

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

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SUMMARY

This chapter provides an assessment of the sulfur (S) and mercury (Hg) status within the Everglades Protection Area (EPA), and Holey Land and Rotenberger wildlife management areas (WMAs) during Water Year 2017 (WY2017; May 1, 2016–April 30, 2017). 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 *2017 South Florida Environmental Report* (SFER) – *Volume I* (Julian et al. 2017).

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 (SO₄²⁻) concentrations, loads, and atmospheric deposition to the EPA. Analytical data are reported for WY2016 for wildlife—Hg in fish tissue for largemouth bass (LMB; *Micropterus salmoides*), sunfish (*Lepomis* spp.), and mosquitofish (*Gambusia* spp.)—and for surface water SO₄²⁻.

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

- WY2017 total mercury (THg) concentrations in mosquitofish from 13 monitoring sites ranged from 0.011 milligram per kilogram (mg/kg) at site CA2NF to 0.228 mg/kg at site WCA2U3, with a median value of 0.020 mg/kg. Mosquitofish THg concentrations during WY2017 exceeded the United States Environmental Protection Agency (USEPA) trophic level 3 (TL3) criterion (0.077 mg/kg) for protection of piscivorous wildlife at one of the 13 sites (WCA2U3).
- In WY2017, median THg concentrations in TL3 sunfish from 13 monitoring sites ranged from 0.025 mg/kg at CA2NF to 0.196 mg/kg at CA315. Median annual sunfish THg

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concentration during WY2017 exceeded the USEPA protection of wildlife criterion at nine stations across the monitoring network. Annual mean THg concentrations in sunfish species from all sites were highest in spotted sunfish (*L. punctatus*; 0.206 mg/kg), intermediate in bluegill (*Lepomis macrochirus*; 0.118 mg/kg), and lowest in redear sunfish (*L. microlophus*; 0.068 mg/kg).

- During WY2017, THg concentrations in largemouth bass were determined from 11 of the 14 locations within the EPA. Annual mean THg concentration from EPA sites ranged from 0.167 mg/kg at site CA3F2 (WCA-3A) to 0.892 mg/kg at site L67F1 (ENP), with a median value of 0.290 mg/kg. During WY2017, four locations exceeded the USEPA recommended criterion for the protection of human health (0.350 mg/kg). A decrease in median Hg concentrations have been observed during the last several water years.
- Most monitoring sites did not display an increasing trend of THg in mosquitofish, sunfish, and largemouth bass. In fact, there have been large interannual variations in fish THg concentration within sites over the period of record (POR).
- Dissolved organic matter (DOM) and Hg dynamics were evaluated at several locations within the EPA suggesting that DOM quality may attenuate methyl mercury (MeHg) entry into the food web influencing bioaccumulation dynamics.
- During WY2017, annual mean inflow SO_4^{2-} concentrations ranged from 8.2 milligrams per liter (mg/L) for ENP to 52.7 mg/L for LNWR. The annual mean SO_4^{2-} concentrations at interior marsh regions ranged from 1.2 mg/L for ENP to 45.9 mg/L for WCA-2.

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 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 = 4,047 square meters) 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 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 in Chapter 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 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 $\text{S}/\text{SO}_4^{2-}$ and MeHg production (Axelrad et al. 2008, 2013, Benoit et al. 1999a, b, 2003, Gilmour et al. 1992, Orem et al. 2011). Since the evolution of the theoretical relationship between SO_4^{2-} and MeHg production, which

states that MeHg production follows a unimodal curve with respect to SO_4^{2-} along the SO_4^{2-} concentration gradient, early S and 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 influenced not only by SO_4^{2-} but a combination of many environmental factors (Gilmour 2011, Julian et al. 2014). Due to this complexity and variability, the SO_4^{2-} -Hg unimodal relationship is not spatially or temporally consistent within the Everglades (Julian et al. 2014, 2015a). The proof of an ecological concept lies in its predictive capability in nature and direct evidence of the SO_4^{2-} 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 an empirically rigorous relationships to explain MeHg formation and bioaccumulation 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*), blue crayfish (*Procambarus alleni*), Florida softshell turtles (*Apalone ferox*), pig frogs (*Rana grylio*), mottled ducks (*Anas fulvigula*), white-tailed deer (*Odocoileus virginianus*), and the endangered Florida panther (*Puma concolor coryi*) (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*), alligators, wading birds, and Florida panthers (Roelke et al. 1991, Spalding et al. 2000, Rumbold et al. 2002, Porcella et al. 2004).

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 (Lange et al. 1993, Rumbold et al. 2001, Frederick et al. 2004, Hammerschmidt and Fitzgerald 2006). 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 Hg in native fish and wading birds from the Everglades region.

SPATIAL AND TEMPORAL TRENDS IN MERCURY LEVELS IN EVERGLADES FISH

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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 is very important in the Everglades system. Fish can be useful indicators of aquatic ecosystem health, as various fish species 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 of multiple trophic levels 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) and all Centrarchid species are also common in the canal and 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. Hg 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 the South Florida Water Management District (SFWMD or District) and the Florida Fish and Wildlife Conservation Commission (FWC).

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 millimeter (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 the District using USEPA Method 7473: *Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry* (USEPA 2007), 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.

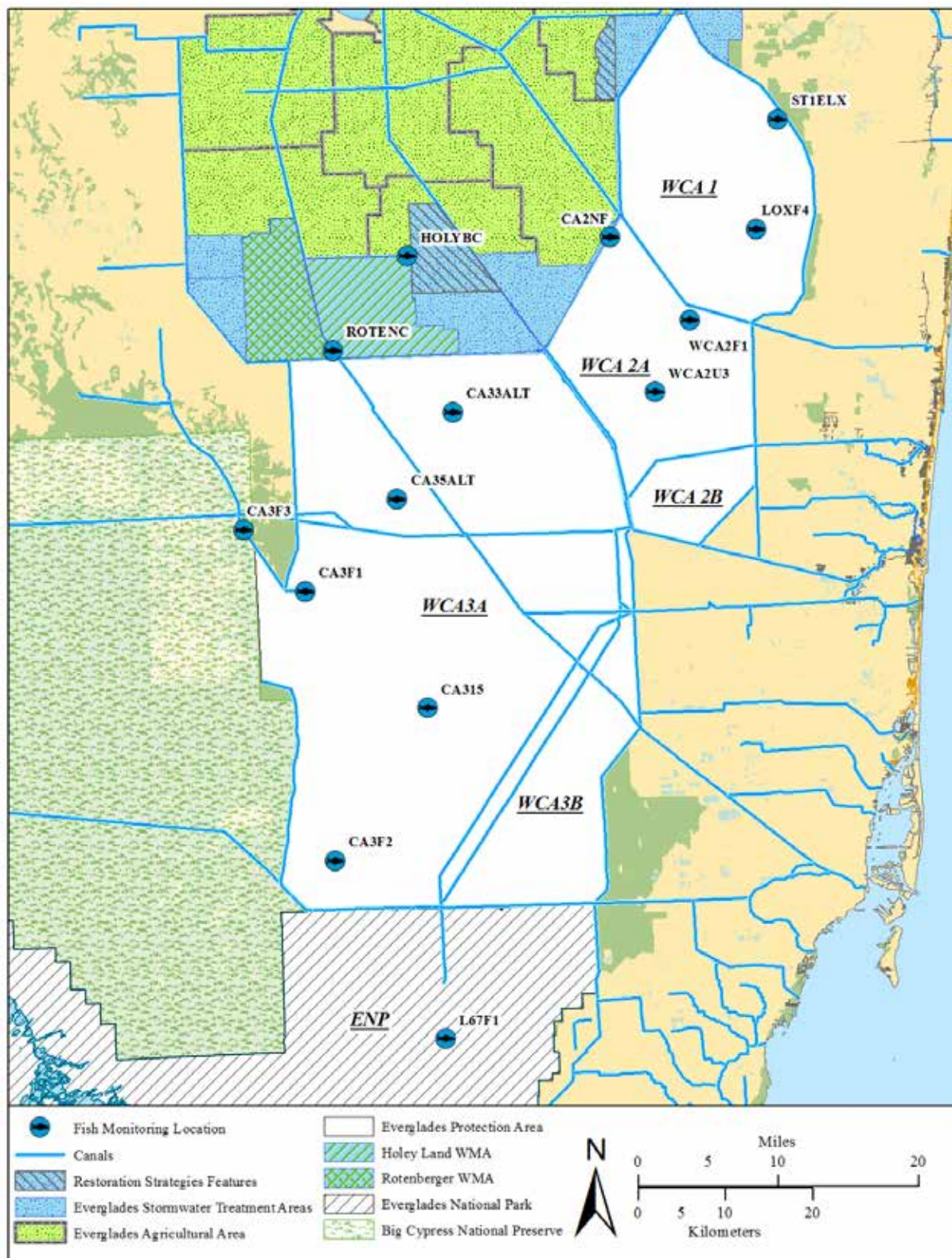


Figure 3B-1. Location of fish tissue monitoring locations within the EPA and Holey Land and Rotenberger WMAs. (Note: Station CA3F1 is an inactive station with fish sampling activity suspended since October 2009. CA3F3 is used to replace CA3F1 since October 2010.)

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 are utilized to assess human health risk from MeHg exposure. The USEPA-recommended MeHg criterion for the protection of human health (0.35 mg MeHg/kg in fish tissue) provides a baseline for these assessments (USEPA 2001). All results are reported as THg on a wet-weight basis as mg/kg.

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 Florida Department of Environmental Protection (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. 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, Water Year 2017, and the entire POR (WY1999–WY2017; May 1, 1998–April 30, 2017). 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 SigmaPlot 17 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 WY2017, two alternative sites were used to replace CA2F1 due to site access issue. THg concentrations in mosquitofish from 13 monitoring sites ranged from 0.011 mg/kg at site CA2NF to 0.228 mg/kg at site WCA2U3, with a median value of 0.020 mg/kg (**Figure 3B-2**), which is on average 40 percent lower than the median value reported in WY2016. The lowest and the highest THg levels in mosquitofish were found at Rotenberger and Holey WMAs in WY2016. However, both lowest and highest values were found in WCA-2 in WY2017. Mosquitofish THg level in WY2017 decreased at 8 stations compared to 4 stations in WY2016. Mosquitofish THg in L67F1 displayed the greatest decrease of 64 percent while WCA2U3 displayed the greatest increase by 84 percent. In fact, 11 of 13 sites in WY2017 were below their POR values (**Figure 3B-2**).

Table 3B-1. Temporal trend analysis (Spearman Rank Correlation of mosquitofish THg concentration at the 13 active monitoring locations within the EPA for WY1999–WY2017.

Area	Station	Spearman's ρ	r - value	Sample Size	Trend Direction
WCA-1	ST1ELX	-0.03	0.9	12	Not Statistically Significant
	LOXF4	-0.68	<0.01	18	Decline
WCA-2	CA2NF	0.07	0.80	12	Not Statistically Significant
	WCA2F1 ^a	0.56	0.02	18	Increase
	WCA2U3	0.09	0.91	19	Not Statistically Significant
WCA-3	CA33ALT	-0.41	0.09	18	Not Statistically Significant
	CA35ALT	0.09	0.75	14	Not Statistically Significant
	CA3F1/F3	-0.17	0.49	19	Not Statistically Significant
	CA315	-0.56	0.02	19	Decline
	CA3F2	-0.54	0.02	18	Decline
ENP	L67F1	-0.08	0.74	18	Not Statistically Significant
WMAs	ROTENC	0.03	0.91	19	Not Statistically Significant
	HOLYBC	-0.07	0.77	19	Not Statistically Significant

a. Data for WY2017 are derived from two alternative sites (CA2F1ALT1 and CA2F1ALT2).

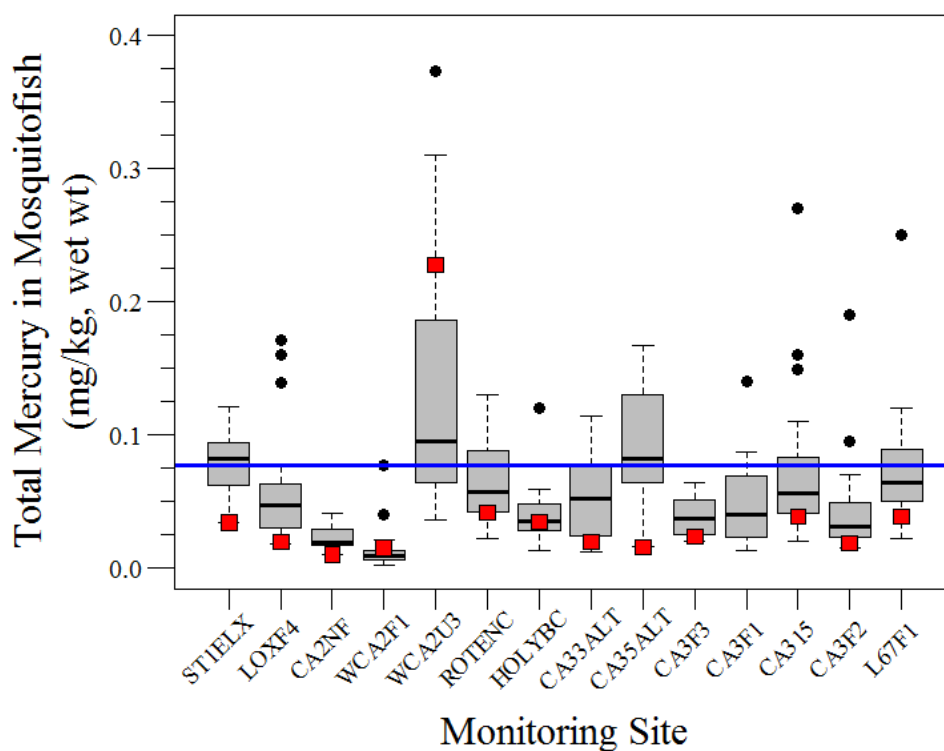


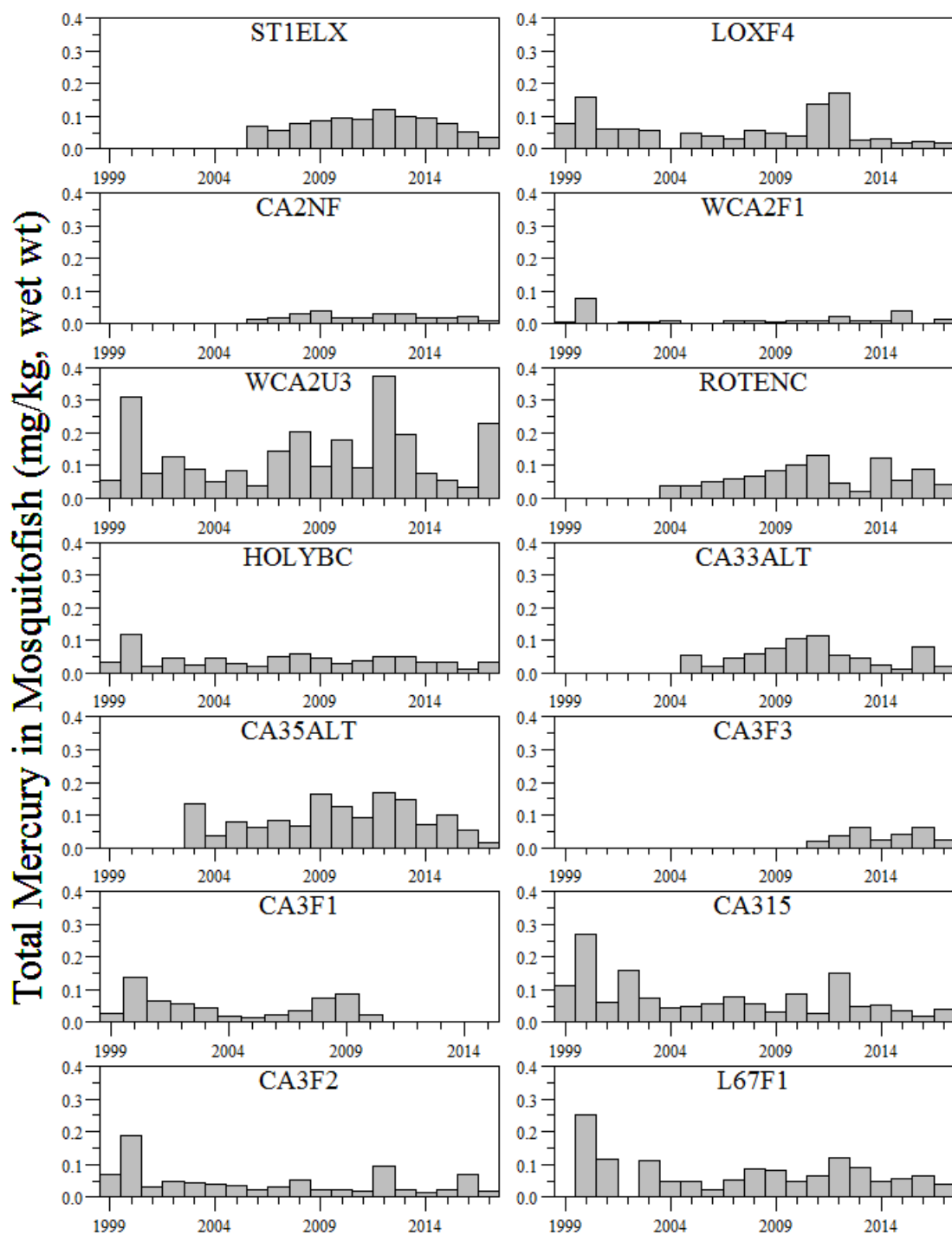
Figure 3B-2. Box plots of THg concentrations in mosquitofish in mg/kg, wet weight (wt), at each monitoring site in the EPA for WY1999–WY2017. Red boxes indicate WY2016 mean THg concentrations and the blue line denotes the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of piscivorous wildlife.

Mosquitofish THg concentrations in WY2017 exceeded the federal criterion of 0.077 mg/kg MeHg for TL3 fish at one of the 13 active monitoring sites (WCA2U3) (**Figure 3B-2**). For the POR, the median value of THg in mosquitofish is 0.048 mg/kg and 24 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 0.010 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.

Interannual and intersite variations in mosquitofish THg concentrations between consecutive years remains high (**Figure 3B-3**). During WY2017, the highest observed mosquitofish THg concentration occurred at WCA2U3 with a concentration of 0.228 mg/kg. During WY2015, this site reported a THg concentration of just 0.036 mg/kg. This one-year change is over a six-fold increase in THg at this site. By contrast, several sites (CA33ALT, CA35ALT, and CA3F2) experienced over 70 percent decline in mosquitofish THg concentrations between WY2016 and WY2017. 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 interannual precipitation (i.e., wet years versus dry years) and site-specific biogeochemistry including SO_4^{2-} , available inorganic mercury (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 (Kruskal-Wallis One Way Analysis of Variance on Ranks, $H = 0.75$, $df = 1$, $p = 0.386$). 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.

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 (variance = 0.00268) than canal habitat (variance = 0.00119). This high degree of variation in marsh habitat could be due to relatively dynamic hydrology (i.e., dry-down, dry-out, water level changes, etc.), and the dynamics of marsh trophic structure and biogeochemistry associated with dynamic hydrology. The median THg concentration is 0.050 mg/kg for marsh area and 0.048 mg/kg for canal and do not show statistical difference between habitat (Kruskal-Wallis Analysis, $H = 0.499$, $p = 0.484$). (**Figure 3B-5**).

During the entire POR, three sites (LOXF4, CA315, and CA3F2) experienced a significantly declining temporal trend in mosquitofish THg while one site (CA2F1) showed a significant increasing trend (**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, dietary sources, internal marsh sources of THg or MeHg from tree islands (Zhu et al. 2014), or other factors.



Florida Water Year

Figure 3B-3. Annual THg concentrations in mosquitofish composite samples at each monitoring site with the EPA for WY1999–WY2017.

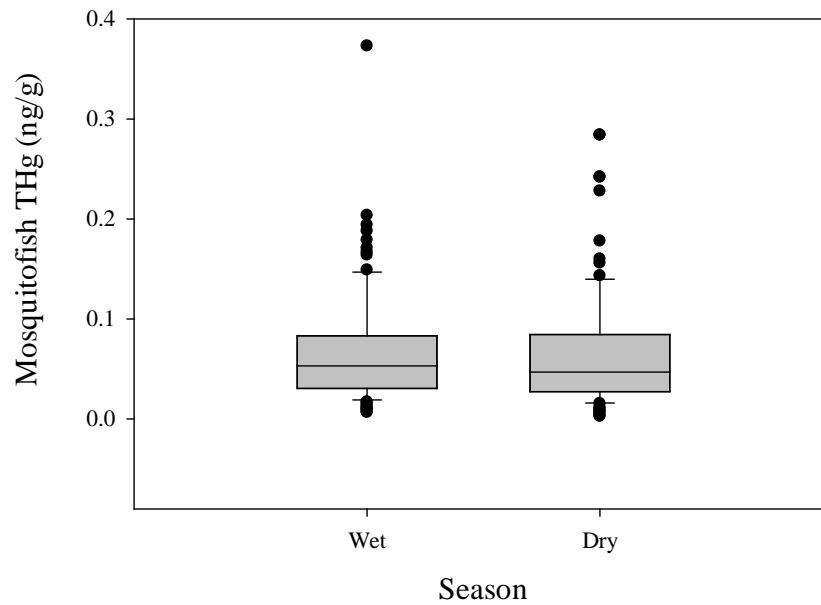


Figure 3B-4. Comparison of mosquitofish THg concentrations collected during wet and dry years within the EPA for WY1999–WY2017.

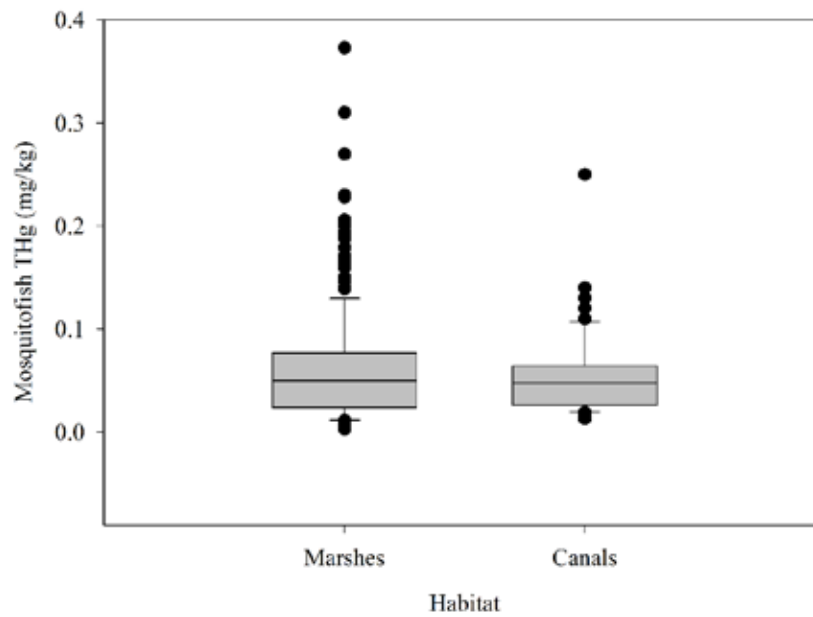


Figure 3B-5. Comparison of mosquitofish THg concentrations between marsh and canal habitats from data collected in the EPA for WY1999–WY2017.

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 0.179 ± 0.003 mg/kg (sample size [n] = 2,983). Throughout the POR, 87 percent of annual mean sunfish THg concentrations exceeded the USEPA MeHg criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. Except WCA2F1 (average = 0.050 mg/kg), all current monitored stations observed annual mean sunfish THg concentration above the USEPA MeHg criterion, with the enriched WCA2F1 experiencing the least number of exceedances (1 out of 6) during the POR.

The average THg concentration for the POR was highest at the ENP site L67F1 (0.359 mg/kg) and lowest (0.042 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. 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 WY2017, the mean THg concentration in the TL3 sunfish species from 11 of the 13 active monitoring sites was 0.120 mg/kg (n = 201), with a range from 0.036 mg/kg at CA2NF to 0.218 mg/kg at CA35ALT. Compared to WY2016 (0.167 mg/kg), a 30 percent decrease in mean sunfish THg concentrations occurred. THg concentrations in these species from all sites were highest in spotted sunfish (*L. punctatus*; 0.206 mg/kg), intermediate in bluegill (*L. macrochirus*, 0.118 mg/kg), and lowest in redear sunfish (*L. microlophus*; 0.068 mg/kg).

THg concentration varied between sunfish species during WY2017 (Kruskal-Wallis Analysis; $H = 4.38$, $df = 2$, $p < 0.01$, **Figure 3B-8**). Throughout the entire POR all three species (annual mean) statistically differed in THg concentrations (Kruskal-Wallis Analysis, $H = 34.4$, $df = 2$, $p < 0.01$) with the highest THg concentration in spotted sunfish (0.253 mg/kg), followed by bluegill (0.198 mg/kg), and redear sunfish (0.126 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).

Table 3B-2. Temporal trend analysis of TL3 sunfish THg concentration at the 13 active monitoring locations within the EPA for WY1999–WY2017.

Area	Station	Spearman's ρ	r - value	Sample Size	Trend Direction
WCA-1	ST1ELX	0.333	0.356	9	Not Statistically Significant
	LOXF4	-0.066	0.795	17	Not Statistically Significant
WCA-2	CA2NF	-0.209	0.520	11	Not Statistically Significant
	WCA2F1 ^a	-0.543	0.297	6	Not Statistically Significant
	WCA2U3	0.482	0.042	18	Increase
	CA33ALT ^a	0.297	0.384	10	Not Statistically Significant
WCA-3	CA35ALT	0.684	0.006	14	Increase
	CA3F1/F3	-0.228	0.356	18	Not Statistically Significant
	CA315	-0.166	0.503	18	Not Statistically Significant
	CA3F2	-0.259	0.293	18	Not Statistically Significant
ENP	L67F1	-0.067	0.786	18	Not Statistically Significant
WMAs	ROTENC	0.336	0.296	11	Not Statistically Significant
	HOLYBC	0.199	0.437	17	Not Statistically Significant

a. No data for WY2015 and WY2016.

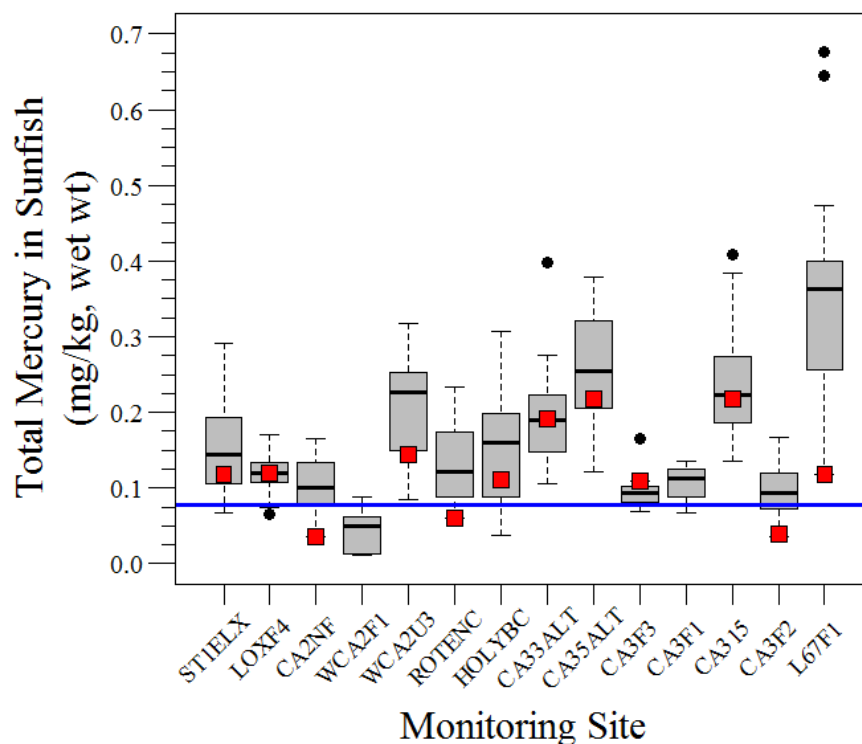


Figure 3B-6. Box plots of THg concentrations in sunfish at each monitoring site in the EPA for WY1999–WY2017. Red boxes indicate WY2017 mean THg concentrations and the blue line denotes the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of piscivorous wildlife.

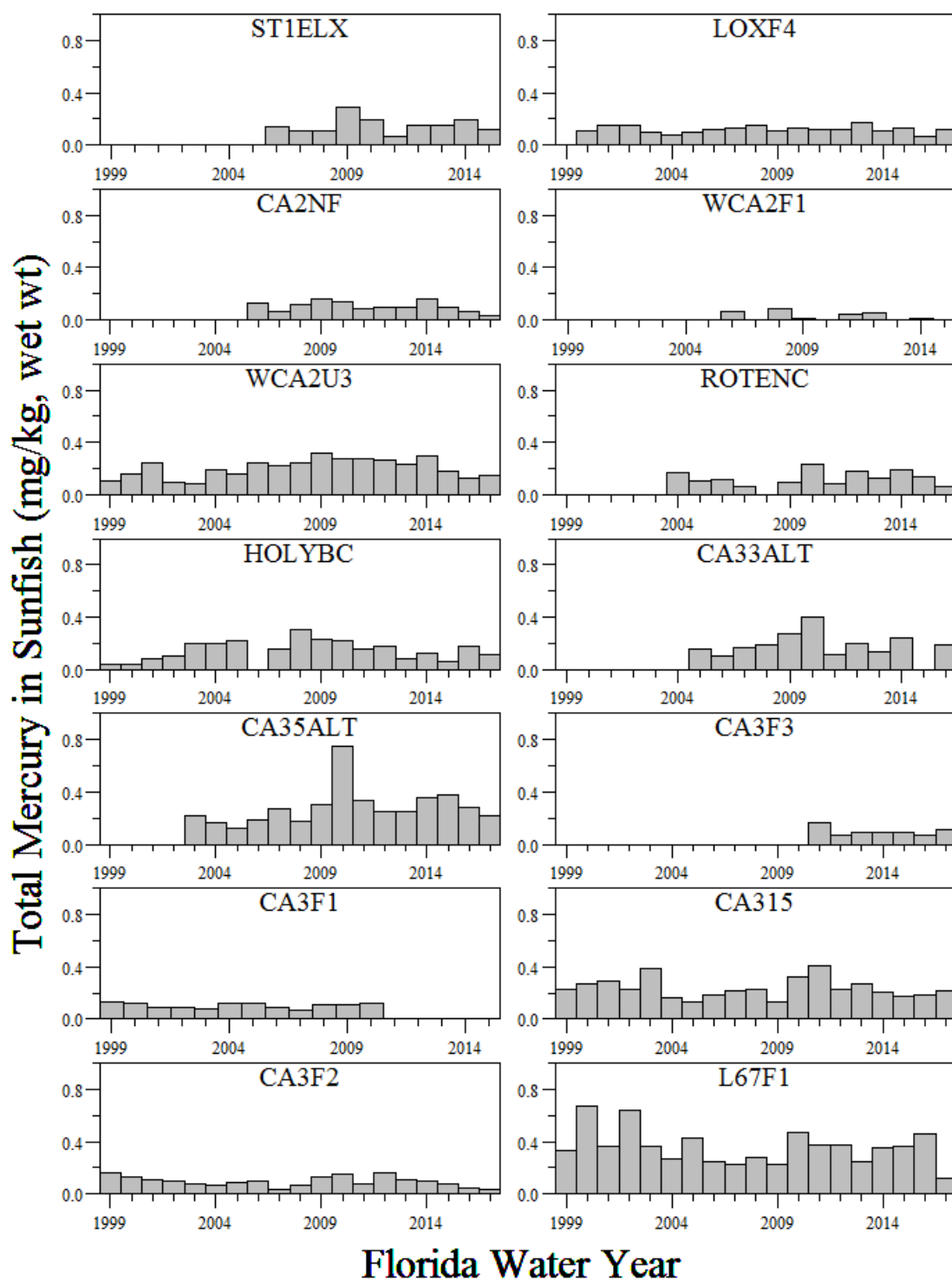
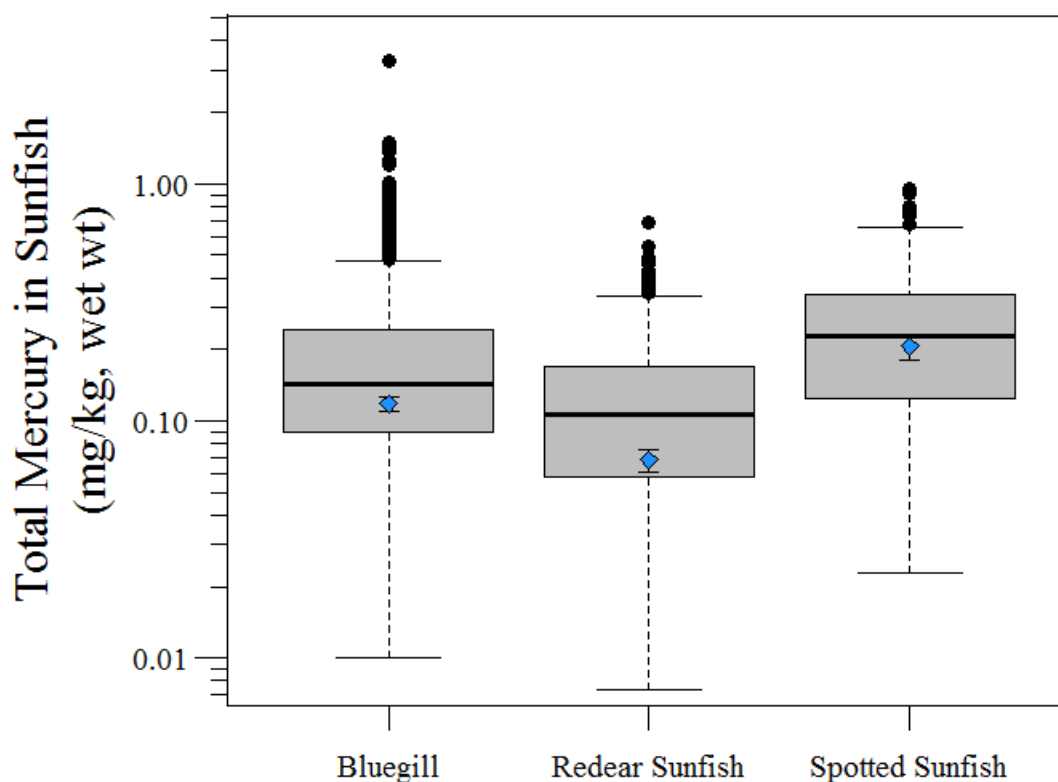


Figure 3B-7. Annual THg in TL3 sunfish whole-body samples at each monitoring site in the EPA for WY1999–WY2017.



Sunfish Species

Figure 3B-8. Comparison of TL3 sunfish species collected in the EPA for WY1999–WY2017. Blue diamonds indicate WY2016 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 WY2017, no fish were collected from three of the monitoring stations. Average THg concentrations in LMB ranged from 0.167 mg/kg at site CA3F2 (WCA-3A) to 0.892 mg/kg at site L67F1 (ENP), with an overall WY2017 median value of 0.290 mg/kg. This represents a 31 percent decrease in the reported median value from WY2016 (0.395 mg/kg). The lowest and highest THg concentration in LMB during WY2017 were observed at CA2NF (0.054 mg/kg) and L67F1 (1.690 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 (pH, alkalinity, nutrient availability, etc.), trophic position, and habitat structure (Julian and Gu 2015).

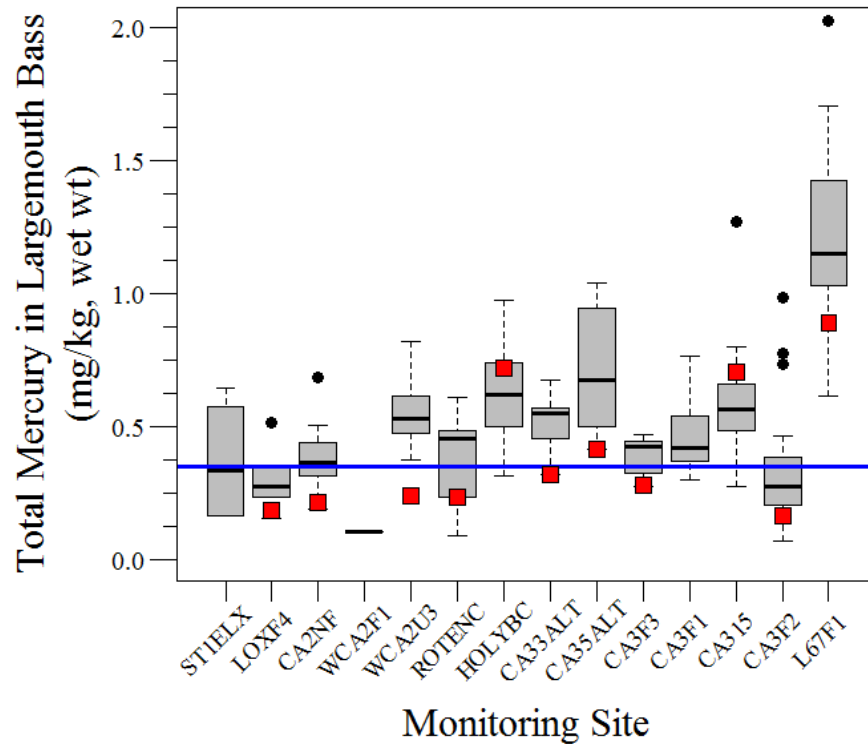


Figure 3B-9. Box plots of THg concentrations in LMB at each monitoring site for WY1999–WY2017. Red boxes indicate WY2017 mean THg concentrations and the blue line denotes the 0.350 mg/kg USEPA MeHg criterion for protection of human health.

During WY2017, 36 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**). This rate decreased from 75 percent of the monitoring locations observed in WY2016. Overall, exceedance rates of the recommended criterion have 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 approximately half of the stations exceeding the recommend criterion. 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–WY2016), except for station HOLYBC, 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) (**Figure 3B-10**).

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 (0.183 mg/kg) and LMB (0.583 mg/kg) has been above the wildlife and human health protection criterion, respectively. During WY2016, mosquitofish THg concentrations exceeded the USEPA criterion in 1 of the 13 sampled monitoring sites. By contrast, during WY2016 sunfish THg concentrations exceeded the USEPA criterion in 3 of the 9 (of the 13 active stations) sampled monitoring sites. Furthermore, during WY2016 LMB THg concentration exceeded the recommend USEPA criterion in 1 of the 8 (of the 13 active stations) sampled monitoring sites. Several sites experienced THg concentration declines in POR annual mosquitofish THg concentrations (sites LOXF4, CA315, and CA3F2), while inclining trends in POR annual mosquitofish

(CA2F1) sunfish THg concentrations (WCA2U3 and CA35ALT). One of 13 sites (HOLYBC) exhibited a statistically significant temporal trend in annual LMB THg concentration throughout the 18-year POR.

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). Furthermore, dietary composition and trophic interactions among fish of different trophic levels might also lead to greater Hg accumulation in fish, especially those at higher trophic level.

Table 3B-3. Temporal trend analysis of TL3 LMB THg concentration at the 13 active monitoring locations within the EPA for WY1999–WY2017.

Area	Station	Spearman's ρ	p-value	Sample Size	Trend Direction
WCA-1	ST1ELX	0.200	0.917	4	Not Statistically Significant
	LOXF4	-0.436	0.078	17	Not Statistically Significant
WCA-2	CA2NF	-0.091	0.776	11	Not Statistically Significant
	WCA2F1				Not Enough Data
	WCA2U3	0.250	0.309	18	Not Statistically Significant
	CA33ALT	-0.500	0.450	5	Not Statistically Significant
WCA-3	CA35ALT	-0.200	0.714	6	Not Statistically Significant
	CA3F1/F3	-0.385	0.112	18	Not Statistically Significant
	CA315	-0.400	0.109	17	Not Statistically Significant
	CA3F2	-0.416	0.084	18	Not Statistically Significant
ENP	L67F1	0.203	0.411	18	Not Statistically Significant
WMAs	ROTENC	0.417	0.243	9	Not Statistically Significant
	HOLYBC	0.511	0.030	18	Increase

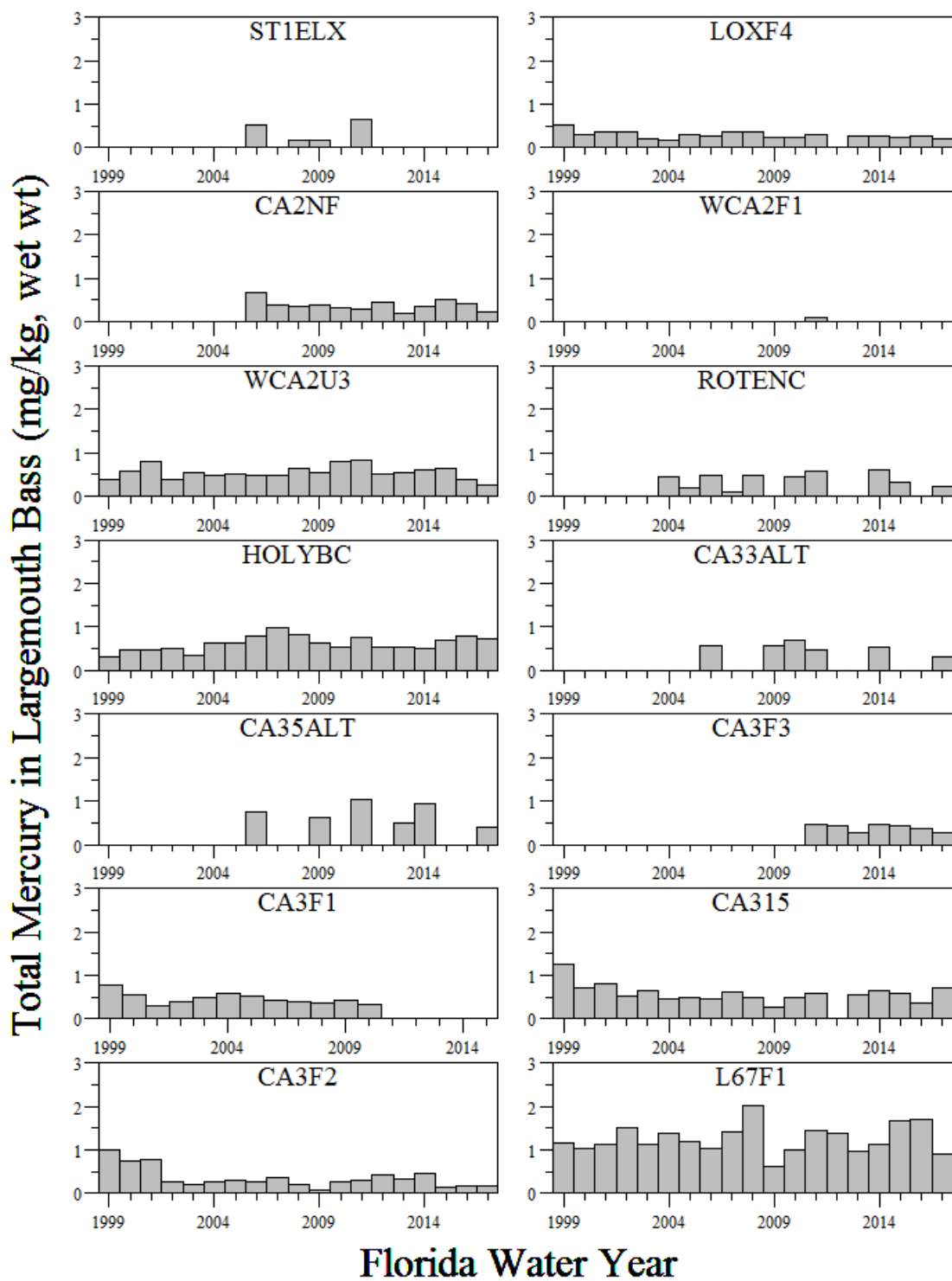


Figure 3B-10. Annual THg concentrations in LMB axial fillet samples at each monitoring site in the EPA for WY1999-WY2017.

MERCURY BIOGEOCHEMISTRY

ASSESSING THE ROLE OF DISSOLVED ORGANIC MATTER IN THE EVERGLADES MERCURY CYCLE

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Janelle A. Potts³, and Nichole R. Larson³, Karen Hileman³, and
Dawn Sierer Finn³

Introduction

Dissolved organic matter (DOM) is naturally abundant in wetlands, including the Everglades. Hg^{2+} and MeHg associate strongly with DOM, especially in oxic surface water. Therefore, many aquatic ecosystems express positive correlations between concentrations of DOM and Hg in the water (Grigal 2002, Brigham et al. 2009, Tsui and Finlay 2011, Chaves-Ulloa et al. 2016) including the Everglades (Liu et al. 2008). Because of the high level of interactivity between DOM and Hg, DOM can be highly influential in the Hg cycle. DOM affects chemical aspects of the Hg cycle in remarkable ways (Ravichandran 2004, Zhang and Hsu-Kim 2010, Gerbig et al. 2011), but it is most frequently discussed as altering, broadly, the bioavailability of Hg. Though rarely (but increasingly) explicitly distinguished, there are two separate aspects of Hg bioavailability relevant to Hg contamination of biota, which is the key environmental component of concern for Hg enrichment. First, the bioavailability of Hg^{2+} to methylating microorganisms often limits the rate of MeHg production (Benoit et al. 2003, Schaefer et al. 2011). Second, the produced MeHg must be bioavailable to consumers to enter the food web.

On the processes of Hg^{2+} methylation and MeHg uptake, DOM has highly complex effects. Contradictory findings are common in the literature, and opposing examples of enhancement and inhibition can be found. For example, Barkay et al. (1997) found that the uptake of Hg^{2+} by model bacteria decreased with increasing DOC concentrations, while Graham et al. (2012) reported that DOM additions enhanced Hg^{2+} uptake and MeHg production by pure-culture sulfate reducing bacteria (SRB) in sulfidic solution. These opposing effects may be antagonistic and the net effect can differ among ecosystems. A growing body of research has focused on this antagonism and identified a threshold-type effect, where, at low concentrations, DOM stimulates methylation and bioaccumulation, but at high concentrations, DOM reduces MeHg bioavailability by strongly complexing Hg (Chiasson-Gould et al. 2014, French et al. 2014, Chaves-Ulloa et al. 2016).

Due to its potential importance, the effects of DOM on Hg methylation and bioaccumulation is one of two prominent research questions receiving a great deal of attention globally, along with a focus on methylation by microbial groups other than obligate SRB (Bae et al. 2014), such as syntrophs and methanogens. Despite this, DOM has received relatively little study in Everglades mercury research, especially compared to sulfate and sulfide concentrations, and mercury deposition. Studies investigating the influence of DOM on biotic Hg concentrations are especially rare (Gilmour et al. 2004, Liu et al. 2008). Thus, the important question remains: what is the role of DOM in the Everglades Hg cycle, particularly with respect to biotic Hg levels?

To better understand the role DOM plays in the Everglades mercury cycle, since 2011 our research team has measured DOM quantity (as the concentration of DOC) and character (as specific ultraviolet absorbance, or SUVA, a measure of the relative size and complexity of DOM) alongside measurements of mercury in the water and several biotic matrices at our network of Hg study sites within the phosphorus (P)-unimpacted EPA (**Figure 3B-11**).

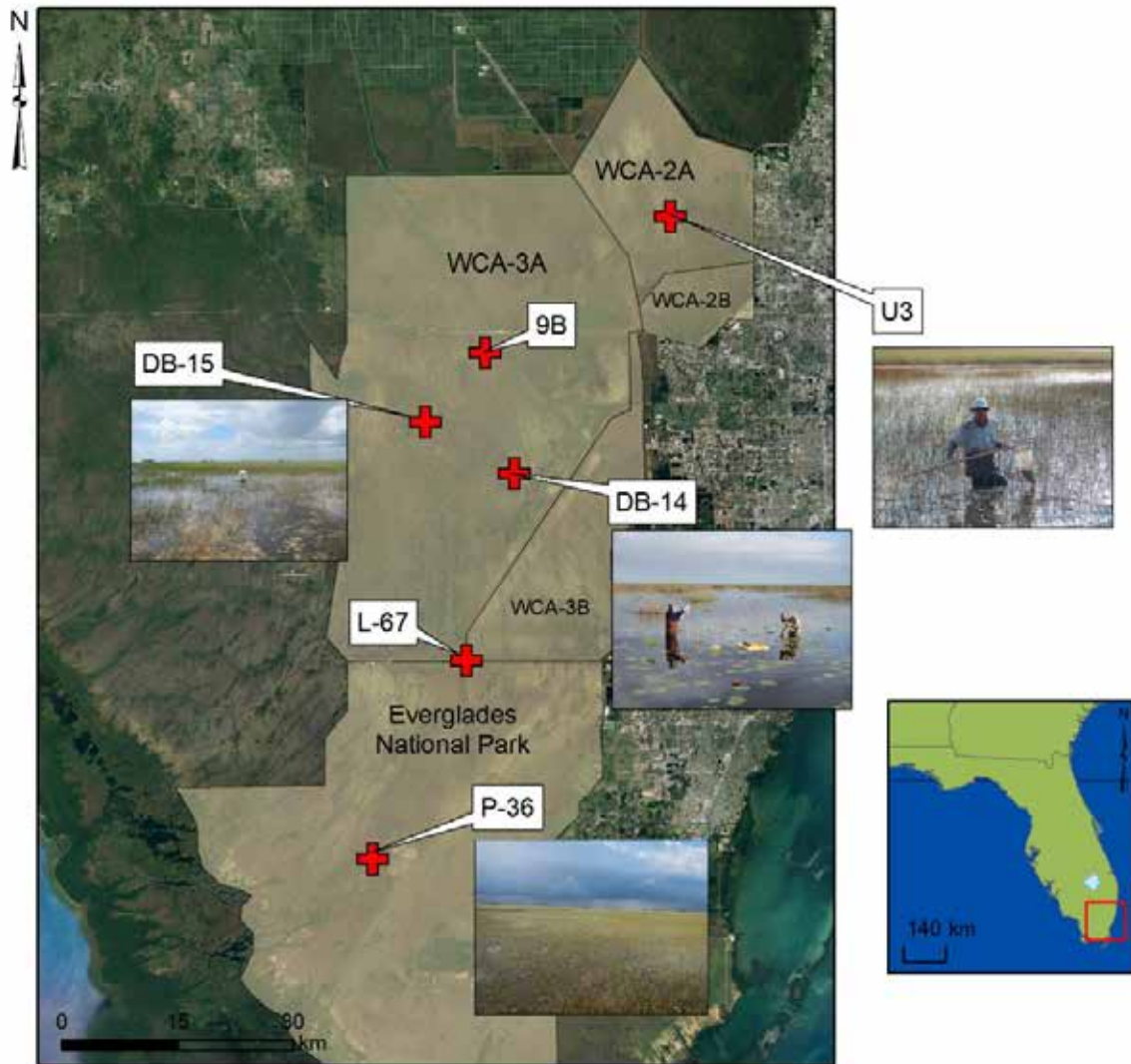


Figure 3B-11. Map showing the locations of the six sites within the EPA where samples were collected from Calendar Years 2011 to 2017.

Results and Discussion

As expected, Hg^{2+} and MeHg in the surface water were very closely associated with DOM, as shown by the strong positive correlation between Hg concentrations and DOC concentration (**Figure 3B-12**). However, to borrow a well-stated phrase from a recent article, “a linear positive relationship between freshwater DOC and dissolved Hg concentration may not translate to a linear increase in MeHg bioavailability to biota” (Chaves-Ulloa et al. 2016). Indeed, Hg concentrations in key carbon sources such as periphyton, detritus (that is, the upper 1 to 2 centimeters [cm] of the surficial floc), and important consumers (the detritivorous amphipod *Hyaella* sp. and the mosquitofish *Gambusia holbrooki*) were not related to water column concentrations of DOC or MeHg (**Figure 3B-13**), despite the wide concentration ranges observed.

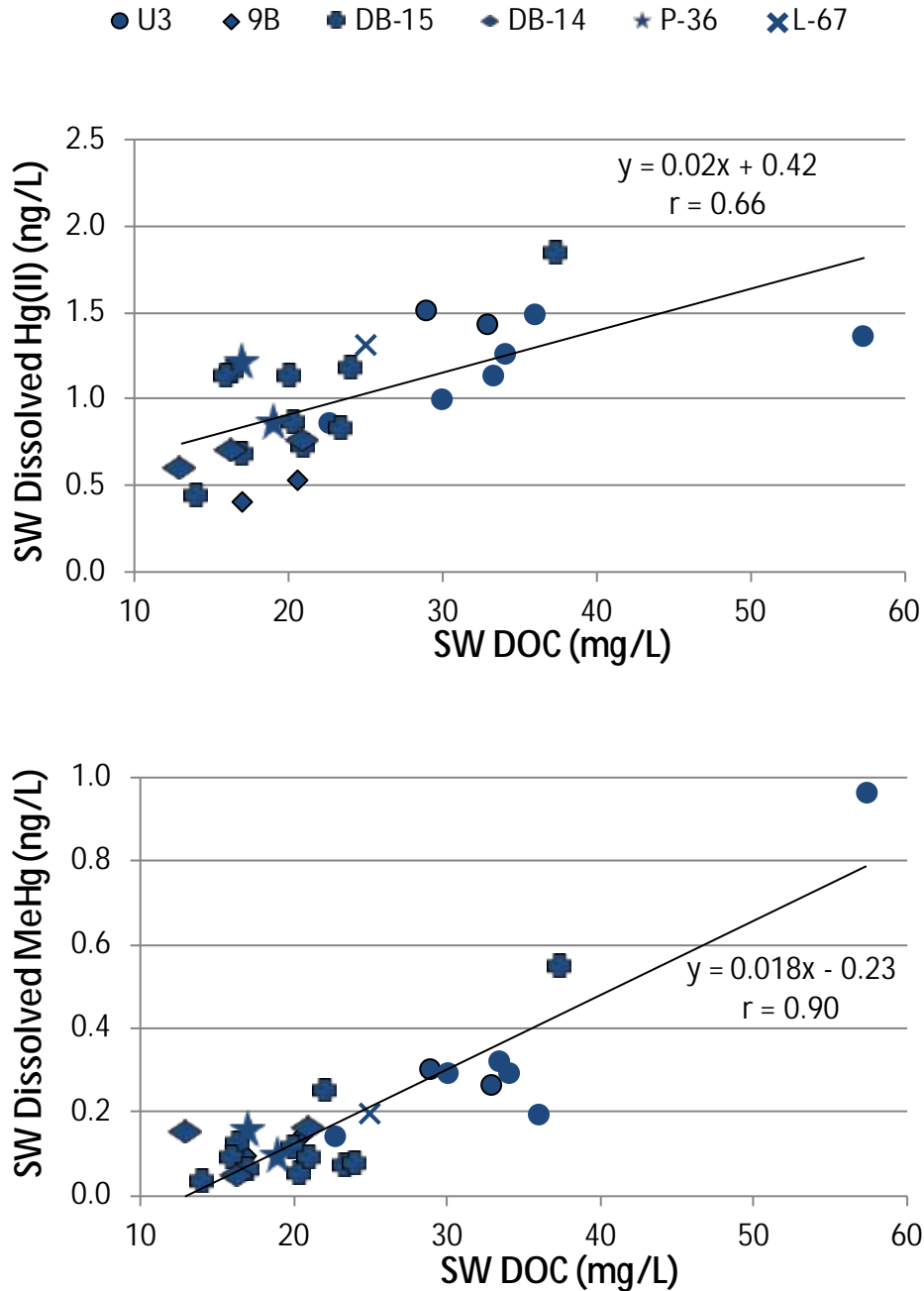


Figure 3B-12. The scatterplots of surface water (SW) DOC to SW dissolved Hg^{2+} and SW dissolved MeHg at six locations in the EPA from Calendar Years 2011 to 2017.

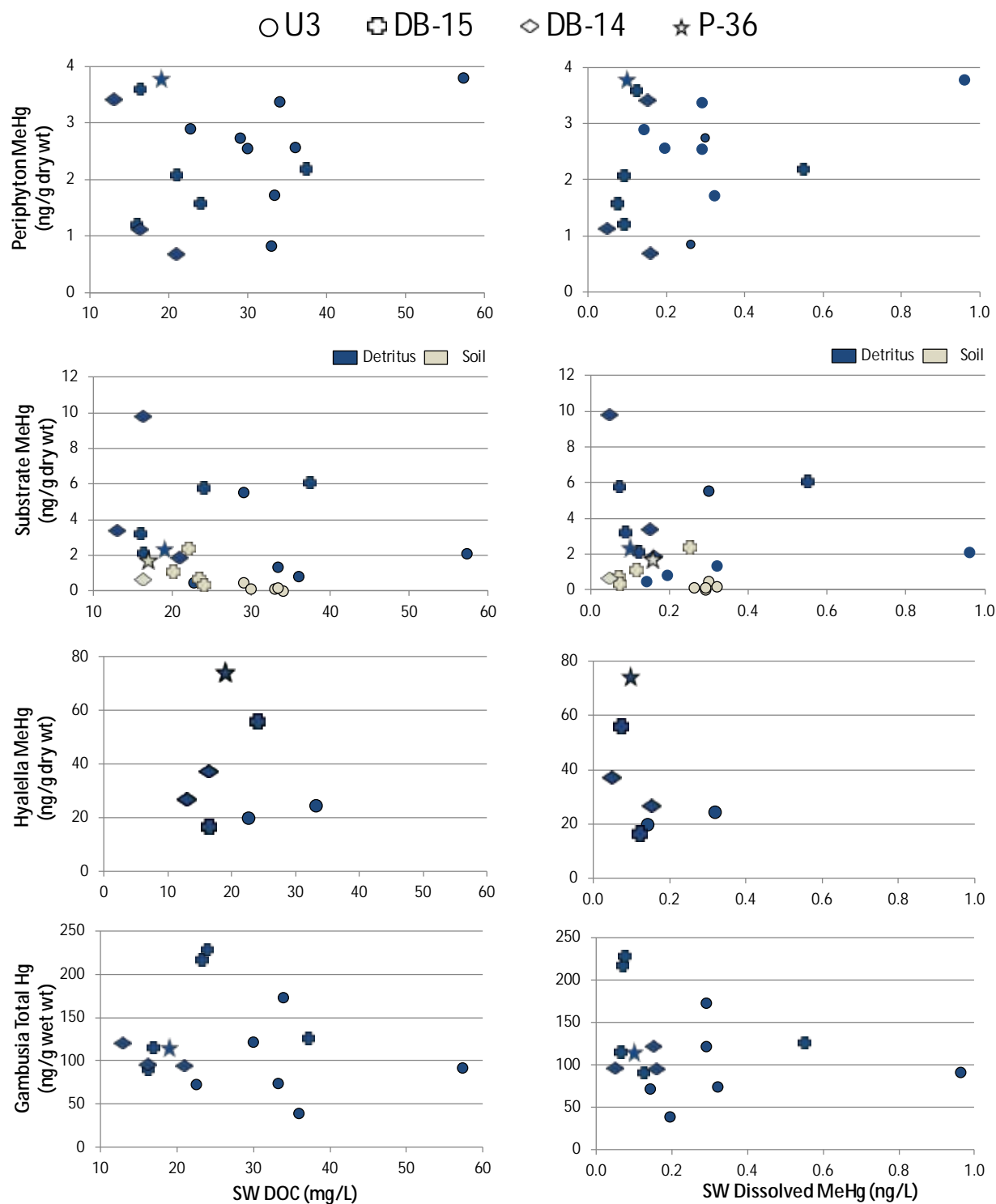


Figure 3B-13. The relationship between SW DOC concentrations and the MeHg concentrations in periphyton, detritus (i.e., surficial 1 to 2cm of floc), soil (top 0 to 5 cm), amphipods (*Hyalella*), and THg concentrations in *Gambusia* at six locations in the EPA from Calendar Years 2011 to 2017. (Note: ng/g – nanograms per gram.)

Of the many potential roles DOM may play in the Hg cycle, our cross-sectional data set emphasizes the mobilization of both Hg^{2+} and MeHg by DOM to the surface water of the P-unimpacted Everglades, as a function of DOC concentration. This solubilization by DOM could theoretically render Hg^{2+} more bioavailable for methylation, especially at sulfidic sites (Graham et al. 2012), like U3, thereby resulting in greater potential for biotic MeHg accumulation. However, the poor relationships between MeHg in potential methylating loci, especially periphyton (Cleckner et al. 1999), and the DOC concentration suggest that DOM does not strongly enhance net methylation in the Everglades.

Furthermore, MeHg complexation with DOM can compete with organic substrates, including food sources such as periphyton, for MeHg, thereby keeping MeHg in solution and unavailable to be taken up by the biota. Indeed, in our data set, the high levels of MeHg in the water column (associated with high DOM concentrations) did not correspond to high MeHg concentrations in carbon sources like periphyton and detritus, or the consumers *Hyaella* and *Gambusia*. Apparently, the MeHg solubilized by DOM was largely not available to the food web.

To summarize, in the P-unimpacted Everglades, DOM mobilizes Hg and especially MeHg to the water, but this probably represents only solubilization, and not stimulation of additional net MeHg production. Further, the “additional” MeHg associated with high DOM concentrations in the water column does not appear to be available to the biota.

This nuanced understanding of the role of DOM in the Everglades Hg cycle is important for the proper evaluation of field and experimental data. For example, measurements of the surface water MeHg concentration will tend to reflect variations in the DOC concentration, and may not be indicative of the Hg risk to biota. Future research on Everglades Hg must be guided by a recognition of the potentially antagonistic effects of DOM on MeHg production and bioaccumulation. In particular, aspects of DOM quality (e.g., reduced S content) that affect Hg interactivity (Poulin et al. 2017) may be as likely to attenuate MeHg from entering the food web as to facilitate MeHg synthesis.

SULFUR SOURCES TO THE EVERGLADES

SULFATE WITHIN THE EPA

Paul Julian II¹

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 SO_4^{2-} to metabolize organic matter under anaerobic conditions. During this process, some SRB have been observed to methylate THg (Gilmour et al. 1998, 2013). The exact quantitative role that 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 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 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 SO_4^{2-} within the EPA, although its role in the Hg problem remains uncertain.

Methods

A regional synoptic approach similar to that used for water quality evaluations in previous SFERs was applied to SO_4^{2-} data for WY2017 to provide an overview of SO_4^{2-} concentrations within the EPA. Consolidating regional water quality data provides the ability to analyze data over time 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 and 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. The majority of the water quality data evaluated in this chapter were retrieved from the District's DBHYDRO database (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 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–WY2016), and (4) the current water year (WY2017).

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 the EAA BMP Program was being implemented 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 *Everglades Protection Area Tributary Basins Long-Term Plan for Achieving Water Quality Goals* (Burns and McDonnell 2003) and the Comprehensive Everglades Restoration Plan (CERP). Because optimization, enhancement, and other restoration activities are expected to continue for years, the Phase II period will continue to expand in future SFERs to incorporate additional years of sampling. In addition, data for the current water year (in this case, WY2017) 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 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 SO_4^{2-} concentration for inflow and interior regions of the EPA using the Kendall's τ 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 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, 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. SO_4^{2-} monitoring results are presented in this section to provide an overview of current concentrations and evaluate temporal and spatial patterns. SO_4^{2-} summary statistics relative to the Baseline, Phase I, Phase II, and current year (WY2017) are shown in **Table 3B-6**.

SO_4^{2-} concentrations follow a general north-to-south gradient (**Figure 3B-14**) similar to other nutrients assessed elsewhere in this report. Annual mean SO_4^{2-} concentrations observed at inflow regions to the EPA during WY2017 range from 52.7 mg/L (LNWR) to 8.2 mg/L (ENP). Inflows into WCA-2, WCA-3, and ENP experienced a slight decrease in annual mean (arithmetic and geometric) and median SO_4^{2-} concentrations relative to the Phase II period. Meanwhile, annual mean (arithmetic and geometric) and median inflow SO_4^{2-} concentrations into LNWR have remained relatively constant since implementation of Phase I (**Table 3B-6** and **Figure 3B-14**). Across the POR, annual average SO_4^{2-} concentrations have significantly declined for LNWR, WCA-3, and ENP (**Table 3B-7**). Inflow concentrations to WCA-2 have not significantly changed along the entire POR. However, since the implementation of Phase II, SO_4^{2-} concentrations have significantly declined for WCA-2 inflows (**Table 3B-7**).

559 **Table 3B-6.** Summary statistics of SO₄²⁻ concentrations in mg/L for the Baseline (WY1979–WY1993),
 560 Phase I (WY1994–WY2004), Phase II (WY2005–WY2016), and WY2017 periods.

Region	Class	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
		2005-2016	512	50.8	20.9	46.3	5.4	48.3	10.0	115.0
		2017	79	52.7	19.7	49.3	5.3	50.4	24.8	132.0
	Interior	1979-1993	340	16.6	21.5	10.3	4.9	10.0	2.5	220.2
		1994-2004	1205	5.0	11.5	1.0	5.8	1.0	0.1	110.0
		2005-2016	2756	5.1	11.6	0.6	8.7	0.6	0.1	95.1
		2017	279	6.9	13.4	0.6	11.8	0.4	0.1	65.8
	Outflow	1979-1993	61	45.1	36.6	35.8	5.5	34.4	7.3	257.2
		1994-2004	70	50.5	50.8	38.8	5.8	40.6	4.2	418.9
		2005-2016	164	30.0	19.4	22.7	5.5	26.4	1.4	85.4
		2017	16	38.6	11.8	36.8	5.0	35.6	19.6	55.6
	Rim	1979-1993	66	42.2	37.1	25.2	6.5	34.4	2.5	139.8
		1994-2004	345	57.2	26.9	51.0	5.6	49.6	1.6	210.0
		2005-2016	285	49.3	22.6	43.9	5.5	44.6	3.5	185.0
		2017	48	51.8	14.9	49.5	5.3	53.0	24.3	85.1
WCA-2	Inflow	1979-1993	73	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
		2005-2016	526	47.8	17.5	42.9	5.6	47.6	0.1	106.0
		2017	63	43.0	14.6	40.4	5.1	43.1	18.0	76.2
	Interior	1979-1993	742	42.2	35.9	32.7	5.6	36.9	2.5	344.3
		1994-2004	1354	43.1	23.5	35.1	5.7	40.9	0.1	180.0
		2005-2016	1781	42.1	18.6	36.5	5.4	43.4	1.8	128.0
		2017	152	45.9	18.3	40.1	5.8	45.6	0.1	87.4
	Outflow	1979-1993	103	41.2	21.0	36.4	5.3	38.7	7.6	131.7
		1994-2004	95	28.6	10.9	26.2	4.8	27.9	5.8	54.3
		2005-2016	397	28.4	15.6	23.7	5.1	26.7	3.9	74.7
		2017	43	30.2	16.3	25.8	5.1	26.9	4.4	66.9
WCA-3	Inflow	1979-1993	268	36.7	35.2	24.2	5.9	29.8	1.0	286.0
		1994-2004	182	20.6	16.6	13.3	5.5	16.3	0.5	62.9
		2005-2016	736	18.6	18.9	7.7	7.5	9.6	0.1	74.7
		2017	144	13.1	18.4	3.1	9.4	4.0	0.1	66.9
	Interior	1979-1993	450	14.9	17.3	10.5	4.6	10.7	2.0	261.5
		1994-2004	1620	10.8	34.8	3.8	6.6	4.5	0.1	1,300.0
		2005-2016	1282	13.1	15.7	3.3	10.2	4.8	0.1	126.0
		2017	72	7.6	10.2	1.9	8.7	2.3	0.1	40.0
	Outflow	1979-1993	137	15.9	16.7	10.3	5.0	12.4	1.0	107.6
		1994-2004	134	6.9	7.7	2.5	7.1	4.5	0.1	36.5
		2005-2016	133	9.1	9.5	2.2	11.0	7.4	0.1	39.3
		2017	37	8.4	6.1	5.9	4.4	7.0	0.6	22.7
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	0.1	36.5
		2005-2016	166	7.8	7.5	3.4	6.8	6.0	0.1	35.8
		2017	40	8.2	5.9	5.8	4.5	7.1	0.4	22.7
	Interior	1979-1993	572	9.0	19.5	4.3	4.4	4.3	0.8	205.5
		1994-2004	864	5.5	17.7	2.1	4.9	2.6	0.1	403.0
		2005-2016	796	5.3	20.6	1.0	6.4	1.2	0.1	242.0
		2017	61	1.2	1.6	0.3	4.8	0.4	0.1	6.1

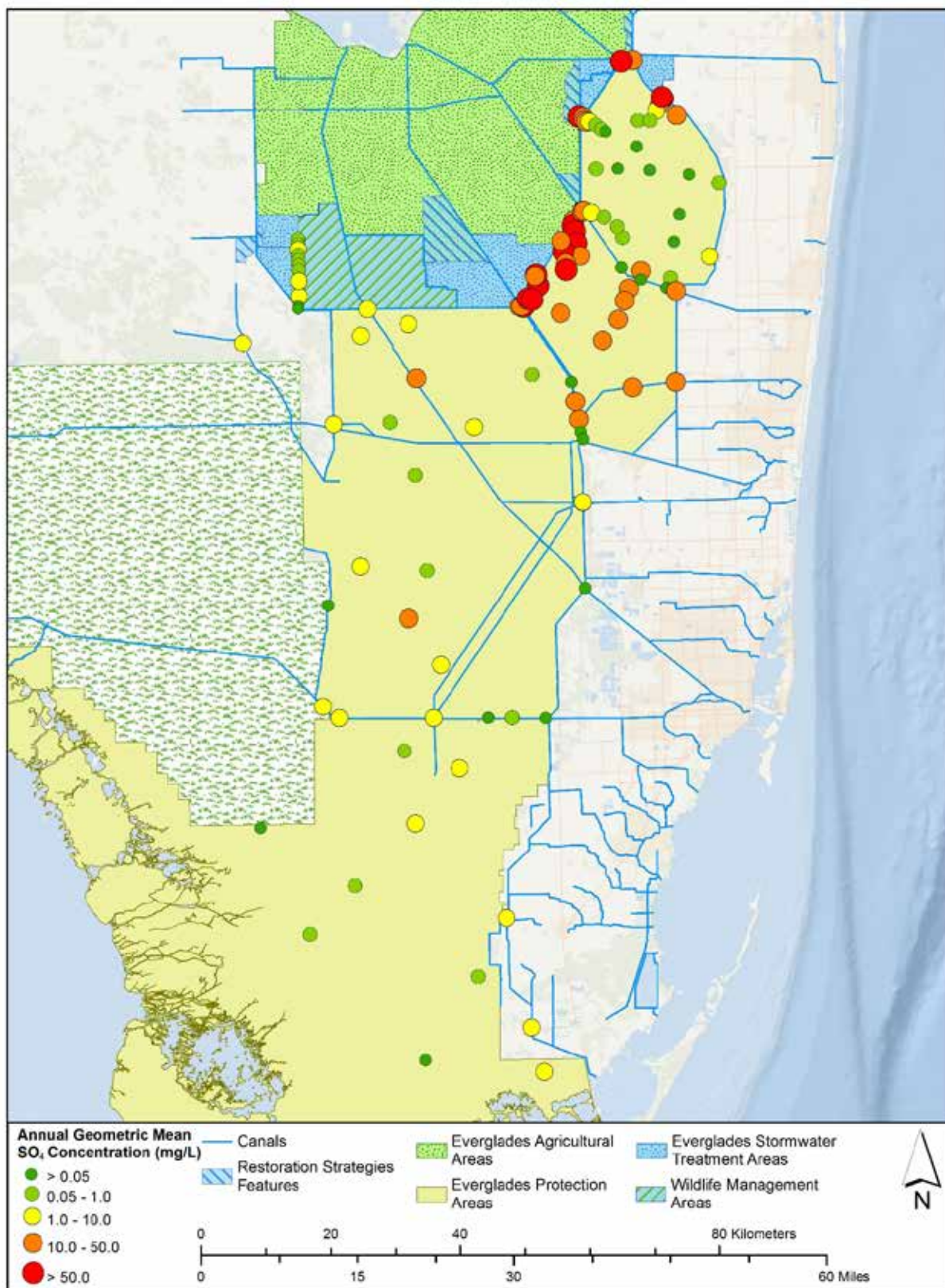


Figure 3B-14. Annual geometric mean SO_4^{2-} concentrations for all classifications at stations across the EPA in WY2017.

Table 3B-7. Kendall's t annual arithmetic mean SO_4^{2-} concentration trend analysis results for each region's inflow and interior classification within the EPA for the entire POR (WY1979–WY2017) and the period of WY2005 to present. Statistically significant r-values are italicized.

		POR (WY1979–WY2016)			Phase II & Current Water Year (WY2005–WY2017)		
Area	Class	Kendall's t	r-value	Sen's Slope Estimate ^a	Kendall's t	r-value	Sen's Slope Estimate ^a
LNWR	Inflow	-0.34	<0.01	-0.82	0.00	1.00	0.06
	Interior	-0.38	<0.01	-0.23	0.05	0.86	0.06
WCA-2	Inflow	-0.19	0.12	-0.33	-0.56	<0.05	-1.06
	Interior	0.18	0.14	0.14	-0.17	0.44	-0.55
WCA-3	Inflow	-0.45	<0.01	-0.50	-0.41	0.06	-1.06
	Interior	-0.15	0.24	-0.01	-0.33	0.13	-0.37
ENP	Inflow	-0.32	<0.05	-0.23	0.08	0.77	0.03
	Interior	-0.31	<0.05	-0.14	-0.46	<0.05	-0.40

a. Expressed as microgram per liter ($\mu\text{g/L}$) per water year.

Some annual trends are more pronounced than others, as shown in **Figure 3B-15**. The trend in annual mean SO_4^{2-} concentrations entering seems high even though throughout the POR, a significantly declining trend is apparent (**Table 3B-7**). 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 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 SO_4^{2-} from the soil to the water column. This dryout and 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.

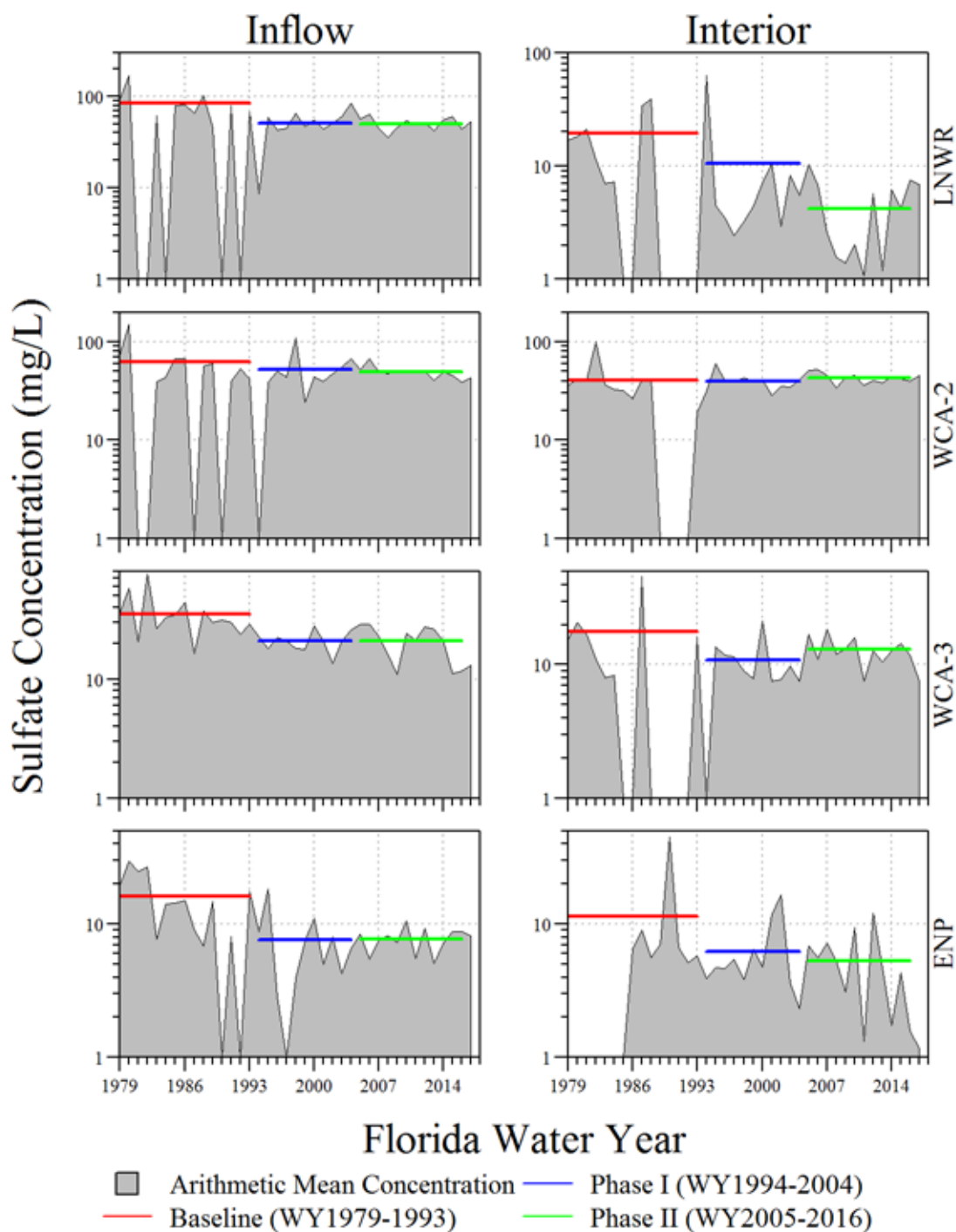


Figure 3B-15. Annual arithmetic mean SO_4^{2-} concentrations for inflow (left panel) and interior (right panel) areas of the LNWR, WCA-2, WCA-3, and ENP during WY1978–WY2017. Bars indicate arithmetic mean when flowing for inflow locations. The horizontal lines indicate the mean annual geometric mean SO_4^{2-} concentrations for the Baseline (WY1979–WY1993), Phase I (WY1994–WY2004), and Phase II (WY2005–WY2016) periods. (Note: Area with no gray indicates data gaps.)

Much like other nutrients in the EPA (see Chapter 3A of this volume), the typical north-to-south gradient is disrupted slightly at interior monitoring stations within the EPA. During WY2017, WCA-2 had the highest annual mean SO_4^{2-} concentration of 45.9 mg/L, followed by WCA-3 (7.6 mg/L), LNWR (6.9 mg/L) and ENP (1.2 mg/L). Across the POR (WY1979 – WY2017), LNWR and ENP have experienced statistically significant decreases in annual arithmetic mean SO_4^{2-} concentrations, all other areas experienced non-significant trends (Table 3B-7). During the shorter POR (WY2005–WY2017), ENP interior continued to experience significantly declining trends while all other areas have non-significant trends (Table 3B-7). Qualitative comparison of periodwide concentrations indicates SO_4^{2-} concentrations within LNWR significantly decreased between the Phase I and Phase II periods (Figure 3B-15), 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 SO_4^{2-} concentrations and loads by a small portion, approximately 10 percent of the SO_4^{2-} from the water column (SFWMD unpublished data). Other factors influencing this trend of decreasing 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 as a soil amendment to agricultural fields in this region of the EAA. It should be noted that the BMPs implemented were not used to directly mitigate SO_4^{2-} ; however, these BMPs could have provided ancillary benefits. It is also important to note that 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 SO_4^{2-} , but P and nitrogen also spiked during these periods (Chapter 3A of this volume). The very low SO_4^{2-} concentrations observed for the interior portion of LNWR indicate that either assimilation of 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 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. To further understand marsh SO_4^{2-} dynamics, S speciation and a more in-depth analysis of iron biogeochemistry is needed.

Annual mean SO_4^{2-} concentrations within WCA-2 are approximately twice that of other regions within the EPA. This is due to historical EAA runoff containing both local and regional inputs of SO_4^{2-} . The hydrology of WCA-2A spreads the canal inflow broadly, and WCA-2 soils have relatively high nutrient concentrations including S. 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. More recently, soil samples were collected along the impacted gradient within WCA-2A indicate that soil S concentrations have not qualitatively changed (unpublished data, University of Florida). 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. These high concentrations of S within the soils could result in enhanced internal S loading, which explains why interior mean concentrations are higher than inflow mean concentrations. Due to these relatively high marsh concentrations within eutrophic/impacted portions of the WCA-2, it is reasonable to suggest that growth of biota within this region of the EPA is not S or SO_4^{2-} growth limited and corroborate 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; SFWMD 2013, 2014) 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 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 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.

In an effort to provide more information on the role of SO_4^{2-} in Hg cycling, FDEP is funding research to investigate Hg methylation potential at low SO_4^{2-} concentrations in surface water. The results will provide evidence on the importance of background SO_4^{2-} levels on methylation and will also help to assess if reduction of S or SO_4^{2-} will cause a positive or negative ecological response. So far this study has yielded interesting results that shows that relatively low SO_4^{2-} additions (i.e., 0.5 to 1.0 mg/L) significantly increase water column MeHg concentrations indicating that non-abatable sources of 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 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 SO_4^{2-} goal is not consistently associated with any particular level of Hg in the Everglades (Julian et al. 2014, 2015a, b). 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 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.

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