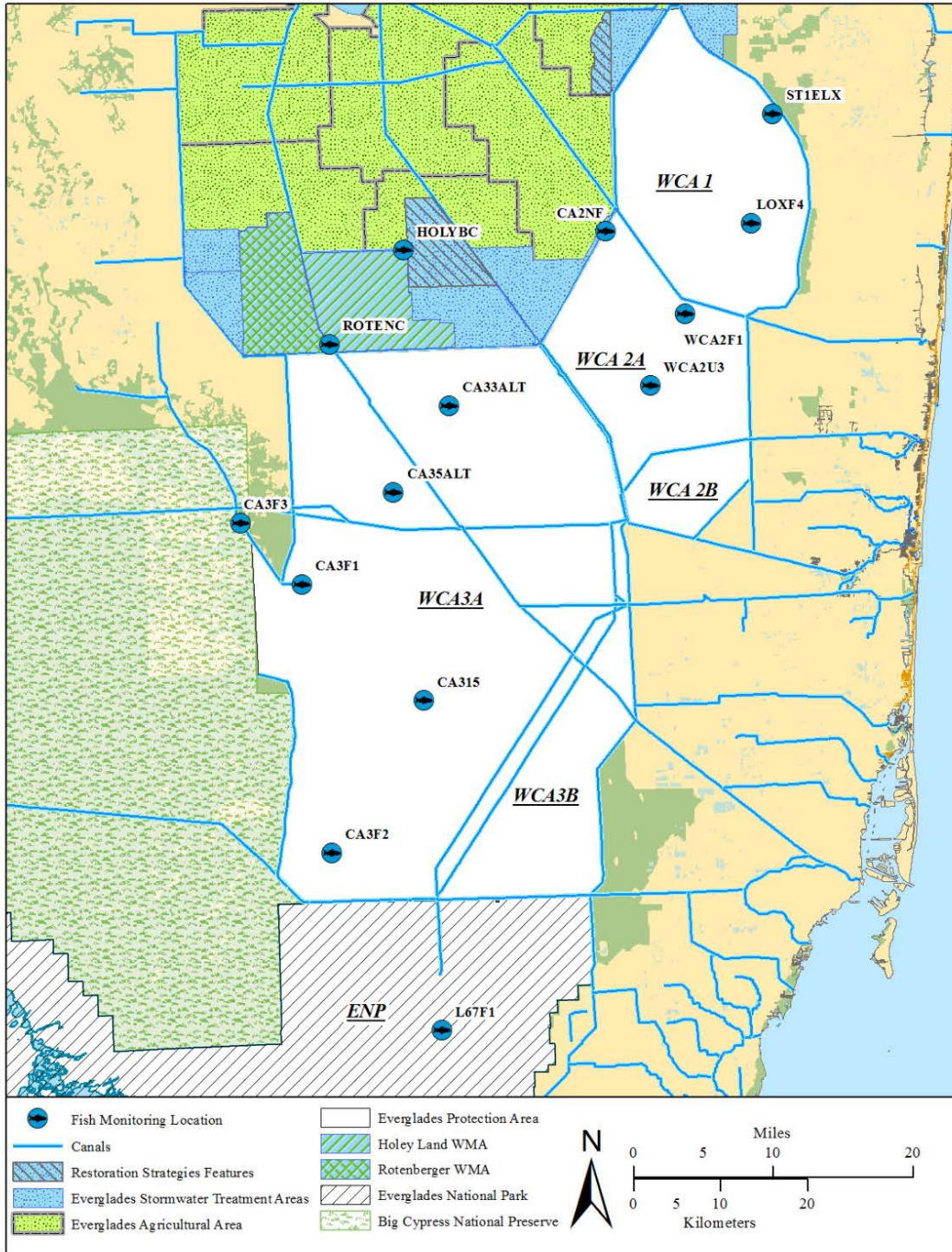
This section presents an update to Hg tissue concentrations in native Everglades fish along a trophic gradient of species and provides an opportunity to evaluate spatial and temporal trends in MeHg exposure levels for both wildlife and humans. Hg data from fish representing three distinct trophic levels and with varying life histories allow for assessment of various bioaccumulation and health assessment endpoints. Mosquitofish represent short-term changes in bioaccumulation due to their relatively short life span and limited home range, although they are widely distributed throughout 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 are thought to live up to 1.5 years).

Sunfish (bluegill, redear sunfish, and spotted sunfish) are also common in the canal/marsh complex and provide a longer-term environmental exposure estimate over a more expanded spatial scale. Sunfish are thought to have an average life span of four to seven years in the wild, but the size classes selected are typically in the age class of 1 to 3 years. These three centrarchid species overlap with diverse diets and may compete across species and age classes for prey items. Larger bluegill feed on a broad array of invertebrates and small fish and may appear higher in the food web structure than redear or spotted sunfish (Loftus 2000). Overall, both mosquitofish and sunfishes represent intermediate links within the Everglades aquatic food web and are preferred prey items for several fish-eating species; therefore, whole body Hg concentrations of these species are utilized to assess potential wildlife health risks. THg concentrations in LMB provide a spatially integrated measure of exposure to a long-lived top predator and, as such, are primarily utilized to assess human exposure to MeHg. Mercury concentrations in axial muscle tissue (fillets) from individual bass are used to assess human health risks associated with Hg exposure. Hg effects on Everglades fish health from actual environmental exposure have been documented (Scheuhammer et al. 2007, Wiener et al. 2003).

### **Methods**

#### ***Fish Sampling within the Greater Everglades Ecosystem***

To assess THg concentrations and trends in fish, samples were collected at 13 monitoring stations within the EPA and Holey Land and Rotenberger WMAs (**Figure 3B-1**). These stations are part of the long-term Hg monitoring projects of SFWMD and the Florida Fish and Wildlife Conservation Commission (FWC).



**Figure 3B-1.** Location of fish tissue monitoring locations within the EPA and Holey Land and Rotenberger WMAs. [Note: Station CA3F1 is an inactive station with fish sampling activity suspended since October 2009.]

Annual fish collections generally occur during September and November. Mosquitofish were collected using a dip net to obtain a grab sample of between 100 and 250 mosquitofish from each site. After collections, mosquitofish were homogenized and subsamples were analyzed for THg. Sunfish and bass were collected using direct current, electrofishing equipment mounted on either an airboat or Jon boat at each site. For sunfish, up to 10 individuals in the target size range of 102 to 178 millimeters (mm; i.e., 4 to 7 inches) total length (TL) 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 targeted for collected at each location. Similarly, 20 bass ranging in size between 200 and 500 mm TL were targeted for collection at each site and collected concurrently with sunfish. In the laboratory, sunfish and bass were weighed, measured, sexed, and, for bass only, the sagittal otoliths were removed for determination of age. Whole sunfish and whole axial muscle (fillet) samples of bass were preserved at 4 degrees Celsius in plastic bags.

Homogenized samples of mosquitofish, sunfish, and bass axial muscle tissue collected from the EPA were analyzed by SFWMD using USEPA Method 7473 (Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry), with a method detection limit (MDL) of 0.005 mg/kg. All results are reported as THg on a wet weight basis as mg/kg. Because more than 85 percent of the Hg found in fish is in the form of MeHg (Bloom 1992, Grieb et al. 1990), it is assumed that THg concentrations are considered to be representative of MeHg concentrations in fish tissue samples.

Both mosquitofish and sunfish were processed as whole body homogenates to assess potential ecological risk from MeHg exposure to fish-eating wildlife. These data were evaluated against the USEPA TL3 MeHg criterion of 0.077 mg/kg for protection of wildlife (USEPA 1997). Human exposure to MeHg occurs primarily through consumption of fish; therefore, axial muscle tissue (fillets) from bass utilized to assessment human health risk from MeHg exposure. The USEPA-recommended MeHg criterion for the protection of human health (0.35 mg/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.

### ***Data Screening and Handling***

Hg data evaluated in this section of the chapter were retrieved from the District's corporate environmental database, DBHYDRO. Similar to water quality analysis within this section 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 used both by laboratories for sample analyses and data users for reporting to indicate that the quality or accuracy of the data may not be suitable for water quality evaluations.

### ***Quantitative Analysis***

Fish tissue THg concentrations were summarized by station, region, and species using basic descriptive statistics for the current water year, WY2015, and the entire period of record (POR; WY1999–WY2015). Mosquitofish THg concentrations were assessed between climatic years (i.e., wet versus dry years) and habitat (i.e., canal and marsh) separately using the Kruskal-Wallis rank sum test. Wet and dry years were determined based on the historical rainfall amount observed at long-term rainfall monitoring stations in the EPA. THg concentrations of TL3 sunfish species (i.e., bluegill, redear sunfish, and spotted sunfish) were compared using the Kruskal-Wallis rank sum test and Dunn's test of multiple comparisons for both the entire POR and current water year. All statistical operations were performed with R© (Version 3.1.2, R Foundation for Statistical Computing, Vienna Austria) and the critical level of significance was set at  $\alpha = 0.05$ .

## Results and Discussion

### Mosquitofish

Mosquitofish composite samples from across the EPA have been collected for THg analysis since WY1999 (**Table 3B-1**). During WY2015, THg concentrations in mosquitofish from 13 monitoring sites ranged from 0.012 mg/kg at site CA33ALT to 0.099 mg/kg at site CA35ALT, with a median value of 0.040 mg/kg (**Figure 3B-2**), which is 13 percent lower than the median value reported in WY2014. The lowest and the highest THg concentrations in mosquitofish were found at different sites in WY2014, two northern sites WCA2F1 and Rotenberger WMA. Similar to WY2013 and WY2014, the majority of the sites showed lower THg concentrations in WY2015 than the previous water year. In fact, 10 of the 13 sites in WY2015 were below their POR median values (**Figure 3B-2**).

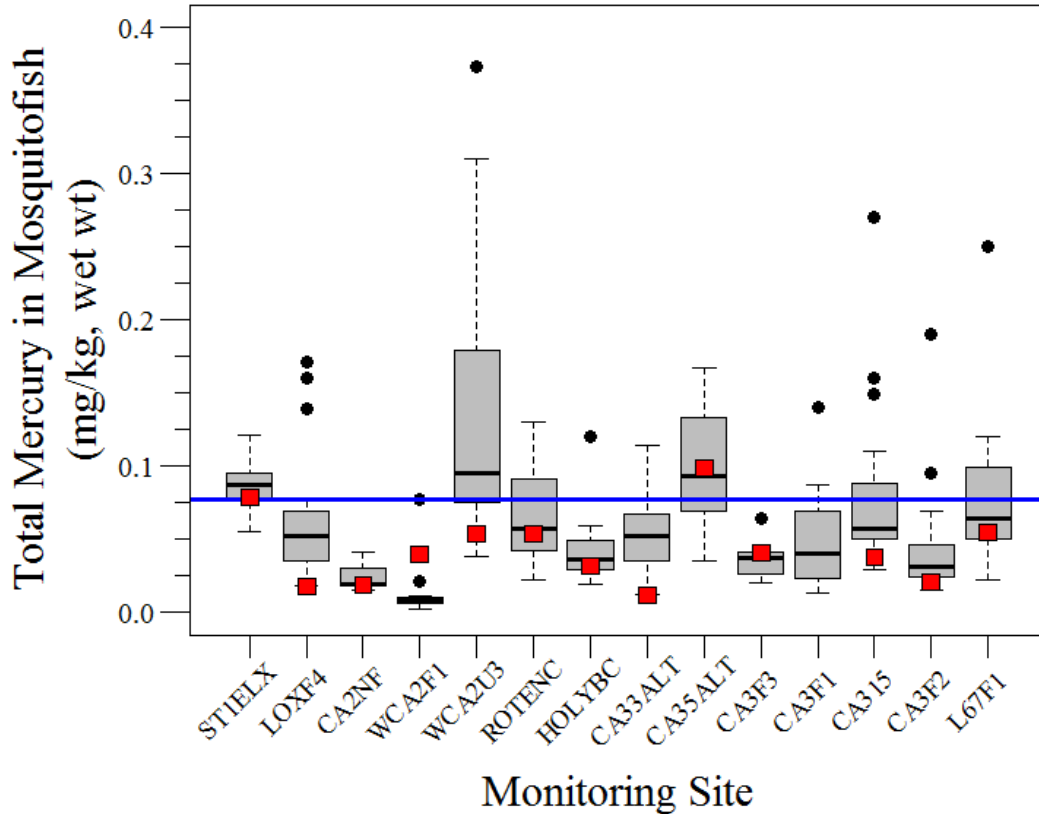
Identical to WY2014, mosquitofish THg concentrations in WY2015 still exceeded the federal criterion of 0.077 mg/kg MeHg for TL3 fish at two of the 13 active monitoring sites (ST1ELX and CA35ALT) (**Figure 3B-2**). For the POR, the median value of THg in mosquitofish is 0.050 mg/kg ( $n = 172$ ) and 28 percent of the data exceeded the federal criterion. The highest median value of mosquitofish THg throughout the POR was 0.373 mg/kg observed at WCA2U3, while the lowest observed value of 0.002 mg/kg was recorded at CA2NF. Site CA2NF near the L-6 canal and site WCA2F1 near the Hillsborough Canal had no exceedance for the entire monitoring period and displayed the lowest mosquitofish median THg value of 0.019 and 0.008 mg/kg, respectively. It is noteworthy that CA2NF and WCA2F1 are located in the northern portion of WCA-2A near the Stormwater Treatment Area (STA-) 2 outflow and within the nutrient enriched areas of the marsh. Additionally, sites WCA2U3 and CA35ALT, which have relatively elevated mosquitofish THg tissue concentrations are located in the nutrient-poor area on the mid-southern end of the marsh.

**Table 3B-1.** Temporal trend analysis of mosquitofish THg concentration at the 13 active monitoring locations within the EPA during WY1999–WY2015.

[Note: NS – not statistically significant].

Area	Station	Test Statistic	Spearman's $\rho$	$p$ -value	Trend Direction
WCA-1	ST1ELX	62.0	0.62	0.06	NS
	LOXF4	1058.0	-0.56	<0.05	Declining
WCA-2	CA2NF	132.9	0.19	0.59	NS
	WCA2F1	281.0	0.50	0.06	NS
	WCA2U3	684.0	0.16	0.53	NS
	CA33ALT	268.0	-0.22	0.52	NS
WCA-3	CA35ALT	228.0	0.37	0.21	NS
	CA3F3	10.0	0.50	0.45	NS
	CA3F1 <sup>a</sup>	330.0	-0.15	0.64	NS
	CA315	1242.0	-0.52	<0.05	Declining
	CA3F2	1379.3	-0.69	<0.05	Declining
ENP	L67F1	665.1	-0.19	0.5	NS
WMAs	ROTENC	200.0	0.30	0.34	NS
	HOLYBC	657.9	0.19	0.46	NS

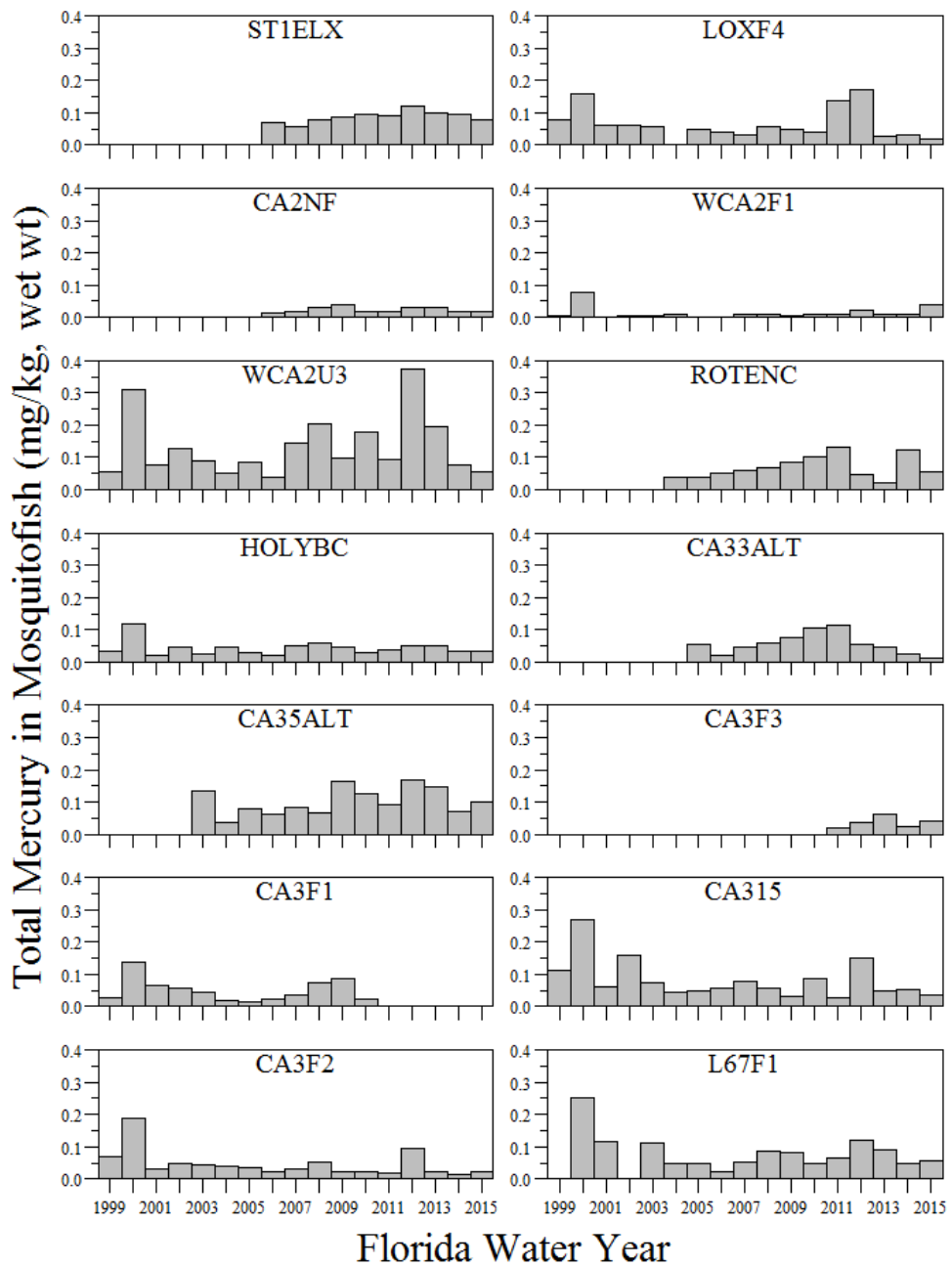
a. Inactive monitoring station. No data has been collected since October 2009.



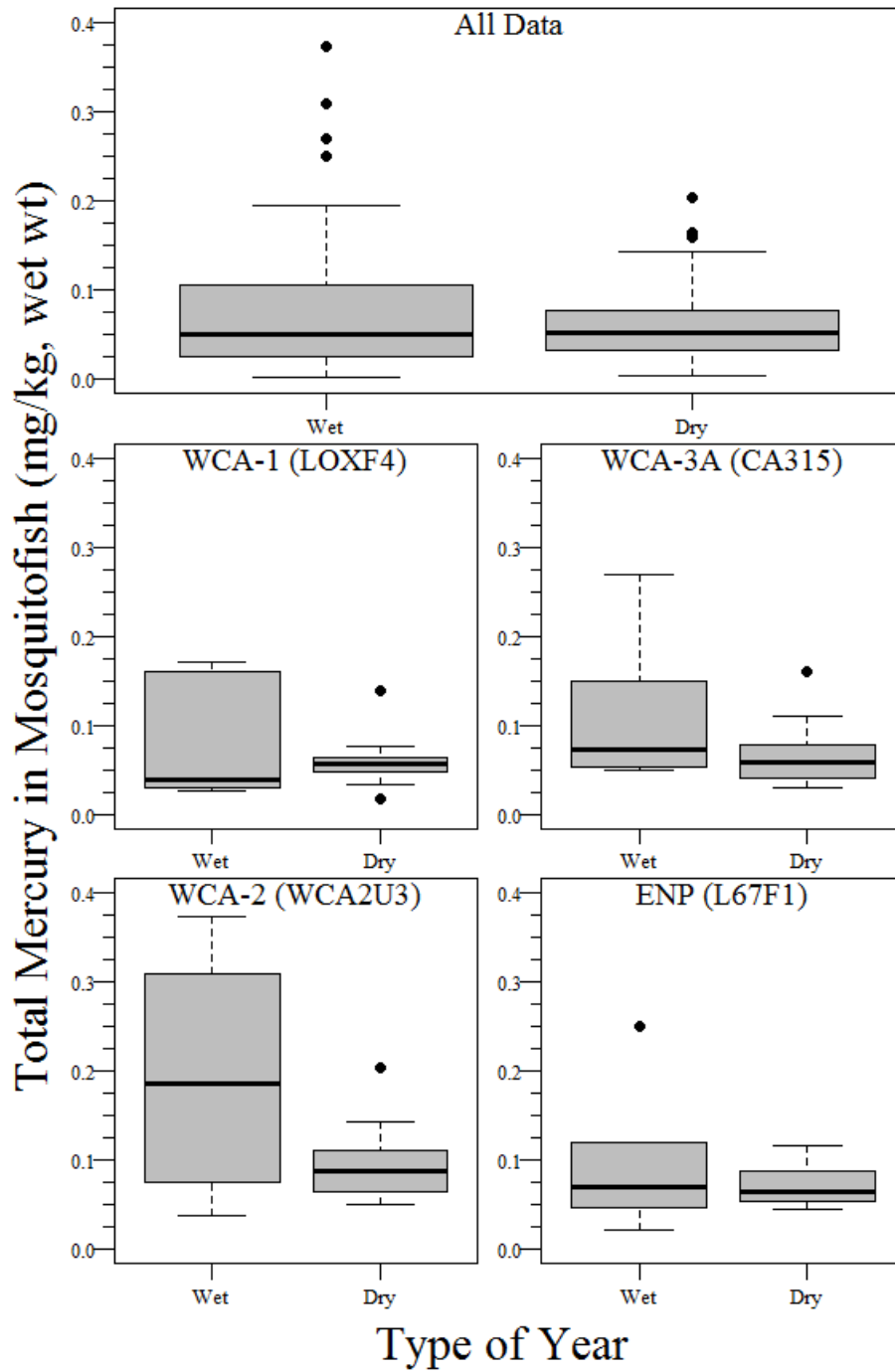
**Figure 3B-2.** Box plots of THg concentrations in mosquitofish at each monitoring site in the EPA during WY1999–WY2015. Red boxes indicate WY2015 mean THg concentrations and the blue line denotes the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of piscivorous wildlife.

Since WY2006, variation in mosquitofish THg concentrations between consecutive years remains high (**Figure 3B-3**). During WY2015, the highest observed mosquitofish THg concentration occurred at WCA2F1 with a concentration of 0.40 mg/kg. During WY2014, this site reported a THg concentration of just 0.008 mg/kg. This one-year change is over a 400 percent increase in THg at this station. By contrast, ROTENC experienced a 79 percent decline in mosquitofish THg concentrations between WY2014 and 2015 (0.125 mg/kg and 0.054 mg/kg, respectively). To date, it is not clear what factor(s) control the dramatic intra-site temporal variations in mosquitofish THg concentration. It hypothesized that changes in inter-annual precipitation (i.e., wet years versus dry years) and site specific biogeochemistry including  $\text{SO}_4^{2-}$ , available  $\text{Hg}^{2+}$ , dissolved organic carbon (DOC), and reduction-oxidation (redox) have the ability to influence prey mercury concentrations. Additionally site-specific trophic dynamics can each can play an important role in controlling THg concentration in mosquitofish. However, a comparison of mosquitofish THg collected between the wet and dry years (**Figure 3B-4**) did not reveal a statistically significant difference ( $\chi^2 = 0.69$ ,  $df = 1$ ,  $p = 0.40$ ). It is possible that the difference in precipitation between wet and dry years alone was not sufficient to result in significant changes in mosquitofish THg. This could be the result of synergistic and competing interactions involving biogeochemistry, water quality conditions, predation or food sources, and trophic structure.



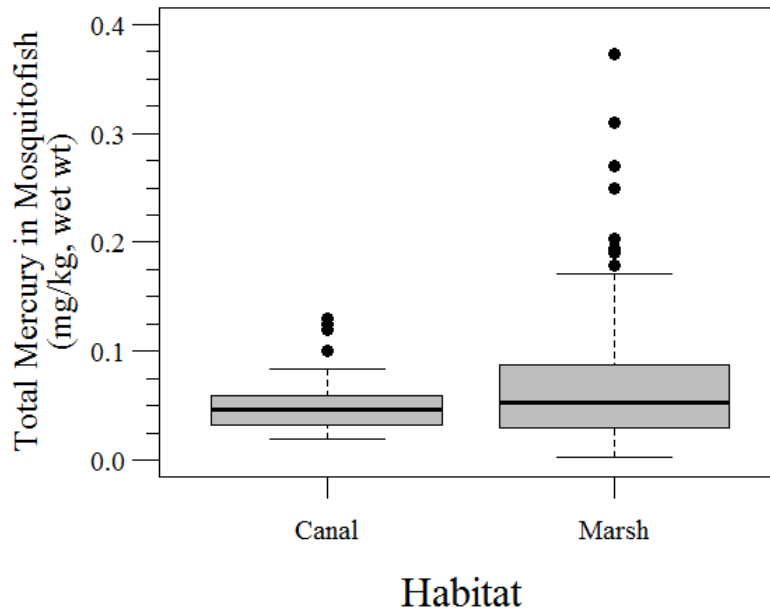


**Figure 3B-3.** Annual THg concentrations in mosquitofish composite samples at each monitoring site with the EPA during WY1999–WY2015.



**Figure 3B-4.** Box plots comparing site-specific mosquitofish THg concentrations collected during wet and dry years during WY1999–WY2015 within the EPA.

Mosquitofish THg concentrations were compared by habitat with stations either characterizing canal or marsh habitat types. Overall variation in mosquitofish THg concentration was greatest in marsh habitat [coefficient of variation (CV) = 85%; Variance = 0.003] than canal habitat (CV = 58%; Variance = 0.0008). This high degree of variation in marsh habitat could be due to relatively dynamic hydrology (i.e., drydown, dryout, water level changes, etc.), the dynamics of marsh trophic structure and biogeochemistry associated with dynamic hydrology. THg concentrations did not statistically differ between habitat ( $\chi^2 = 1.76$ ,  $df = 1$ ,  $\rho = 0.18$ ). The average THg concentration in mosquitofish collected from marsh sites throughout the POR was  $0.069 \pm 0.005$  mg/kg ( $n = 153$ ) while the THg concentration in mosquitofish collected from canal sites was  $0.050 \pm 0.005$  mg/kg ( $n = 34$ ) (**Figure 3B-5**).



**Figure 3B-5.** Box plot comparing mosquitofish THg concentrations between marsh and canal habitats from data collected in the EPA during WY1999–WY2015.

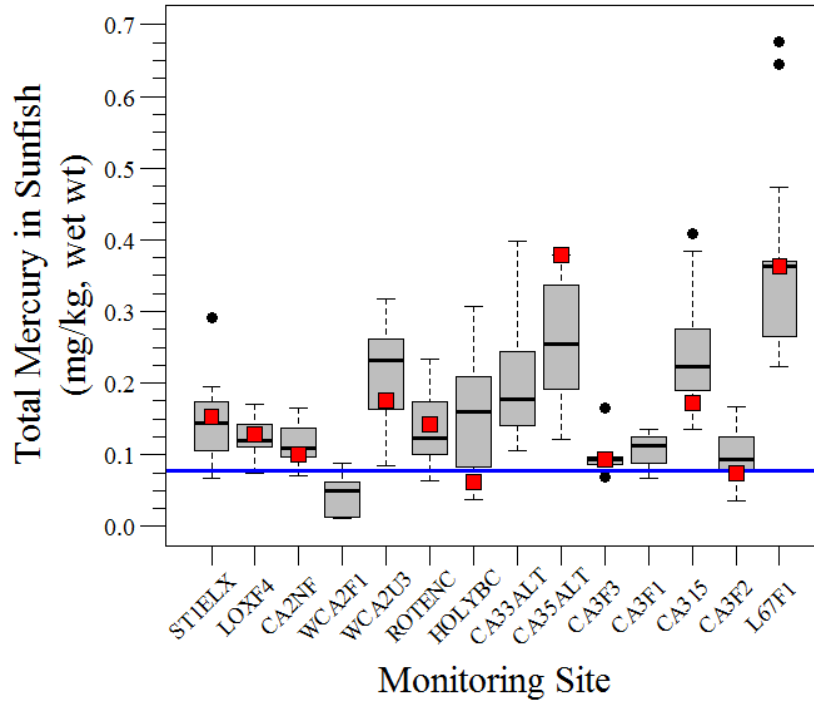
During the entire POR, three stations experienced a significantly declining temporal trend in mosquitofish THg (**Table 3B-1**). Considerable interannual variations of THg concentrations were observed within sites with low nutrient concentrations including interior stations such as LOXF4, WCA2U3, CA3A15, and L67F1 (**Figure 3B-3**). It is not known if the large variations were associated with internal factors such as wading bird feeding, which has the potential to alter trophic structure, internal marsh sources of THg or MeHg from tree islands (Zhu et al. 2014), or other factors.

### **Sunfish**

TL3 sunfish species including bluegill, redear sunfish, and spotted sunfish have been sampled for THg analysis in the EPA since WY1999. The overall average sunfish whole body concentration of THg for data pooled from all sites and years was  $0.185 \pm 0.003$  mg/kg ( $n = 2600$ ). Throughout the POR, 89 percent of annual mean sunfish THg concentrations exceeded the USEPA MeHg criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. All monitored stations observed annual mean sunfish THg concentration above the USEPA MeHg criterion, with the enriched WCA2F1 experiencing the least number of exceedances ( $n = 1$ ; WY2008; mean THg = 0.088 mg/kg) during the POR.

The average THg concentration for the POR was highest at the ENP site L67F1 (0.366 mg/kg) and lowest (0.046 mg/kg) at a WCA-2A site (WCA2F1) near the Hillsborough Canal (**Figure 3B-1**). This pattern of THg concentrations in sunfish is consistent with THg concentrations observed in mosquitofish within the EPA (discussed above). Several interior sites in WCA-2 and WCA-3 displayed high long-term (i.e., POR) average THg concentrations above 0.200 mg/kg. The THg concentration in sunfish tended to increase from north to south (**Figure 3B-6**). Only two monitoring stations showed a significant increasing temporal trend in mean sunfish THg concentration throughout the POR, while all other stations had no significant temporal trend (**Table 3B-2** and **Figure 3B-7**) and showed little pattern consistency across stations.

During WY2015, the mean THg concentration in the TL3 sunfish species from 13 active monitoring sites was 0.168 mg/kg, with a range from 0.06 mg/kg at HOLYBC to 0.379 mg/kg at CA35ALT. Compared to WY2014 (0.186 mg/kg), a 10 percent decrease in mean sunfish THg concentrations occurred. THg concentration significantly varied between sunfish species during WY2015 ( $\chi^2 = 23.93$ ,  $df = 2$ ,  $\rho < 0.001$ ; **Figure 3B-8**). Bluegill were significantly different from redear sunfish ( $z = -4.19$ ,  $\rho < 0.001$ ) and spotted sunfish ( $z = 4.06$ ,  $\rho < 0.001$ ), meanwhile redear did not differ from spotted sunfish ( $z = 1.15$ ,  $\rho = 0.12$ ). Throughout the entire POR, all three species statistically differed in THg concentrations ( $\chi^2 = 289.81$ ,  $df = 2$ ,  $\rho < 0.001$ ) with the highest THg concentration in spotted sunfish ( $0.265 \pm 0.009$  mg/kg), followed by bluegill ( $0.207 \pm 0.005$  mg/kg), and redear sunfish ( $0.130 \pm 0.003$  mg/kg) (**Figure 3B-8**). These differences could be due to feeding preferences among these three species. Depending on size class and hydrologic conditions, bluegill prefer omnivorous invertebrates, redear sunfish prefer herbivorous invertebrates and spotted sunfish prefer decapods and omnivorous invertebrates (Loftus 2000).

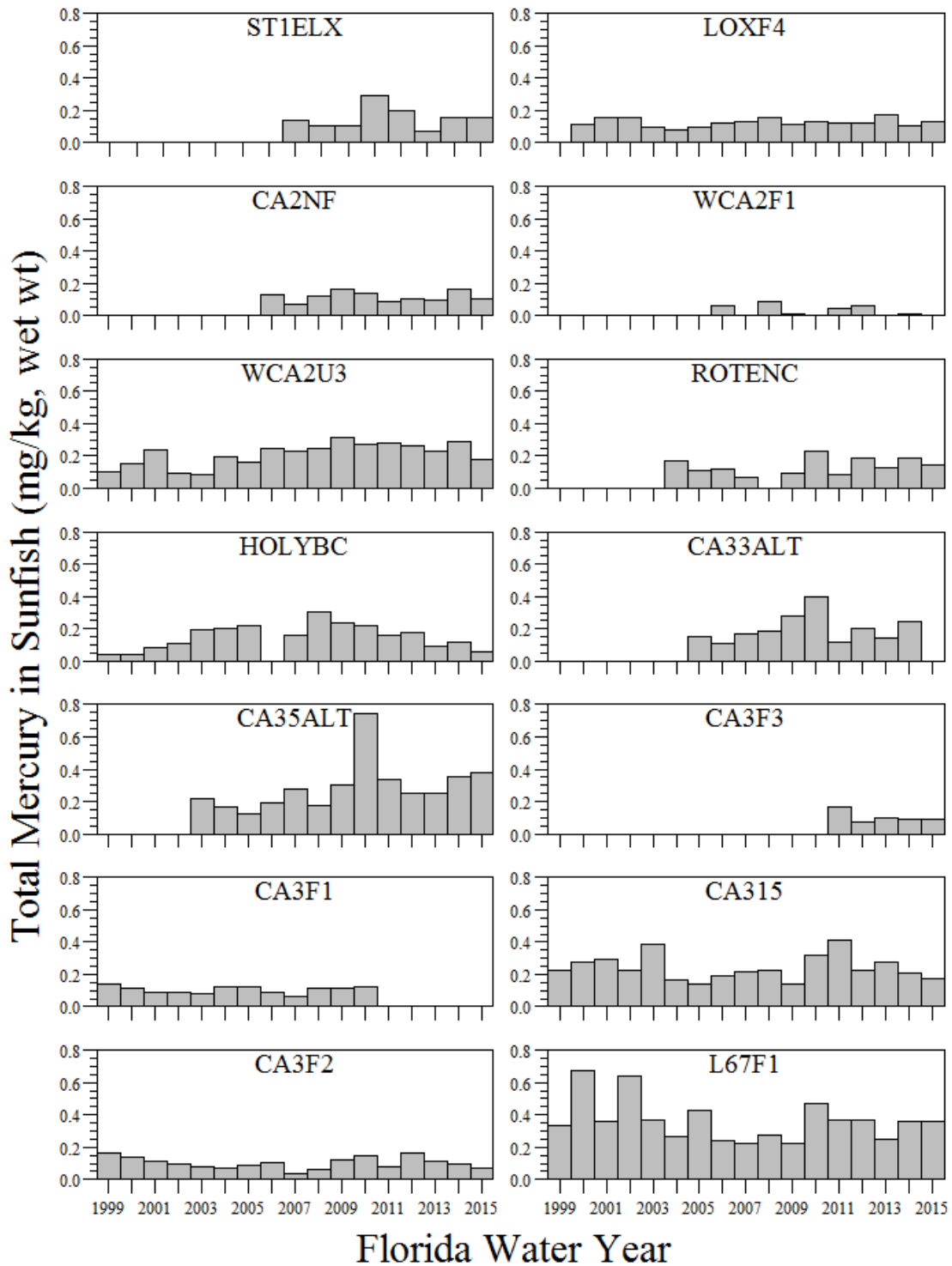


**Figure 3B-6.** Box plots of THg concentrations in sunfish at each monitoring site in the EPA during WY1999–WY2015. Red boxes indicate WY2015 mean THg concentrations and the blue line denotes the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of piscivorous wildlife.

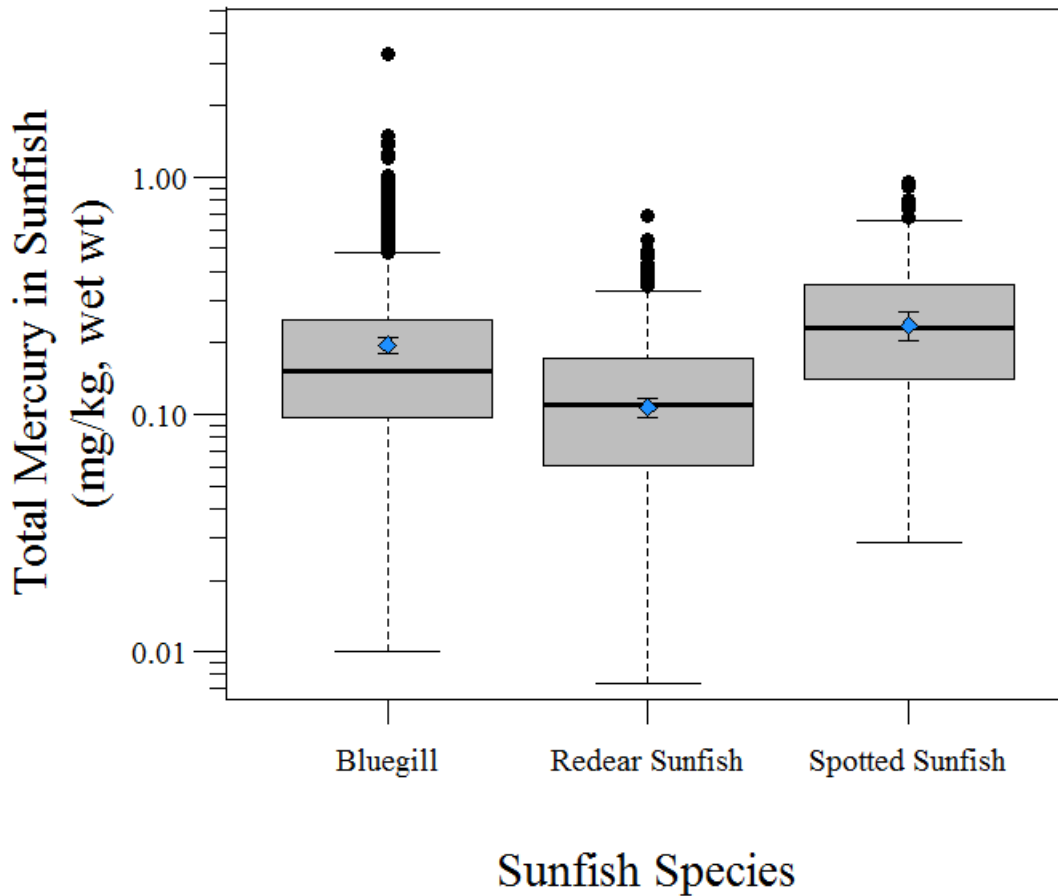
**Table 3B-2.** Temporal trend analysis of mean sunfish THg concentrations at the 13 active monitoring locations within EPA during WY1999–WY2015. [Note: NS=not statistically significant].

Area	Station	Test Statistic	Spearman's $\rho$	$\rho$ -value	Trend Direction
WCA-1	ST1ELX	62	0.26	0.54	NS
	LOXF4	596	0.12	0.65	NS
WCA-2	CA2NF	156	0.05	0.89	NS
	WCA2F1	54	-0.54	0.30	NS
	WCA2U3	298	0.63	<0.05	Inclining
WCA-3	CA33ALT	116	0.30	0.41	NS
	CA35ALT	102	0.72	<0.05	Inclining
	CA3F3	26	-0.30	0.68	NS
	CA3F1 <sup>a</sup>	304	-0.06	0.85	NS
	CA315	886	-0.09	0.74	NS
ENP	CA3F2	904	-0.11	0.68	NS
	L67F1	962	-0.18	0.49	NS
WMA's	ROTENC	146	0.34	0.31	NS
	HOLYBC	536	0.21	0.43	NS

a. Inactive monitoring station. No data has been collected since October 2009.



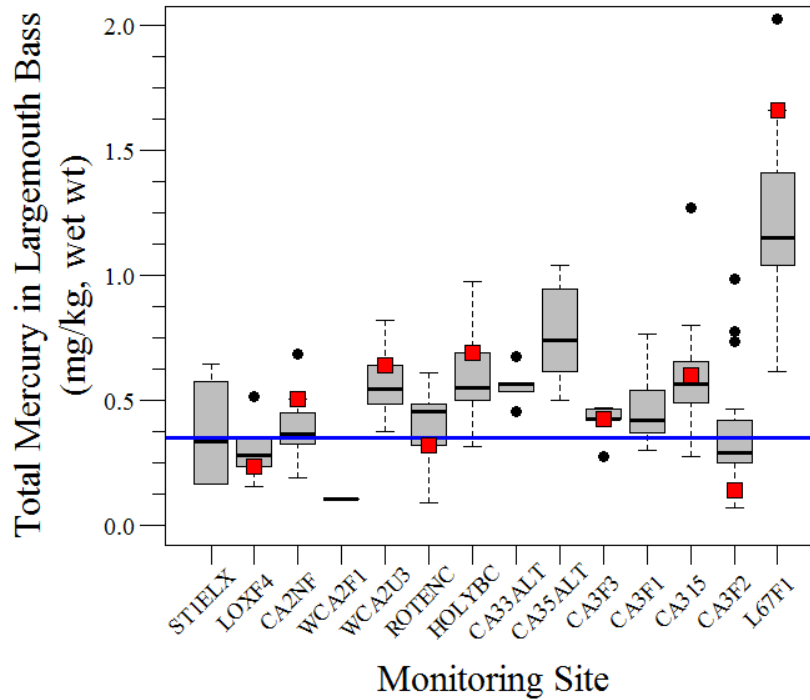
**Figure 3B-7.** Annual THg in TL3 sunfish whole body samples at each monitoring site in the EPA during WY1999–WY2015.



**Figure 3B-8.** Comparison of TL3 sunfish species collected in the EPA during WY1999–WY2015. Blue diamonds indicate WY2015 mean ( $\pm$  standard error) THg concentrations for each species.

### ***Largemouth Bass***

LMB axial tissue fillet samples have been collected across the EPA for THg analysis since WY1999. During WY2015, mean THg concentrations in LMB ranged from 0.141 mg/kg at site CA3F2 (WCA-3A) to 1.660 mg/kg at site L67F1 (ENP), with an overall WY2015 median value of 0.433 mg/kg. This represents a 13 percent decrease in the reported median value for WY2015 (0.494 mg/kg). The lowest and highest THg concentration in LMB during WY2014 were observed at LOXF4 (0.265 mg/kg) and L67F1 (1.125 mg/kg), respectively. Generally, LMB THg concentrations follow a strong north-to-south gradient with concentrations being lower in WCA-1 and WCA-2 and higher in WCA-3 and ENP (**Figure 3B-9**). Along this gradient, several key factors could influence THg conditions including water quality conditions (i.e., pH, alkalinity, nutrient availability, etc.), trophic position, and habitat structure (Julian and Gu 2015). Water column variables such as alkalinity, chloride, nutrient concentrations, and pH can either alter fish physiology or alter Hg cycling making it easier for absorption (Lange et al. 1993, Spry and Wiener 1991). Furthermore factors that influence trophic position including hydrology, vegetation density, and prey abundance influence Hg accumulation dynamics (Julian and Gu 2015, Rawlik et al. 2002).

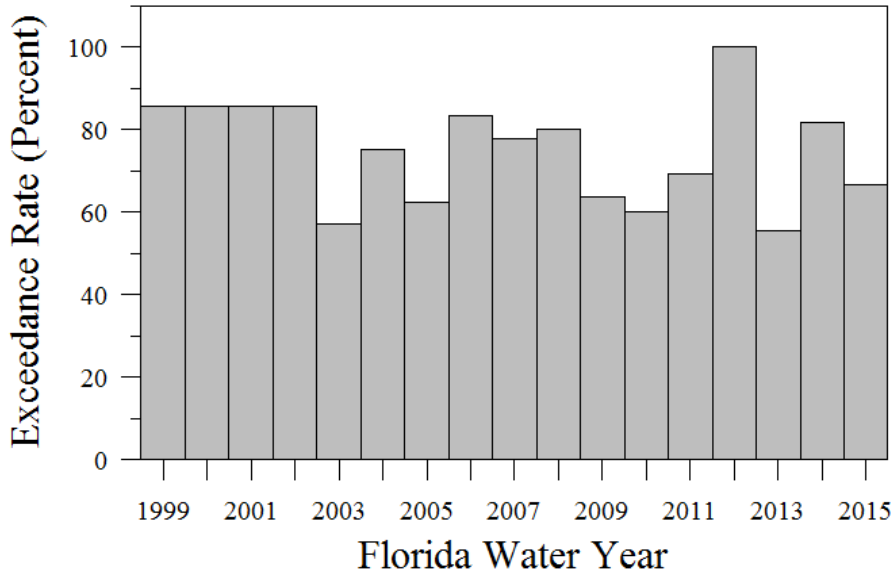


**Figure 3B-9.** Box plots of THg concentrations in LMB at each monitoring site during WY1999–WY2015. Red boxes indicate WY2015 mean THg concentrations and the blue line denotes the 0.350 mg/kg USEPA MeHg criterion for protection of human health.

During WY2015, 67 percent of the monitoring locations in the region had mean THg concentration above the USEPA recommended MeHg criterion for the protection of human health (0.35 mg/kg) (USEPA 2001) (**Figure 3B-9**). It is important to note that six of the nine stations sampled during WY2015 were greater than historic values, the largest increases was observed at stations L67F1 in ENP, which exhibits very low  $\text{SO}_4^{2-}$  water column concentrations. This rate decreased from 81 percent of the monitoring locations observed in WY2014. Overall, exceedance rates of the recommended criterion has improved from the POR start (WY1999) from exceedance rates of 86 percent for several years followed by several years with variable exceedance rates and after WY2003/WY2004 some years achieved 60 percent of the stations exceeding the recommend criterion (**Figure 3B-10**). These exceedances of the recommend criterion could potentially be driven by hydrologic factors (i.e., wet versus dry years) and/or changes in water quality, quantity, and timing.

Throughout the POR (WY1999–WY2015), no statistically significant temporal trends in LMB THg tissue concentration were evident (**Table 3B-3**). The lack of temporal trend in tissue THg could be due to gaps in the data for some stations and/or little to no variation (i.e., WCA2U3) or too much variation (i.e., ROTENC) in interannual concentrations at some sites, which could be driven by unexplained underlying conditions (discussed above), external drivers such as changes in atmospheric deposition, or highly variable trophic interactions that alter food webs and available Hg for accumulation (**Figure 3B-11**).



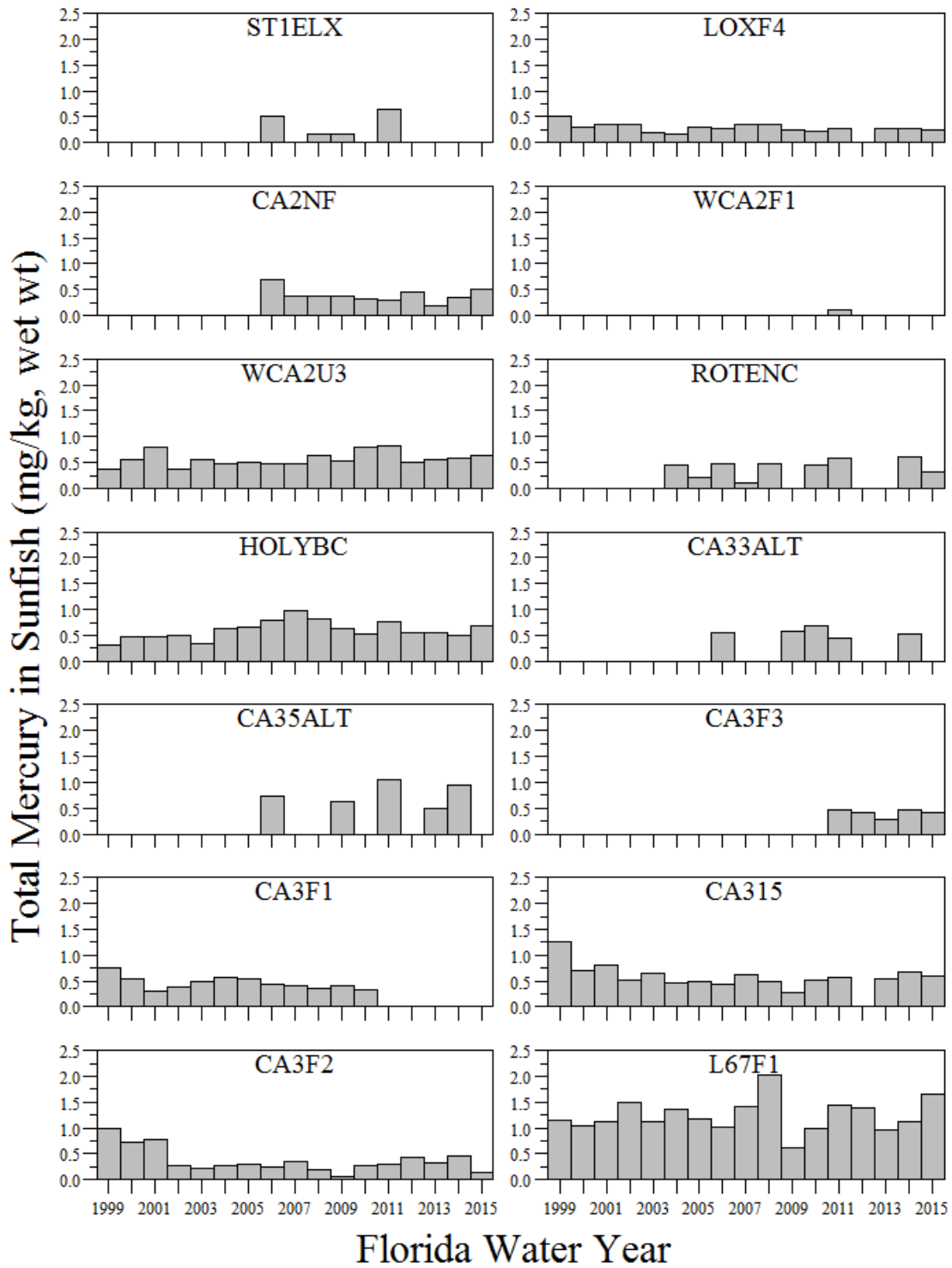


**Figure 3B-10.** Annual exceedance rate of LMB mean THg concentrations relative to the USEPA MeHg criterion for protection of human health.

**Table 3B-3.** Temporal trend analysis of mean LMB THg concentration at the 13 active monitoring locations within the EPA during WY1999–WY2015. [Note: NS=not statistically significant.]

Area	Station	Test Statistic	Spearman's $\rho$	$\rho$ -value	Trend Direction
WCA-1	ST1ELX	8	0.20	0.92	NS
	LOXF4	970	-0.43	0.10	NS
WCA-2	CA2NF	210	-0.27	0.45	NS
	WCA2F1	---	---	---	Not Enough Data
	WCA2U3	469	0.43	0.09	NS
WCA-3	CA33ALT	30	-0.50	0.45	NS
	CA35ALT	18	0.10	0.95	NS
	CA3F3	24	-0.20	0.78	NS
	CA3F1 <sup>a</sup>	418	-0.46	0.13	NS
	CA315	882	-0.30	0.26	NS
	CA3F2	1082	-0.33	0.20	NS
ENP	L67F1	764	0.06	0.81	NS
WMAs	ROTENC	70	0.42	0.27	NS
	HOLYBC	420	0.49	0.05	NS

a. Inactive monitoring station. No data has been collected since October 2009.



**Figure 3B-11.** Annual THg concentrations in LMB axial fillet samples at each monitoring site in the EPA during WY1999–WY2015.

Over the entire POR, the median mosquitofish THg concentration (0.050 mg/kg) has been below the federal criterion for wildlife protection. Meanwhile, POR THg concentration for sunfish (0.140 mg/kg) and LMB (0.460 mg/kg) has been above the wildlife and human health protection criterion, respectively. During WY2015, mosquitofish THg concentrations exceeded the USEPA criterion in two of the 13 sampled monitoring sites (15 percent). By contrast, during WY2015 sunfish THg concentrations exceeded the USEPA criterion in nine of the 10 (of the 13 active stations) sampled monitoring sites (89 percent). Furthermore, during WY2015 LMB THg concentration exceeded the recommended USEPA criterion in six of the nine (of the 13 active stations) sampled monitoring sites (67 percent). Several sites experienced THg concentration declines in POR annual mosquitofish THg concentrations (sites CA315 and CA3F2), while inclining trends in POR annual sunfish THg concentrations occurred at two monitoring sites (sites WCA2U3 and CA35ALT). None of the sites exhibited a statistically significant temporal trend in annual LMB THg concentration throughout the 17-year POR.

Whether THg concentrations in fish are remaining constant over the past decade, as reported in previous SFERs, or whether there are recent increases in fish tissue THg concentrations, Hg bioaccumulation continues to be a significant water quality issue within the EPA and Greater Everglades. THg concentrations in higher trophic level fish (i.e., sunfish and LMB) are highly variable across the landscape but continue to exceed criteria concentrations for the protection of piscivorous wildlife and humans at many locations. Future rates of Hg emissions and atmospheric deposition are highly uncertain (Krabbenhoft and Sunderland 2013), the response of fisheries to Hg load reductions could take decades (Munthe et al. 2007), and repeated attempts to gain a better understanding of system controls on methylation and bioaccumulation have found little consistent patterns. These basic findings do not provide a basis to develop a comprehensive strategy to manage the Everglades mercury issue beyond the state's total maximum daily load (FDEP 2013).

## **PERSPECTIVES ON THE SPATIAL VARIABILITY OF MERCURY IN EASTERN MOSQUITOFISH IN THE EVERGLADES PROTECTION AREA**

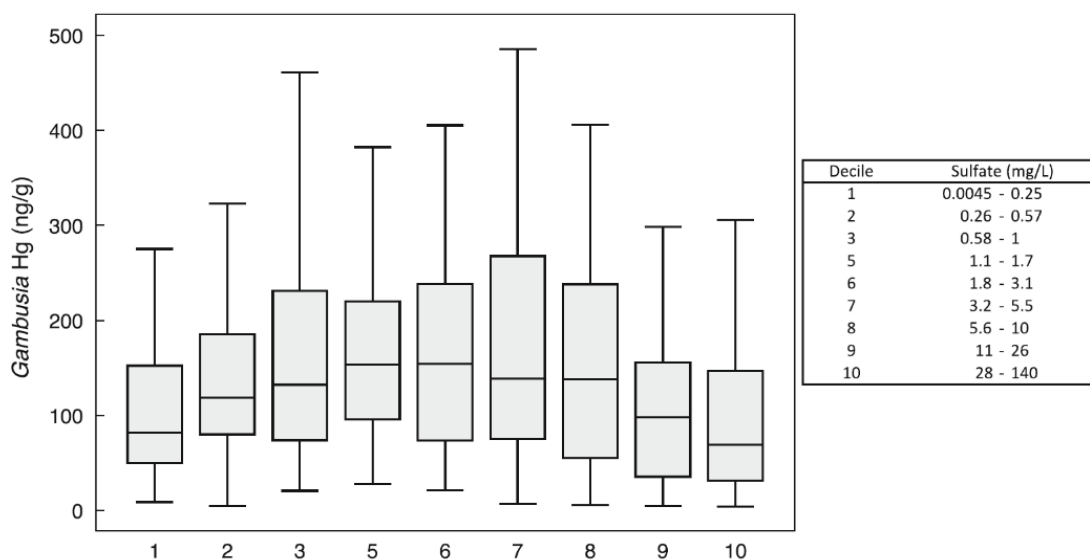
Forrest E. Dierberg<sup>6</sup>, Mike Jerauld<sup>6</sup>,  
Thomas A. DeBusk<sup>6</sup>, Michelle D. Kharbanda<sup>6</sup>,  
Janelle A. Potts<sup>6</sup> and Nichole R. Larson<sup>6</sup>

Persistent spatial variability in Eastern mosquitofish (*Gambusia holbrooki*) tissue Hg concentrations across the Everglades has been recognized since at least 1996 (Scheidt and Kalla 2007, Stober et al. 2001). These patterns have been attributed to the distribution of Hg methylation rates, as determined by the intersection of the distributions of  $\text{SO}_4^{2-}$  [promotes Hg methylation by the key microbial group, sulfate-reducing bacteria (SRB)] and sulfide ( $\text{S}^{2-}$ ) (inhibits Hg methylation by reducing the availability of inorganic Hg to methylating organisms) levels (Benoit et al. 2003, Gilmour et al. 1998, Orem et al. 2011). In particular, analyses of broad-level ecosystem monitoring data have suggested a unimodal relationship exists between fish tissue Hg and surface water  $\text{SO}_4^{2-}$  concentrations across the Everglades (**Figure 3B-12**; (Axelrad et al., 2013; Gabriel et al., 2014; Pollman, 2012). It has also been speculated that changing  $\text{SO}_4^{2-}$  availability contributed to observed temporal variability in mosquitofish Hg concentrations (Axelrad et al. 2005). However, it has been recognized that, despite the appearance of this apparent trend, there is unexplained variability in the fish Hg/surface water  $\text{SO}_4^{2-}$  relationship that must be explained if an effective MeHg mitigation

---

<sup>6</sup>DB Environmental, Rockledge, FL

policy is to be devised (Axelrad et al., 2013). Several recent studies have been conducted in areas of persistently high and low mosquitofish Hg, in an effort to resolve the suite of controlling factors.

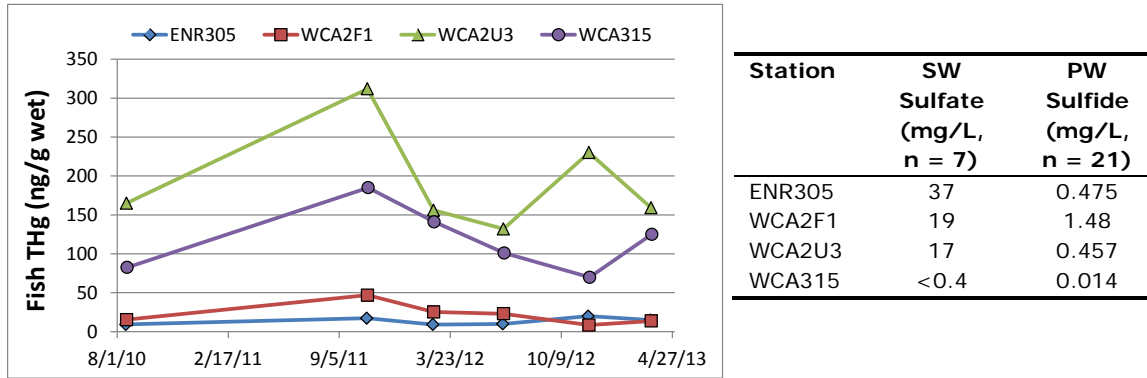


**Figure 3B-12.** Box plot of the distribution of *Gambusia* spp. Hg concentrations as a function of decile surface water  $\text{SO}_4^{2-}$  concentrations. Data from all Regional Environmental Monitoring and Assessment Program (REMAP) samples collected in the EPA during 1995, 1996, 1999, and 2005 sampling cycles. Figure and caption text from Pollman and Axelrad, (2014).

### Long-term, Synoptic Studies at Mosquitofish Mercury Hotspots

In the recent Everglades Mercury Hot Spot Study, four stations were monitored from 2010 to 2013. Sites U3 (central WCA-2A) and 3A-15 (central WCA-3A) consistently exhibited elevated mosquitofish tissue Hg levels, with some temporal variability, while two other locations (ENR305, near the outflow of STA-1 West) and F1 (northern WCA-2A) contained mosquitofish with consistently low tissue Hg levels (**Figure 3B-13**; see **Figure 3B-1** for site locations). These findings were generally consistent with those of USEPA's Regional Environmental Monitoring and Assessment Program (REMAP), which measured mosquitofish Hg in these marshes several times between 1995 and 2005 (Scheidt and Kalla 2007, Stober et al. 2001), and indicated the persistence of these spatial patterns. However, these patterns only partially conform to the expectations of the unimodal hypothesis described above, based on the  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  conditions measured at these sites. For example, the difference in mosquitofish Hg at F1 and U3, which had nearly identical average surface water  $\text{SO}_4^{2-}$  concentrations during the study period, could be attributed to a disparity in porewater  $\text{S}^{2-}$  levels (F1: 1.5 mg/L; U3: 0.5 mg/L), and the expected inverse relationship between  $\text{S}^{2-}$  and MeHg production (Gilmour et al. 1998). Conversely, ENR305 had very high surface water  $\text{SO}_4^{2-}$  availability (approximately 35 mg/L) with modest average porewater  $\text{S}^{2-}$  (0.5 mg/L; nearly identical to U3, the site with the highest mosquitofish Hg levels), so conceptually should have been the most effective MeHg producer. Instead, ENR305 had the lowest MeHg of all four sites in nearly every sampled matrix (including THg in mosquitofish). In addition, it is remarkable that site 3A-15 maintains such high mosquitofish mercury levels despite a near complete absence of surface water  $\text{SO}_4^{2-}$ . This contrasts with the position advanced by Corrales et al. (2011) that  $\text{SO}_4^{2-}$  concentrations below 1 mg/L should curtail MeHg production and bioaccumulation. Evidently, some factor(s) other than the balance of  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  strongly affect the Hg accumulation by

mosquitofish among these sites. SFWMD and FDEP are examining this database further to evaluate potential factors that can explain the observed variability in fish Hg levels among sites.

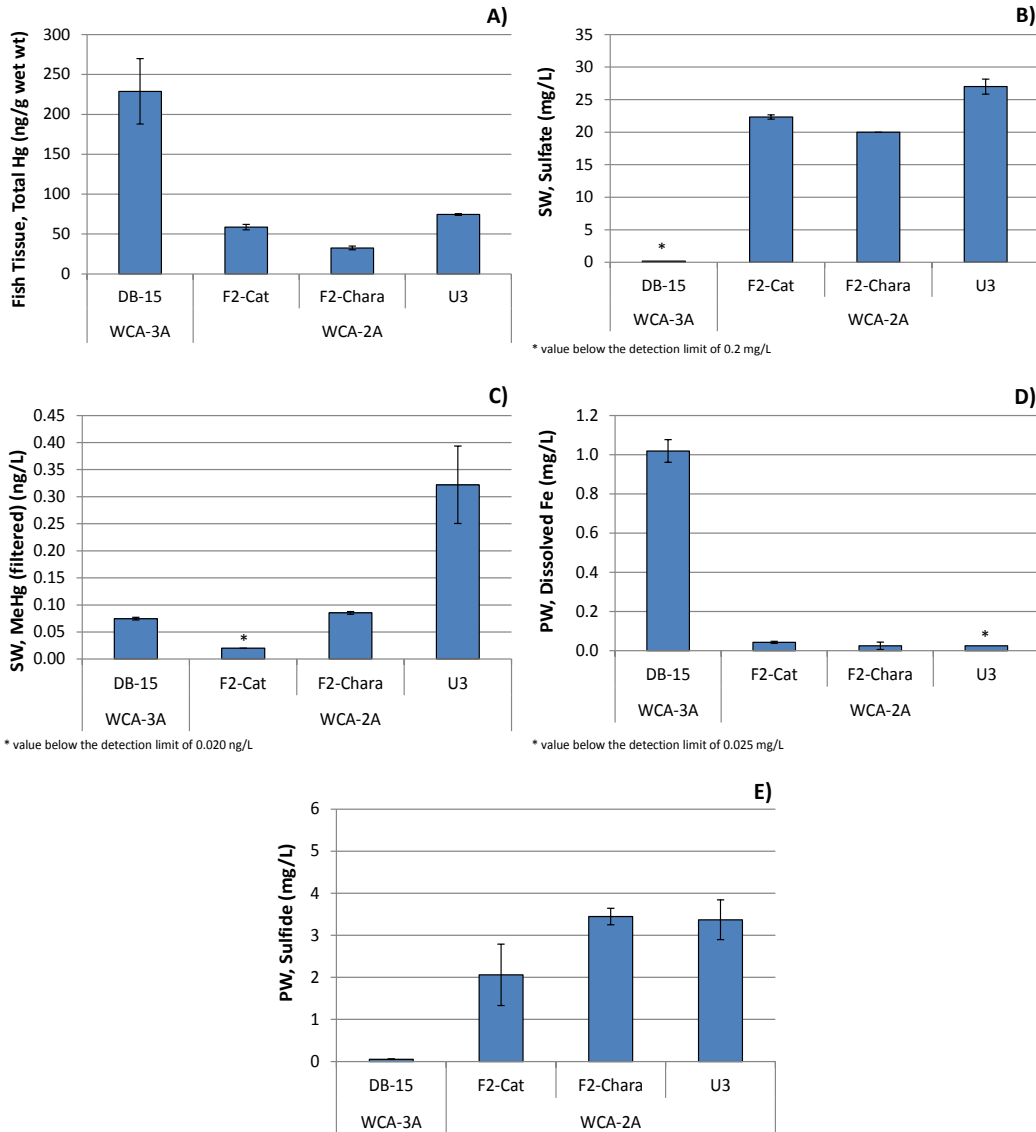


**Figure 3B-13.** THg concentrations (n = 1) in nanograms per grams (ng/g) wet weight in mosquitofish collected from August 2010 to March 2013 in the Everglades Mercury Hot Spot data set. The mean surface water (SW) SO<sub>4</sub><sup>2-</sup> and porewater (PW) S<sup>2-</sup> concentrations for the period at each station are shown to the right of the figure.

As part of an ongoing research program, in late 2013, DB Environmental, Inc. began monitoring mosquitofish tissue Hg concentrations (alongside a suite of other matrices and parameters) at several similar locations in WCA-2A and WCA-3A. A broad suite of surface water and porewater chemical parameters are being characterized at these sites to facilitate comparisons among MeHg levels in soils, water, and periphyton, as well as with total Hg levels in fish tissues. The research team also is sampling omnivorous fish (such as mosquitofish), herbivorous fish (such as flagfish (*Jordanella floridae*) and sailfin molly (*Poecilia latipinna*), and assorted invertebrates at selected locations to characterize potential spatial and temporal differences in food webs. In addition to Hg analyses of these organisms, stable carbon and nitrogen isotope analyses are being performed to help pinpoint the trophic status of the various organisms among the northern, central, and southern Everglades hydrologic units; the length and character of the food web is an important contributor to biological Hg accumulation (Loftus 2000) and is known to vary across space and time in the Everglades (Abbey-Lee et al. 2013).

Data from this monitoring program are still being collected and analyzed. However, initial data have not followed expectations based on a unimodal relationship between mosquitofish Hg and surface water SO<sub>4</sub><sup>2-</sup> (**Figure 3B-14**). For example, mosquitofish collected in January/February 2015 show modest tissue levels of Hg in mosquitofish at all sites, with the exception of site DB-15 (near 3A-15) in WCA-3A where the fish contained high levels of Hg in their tissues (**Figure 3B-15**). Surface waters at this site, however, have exhibited undetectable levels of SO<sub>4</sub><sup>2-</sup> (below 0.2 mg/L) since 2011, at which time a drydown event caused a slight increase in SO<sub>4</sub><sup>2-</sup> (to about 1.5 mg/L) in the marsh waters. The high tissue Hg levels for mosquitofish at site DB-15 suggest that extremely low, background SO<sub>4</sub><sup>2-</sup> levels per se are not adequate to ensure acceptably low Hg bioaccumulation in all Everglades marshes. Several hypotheses are under consideration, including various influences of the differing vegetation communities in intercepting, translocating, and assimilating Hg; other microbial consortia (such as iron-reducing bacteria) could be responsible for the net accumulation of MeHg (and resulting fish Hg contamination) at this site; or the character of the food web could make this site particularly effective at transferring MeHg from the environment into mosquitofish. Also of interest, dissolved iron levels in the soil porewaters are



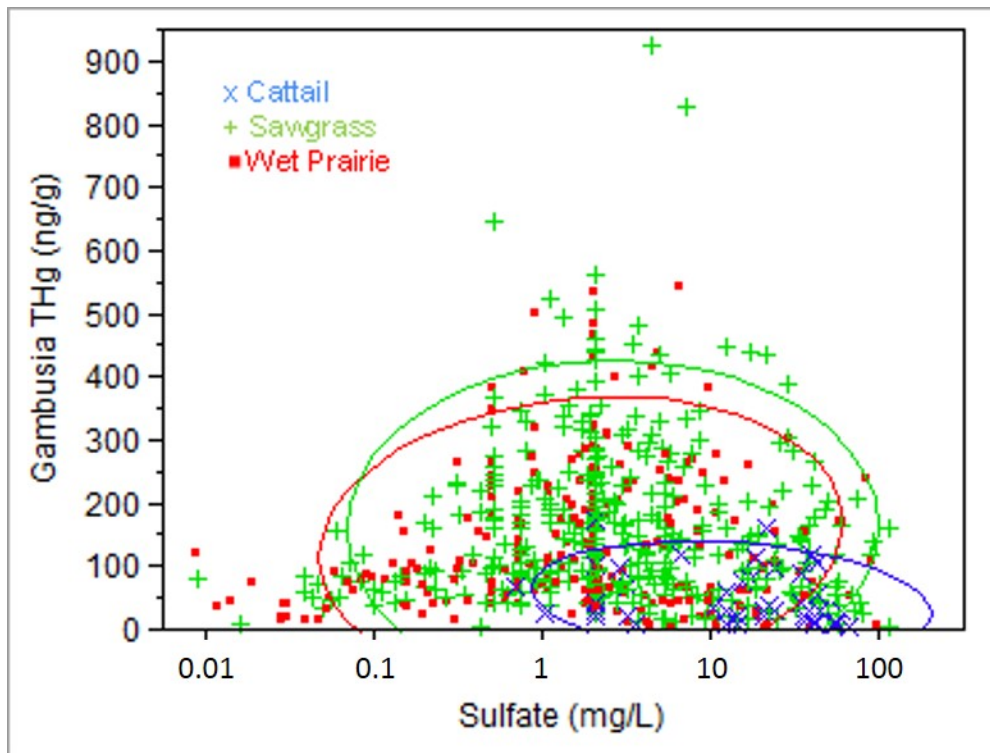


**Figure 3B-15.** (A) Mosquitofish THg, (B) surface water  $SO_4^{2-}$ , (C) filtered surface water MeHg, (D) porewater dissolved iron (Fe), and (E) porewater  $S^{2-}$  concentrations measured by DB Environmental at four sites in WCA-2A and WCA-3A during January and February 2015. [Note: DB-15 – oligotrophic open-water slough with submerged and sparse emergent macrophytes; F2-Cat – phosphorus-enriched monotypic cattail (*Typha*); F2-Chara – phosphorus-enriched open water dominated by the submerged plant *Chara*; and U3 – oligotrophic open-water slough with submerged and sparse emergent macrophytes.]

## Alternative Controls on Mosquitofish Mercury Bioaccumulation

As stated previously, marked differences in mosquitofish body THg were measured between sites of different vegetation communities that were poorly accounted for by differences in  $\text{SO}_4^{2-}$  or  $\text{S}^{2-}$  concentrations (**Figure 3B-14**). We hypothesized that the physical or ecological structure imposed by different vegetation types (P-enriched monotypic cattail (*Typha*) versus P-enriched open water with submerged macrophyte *Chara* versus typical oligotrophic open-water Everglades slough with submerged and sparse emergent macrophytes) was an important factor mediating the uptake of Hg by mosquitofish (and other biota). Differences in the redox conditions, atmospheric Hg interception and translocation, food webs, DOC concentrations and content, and predation can be influenced by the habitat structure associated with different vegetation communities.

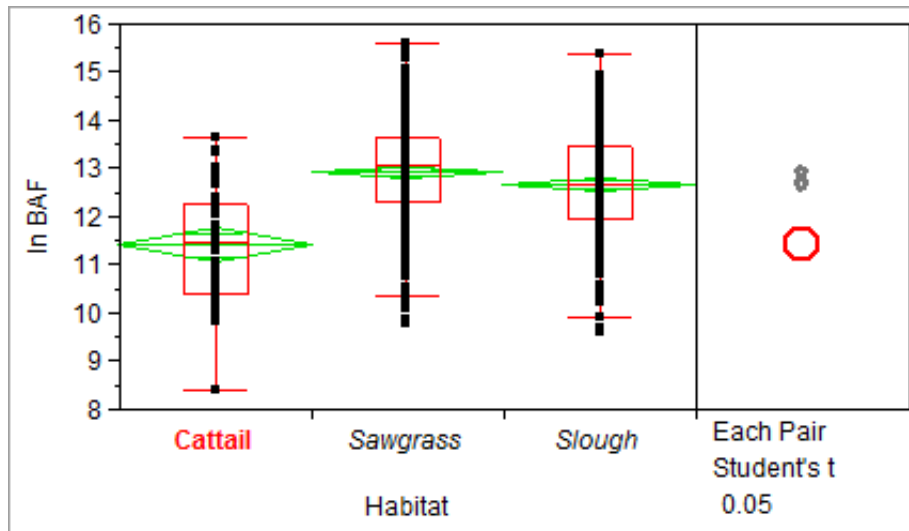
As an initial investigation into this hypothesis, a novel analysis of USEPA's Everglades REMAP data was undertaken. To begin, the REMAP data set was segregated by the vegetation community of each sampling location [i.e., cattail, sawgrass (ridge), or wet prairie (slough)], and then the mosquitofish THg concentrations with respect to the surface water  $\text{SO}_4^{2-}$  concentration were graphed (**Figure 3B-16**). Samples collected in sawgrass (ridge) and wet prairie (slough) spanned the observed range of  $\text{SO}_4^{2-}$  and fish THg concentrations. However, samples collected from cattail communities, while typically elevated in  $\text{SO}_4^{2-}$ , had uniformly low fish THg concentrations.



**Figure 3B-16.** Relationship between mosquitofish tissue THg and surface water  $\text{SO}_4^{2-}$  concentrations within the REMAP data set (1995–2005) for each of three vegetation community types. Data points enclosed by each ellipse is where 90 percent of the data is expected to lie, assuming a bivariate normal distribution.



To determine if the low fish Hg values found in cattail communities were the result of biogeochemically-mediated low MeHg production rates or ecologically-mediated low MeHg uptake or trophic transfer efficiency, bioaccumulation factor (BAF; ratio of mosquitofish tissue THg to surface water MeHg) was calculated for each REMAP sample point, and then they were grouped by vegetation community type. Calculated BAFs were markedly ( $p < 0.05$ ) lower at sites in cattail habitat, compared to those in sawgrass or slough regions (**Figure 3B-17**). It must be acknowledged that dense cattail occurs most commonly in upstream areas, rather than randomly distributed through the Everglades, and so is often coincident with elevated  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$ , which can affect the production of MeHg by SRB, as described above. On the other hand, there is no mechanism by which S chemistry should, conceptually, affect the efficiency of transfer of MeHg from the environment into fish (approximated by the BAF). From this, it appears very likely that the vegetation community is an ecological driver of Hg bioaccumulation, perhaps disrupting the expected unimodal relationship between fish Hg and surface water  $\text{SO}_4^{2-}$  (e.g., Gilmour and Henry 1991). The ongoing research program by DB Environmental, Inc. has been modified to include analysis of stable carbon and nitrogen isotopes and analysis of Hg concentrations in additional ecosystem components like detritus and invertebrates in an effort to identify the mechanism(s) of this phenomenon.



**Figure 3B-17.** Distributions of BAF for mosquitofish collected from each of three vegetation communities in the Everglades, calculated from the REMAP data set (1995–2005). The vertical axis is transformed to a natural log scale. The box-and-whiskers plot (in red horizontal lines on the left side of each panel) represents the median, upper and lower quartiles, and the range (maximum and minimum). Green diamond represents the 95 percent confidence interval with the horizontal line through the diamond indicating the arithmetic mean. Horizontal overlap lines within the diamond above and below the mean line provide a visual comparison of significance between two means. Overlapping circles on the right-hand side of each panel indicate that group means are not significantly different at the 95 percent confidence interval.

---

## MERCURY SOURCES TO THE EVERGLADES

---

### ATMOSPHERIC MERCURY DEPOSITION TRENDS

Paul Julian II<sup>1</sup>

The source of inorganic mercury ( $\text{Hg}^{2+}$ ) to the Everglades, as in most aquatic/semi-aquatic ecosystems, is through atmospheric deposition (Atkeson and Axelrad 2004, Hammerschmidt and Fitzgerald 2005, Liu et al. 2008). Due to amendments to the Clean Air Act (Public Law 1990), near-field (i.e., local) sources of Hg have been significantly reduced in the United States (FDEP 2013). However, far-field (i.e., global) sources are still relatively unregulated and are the primary sources of Hg to the Everglades (Driscoll et al. 2013).  $\text{Hg}^{2+}$  from these distant sources are transported via the atmosphere and delivered largely from wet deposition as the result of scavenging of aerosol 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.

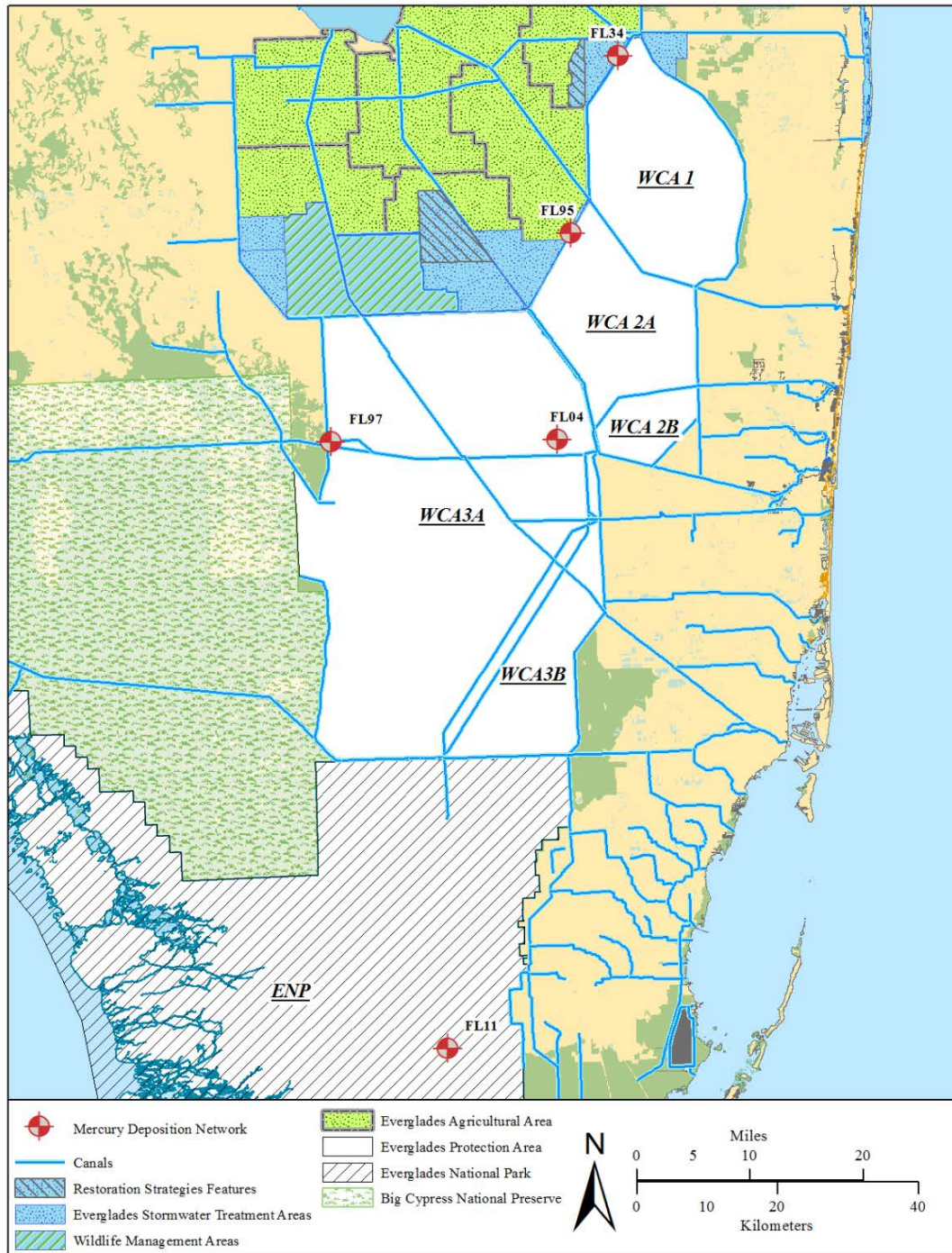
#### Methods

Hg wet deposition data was retrieved from the National Atmospheric Deposition Program (NADP) Mercury Deposition Network for the monitoring locations within the EPA (**Figure 3B-18**). 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 (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 USEPA.

There are only three active Mercury Deposition Network stations located within the EPA. Monitoring was discontinued at site FL04 during October 2006, at which time site FL97 began operation. Furthermore monitoring at site FL34 was discontinued at the end of WY2015, at which time FL95 began operations. To provide a regional assessment of Hg wet deposition, monitoring locations were assigned to different regions of the EPA. Monitoring station FL34 and FL95 were 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). It is acknowledged that data from three sites at any given time are difficult to justify as representative of the EPA, but what is lacking in spatial coverage is somewhat countered by long-term records and consistent quality assurance.

Monthly Hg atmospheric deposition data were summarized by water year for the POR (WY1996–WY2014). For purposes of this 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 precipitation-weighted 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 geographically 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  $\tau$  correlation

analysis. All statistical operations were performed with R© (Version 3.1.2, R Foundation for Statistical Computing, Vienna, Austria) and the critical level of significance was set at  $\alpha = 0.05$ .



**Figure 3B-18.** Locations of Mercury Deposition Network atmospheric monitoring locations within the EPA (WCA-1, WCA-2, WCA-3, and ENP).

## Results and Discussion

Annual Hg wet deposition has remained relatively constant (for water years with an entire data set) throughout the current POR for the northern, central, and southern EPA, as indicated by no apparent significant trends for the different regions of the EPA (**Table 3B-4**). During WY2014, wet deposition values ranging from 15.1 to 19.1 micrograms per square meter ( $\mu\text{g}/\text{m}^2$ ) for all regions (**Figure 3B-19**) with an overall mean value of  $16.7 \pm 1.2 \mu\text{g}/\text{m}^2$ . Wet deposition appears to follow a slight south-to-north gradient, with the southern region exhibiting the highest POR mean (WY1996–WY2014) Hg wet deposition ( $17.5 \pm 0.5 \mu\text{g}/\text{m}^2$ ), followed by the central ( $16.9 \pm 0.8 \mu\text{g}/\text{m}^2$ ), and northern ( $14.9 \pm 0.5 \mu\text{g}/\text{m}^2$ ) regions. As the primary source of atmospheric Hg is international, the deposition patterns could potentially be driven by local weather patterns.

**Table 3B-4.** Kendall's  $\tau$  trend analysis results for both Hg wet deposition and PWM concentrations for each region of the EPA for the entire POR (WY1996–WY2014).

Region	Wet Deposition			PWM Concentration		
	Statistic	Kendall's $\tau$	$\rho$ -value	Statistic	Kendall's $\tau$	$\rho$ -value
Northern	96	0.25	0.15	0.61	0.10	0.54
Central	84	0.10	0.60	1.02	0.18	0.31
Southern	78	-0.17	0.29	0.29	0.05	0.77

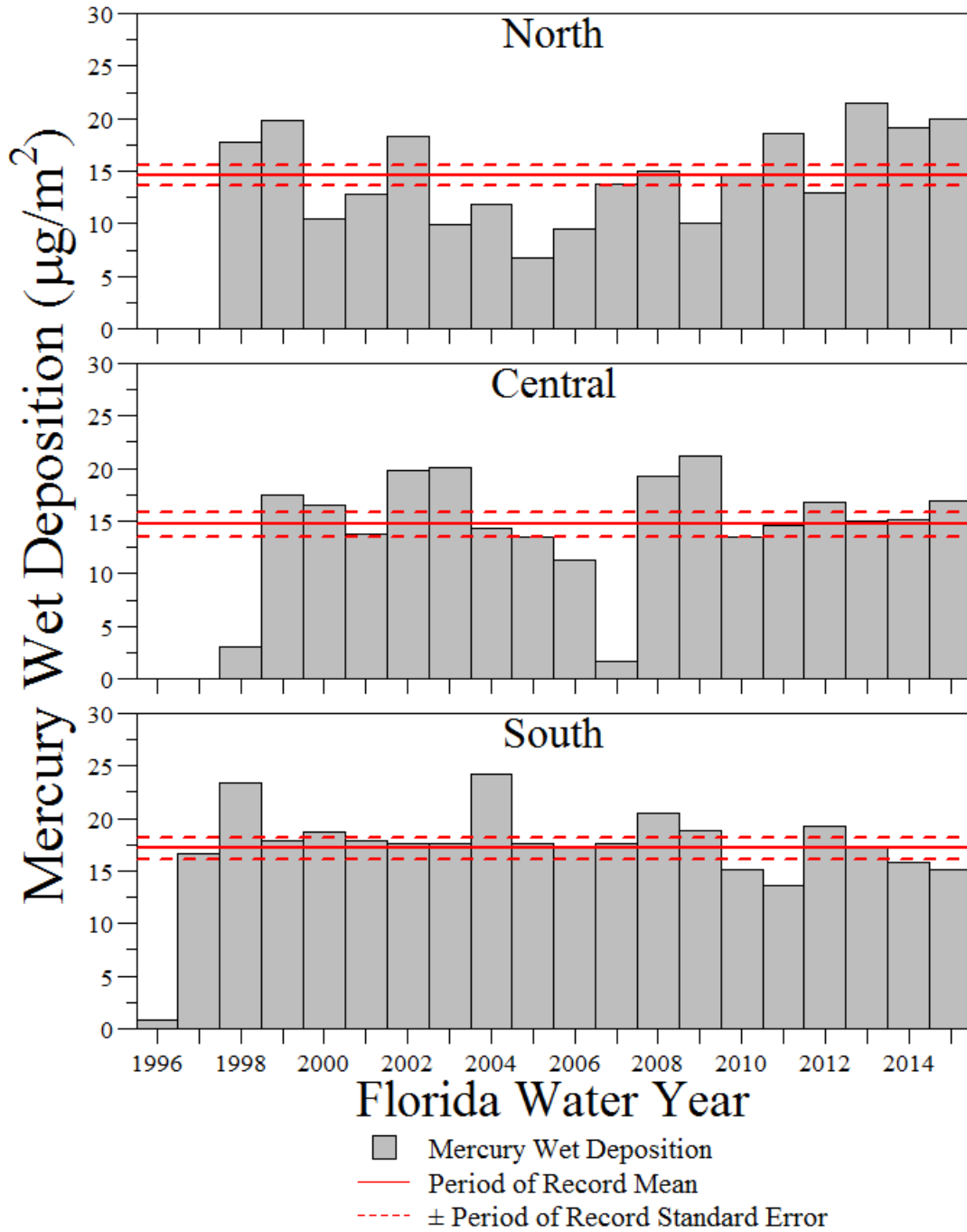
Similar to the wet deposition trend, Hg PWM concentrations remained relatively constant throughout the POR for the southern and central regions of the EPA, with the northern region experiencing slight fluctuations among years (**Table 3B-4**). During WY2014, PWM concentrations ranging from 11.2 to 14.2 nanograms per liter (ng/L) with an overall mean concentration of  $13.1 \pm 0.9 \text{ ng/L}$ .

During WY2014, atmospheric loading in the EPA was highest within ENP followed by WCA-3, WCA-1, and WCA-2 (**Table 3B-5**). Furthermore, data presented within **Table 3B-5** supports the claim that the primary source of Hg to the Everglades is through atmospheric deposition with percent atmospheric contribution range from 95 to 98 percent throughout the EPA. (Hammerschmidt and Fitzgerald (2006) suggested that accumulation of Hg in fish population is linked to atmospheric Hg loading. When taking these deposition values in context to fish tissue Hg concentrations (other sections of this report), there is a qualitatively weak relationship between fish tissue Hg and deposition. While more quantitative analysis is needed, limited data and small regional differences limit investment in more detailed data collection and analysis.

**Table 3B-5.** Atmospheric load of THg to each region of the EPA during WY2014 and mean ( $\pm$  standard error) surface water load estimated during WY2001–WY2008.

Region	Atmospheric Load (kilograms)	WY2001–WY2008 Surface Water Inflow Load <sup>a</sup> (kilograms)	Percent Atmospheric Contribution
LNWR	10.8	$0.27 \pm 0.03$	98
WCA-2	10.2	$0.51 \pm 0.06$	95
WCA-3	36.3	$1.89 \pm 0.18$	95
ENP	62.5	$1.12 \pm 0.21$	98

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



**Figure 3B-19.** Annual Hg deposition relative to the POR mean ( $\pm$  standard error) for the (A) northern (Stations FL34 and FL95), (B) central (Stations FL04 and FL97), and (C) southern (Station FL11) regions of the EPA during WY1996–WY2014.

Annually wet deposition rates and concentrations were relatively consistent, with southern and central regions experiencing very little change from year to year. While the northern region has experienced a slight increase in recent years after WY2006, 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 one or two 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–WY2014. **Figure 3B-19** includes data for WY2015, but it should be noted that this data set is currently incomplete. Therefore, values presented for WY2015 should be used with caution and are expected to be updated in the following SFER.

---

## SULFUR SOURCES AND EFFECTS

---

### SULFATE WITHIN THE EVERGLADES PROTECTION AREA

Paul Julian II<sup>1</sup>

The primary source of Hg to the Everglades is through global transport and atmospheric deposition, as previously noted. Once deposited, Hg can be converted to MeHg, primarily by reducing bacteria, particularly SRB which utilize  $\text{SO}_4^{2-}$  to metabolize organic matter under anaerobic conditions. During this process, some SRB have been observed to methylate THg (Gilmour et al. 2013, 1998, Gilmour and Henry 1991). The exact quantitative role that  $\text{SO}_4^{2-}$  plays in the S/Hg biogeochemical cycle in Everglades marshes is still not clear; biogeochemical cycling of Hg within the Everglades is confounded by many variables, particularly food web dynamics, water quality, and hydrological conditions (Julian 2013, Julian and Gu 2015). In spite of this complexity, research suggests that  $\text{SO}_4^{2-}$  can potentially influence the Hg/MeHg cycle under some suite of ambient conditions. From an environmental management perspective, the mercury-related end products of these complexities must be predictable and quantified before an effective control or management strategy can be considered. Furthermore, various  $\text{SO}_4^{2-}$  sources to the Everglades originate from both natural (i.e., oxidation of peat soil, groundwater, etc.) and anthropogenic sources (i.e., atmospheric deposition, fertilizer application, etc.). Within this context, this section provides an update to the status of  $\text{SO}_4^{2-}$  within the EPA, although its role in the Hg problem is not certain at this time.

#### Methods

A regional synoptic approach similar to that used for water quality evaluations in previous SFERs was applied to  $\text{SO}_4^{2-}$  data for WY2015 to provide an overview of  $\text{SO}_4^{2-}$  concentrations within the EPA. Consolidating regional water quality data provides the ability to analyze data over time across a limited spatial scale within each region.

#### *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 in Chapter 3A of this volume). These sites are part of the District's long-term monitoring network and are sampled 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 (i.e., 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. 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](http://www.sfwmd.gov/environmentalmonitoring). The majority of the water quality data evaluated in this chapter were retrieved from the District's DBHYDRO database ([www.sfwmd.gov/dbhydro](http://www.sfwmd.gov/dbhydro)). 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***

This section summarizes  $\text{SO}_4^{2-}$  concentrations within the EPA during WY2015 and describes 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, including WY1994–WY2004, (3) Phase II best management practices (BMP)/STA implementation period after WY2004 (WY2005–WY2014), and (4) the current water year (WY2015).

The baseline period corresponds to the timeframe prior to implementation of the 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 SFRs to incorporate additional years of sampling. In addition, data for the current water year (in this case, WY2015) will be used to make comparisons with the historical periods and will be analyzed independently as the fourth period. These periods of analysis are also used in Chapter 3A of this volume.

### ***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. 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.

## Data Analyses

Unless otherwise noted, all inflow and outflow summary statistics (geometric mean, minimum, maximum, etc.) were performed using data collected on flow events only. All valid data (i.e., non-qualified data) were used to compute summary statistics for all other regions (i.e., interior and rim). Surface water  $\text{SO}_4^{2-}$  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. However, due to low sample size at each station, arithmetic mean concentrations were also employed for some monitoring locations. Trend analysis was performed on annual arithmetic mean  $\text{SO}_4^{2-}$  concentration for inflow and interior regions of the EPA using the Kendall's  $\tau$  correlation analysis (Base stats R package) and Sen's slope estimate (zyp R package). All statistical operations were performed with R© (Version 3.1.2, R Foundation for Statistical Computing, Vienna, Austria) and the critical level of significance was set at  $\alpha = 0.05$ .

## Results and Discussion

### *Sulfate Concentrations*

S is an essential plant macro-nutrient (Bellinger and Van Mooy 2012) and enters the Everglades ecosystem primarily as  $\text{SO}_4^{2-}$  (Orem et al. 2011), but the role of organic S in the total mass of S entering the region remains undetermined. As stated above,  $\text{SO}_4^{2-}$  is of concern due to its ability under some circumstances to influence biogeochemical processes that lead to Hg methylation and support the production of reduced S compounds under anaerobic conditions.  $\text{SO}_4^{2-}$  monitoring results are presented in this section to provide an overview of current concentrations and evaluate temporal and spatial patterns. Sulfate summary statistics relative to the Baseline, Phase I, Phase II, and current year (WY2015) are shown in **Table 3B-6**.

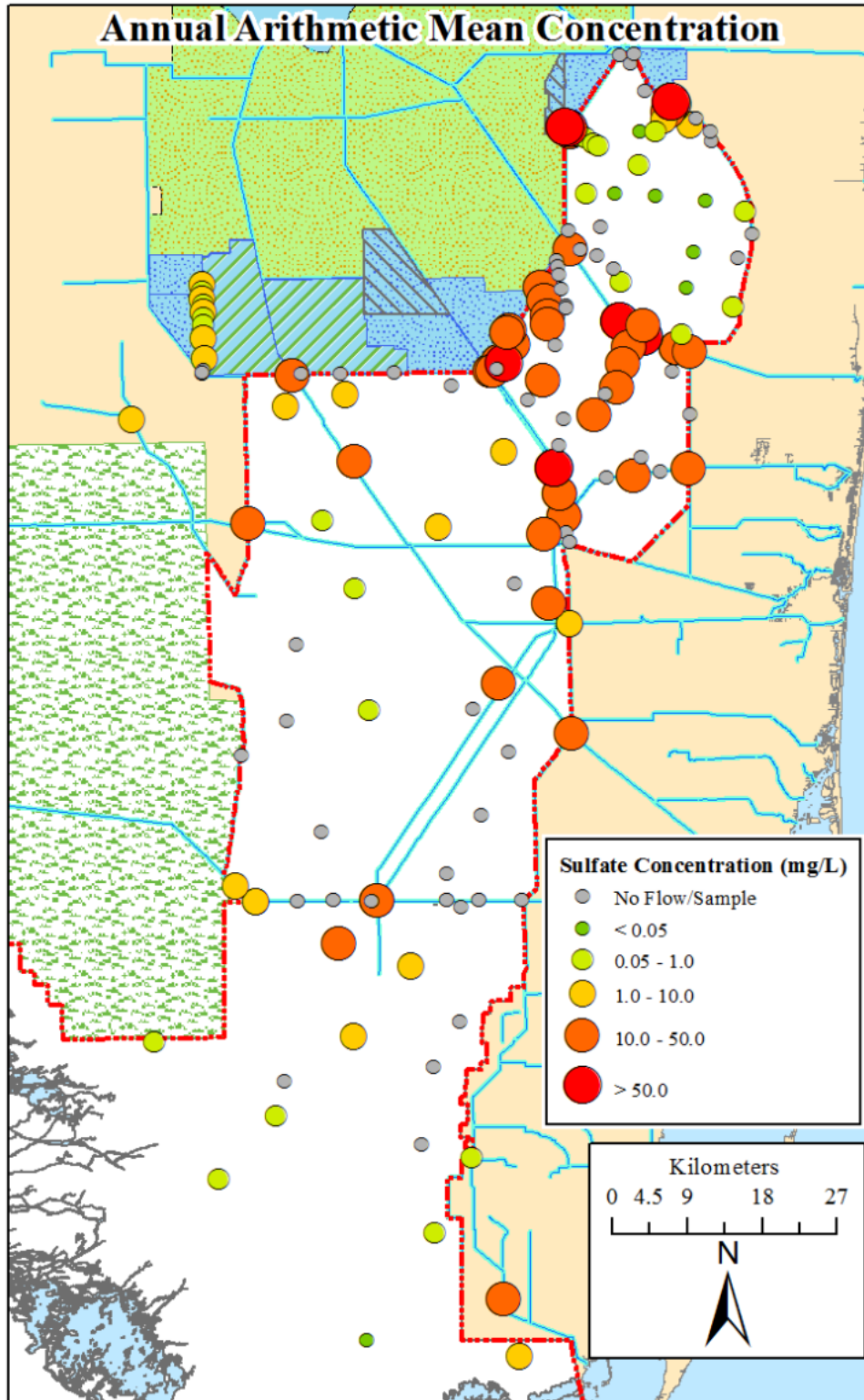
Similar to other water quality parameters within the EPA,  $\text{SO}_4^{2-}$  follows a general north-to-south concentration gradient (**Figure 3B-20**). This gradient is apparent for inflow regions within the EPA for WY2015, with the highest mean  $\text{SO}_4^{2-}$  concentrations observed in the LNWR peripheral canals (60.1 mg/L), followed by WCA-2 (45.6 mg/L), WCA-3 (11.4 mg/L), and ENP (8.8 mg/L) inflows. Inflows into WCA-2, WCA-3, and ENP experienced a slight decrease in annual mean (arithmetic and geometric) and median  $\text{SO}_4^{2-}$  concentrations relative to the Phase II period. Meanwhile, annual mean (arithmetic and geometric) and median inflow  $\text{SO}_4^{2-}$  concentrations into LNWR were elevated relative to the Phase II period.



**Table 3B-6.** Summary statistics of SO<sub>4</sub><sup>2-</sup> concentrations in mg/L for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), Phase II (WY2005–WY2014), and WY2015 periods.

Region	Class <sup>a</sup>	Period	Sample Size	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Standard Deviation	Median	Minimum	Maximum
LNWR	Inflow	1979–1993	64	101.6	80.1	84.0	6.2	82.3	28.8	455.8
		1994–2004	309	55.6	34.7	48.9	5.6	50.7	6.7	460.7
		2005–2014	312	50.4	21.2	45.6	5.4	48.3	10.0	115.0
		2015	71	60.1	17.7	57.4	5.4	57.5	21.3	100.0
	Interior	1979–1993	500	45.1	36.6	35.8	5.5	34.4	7.3	257.2
		1994–2004	1219	48.2	48.8	36.9	5.7	40.0	4.2	418.9
		2005–2014	638	28.6	20.6	20.6	5.5	23.9	1.4	85.4
		2015	336	38.7	16.7	35.1	5.1	39.7	14.6	77.3
	Outflow	1979–1993	65	42.2	37.1	25.2	6.5	34.4	2.5	139.8
		1994–2004	78	57.2	26.9	51.0	5.6	49.6	1.6	210.0
		2005–2014	102	50.8	25.5	43.9	5.6	45.8	3.5	185.0
		2015	31	50.6	14.5	48.7	5.2	47.9	28.0	91.0
	Rim	1979–1993	96	16.6	21.5	10.3	4.9	10.0	2.5	220.2
		1994–2004	341	5.0	11.5	1.0	5.8	1.0	<0.05	110.0
		2005–2014	20	5.0	11.7	0.6	8.3	0.6	<0.05	95.1
		2015	48	4.3	10.1	0.4	8.6	0.2	<0.05	77.1
WCA-2	Inflow	1979–1993	71	75.8	114.9	53.6	6.1	53.8	7.3	945.3
		1994–2004	127	55.3	38.9	48.2	5.6	52.3	7.8	418.9
		2005–2014	300	49.6	17.9	44.3	5.7	49.2	<0.05	106.0
		2015	90	45.6	14.1	43.5	5.1	44.1	25.0	77.8
	Interior	1979–1993	1484	41.2	21.0	36.4	5.3	38.7	7.6	131.7
		1994–2004	1640	28.6	10.9	26.2	4.8	27.9	5.8	54.3
		2005–2014	593	28.5	16.6	23.0	5.2	27.3	3.9	74.7
		2015	196	30.0	11.9	27.9	4.8	25.0	14.4	61.4
	Outflow	1979–1993	106	42.2	35.9	32.7	5.6	36.9	2.5	344.3
		1994–2004	95	43.1	23.5	35.1	5.7	40.9	0.1	180.0
		2005–2014	233	42.3	19.1	36.3	5.5	44.4	1.8	128.0
		2015	62	42.2	16.7	38.8	5.2	40.8	10.3	89.3
WCA-3	Inflow	1979–1993	258	36.7	35.2	24.2	5.9	29.8	1.0	286.0
		1994–2004	192	21.1	16.5	13.7	5.5	17.2	0.5	62.9
		2005–2014	380	23.3	19.7	11.7	7.1	20.5	<0.05	74.7
		2015	100	11.4	16.3	2.2	10.7	2.4	<0.05	61.4
	Interior	1979–1993	611	16.3	16.7	10.7	5.0	12.9	1.0	107.6
		1994–2004	1645	7.4	8.0	2.7	7.2	4.7	<0.05	36.5
		2005–2014	325	8.8	10.3	1.6	12.3	3.9	<0.05	39.3
		2015	82	12.1	10.8	8.7	4.6	5.9	4.0	28.0
	Outflow	1979–1993	146	14.9	17.3	10.5	4.6	10.7	2.0	261.5
		1994–2004	141	10.8	34.8	3.8	6.6	4.5	<0.05	1300.0
		2005–2014	98	13.1	15.9	3.2	10.3	4.9	<0.05	126.0
		2015	5	14.5	15.7	3.7	10.4	6.9	<0.05	58.6
ENP	Inflow	1979–1993	142	15.4	16.3	10.1	4.9	11.5	1.0	107.6
		1994–2004	134	7.4	7.2	3.7	5.9	6.0	<0.05	36.5
		2005–2014	110	7.4	8.0	2.7	7.5	4.6	<0.05	35.8
		2015	9	8.8	9.8	4.2	5.6	4.2	0.6	28.0
	Interior	1979–1993	572	9.0	19.5	4.3	4.4	4.3	0.8	205.5
		1994–2004	1044	5.5	17.7	2.1	4.9	2.6	<0.05	403.0
		2005–2014	269	5.7	21.6	1.1	6.6	1.3	<0.05	242.0
		2015	77	4.4	17.7	0.7	6.3	0.7	<0.05	134.0

a. Inflow and outflow values only utilize data when structures are flowing.



**Figure 3B-20.** Annual arithmetic mean  $\text{SO}_4^{2-}$  concentrations for all classifications at stations across the EPA in WY2015.

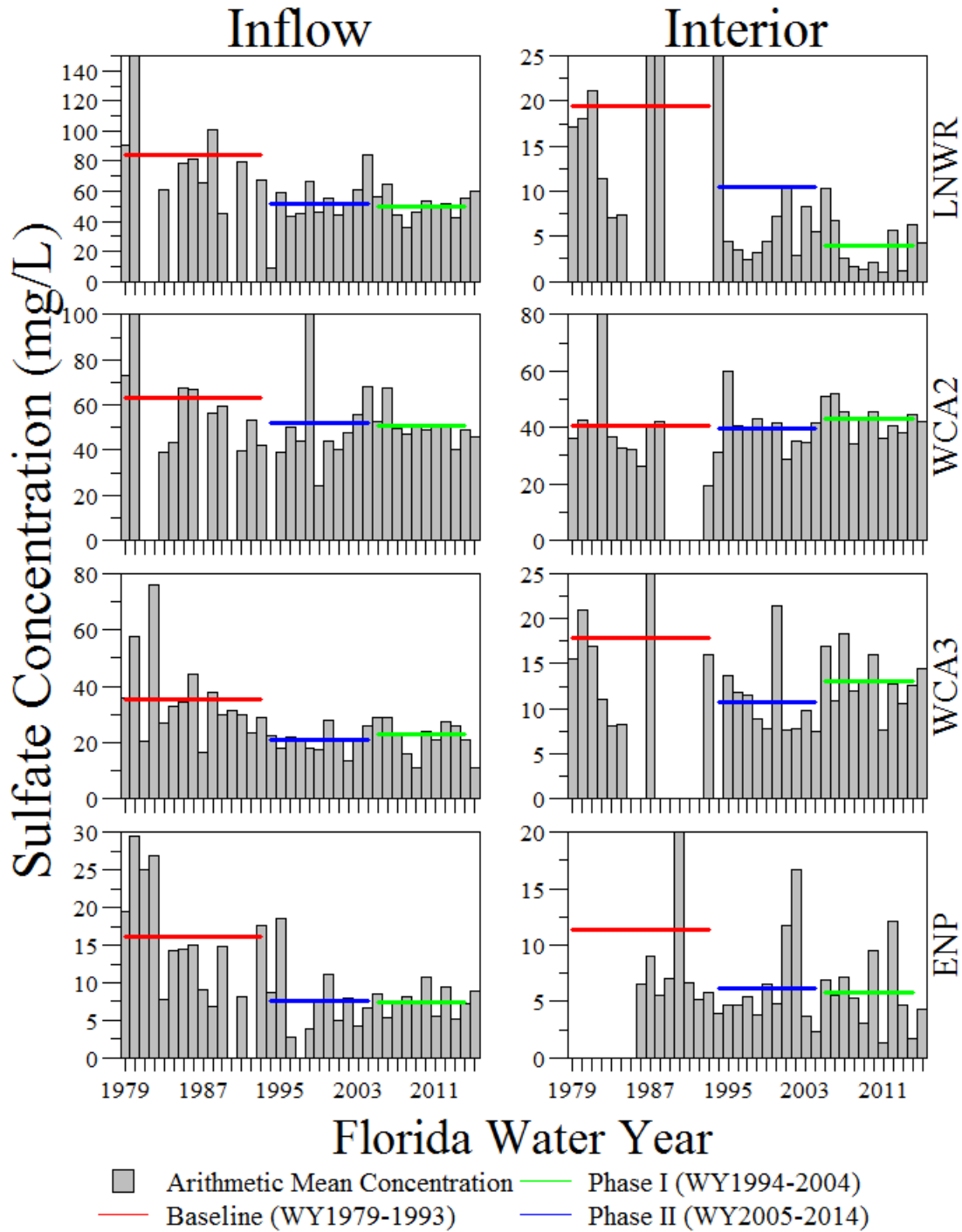
Although LNWR experienced a slight increase of  $\text{SO}_4^{2-}$  concentrations in recent years, the entire POR (WY1979–WY2015) reflects a statistically significant decrease in mean concentrations were observed for LNWR inflow and interior regions. WCA-3 and ENP inflow regions also experienced a significant decreasing trend in mean  $\text{SO}_4^{2-}$  concentrations. No significant trend was observed for both WCA-2 and WCA-3 inflow region mean concentrations (**Table 3B-7**). Due to the abundance of relative low concentration stations, data distribution, and higher values being spread out over a wide range, most valid data within the POR is extremely right-skewed with concentrations ranging from at or below the MDL (0.05 mg/L or 0.10 mg/L, depending on the time period) to 403.0 mg/L within ENP and 1,300 mg/L within WCA-3.

**Table 3B-7.** Kendall's  $\tau$  annual arithmetic mean  $\text{SO}_4^{2-}$  concentration trend analysis results for each region's inflow and interior classification within the EPA for the entire POR (WY1979–WY2015). Statistically significant  $p$ -values are italicized.

		POR (WY1979–WY2015)		
Area	Class	Kendall's $\rho$	$p$ -value	Sen's Slope Estimate <sup>a</sup>
LNWR	Inflow	-0.33	<i>&lt;0.01</i>	-0.92
	Interior	-0.46	<i>&lt;0.01</i>	-0.22
WCA-2	Inflow	-0.12	0.34	-0.25
	Interior	0.16	0.21	0.12
WCA-3	Inflow	-0.39	<i>&lt;0.01</i>	-0.41
	Interior	-0.10	0.47	-0.21
ENP	Inflow	-0.37	<i>&lt;0.01</i>	-0.29
	Interior	-0.22	0.09	-0.14

a. Expressed as mg/L per water year.

Some trends are more pronounced than others, as shown in **Figure 3B-21**, with LNWR 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 Axelrad et al., (2013), connate seawater could potentially be a relatively large source of  $\text{SO}_4^{2-}$ , chloride, and dissolved solids (i.e., other minerals) to the EPA, more specifically to the LNWR. Another driving factor of interior trends are the biogeochemical processes associated with marsh dryout. During relatively dry periods, when water levels in the marsh recede below the soil surface, oxidation of organic matter occurs readily. Once the area is reflooded, a large upward flux of nutrients occurs including  $\text{SO}_4^{2-}$  from the soil to the water column. This dryout/flux phenomena explains the relatively high annual concentrations experienced during the extremely dry period in the mid-1980s and the relatively dry period during the early to mid-2000s.



**Figure 3B-21.** Annual arithmetic mean  $SO_4^{2-}$  concentrations for inflow (left panel) and interior (right panel) areas of the LNWR, WCA-2, WCA-3, and ENP during WY1978–WY2014. Bars indicate arithmetic mean when flowing for inflow locations. 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–WY2014) periods. [Note: Area with no bars indicates data gaps.]

Much like other nutrients in the EPA (see Chapter 3A of this volume), the typical north-to-south gradient is somewhat muted at interior monitoring stations of the EPA. During WY2015, WCA-2 had the highest annual mean  $\text{SO}_4^{2-}$  concentration of 42.2 mg/L, followed by WCA-3 (14.5 mg/L), ENP (4.4 mg/L), and LNWR (4.3 mg/L). Furthermore, the only region with a significant decreasing annual arithmetic mean  $\text{SO}_4^{2-}$  concentration was LNWR, with all other areas experiencing non-significant trends (**Table 3B-7**).  $\text{SO}_4^{2-}$  concentrations within LNWR significantly decreased during the Phase II period (**Figure 3B-21**), which could possibly be due to the construction and operation of STA-1 West and STA-1 East in combination with the rainfall-driven hydrology. However, it has been suggested that the Everglades STAs only reduce surface water  $\text{SO}_4^{2-}$  concentrations and loads by a small portion, approximately 10 percent of the  $\text{SO}_4^{2-}$  from the water column (SFWMD, unpublished data). Other factors influencing this trend of decreasing  $\text{SO}_4^{2-}$  concentrations with time could be changes in water management, establishing and managing BMPs within the EAA, and potential decreasing application of elemental S to as a soil amendment to agricultural fields. It should be noted that the BMPs implemented were not used to directly mitigate  $\text{SO}_4^{2-}$ ; however, these BMPs could have provided ancillary benefits. It is also important to note that  $\text{SO}_4^{2-}$  concentrations within LNWR spiked after extended periods of dry conditions as observed between WY1985 and WY1994. This was not just isolated to water column  $\text{SO}_4^{2-}$ , but phosphorus and nitrogen also spiked during these periods. The very low  $\text{SO}_4^{2-}$  concentrations observed for the interior portion of LNWR indicate that either assimilation of  $\text{SO}_4^{2-}$  is occurring and potentially could be in growth-limiting concentrations due to its low availability (Bellinger and Van Mooy 2012), or very little to no high  $\text{SO}_4^{2-}$  water reached the interior portion (due to topography and hydrology) of LNWR and these low concentrations reflect deposition-driven water column concentrations.

Annual mean  $\text{SO}_4^{2-}$  concentrations within WCA-2 are approximately twice that of other regions with the EPA. This is due to historical EAA runoff containing both local and regional inputs of  $\text{SO}_4^{2-}$ . The hydrology of WCA-2A spreads the canal inflow broadly, and WCA-2 soils have relatively high concentrations of S. In fact, samples collected between 2003 and 2004 at limited locations within each region indicate that WCA-2A soils had the greatest concentration of S ( $14,025 \pm 1,173$  mg/kg; mean  $\pm$  standard error), followed by WCA-3A ( $9,100 \pm 576$  mg/kg) and LNWR ( $8,825 \pm 1,019$  mg/kg; data source: District's DBHYDRO database). This restricted sampling effort did not take into account soil types or bulk density and was limited to two sampling locations per area. This general trend is also apparent in a more spatially explicit data set (Everglades Soil Mapping Data, Reddy et al. (2005)). This larger effort showed high concentrations of soil S in WCA-2 and around the periphery of WCA-1. This high concentration of S 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 eutrophic/impacted portions of the WCA-2, it is reasonable to suggest that growth of macrophytic biota within this region of the EPA is not S/  $\text{SO}_4^{2-}$ -limited, corresponding to results presented by (Bellinger and Van Mooy 2012).

### ***Feasibility of a Sulfate Criterion***

Previous peer reviews of this SFER chapter (2013 and 2014 SFER Volume 1, Appendix 1-2) as well as peer reviewed literature (Corrales et al. 2011, Gabriel et al. 2014, Orem et al. 2011) have suggested the need to develop a site-specific water quality standard for  $\text{SO}_4^{2-}$  in the EPA. As explained above, the S/Hg biogeochemical cycle has proven to be altered by many environmental factors in the EPA. As a result, empirical evaluation of Hg and  $\text{SO}_4^{2-}$  data provides little predictive power to link water column concentrations or loads to environmental Hg levels. These factors together make development of a site-specific criterion impossible to defend at this time. It is uncertain based on the best available data that reduction of S inputs can reduce Hg methylation at all or even shift methylation hot spots on the landscape or regional scale. Appendix 3B-1 of this volume summarizes recent data from a District-FDEP hotspot investigation.

In an effort to provide more information on the role of  $\text{SO}_4^{2-}$  in Hg cycling, the FDEP is funding research to investigate Hg methylation potential at low  $\text{SO}_4^{2-}$  concentrations in surface water. The results will provide evidence on the importance of background  $\text{SO}_4^{2-}$  levels on methylation and will also help to assess if reduction of S/ $\text{SO}_4^{2-}$  will cause a positive or negative ecological response. So far this study has yielded interesting results that shows that relatively low  $\text{SO}_4^{2-}$  additions (i.e., 0.5 to 1.0 mg/L) significantly increases water column MeHg concentrations indicating that non-abatable sources of  $\text{SO}_4^{2-}$  could support meaningful MeHg production in the presence of bioavailable inorganic Hg (Dierberg et al. 2014, Jerauld et al. 2015).

The commonly referenced 1 mg/L  $\text{SO}_4^{2-}$  CERP performance measure for the Greater Everglades was developed to indicate background marsh concentrations that would be consistent with S limitation of Hg bioaccumulation. However, this performance measure was proposed without detailed technical support. While concerns have been raised that concentrations above this level could stimulate significant Hg methylation, the 1 mg/L  $\text{SO}_4^{2-}$  goal is not consistently associated with any particular level of Hg in the Everglades (Julian et al. 2015a, 2015b, 2014). In addition, this goal lacks empirical evidence on whether 1 mg/L is protective of flora and fauna or if higher concentrations are consistently associated with degraded water quality or ecological integrity. Furthermore, to date, no studies have justified either a numeric  $\text{SO}_4^{2-}$  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.

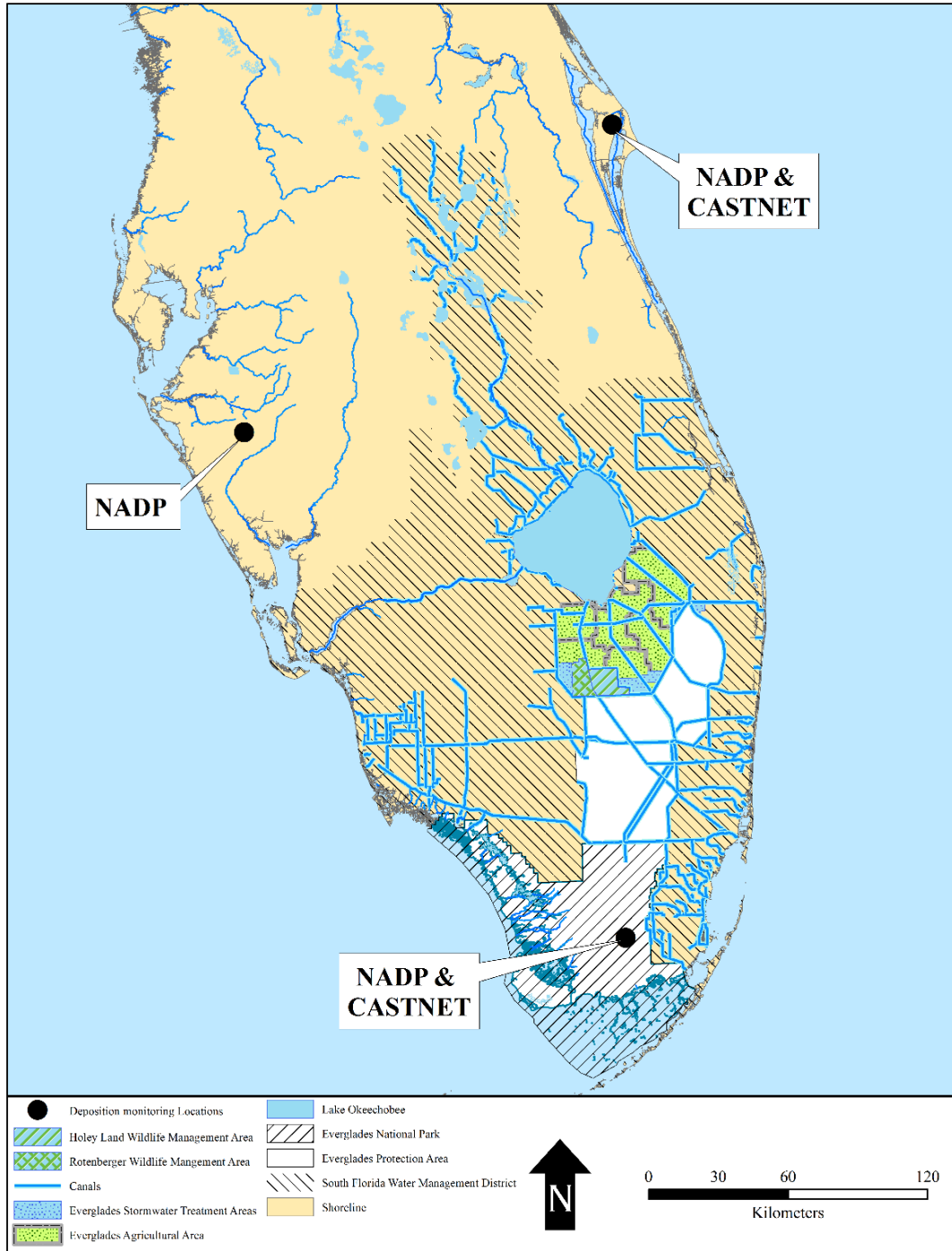
## TRENDS IN ATMOSPHERIC DEPOSITION OF SULFATE

Paul Julian II<sup>1</sup>

Acid precipitation and the associated deposition of acid anions have been widely recognized as an 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 to provide data to 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 United States Congress to amend the Clean Air Act in 1990 (Public Law 1990). This amendment 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  $\text{SO}_4^{2-}$  deposition has resulted in its accumulation in soils and increased loading to surface waters (Alewell et al. 2000). This accumulation within ecosystems such as the Everglades is significant especially as  $\text{SO}_4^{2-}$  has the potential to interact with several biogeochemical cycles including the phosphorus, iron, and Hg cycles (Gilmour et al. 1992, Reddy and DeLaune 2008). To date, very few studies have focused on the quantity and timing of atmospheric  $\text{SO}_4^{2-}$  deposition. Studies that have investigated wet  $\text{SO}_4^{2-}$  deposition have reported rainwater  $\text{SO}_4^{2-}$  concentrations ranging from 0.5 to 2.5 mg/L (Orem et al. 2011). Orem et al. (2011) concludes that rain water may be an important source of  $\text{SO}_4^{2-}$  to unenriched areas, but cannot account for its high loads and concentrations in canals or  $\text{SO}_4^{2-}$ -enriched marshes.

This section reports on the estimated  $\text{SO}_4^{2-}$  deposition flux and associated atmospheric load to the EPA by using data collected from the several atmospheric deposition monitoring locations (**Figure 3B-22**).



**Figure 3B-22.** NADP and Clean Air Status and Trend Network stations used in this analysis.

## Methods

Atmospheric deposition data was retrieved from the NADP National Trend Network and USEPA Clean Air Status and Trends Network for several monitoring locations identified in **Figure 3B-22**. Due to the limited number of stations located within the Everglades region, two other stations outside of the region were used in conjunction with the Everglades station. 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 National Trend Network 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 USEPA. Similar to the NADP National Trend Network, the Clean Air Status and Trend Network is a national air quality monitoring network designed to provide dry deposition data to assess trends in air quality, atmospheric deposition, and ecological effects due to changes in air pollutant emissions.

Annual mean  $SO_4^{2-}$  fluxes were calculated using data collected from the deposition monitoring locations identified in **Figure 3B-22**. These three sites were identified due to their distribution across the region and study location. As data are being used from two different atmospheric deposition networks, the PORs for each fraction and monitoring location vary slightly (i.e., wet deposition data from WY1995– to present; dry deposition data from WY1999–present). In an effort to conduct trend analysis, the POR (WY1999–WY2014) mean dry deposition was calculated to fill in data gaps in the earlier portion of the entire data set; only water years with a complete year of data were used to calculate this average dry  $SO_4^{2-}$  flux of  $85.0 \pm 4.7$  mg/m<sup>2</sup>. Water years with less than 12 months of data were not included in the trend analysis. Trend analysis was performed on wet, dry, and total (wet + dry)  $SO_4^{2-}$  deposition and  $SO_4^{2-}$  PWM concentrations using the Kendall correlation analysis (Base R package). All statistical operations were performed with R© (Version 3.1.2, R Foundation for Statistical Computing, Vienna, Austria), and the critical level of significance was set at  $\alpha = 0.05$ .

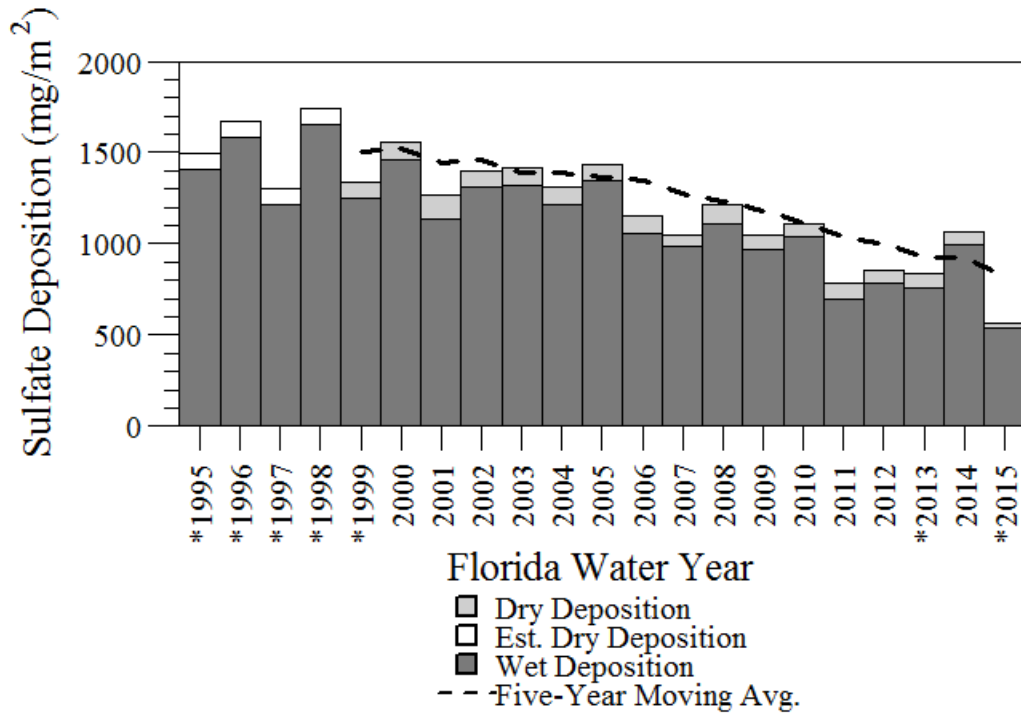
## Results and Discussion

Annual  $SO_4^{2-}$  wet deposition has significantly declined throughout the POR ( $\tau = -0.64$ ,  $\rho < 0.01$ ) at a rate of 37.0 milligrams per square milligrams per year (mg/mg<sup>2</sup>/yr). Water years with complete data range from 695.7 to 1657.1 mg/m<sup>2</sup>/yr (**Figure 3B-23**). Annual  $SO_4^{2-}$  dry deposition has significantly declined throughout the POR ( $\tau = -0.67$ ,  $\rho < 0.05$ ) at a rate of 3.2 mg/m<sup>2</sup>/yr. As a result of the observed declines in wet and dry  $SO_4^{2-}$  deposition, total deposition significantly declined throughout the entire POR ( $\tau = -0.70$ ,  $\rho < 0.01$ ) at a rate of 47.2 mg/m<sup>2</sup>/yr. Since wet deposition is the majority of the  $SO_4^{2-}$  deposited (**Table 3B-8**), the overall total deposition trend and associated magnitude of change is dominated by the trend of wet deposition. However, it is important to note that the magnitude of change between dry and wet  $SO_4^{2-}$  deposition rates trends is of an order of magnitude different and that any reductions in  $SO_4^{2-}$  deposition rates is beneficial. A decline in total  $SO_4^{2-}$  deposition in recent years can likely be attributed to tighter emission controls after a lag period of approximately 10 years.

Similar to the wet deposition trend, PWM  $SO_4^{2-}$  concentrations significantly declined throughout the POR ( $\tau = -0.59$ ,  $\rho = <0.01$ ) at a rate of 0.02 mg/L per year, with concentrations ranging between 0.61 and 1.07 mg/L. The range of annual PWM  $SO_4^{2-}$  concentrations in this assessment is consistent with values summarized by Orem et al. (2011). Unfortunately, due to the data release schedules, the current assessment only spans WY1995–WY2014. Meanwhile **Figure 3B-23** includes data for WY2015 but these data are incomplete. Therefore, values presented for WY2015 should be used with caution and are expected to be updated in the next SFER. The dry deposition data summarized for the Everglades region corresponds to data from other areas of North



America, indicating that dry deposition is unlikely to be a major contributor to the total  $\text{SO}_4^{2-}$  flux (Mitchell et al. 2013, 2011).



**Figure 3B-23.** Annual  $\text{SO}_4^{2-}$  deposition in milligrams per square meter ( $\text{mg}/\text{m}^2$ ) and five-year moving average between WY1995 and WY2014. Stations with less than 12 months of data are identified with an asterisk (\*).

**Table 3B-8.** Atmospheric  $\text{SO}_4^{2-}$  load from wet and dry deposition to each region of the EPA for WY2014.

Area	Atmospheric Deposition Load		
	Dry (metric tons)	Wet (metric tons)	Total (metric tons)
WCA-1	35.6	565.2	600.8
WCA-2	33.7	535.6	569.3
WCA-3	150.5	2389.9	2540.5
ENP	248.9	3951.6	4200.5

During WY2014, atmospheric loading to the EPA was dominated by wet deposition of  $\text{SO}_4^{2-}$  ranging from 535.6 to 3951.6 metric tons of  $\text{SO}_4^{2-}$ . Furthermore  $\text{SO}_4^{2-}$  dry deposition amounts during WY2014 ranged from 33.7 to 248.9 metric tons (**Table 3B-8**). Although an overall decreasing trend in  $\text{SO}_4^{2-}$  deposition has occurred through the POR (**Figure 3B-23**), between WY2013 (6,208.3 metric tons) and WY2014 (7,911.1 metric tons) a 24 percent increase in total deposition load occurred.

---

## LITERATURE CITED

---

- Abbey-Lee, R.N., E.E. Gaiser and J.C. Trexler. 2013. Relative roles of dispersal dynamics and competition in determining the isotopic niche breadth of a wetland fish. *Freshwater Biology*, 58, 780–792.
- Alewell, C., M.J. Mitchell, G.E. Likens and R. Krouse. 2000. Assessing the origin of sulfate deposition at the Hubbard Brook Experimental Forest. *Journal of Environmental Quality*, 29, 759–767.
- Atkeson, T. and D.M. Axelrad. 2004. Chapter 2B: Mercury Monitoring, Research and Environmental Assessment. In: *2004 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- Axelrad, D.M., T.D. Atkeson, C.D. Pollman, T. Lange, D.G. Rumbold and K. Weaver. 2005. Chapter 2B: Mercury Monitoring, Research and Environmental Assessment in South Florida. In: *2005 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Axelrad, D.M., T. Lange, M. Gabriel, T.D. Atkeson, C.D. Pollman, W.H. Orem, D.J. Scheidt, P.I. Kalla, P.C. Federick and C.C. Gilmour. 2008. Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida. In: *2008 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Axelrad, D.M., C.D. Pollman, B. Gu and T. Lange. 2013. Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades. In: *2013 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Bancroft, G.T., W. Hoffman, R.J. Sawicki and J.C. Ogden. 1992. The Importance of the Water Conservation Areas in the Everglades to the Endangered Wood Stork (*Mycteria americana*). *Conservation Biology*, 6, 392–398.
- Bellinger, B.J. and B.A.S. Van Mooy. 2012. Nonphosphorus lipids in periphyton reflect available nutrients in the Florida Everglades, USA. *Journal of Phycology*, 48, 303–311.
- Benoit, J.M., C.C. Gilmour, A. Heyes, R.P. Mason and C.L. Miller. 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In: *ACS Symposium Series*. Washington, DC; American Chemical Society; 1999, pp. 262–297.
- Benoit, J.M., C.C. Gilmour, R.P. Mason and A. Heyes. 1999a. Sulfide Controls on Mercury Speciation and Bioavailability to Methylating Bacteria in Sediment Pore Waters. *Environmental Science & Technology*, 33, 951–957.
- Benoit, J.M., R.P. Mason and C.C. Gilmour. 1999b. Estimation of mercury-sulfide speciation in sediment pore waters using octanol–water partitioning and implications for availability to methylating bacteria. *Environmental Toxicology and Chemistry*, 18, 2138–2141.
- Bloom, N.S. 1992. On the Chemical Form of Mercury in Edible Fish and Marine Invertebrate Tissue. *Canadian Journal of Fisheries and Aquatic Sciences*, 49, 1010–1017.
- Corrales, J., G.M. Naja, C. Dziuba, R.G. Rivero and W. Orem. 2011. Sulfate threshold target to control methylmercury levels in wetland ecosystems. *Science of The Total Environment*, 409, 2156–2162.

- DeAngelis, D.L., L.J. Gross, M.A. Huston, W.F. Wolff, D.M. Fleming, E.J. Comiskey and S.M. Sylvester. 1998. Landscape Modeling for Everglades Ecosystem Restoration. *Ecosystems*, 1, 64–75.
- Dierberg, F.E., T.A. DeBusk, M. Jerauld and B. Gu. 2014. Appendix 3B-1: Evaluation of Factors Influencing Methylmercury Accumulation in South Florida Marshes. In: *2014 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Dochinger, L.S. and T.A. Seliga. 1976. Proceedings of the First International Symposium on Acid Precipitation and Forest Ecosystem. (General Technical Report No. NE-23). United States Department of Agriculture Forest Service, Radnor, PA.
- Driscoll, C.T., R.P. Mason, H.M. Chan, D.J. Jacob and N. Pirrone. 2013. Mercury as a Global Pollutant: Sources, Pathways, and Effects. *Environmental Science & Technology*, 47, 4967–4983.
- FDEP. 2013. Mercury TMDL for the State of Florida (Revised Draft) (Final Report). Florida Department of Environmental Protection, Tallahassee, FL.
- Frederick, P.C., B. Hylton, J.A. Heath and M.G. Spalding. 2004. A historical record of mercury contamination in southern florida (USA) as inferred from avian feather tissue. *Environmental Toxicology and Chemistry*, 23, 1474–1478.
- Gabriel, M.C., N. Howard and T.Z. Osborne. 2014. Fish Mercury and Surface Water Sulfate Relationships in the Everglades Protection Area. *Environmental Management*, 53, 583–593.
- Gilmour, C.C. 2011. A review of the literature on the impact of sulfate on methylmercury in sediments and soils (Technical No. SP689 Task 3). Florida Department of Environmental Protection, Tallahassee, FL.
- Gilmour, C.C. and E.A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environmental pollution*, 71, 131–169.
- Gilmour, C.C., E.A. Henry and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science & Technology*, 26, 2281–2287.
- Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, G.A. Gill and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*, 40, 327–345.
- Gilmour, C., M. Podar, A.L. Bullock, A.M. Graham, S.D. Brown, A.C. Somenahally, A. Johs, R., Hurt, K.L. Bailey and D.A. Elias. 2013. Mercury Methylation by Novel Microorganisms from New Environments. *Environmental Science & Technology*, 47, 11810–11820.
- Grieb, T.M., G.L. Bowie, C.T. Driscoll, S.P. Gloss, C.L. Schofield and D.B. Porcella. 1990. Factors affecting mercury accumulation in fish in the upper michigan peninsula. *Environmental Toxicology and Chemistry*, 9, 919–930.
- Guentzel, J.L., W.M. Landing, G.A. Gill and C.D. Pollman. 2001. Processes influencing rainfall deposition of mercury in Florida. *Environmental Science & Technology*, 35, 863–873.
- Hammerschmidt, C.R. and W.F. Fitzgerald. 2005. Methylmercury in Mosquitoes Related to Atmospheric Mercury Deposition and Contamination. *Environmental Science & Technology*, 39, 3034–3039.

- Hammerschmidt, C.R. and W.F. Fitzgerald. 2006. Methylmercury in freshwater fish linked to atmospheric mercury deposition. *Environmental Science & Technology*, 40, 7764–7770.
- Jerauld, M., F.E. Dierberg, W.F. DeBusk and T.A. DeBusk. 2015. Appendix 3B-1: Evaluation of Factors Influencing Methylmercury Accumulation in South Florida Marshes. In: *2015 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Joy, M.K. and R.G. Death. 2002. Predictive modelling of freshwater fish as a biomonitoring tool in New Zealand. *Freshwater Biology*, 47, 2261–2275.
- Julian, P. 2013. Mercury hotspot identification in Water Conservation Area 3, Florida, USA. *Annals of GIS*, 19, 79–88.
- Julian, P. and B. Gu. 2014. Mercury accumulation in largemouth bass (*Micropterus salmoides* Lacépède) within marsh ecosystems of the Florida Everglades, USA. *Ecotoxicology*,.
- Julian, P. and B. Gu. 2015. Mercury accumulation in largemouth bass (*Micropterus salmoides* Lacépède) within marsh ecosystems of the Florida Everglades, USA. *Ecotoxicology*, 24, 202 – 214.
- Julian, P., B. Gu, R. Frydenborg, T. Lange, A.L. Wright and J.M. McCray. 2014. Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades. In: *2014 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Julian, P., B. Gu and G. Redfield. 2015a. Comment on and Reinterpretation of Gabriel et al. (2014) “Fish Mercury and Surface Water Sulfate Relationships in the Everglades Protection Area.” *Environmental Management*, 55, 1 – 5.
- Julian, P., B. Gu, G. Redfield, K. Weaver, T. Lange, P. Frederick, J.M. McCray, A.L. Wright, F.E. Dierberg, T.A. DeBusk, M. Jerauld, W.F. DeBusk, H. Bae and A. Ogram. 2015b. Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades. In: *2015 South Florida Environmental Report*. South Florida Water Management District, West Palm Beach, FL.
- Krabbenhoft, D.P. and E.M. Sunderland. 2013. Global Change and Mercury. *Science*, 341, 1457–1458.
- Lange, T.R., H.E. Royals and L.L. Connor. 1993. Influence of Water Chemistry on Mercury Concentration in Largemouth Bass from Florida Lakes. *Transactions of the American Fisheries Society*, 122, 74–84.
- Liu, G., Y. Cai, P. Kalla, D. Scheidt, J. Richards, L.J. Scinto, E. Gaiser and C. Appleby. 2008. Mercury mass budget estimates and cycling seasonality in the Florida Everglades. *Environmental Science & Technology*, 42, 1954–1960.
- Loftus, W.F. 2000. Accumulation and fate of mercury in an Everglades aquatic food web. Florida International University, Miami, Florida.
- Lynch, J.A., V.C. Bowersox and J.W. Grimm. 2000. Changes in sulfate deposition in eastern USA following implementation of Phase I of Title IV of the Clean Air Act Amendments of 1990. *Atmospheric Environment*, 34, 1665–1680.
- Miller, W.L. 1988. Description and evaluation of the effects of urban and agricultural development on the surficial aquifer system, Palm Beach County, Florida (Report No. 88-4056). United States Geological Survey, Tallahassee, FL.

- Mitchell, M.J., C.T. Driscoll, P.J. McHale, K.M. Roy and Z. Dong. 2013. Lake/watershed sulfur budgets and their response to decreases in atmospheric sulfur deposition: watershed and climate controls: REGULATION OF SULFUR BUDGETS OF FORESTED LAKE/WATERSHEDS. *Hydrological Processes*, 27, 710–720.
- Mitchell, M.J., G. Lovett, S. Bailey, F. Beall, D. Burns, D. Buso, T.A. Clair, F. Courchesne, L. Duchesne, C. Eimers, I. Fernandez, D. Houle, D.S. Jeffries, G.E. Likens, M.D. Moran, C. Rogers, D. Schwede, J. Shanley, K.C. Weathers and R. Vet. 2011. Comparisons of watershed sulfur budgets in southeast Canada and northeast US: new approaches and implications. *Biogeochemistry*, 103, 181–207.
- Munthe, J., R.A. (Drew) Bodaly, B.A. Branfireun, C.T. Driscoll, C.C. Gilmour, R. Harris, M. Horvat, M. Lucotte and O. Malm. 2007. Recovery of Mercury-Contaminated Fisheries. *AMBIO: A Journal of the Human Environment*, 36, 33–44.
- Newman, S., J. Schuette, J.B. Grace, K. Rutchey, T. Fontaine, K.R. Reddy and M. Pietrucha. 1998. Factors influencing cattail abundance in the northern Everglades. *Aquatic Botany*, 60, 265–280.
- Ogden, J.C., W.B. Robertson Jr, G.E. Davis and T.W. Schmidt. 1973. Pesticide, Polychlorinated Biphenols and Heavy Metals in Upper Food Chain Levels, Everglades National Park and Vicinity. National Park Service, Everglades National Park, Homestead, FL.
- Orem, W., C. Gilmour, D. Axelrad, D. Krabbenhoft, D. Scheidt, P. Kalla, P. McCormick, M. Gabriel and G. Aiken. 2011. Sulfur in the South Florida Ecosystem: Distribution, Sources, Biogeochemistry, Impacts, and Management for Restoration. *Critical Reviews in Environmental Science and Technology*, 41, 249–288.
- Pollman, C.D. 2012. Modeling sulfate and gambusia mercury relationships in the Everglades (Technical No. SP696). Florida Department of Environmental Protection, Tallahassee, FL.
- Pollman, C.D. and D.M. Axelrad. 2014. Mercury Bioaccumulation and Bioaccumulation Factors for Everglades Mosquitofish as Related to Sulfate: A Re-analysis of Julian II (2013). *Bull Environ Contam Toxicol*, 93, 509–516.
- Porcella, D.B., E.J. Zillioux, T.M. Grieb, J.R. Newman and G.B. West. 2004. Retrospective Study of Mercury in Raccoons (*Procyon lotor*) in South Florida. *Ecotoxicology*, 13, 207–221.
- Public Law. 1990. Law 101-549. *Clean Air Act*.
- Rawlik, P.S., C. Kendall, B.E. Bemis and S.D. Wankel. 2002. A conceptual model for seasonal changes in foodwebs in the Everglades: implications for mercury bioaccumulation. South Florida Water Management District, West Palm Beach, FL.
- Reddy, K.R. and R.D. DeLaune. 2008. *Biogeochemistry of wetlands: science and applications*. CRC Press, Boca Raton, FL.
- Reddy, K.R., S. Newman, S. Grunwald, R. Corstanje and R. Rivero. 2005. Everglades soil mapping final report. South Florida Water Management District.
- Roelke, M.E., D.P. Schultz, C.F. Facemire, S.F. Sundlof and H.E. Royals. 1991. Mercury contamination in Florida panthers (A report of the Florida Panther Technical Subcommittee to the Florida Panther Interagency Committee). Florida Game and Fresh Water Fish Commission, Eustis, FL.

- Rumbold, D.G., L.E. Fink, K.A. Laine, S.L. Niemczyk, T. Chandrasekhar, S.D. Wankel and C. Kendall. 2002. Levels of mercury in alligators (*Alligator mississippiensis*) collected along a transect through the Florida Everglades. *Science of The Total Environment*, 297, 239–252.
- Rumbold, D.G., S.L. Niemczyk, L.E. Fink, T. Chandrasekhar, B. Harkanson and K.A. Laine. 2001. Mercury in Eggs and Feathers of Great Egrets (*Ardea albus*) from the Florida Everglades. *Archives of Environmental Contamination and Toxicology*, 41, 501–507.
- Scheidt, D. and P.I. Kalla. 2007. Everglades ecosystem assessment: water management and quality, eutrophication, mercury contamination, soil and habitat: monitoring for adaptive management: a R-EMAP status report. (Technical No. EPA 904-R-07-001). United States Environmental Protection Agency, Athens, GA.
- Scheuhammer, A.M., M.W. Meyer, M.B. Sandheinrich and M.W. Murray. 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *AMBIO: A Journal of the Human Environment*, 36, 12–19.
- SFWMD. 2008. Field Sampling Quality Manual. (No. SFWMD-FIELD-QM-001-04). South Florida Water Management District, West Palm Beach, FL.
- Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton and L.R. McDowell. 2000. Methylmercury accumulation in tissues and its effects on growth and appetite in captive great egrets. *Journal of Wildlife Diseases*, 36, 411–422.
- Spry, D.J. and J.G. Wiener. 1991. Metal bioavailability and toxicity to fish in low-alkalinity lakes: A critical review. *Environmental Pollution*, 71, 243–304.
- Stober, Q.J., K. Thornton, R. Jones, J. Richards, C. Ivey, R. Welch, M. Madden, J. Trexler, E. Gaiser, D. Scheidt and S. Rathbun. 2001. South Florida Ecosystem Assessment: Phase I/II Everglades Stressor Interactions: Hydropatterns, Eutrophication, Habitat Alteration, and Mercury Contamination (Technical No. EPA 904-R-01-003). United States Environmental Protection Agency, Washington DC.
- Sunderland, E.M. 2007. Mercury Exposure from Domestic and Imported Estuarine and Marine Fish in the U.S. Seafood Market. *Environmental Health Perspectives*, 115, 235–242.
- USEPA. 1997. Mercury Study Report to Congress. Volume VI: An Ecological Assessment for Anthropogenic Mercury Emissions in the United States (No. EPA-452/R-97-008). United States Environmental Protection Agency, Washington DC.
- USEPA. 2001. Water Quality Criterion for the Protection of Human Health: Methylmercury (No. EPA-823-R-01-001). United States Environmental Protection Agency, Washington DC.
- Ware, F.J., H. Royals and T. Lange. 1991. Mercury contamination in Florida largemouth bass. In: *Proceedings of the Annual Conference Southeastern Association of Fish and Wildlife Agencies*. Presented at the Annual Conference Southeastern Association of Fish and Wildlife Agencies, pp. 5 – 12.
- Wiener, J.G., D.P. Krabbenhoft, G.H. Heniz and A.M. Scheuhammer. 2003. Ecotoxicology of mercury. In: Hoffman, D.J., Rattner, B., Burton, G.A., Cairns, J. (Eds.), *Handbook of Ecotoxicology*. CRC Press, Boca Raton, FL, pp. 409 – 463.

Zhu, Y., B. Gu, D.L. Irick, S. Ewe, Y. Li, M.S. Ross and L.Q. Ma. 2014. Wading bird guano contributes to Hg accumulation in tree island soils in the Florida Everglades. *Environmental Pollution*, 184, 313–319.