Chapter 3B: Regional Mercury and Sulfur Monitoring and Environmental Assessment

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SUMMARY

This chapter updates the status of mercury and sulfur monitoring in South Florida and highlights the progress on research findings. Along with Volume III, Appendices 3-1 and 3-2, this chapter fulfills the Everglades Forever Act requirement that the South Florida Water Management District and Florida Department of Environmental Protection annually issue a peer-reviewed report that summarizes all data and findings of mercury monitoring and research in South Florida. Additional scientific information is available in the mercury-related chapters of the 1999 Everglades Interim Report, 2000–2004 Everglades Consolidated Reports, and 2005–2011 South Florida Environmental Reports – Volume I.

KEY FINDINGS OF RESEARCH AND MONITORING

- In the Water Conservation Areas (WCAs) over the past 22 years, there has been a significant decline in annual median total mercury concentration in largemouth bass (*Micropterus salmoides*). Mercury in largemouth bass declined 58 percent from a peak level of 1.6 parts per million [(ppm) or milligrams per kilogram (mg/kg)] in 1991 to 0.55 ppm in 2010; however, over the past decade, median mercury concentrations in largemouth bass have not declined and have averaged twice the United States Environmental Protection Agency's recommended human health criterion for fish consumption (0.3 ppm).
- No significant trend in annual median mercury concentration in largemouth bass has been observed over the past 23 years in the Shark River Slough region of Everglades National

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Park. In 2011, the median mercury concentration in largemouth bass was 1.3 ppm, which markedly exceeds both federal wildlife protection and human health criteria.

- Fish within the Everglades Protection Area (EPA) as well as in the Greater Everglades generally exceed mercury criteria set by the Florida Department of Health for the protection of human health. Fish mercury concentrations vary consistently with trophic level with largemouth bass having higher mercury levels than lower trophic level sunfish and exotic species. Fish mercury levels generally decline across the Kissimmee Chain of Lakes south to Lake Okeechobee and then increase southwards across the EPA.
- Largemouth bass mercury concentrations vary widely among monitoring sites and years. These differences may be related to the variations in mercury methylation rates that are affected by the concentrations of mercury, sulfate, and dissolved organic carbon. They may also be related to fish movement and prey availability. Further studies are needed to gain a better understanding of the biogeochemical, ecological, and hydrological conditions that control mercury accumulation in fish, especially conditions that lead to mercury hot spots in largemouth bass populations.
- The contrary effects of sulfate and sulfide on methylmercury production are major drivers of methylmercury accumulation in aquatic ecosystems including the Everglades. Research on the role of sulfur in controlling net methylmercury production has demonstrated that the sulfate concentration at which methylmercury production or accumulation is maximal is generally between 7 and 14 milligrams per liter (mg/L). For fresh waters below that optimal sulfate level, addition of sulfate stimulates methylmercury production. Further studies are needed to better understand other factors, such as dissolved organic carbon, which influence the rate of microbial methylation of mercury in the Everglades.
- National Mercury Deposition Network (MDN) results indicate that mercury wet deposition fluxes to the Everglades consistently rank among the highest in the continental United States. The Everglades National Park MDN site ranked highest nationally for seven years, and one of the other three Everglades MDN sites ranked highest nationally for a further four years of the MDN's period of record (1997-2010). Deposition modeling suggests that atmospheric mercury originating outside of North America is the dominant source of mercury deposited in the Everglades.
- Several lines of evidence plus preliminary results from regional sulfur mass balance studies suggest that the Everglades Agricultural Area (EAA) is a key source of sulfur to the downstream Everglades. Since sulfur affects mercury bioaccumulation, and as there are large uncertainties regarding sources of sulfur to the EAA, there is a need for more accurate sulfur mass balance estimates for the Everglades, the EAA, and Lake Okeechobee.
- A comprehensive study of the potential for high sulfate levels causing soil phosphorus release in South Florida marshes, in contrast to a preliminary study, revealed no increase in either surface or pore water soluble reactive phosphorus (SRP) in response to sulfate enrichment in both Stormwater Treatment Areas (STAs) and WCAs. Low substrate quality, phosphorus-limiting conditions, and/or low iron concentrations in the wetlands likely contributed to the lack of observed soil phosphorus release.

MERCURY IN EVERGLADES FISH AND WILDLIFE

Methylmercury (MeHg), the highly toxic and bioaccumulative form of mercury (Hg), can reach toxicologically significant concentrations in Everglades aquatic food webs where it becomes a risk for wildlife and humans who consume fish (Barron et al., 2004; FDOH, 2011, Frederick and Jayasena, 2010; Rumbold et al. 2008). Because fish are the main vector for MeHg exposure to both human and wildlife consumers (Harris et al., 2007a), monitoring programs are necessary to (1) assess human and wildlife risks from consumption of Hg-contaminated fish, (2) describe spatial and temporal patterns in Hg bioaccumulation, and (3) gain a better understanding of the ecological significance of Hg bioaccumulation in fish and wildlife. This section summarizes research on the status and trends of Hg in sport fish. Hg accumulation in the American alligator (*Alligator mississippiensis*), Florida panther (*Puma concolor coryi*), and Burmese python (*Python molurus bivittatus*) is available in Axelrad et al. (2011).

FISH COLLECTION

Total mercury (THg) concentrations in largemouth bass and other sport fish collected from the Everglades Protection Area (EPA) and other South Florida sites (**Figure 3B-1**) during Water Year 2011 (WY2011) (May 1, 2010–April 30, 2011) are reported. All fish were collected using direct-current, electrofishing equipment mounted on either an airboat or jon boat. Results are included here from two independent sampling programs and include fish collected from EPA downstream receiving waters as part of South Florida Water Management District (SFWMD or District) permit compliance under the Everglades Forever Act (EFA) and reported in Appendix 3B-1 and fish collected for human health risk assessments and identification of impaired surface waters [Chapter 62-303, Florida Administrative Code (F.A.C.)] under programs funded by the Florida Department of Environmental Protection (FDEP) and coordinated with the Florida Department of Health (FDOH). During WY2011, a large number of sport fish were collected for human health risk assessment from the EPA and this additional data was used to report on the current status of risk assessment data for the Everglades region. Although collected in a similar manner, each sampling program relied on different analytical methodologies for mercury determinations. Monitoring data for largemouth bass, as well as sport fish collected for human health risk assessments for THg from key Everglades fisheries, are reported in Volume III, Appendix 3-2, Attachment F.

In the laboratory, fish were weighed, measured, sexed, and, for largemouth bass (LMB) only, the sagittal otoliths were removed for age determination. Fish collected from the EPA and reported in Appendix 3B-1 as per the EFA, were analyzed by SFWMD using United States Environmental Protection Agency (USEPA) Method 7473 (Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry). The method detection limit (MDL) was 0.005 ppm. At the same time, fish collected from important fisheries within the EPA and other areas within the Greater Everglades for human health risk assessments were analyzed by the FDEP Central Laboratory in Tallahassee where THg determinations were made using USEPA Method 245.6 (Mercury in Tissues by Cold Vapor AAS). The MDL was 0.02 ppm. A portion of all samples were analyzed by both laboratories and evaluated for consistency. All results are reported as THg on a wet weight basis as milligrams per kilogram or parts per million. Because more than 85 percent of the Hg found in top level predatory fish such as LMB is in the form of MeHg (Grieb et al., 1990; Bloom, 1992), the assumption is made that THg is equal to MeHg concentration in fish axial muscle tissue.

Using relatively long-lived LMB as a monitoring tool is a distinct advantage because these fish accumulate high concentrations of MeHg that are integrated over a wide range of habitats over their life span (typically >3 yrs). Therefore, MeHg concentrations in LMB and other large predators are highly dependent on fish size and age, as well as trophic position (Lange et al., 1994; Wiener and Spry, 1996). Landscape-level factors (i.e., hydrologic variations) that influence LMB growth, movement, trophic dynamics, and life histories play an important but unquantified influence on variations in MeHg bioaccumulation. However, it is evident that across the EPA, MeHg concentration in LMB and other predators is strongly influenced by ambient levels of MeHg (Krabbenhoft et al., 2008; Fink, 2003), which in turn are tightly linked to inputs of Hg, sulfate, and dissolved organic carbon (DOC) and MeHg production by sulfate-reducing bacteria (Gilmour, 2011), which is further discussed below.

Because of size dependence in Hg bioaccumulation, Hg concentrations must be normalized to allow temporal and spatial comparisons. Calculation of an age-standardized Hg concentration can be informative in detecting gradients in Hg bioaccumulation across the Everglades landscape. However, the approach here is to evaluate broad-scale trends in Hg bioaccumulation in largemouth bass over a regional scale within the Everglades. Therefore, site-specific trends are utilized (as reported in Volume III, Appendix 3-2), but trends are evaluated using size (length)-adjusted THg concentrations in LMB among regions of the EPA.

This approach takes advantage of multiple monitoring programs and focuses on a broader set of data utilizing largemouth bass length measurements, which are more readily available, to normalize individual largemouth bass to a 14 inch [356 millimeter (mm)] total length THg concentration (THg14). The *2010 South Florida Environmental Report* (SFER) – Volume I, Chapter 3B provides specific normalization methods. The rationale for normalizing to a total length of 14 inches comes from current Florida Fish and Wildlife Conservation Commission (FWC) bag restrictions for largemouth bass caught within the EPA where anglers are allowed to keep up to five largemouth bass per day that measure up to 14 inches in total length, including one that may exceed 14 inches. In waters north of Lake Okeechobee, anglers are allowed to keep up to five largemouth bass all of which must be greater than 14 inches in total length. Normalization to a 14 inch total length provides a human health endpoint for assessments that is conservative in representing the upper size range of 80 percent of largemouth bass available for consumption within the EPA and is consistent with bag restrictions for largemouth bass caught from waters north of Lake Okeechobee. Consistent with previous reports, regional comparisons were made between Shark River Slough (SHARK region) and Water Conservation Areas 1, 2, and 3 (WCA-1, WCA-2, and WCA-3, respectively) (WCA region). From north of the EPA, sites previously compared, such as Stormwater Treatment Area 1 West (STA-1W), Holey Land Wildlife Management Area, and the Kissimmee Chain of Lakes are not included as individual sites are discussed in either Volume III, Appendices 3-1 and 3-2, or are reported below with fish consumption advisory results. Locations for long-term monitoring sites are presented in Volume III, Appendix 3-2, Attachment F.

For the section on fish consumption advisories, data on multiple species of fish, including largemouth bass, are summarized by average THg concentrations within a water body with no normalization by total length. Fish reported are all of legally harvestable size, representative of a typical angler catch, and summarized in a manner consistent with FDOH risk assessment procedures for fish contaminants.

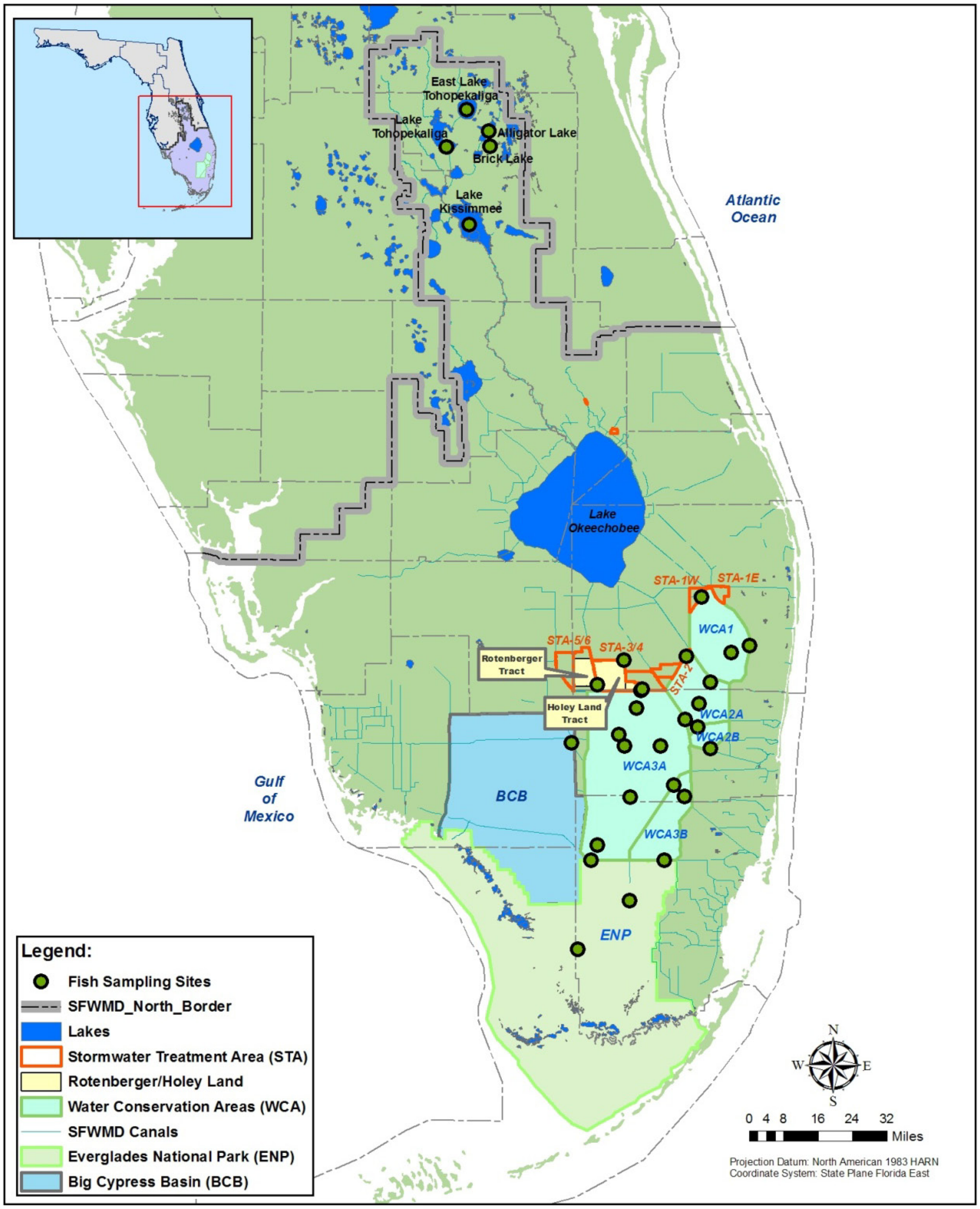


Figure 3B-1. Map of South Florida showing sampling sites for fish.

MERCURY ACCUMULATION IN FISH IN THE EVERGLADES PROTECTION AREA

During WY2011, 286 largemouth bass were collected from the WCAs and 40 were collected from Shark River Slough in Everglades National Park (ENP or Park). Within the WCAs, 19 locations were sampled, including 9 as part of downstream Everglades Construction Project monitoring and 10 as part of a reevaluation of human health risk assessments for state waters (**Table 3B-1**). Two sites were sampled within Shark River Slough: Everglades Construction Project site L67F1 and health assessment site ENPNP in North Prong Creek at the ecotonal marsh interface with Shark River. Across all sites within the WCAs, largemouth bass total length ranged from 110 to 516 mm with a median length of 311 mm while in Shark Slough total length ranged from 232 to 523 mm with a median of 388 mm. Size (total length) distributions of largemouth bass varied widely among sites (**Table 3B-1**) and when pooled among individual WCAs and SHARK region sites, median largemouth bass total length varied significantly [Kruskal-Wallis Analysis of Variance (ANOVA) on Ranks; df = 3; H = 1870.7; $p < 0.001$) making normalization by fish size preferable for comparison of Hg bioaccumulation among areas.

During WY2011, median THg14 for the WCA region ranged from 0.08 to 1.86 mg/kg among sites with a systemwide regional median of 0.66 mg/kg (**Table 3B-2**). This was a 20 percent increase from 2009 but an overall decline of 58 percent from the regional maximal THg14 median of 1.59 mg/kg reported in 1991. Similarly, the median THg14 for the SHARK region was 1.50 mg/kg (**Table 3B-2**), representing a 27 percent increase from 2009 and an overall decline of 43 percent from the regional maximum median THg14 of 2.58 mg/kg in 1997 (**Figure 3B-2**).

It is evident that declines in largemouth bass Hg levels have occurred over the period of record for the WCA region (1988–2010) (refer to 2011 SFER – Volume I, Chapter 3B). However, declines have not been consistent across the individual WCAs. Although overall declines in median THg14 have occurred within each WCA (**Figures 3B-3** through **3B-5**), the most significant declines have been observed in WCA-3 (**Figure 3B-3**) where median THg14 declined from 1.74 mg/kg in 1990 to 0.79 mg/kg in 2010, which follows a three-year increase from 2007 when THg14 reached its lowest level for the period of record at 0.43 mg/kg.

Trends for the WCAs were evaluated using Spearman Rank Correlations of annual THg14 concentrations. Over the period of record, WCA-3 declined most significantly ($p < 0.001$, $r = -0.736$, $n = 22$ years), followed by WCA-1 ($p = 0.002$, $r = -0.67$, $n = 18$ years) and WCA-2 ($p = 0.034$, $r = -0.486$, $n = 19$ years), while the SHARK region showed no change over the period of record ($p = 0.753$, $r = -0.07$, $n = 20$ years).

Although the range and median THg14 concentrations varied greatly within the SHARK region for the period of record (1989–2011; **Figure 3B-2**) no significant trends were evident. Moreover, for the entire period of record, all largemouth bass from the two sites within region SHARK have continued to exceed the 0.3 ppm USEPA MeHg criterion for the protection of human health. Similarly, sunfish THg concentrations (reported in Volume III, Appendix 3-2, Attachment F) were highest among all EPA monitoring sites with a concentration of 0.46 mg/kg. Shark River Slough continues to be a significant mercury hot spot within the EPA.

Based on site-specific largemouth bass THg concentrations in the EPA as reported in Volume III, Appendix 3-2, Attachment F, spatial patterns in largemouth bass Hg bioaccumulation continue to occur across the EPA. A north to south gradient was evident with the northernmost sites (LOXF4, WCA2F1, and CA2NF) and a site in WCA-3 (CA3F2) low in fish THg concentration compared to more southern sites (WCA2U3, WCA315, and L67F1). Similar gradients in largemouth bass THg14 were observed among the regions. Significant regional gradients existed during WY2011, with median THg14 increasing from north to south with WCA-1 less than WCA-2, WCA-2 the same as WCA-3, and WCA-3 less than SHARK with medians of 0.30, 0.71, 0.79, and 1.50 mg/kg, respectively (Kruskal-Wallis ANOVA on Ranks; df = 3; H = 141.2; $p < 0.001$; followed by Dunn's Method comparing ranks, $p < 0.05$). Site specific trends cannot be ignored when considering regional trends in that they indicate localized site specific factors impacting Hg methylation rates. For example, at site WC2U3 in WCA-2, a significant increasing trend in age-3 largemouth bass THg was observed (Volume III, Appendix 3-2, Attachment F) and similarly, the median THg14 at site WC2U3 was 1.08 mg/kg, well in excess of other sites in WCA-2.

Table 3B-1. Range and medians for largemouth bass (*Micropterus salmoides*) by total length and THg14* for individual sites within the Water Conservation Area (WCA) and SHARK regions in WY2011.

Site	N	Total Length (mm)			THg14 (mg/kg)		
		Min	**Max**	**Median**	**Min**	**Max**	**Median**
WCA Region							
L-40 Canal	12	240	436	310	0.23	0.91	0.47
L-7 Canal	20	210	482	315.5	0.10	0.50	0.27
LOXF4[1]	20	163	508	270	0.14	0.53	0.25
WCA-1 Total	**52**	**163**	**508**	**300**	**0.10**	**0.91**	**0.30**
L-35B Canal	20	211	516	325.5	0.23	1.41	0.88
WCA2F1[1]	3	110	164	141	0.08	0.68	0.08
CA2NF[1]	20	157	496	283	0.10	1.01	0.31
WCA2U3[1]	20	162	437	311.5	0.32	1.47	1.08
WCA2B Marsh	12	230	439	301	0.42	1.27	0.59
WCA-2 Total	**75**	**110**	**516**	**308**	**0.08**	**1.47**	**0.71**
Alligator Alley Canal	36	279	502	349	0.63	1.86	1.14
L-38W Canal	12	275	490	348.5	0.48	1.45	0.83
L-5 Canal	10	263	433	295.5	0.44	0.88	0.61
L-67A Canal	20	228	492	307.5	0.39	1.09	0.66
Tamiami Canal	21	211	484	318	0.30	0.92	0.60
CA315[1]	20	187	390	275	0.40	1.38	0.82
WCA33ALT[1]	3	170	191	174	0.81	1.08	0.86
WCA35ALT[1]	2	201	296	248.5	1.06	1.79	1.43
CA3F2[1]	4	145	376	244	0.28	0.52	0.40
CA3F3[1]	19	206	431	283	0.41	0.86	0.54
WCA3B North	12	251	473	331.5	0.50	1.31	0.92
WCA-3 Total	**159**	**145**	**502**	**314**	**0.28**	**1.86**	**0.79**
WCA Region Total	**286**	**110**	**516**	**311**	**0.08**	**1.86**	**0.66**
SHARK Region							
ENPNP	20	290	523	407	0.89	2.46	1.48
L67F1[1]	19	232	457	337	0.75	1.78	1.52
SHARK Region Total	**39**	**232**	**523**	**388**	**0.75**	**2.46**	**1.50**

*THg14 is the total mercury (THg) concentration normalized to a total fish length of 14 inches.

[1] Indicates downstream receiving water sites reported in Volume III, Appendix 3-2, Attachment F.

Table 3B-2. Mean THg concentrations (mg/kg) and number of sport fish collected for human health risk assessment from important fisheries within the Greater Everglades region during Water Year 2011 (WY2011) (May 1, 2010–April 30, 2011).

Location	Sites	Mean THg (Number of Fish Collected)						
		Largemouth Bass		Warmouth	Spotted Sunfish	Bluegill	Mayan Cichlid	Redear Sunfish
		≥ 14 inches	< 14 inches					
Kissimmee Chain of Lakes	5	0.50 (81)		0.17 (7)		0.23 (54)		0.10 (48)
Rotenberger Wildlife Management Area	1		0.59 (13)					
STA-3/4 (Campbell Public Use Area)	1	0.59 (3)	0.52 (7)			0.11 (12)	0.36 (6)	0.08 (12)
Holeyland Wildlife Management Area	1	1.06 (7)	0.67 (13)					
WCA-1	3	0.54 (10)	0.26 (22)	0.32 (10)		0.18 (24)		0.15 (24)
WCA-2A	4	1.28 (11)	0.58 (47)	0.61 (12)	0.58 (12)	0.27 (12)		0.29 (12)
WCA-2B	1	0.78 (3)	0.55 (9)	0.43 (8)				0.16 (12)
Big Cypress Preserve	1	0.45 (1)	0.41 (9)					
WCA-3A	12	1.08 (42)	0.65 (91)	0.60 (56)	0.38 (16)	0.47 (74)	0.10 (10)	0.27 (73)
WCA-3B	1	1.32 (5)	0.65 (7)			0.24 (12)	0.32 (12)	
ENP – Shark River Slough	5	1.79 (35)	1.01 (24)		0.52 (11)			
ENP – other	1	0.96 (14)	0.33 (16)					
Grand Mean		0.81	0.60	0.56	0.48	0.31	0.25	0.20
Total Number of Fish		212	258	93	39	188	28	181

THg – total mercury
STA – Stormwater Treatment Area
WCA – Water Conservation Area
ENP – Everglades National Park

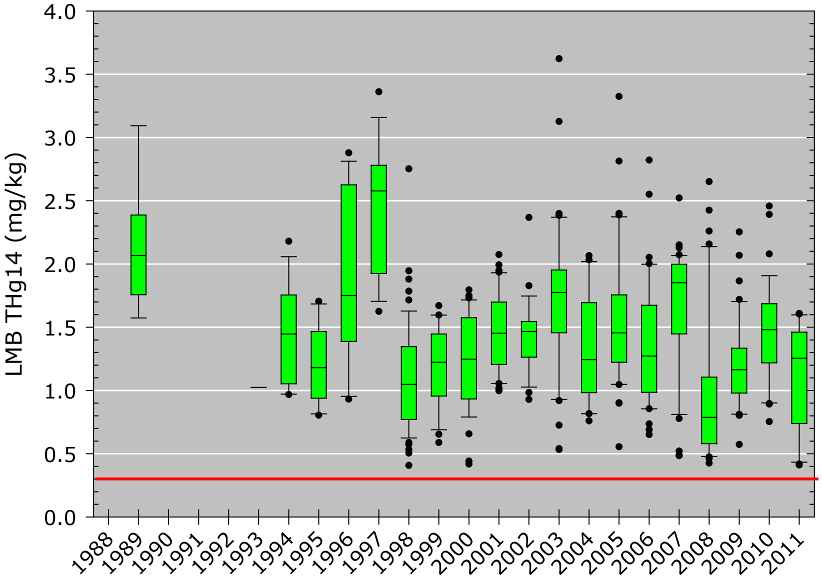


Figure 3B-2. Annual summaries of THg concentrations (normalized to total fish length = 356 mm) for largemouth bass collected from the SHARK region (sites L67F1 and ENPNP) from 1989 to 2011. Box plots represent the median, 25th, and 75th percentiles; whiskers the 10th and 90th percentile; and points are outliers. The 0.3 ppm U.S. Environmental Protection Agency (USEPA) methylmercury (MeHg) criterion is indicated in red.

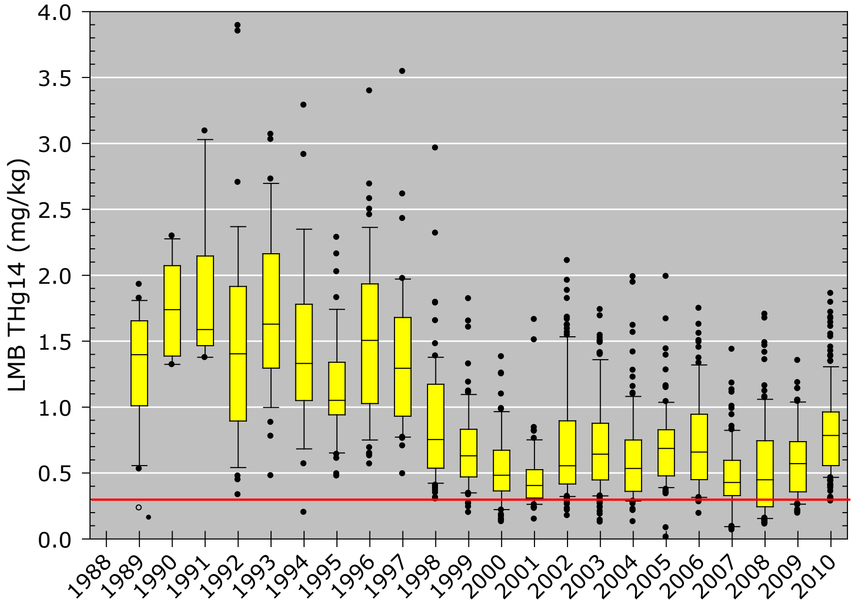


Figure 3B-3. Annual pooled summaries of THg concentrations (normalized to total fish length = 356 mm) in largemouth bass collected from canal and marsh sites in WCA-3 from 1989 to 2010. See **Table 3B-1** for sites sampled during WY2011. Box plots represent the median, 25th, and 75th percentiles; whiskers the 10th and 90th percentile; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

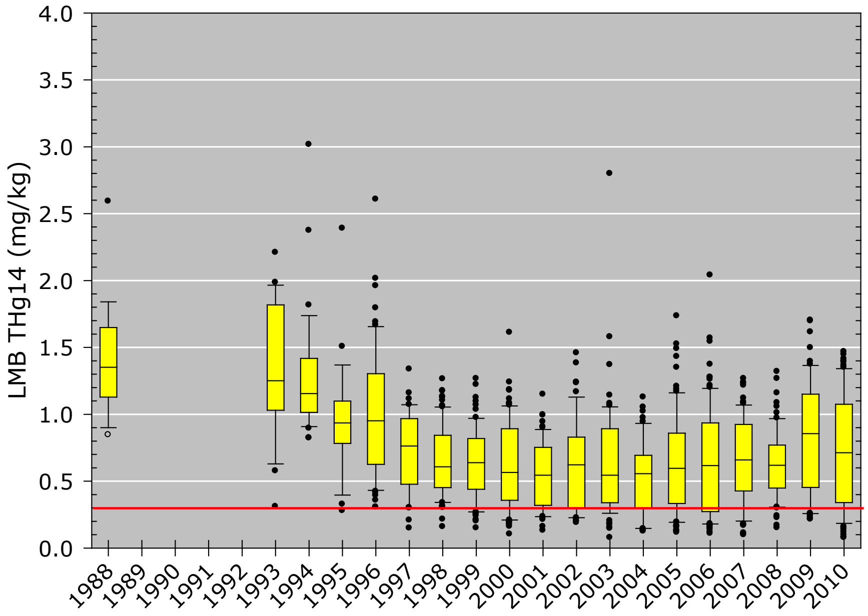


Figure 3B-4. Annual pooled summaries of THg concentrations (normalized to total fish length = 356 mm) in largemouth bass collected from canal and marsh sites in WCA-2 from 1988 to 2010. See **Table 3B-1** for sites sampled during WY2011. Box plots represent the median, 25th, and 75th percentiles; whiskers the 10th and 90th percentile; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

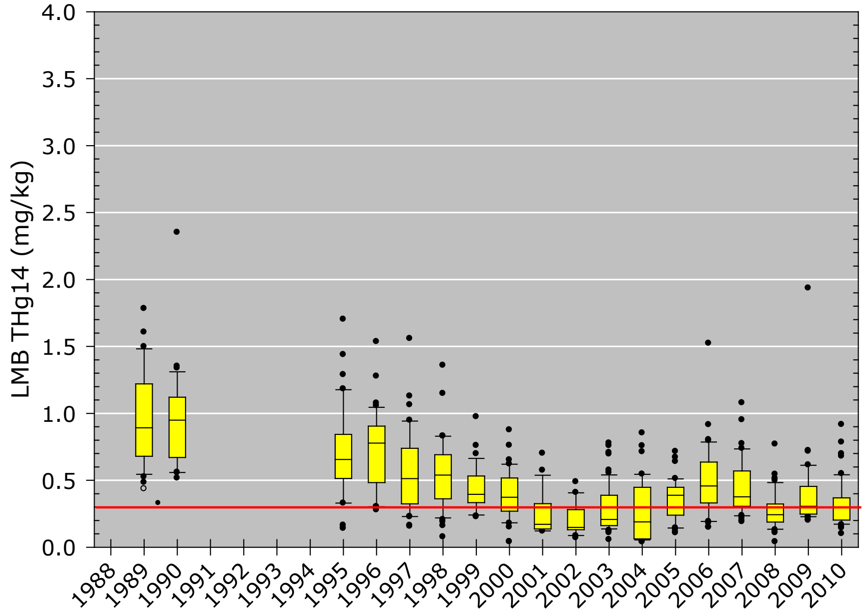


Figure 3B-5. Annual pooled summaries of THg concentrations (normalized to total fish length = 356 mm) in largemouth bass collected from canal and marsh sites in WCA-1 from 1989 to 2010. See **Table 3B-1** for sites sampled during 2010. Box plots represent the median, 25th, and 75th percentiles; whiskers the 10th and 90th percentile; and points are outliers. The 0.3 ppm USEPA MeHg criterion is indicated in red.

FISH CONSUMPTION ADVISORIES

Currently, the FDOH advises anglers not to consume largemouth bass with a total length of more than 14 inches caught from any waters in the WCA-1, WCA-2, WCA-3, ENP, Holeyland Wildlife Management Area, and other Everglades locations. Advice for consuming largemouth bass less than 14 inches in total length varies but is restrictive across the Greater Everglades. The FDOH also advises anglers to restrict consumption of 13 other freshwater sport fish species found in the Everglades region. During WY2011, intensive sampling was conducted to update data risk assessments that form the basis of FDOH fish consumption advisories. A total of 1,206 fish representing 13 species were collected from 36 sites to assess human health risks from key Everglades fisheries (**Table 3B-2**). Results were provided to the Florida Fish Consumption Advisory Working Group composed of representatives from the FDEP, FDOH, FWC, and Florida Department of Agriculture and Consumer Services (FDACS) working on behalf of FDOH's State Health Officer who promulgates specific fish consumption advice for the public. Results additionally serve to provide data on the status of Hg contamination in important state freshwater fisheries through periodic sampling and to identify surface waters impaired because of Hg in fish (Chapter 62-303, F.A.C.). For risk assessments, the FDOH generally utilizes the average THg concentration for a group of legally harvestable fish, preferably of a sample size of 12 inches or longer and representative of the water body being assessed. Here, results are grouped within appropriate water bodies for assessment and average concentrations are provided (**Table 3B-2**). Additional samples are being collected and processed prior to updating fish consumption advisories.

Most effort was focused on largemouth bass and sunfish from the WCAs where 633 samples were collected from 21 locations, principally canal sites (**Table 3B-1**). However, a number of other important fisheries were sampled within the Everglades region. Largemouth bass larger than 14 inches had the highest overall THg concentration with a grand mean for all largemouth bass of 0.81 mg/kg and a range of 0.02 to 2.9 mg/kg. Water body average THg in largemouth bass less than 14 inches, which are the size most commonly caught by anglers, ranged from 0.26 mg/kg in the WCA-1 to 1.01 mg/kg in Shark River Slough within the ENP. Although largemouth bass are an important sport fish, catch and release fishing is becoming more prevalent among anglers who practice conservation. Angler creel surveys in the L67A canal, a popular fishing location in WCA-3, during recent years documented that anglers voluntarily released 96 percent of largemouth bass less than 14 inches in total length and 94 percent of largemouth bass greater than 14 inches in total length (FWC, unpublished data).

With the increasing rate of catch and release fishing for largemouth bass, human health risk from other species needs to be assessed as anglers look for alternatives for consumption. Sunfish species and the exotic Mayan cichlid (*Cichlasoma urophthalmus*) offer a lower THg alternative to anglers but still contain THg at levels of concern regarding human health. In general order of decreasing THg concentration based on means across all sites are warmouth (*Lepomis gulosus*), spotted sunfish (*L. punctatus*), bluegill (*L. macrochirus*), Mayan cichlid, and redear sunfish (*L. microlophus*) (**Table 3B-2**). These THg concentration patterns generally hold for individual sites. Black crappie (*Pomoxis nigromaculatus*) from the northern Everglades has intermediate level of THg (**Figure 3B-6**).

Similarly, gradients in Hg bioaccumulation exist across the Greater Everglades. Species composition varies across these sites, which include lakes, rivers, canals, marsh, and estuarine creeks; however, largemouth bass are consistently sought by anglers throughout this range. Average THg concentrations in fish generally decline through the Kissimmee Chain of Lakes and south through the Kissimmee River, reaching their lowest levels in fish from Lake Okeechobee while to the south, concentrations generally increase through the Refuge, WCA-2, WCA-3, and

Shark River Slough (see **Figure 3B-6**). Within freshwater areas of the ENP, THg levels remain at levels of concern and are generally highest in Shark River Slough.

Results demonstrate the variability in Hg bioaccumulation across the Greater Everglades and in particular within the EPA. Hg bioaccumulation within the Everglades fisheries resources are a serious water quality issue. Short-term management includes proper identification of important fisheries, testing, and notification of the public for protection of human health. Long-term management for the protection of human health, and the health of other wildlife species, must include a better understanding of the causes for the high rates of Hg bioaccumulation within compartments of the Everglades.

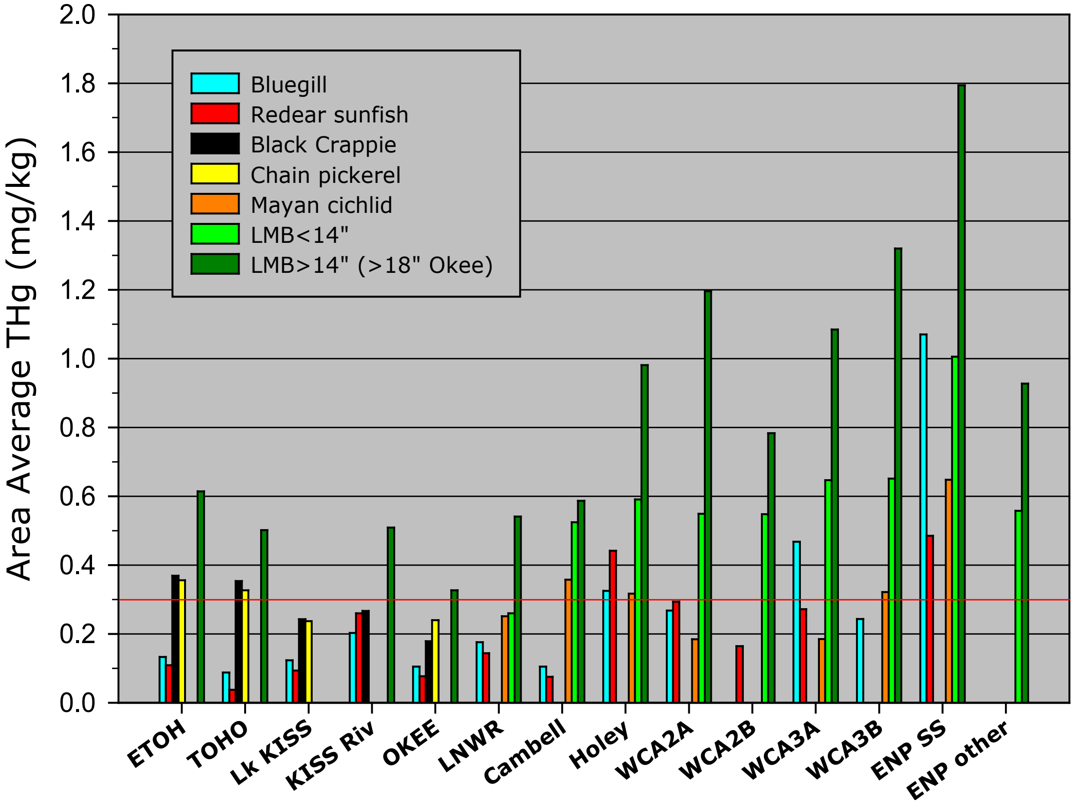


Figure 3B-6. Average THg concentration for select sport fish, including two size classes of largemouth bass (LMB) collected for human health risk assessment from water bodies from the Greater Everglades including, from north to south, East Lake Tohopekaliga (ETOH), Lake Tohopekaliga (TOHO), Lake Kissimmee (Lk KISS), Kissimmee River (KISS Riv), Lake Okeechobee (OKEE), Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR) or WCA-1, Campbell Public Use Area (Campbell), Holeyland Wildlife Management Area (Holey), WCA-2A, WCA-2B, WCA-3A, WCA-3B, Shark River Slough (ENP SS), and other ENP areas (ENP other). The 0.3 ppm USEPA MeHg criterion is indicated in red.

MERCURY, SULFUR AND DISSOLVED ORGANIC CARBON

Methylmercury (MeHg) is a highly toxic and bioaccumulative form of Hg (Mergler et al., 2007), commonly produced by naturally occurring sulfate-reducing bacteria (SRB) enzymatically catalyzing the methylation of inorganic Hg in anaerobic zones of water bodies. Elevated MeHg levels in Everglades fish represent a risk to anglers and wildlife (FDOH, 2011; Frederick and Jayasena, 2010; Rumbold et al., 2008).

In many respects, the Everglades is an optimal environment for Hg methylation because: (1) it is a shallow wetland area with anoxic conditions in organic-rich soils, (2) the deposition rate of inorganic Hg from the atmosphere is high, (3) it has high dissolved organic carbon (DOC) concentrations that hold Hg in solution and can enhance methylation, (4) pH is near neutral, (5) water temperature is high, and (6) it receives high sulfate loads to drive microbial sulfate reduction (Orem et al., 2011).

MeHg production by SRB and MeHg levels in fish are dominantly controlled by factors related to inputs of Hg, sulfate, and DOC to aquatic ecosystems (Gilmour, 2011). Control of these represents an opportunity to reduce MeHg levels in Everglades fish. The feasibility of reducing levels of these inputs to the Everglades is examined below.

MERCURY

The MeHg production rate is directly related to the rate of inorganic Hg deposition to the surface of a water body (2007 SFER – Volume I, Appendix 3B-2; Harris et al., 2007b). Mercury is deposited from the atmosphere to land and water via one of two pathways. Either as wet deposition, which includes dissolved Hg and particulate Hg scavenged from the atmosphere during rainfall events; or as dry deposition, which includes particulate Hg removed from the atmosphere by gravitational settling and particle impaction, and gaseous Hg (predominantly reactive gaseous mercury or RGM) reacting with surfaces. Hg sourced to the Everglades is almost entirely (greater than 95 percent) from wet and dry atmospheric deposition (Guentzel et al., 1998, 2001; Landing et al., 1995; Pollman et al., 1995; Stober et al., 1996, 1998, 2001).

About two-thirds of the Hg in the atmosphere distributed globally is from sources associated with human activities (e.g., coal-fired power plants, smelting, incineration of wastes, and cement production). Hg wet deposition to the Everglades consistently ranks among the highest in the continental United States. Hg atmospheric deposition is now predominantly from global (international) rather than local (within Florida) sources (Pollman et al., 2007).

Deposition modeling conducted by a number of researchers suggests that sources originating outside North America are the dominant sources of Hg deposited in the Everglades. For example, research by Seigneur et al. (2003) based on two nested chemical transport models (global and continental scale) suggest that only 17 percent of the total mercury deposition in the Everglades originates from within North America, with the largest contributions coming from Asia (29 percent). Subsequent modeling reported by Carlton et al. (2004) using the same model but at a finer scale of spatial resolution (20 km by 20 km compared to a 100 km by 100 km grid used by Seigneur et al. (2003) yielded North American contributions of 8 percent for the Everglades. More recently, modeling conducted by using REMSAD coupled with inputs averaged from three different global scale models indicated approximately 90 percent of the Hg deposited in the Everglades originates outside the REMSAD model domain (which includes the continental United States and parts of Mexico and Canada) (USEPA, 2008; D. Atkinson, personal communication, May 2009). Clearly, significantly reducing mercury sources to the Everglades will require reduction of global Hg sources via mechanisms such as international treaties; this may not be feasible in the short term.

DISSOLVED ORGANIC CARBON

DOC is a substrate and energy source for SRB, which methylate inorganic Hg. Further, DOC, along with sulfide, is the main control on inorganic Hg partitioning and bioavailability through formation of DOC-Hg complexes (Aiken et al., 2011; Gilmour 2011). The highly organic soils of the Everglades formed over thousands of years under conditions where organic matter production exceeded decomposition (Wright and Snyder, 2009; Orem et al., 2011). Considering the stores of organic matter in Everglades soils, there seems to be little possibility of reducing DOC in the Everglades so as to reduce Hg methylation rates to acceptable levels without fundamentally changing the ecosystem.

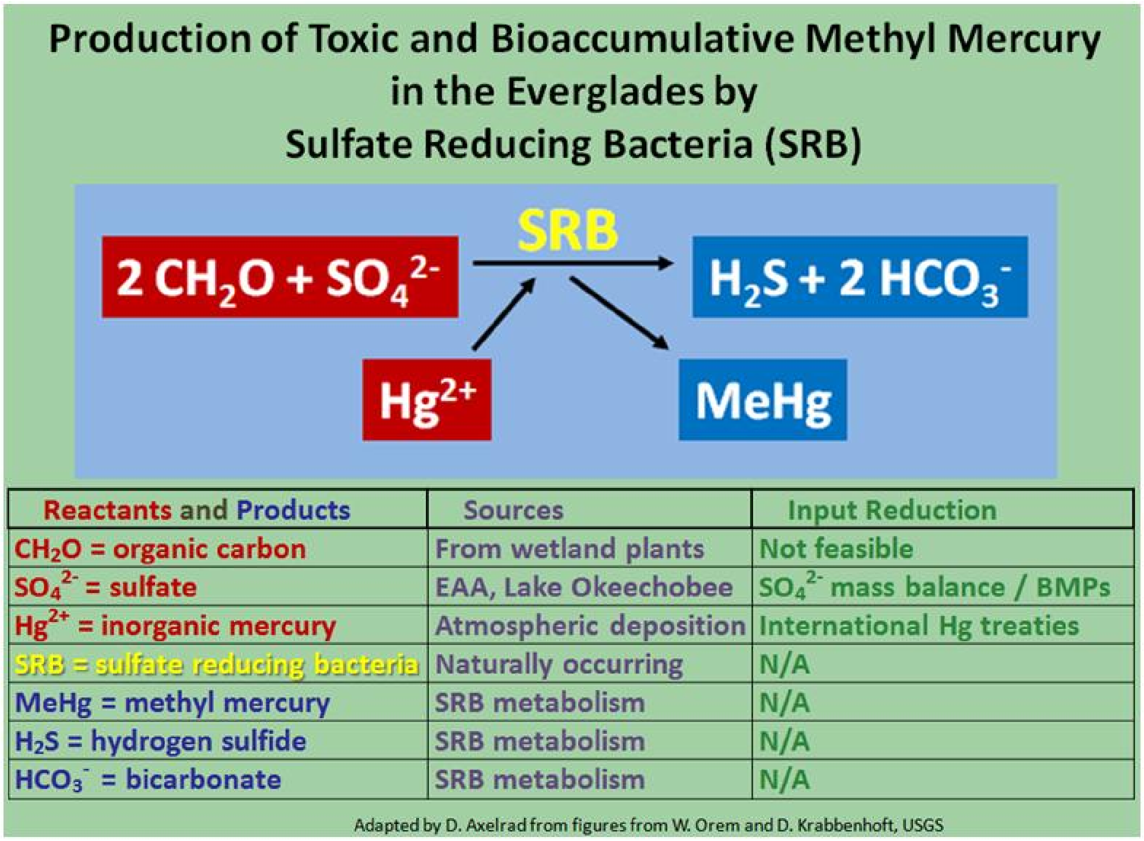
However, there are two considerations regarding the potential use of DOC input management to reduce Everglades MeHg levels. The Central and Southern Florida Flood Control Project (C&SF Project) that was largely responsible for the dikes and levees and helped establish the Everglades Agricultural Area (EAA) arguably altered the organic carbon budget of the Everglades. Whereas, historically, water flowing south from Lake Okeechobee moved as sheetflow across the landscape, water regulation in the EAA necessary for crop management has introduced a vertical drainage component — percolation — through organic soils, that has fundamentally altered the geochemistry of waters leaving the EAA. This altered geochemistry almost certainly includes the introduction of higher concentrations of DOC. Further, aromatic DOC produced via peat oxidation in the EAA may enhance the rate of Hg methylation, possibly due to inorganic Hg being partitioned into aromatic DOC and made more bioavailable for methylation [D. Krabbenhoft, United States Geological Survey (USGS), personal communication, 2011]. Scheidt and Kalla (2007) concluded that Everglades areas strongly influenced by EAA storm water have higher DOC concentrations and this EAA-sourced DOC is more reactive with Hg than DOC in more pristine areas of the Everglades.

SULFATE

Sulfate is a terminal electron acceptor that allows sulfate-reducing bacteria (SRB) to metabolize organic matter and methylate inorganic Hg. SRB can compete for organic carbon when electron acceptors that yield more energy than sulfate (i.e., oxygen, nitrate, manganese, and ferrous iron) are unavailable (Orem et al., 2011). Everglades soils exhibit rapid loss of oxygen with depth due to high concentrations of organic carbon and microbial oxygen demand. Nitrate, manganese, and ferrous iron concentrations are too low in Everglades soils to support significant denitrification and manganese and iron reduction, and so do not greatly inhibit microbial sulfate reduction (Orem et al., 2011). Sulfate is sourced to the Everglades via the EAA and Lake Okeechobee; input estimates range from 40 to 90 metric tons per year (mt/yr). Presently, sulfate concentrations in the ecosystem range up to 70 mg/L; historically, it is believed sulfate levels in much of the Everglades were relatively low (approximately 0.1 mg/L).

Significantly reducing Hg sources to the Everglades which are dominantly from international sources is not achievable in the short term, nor would control of organic carbon in the Everglades be easily achieved. Reducing sulfur loading to the Everglades from agricultural activities (e.g., agricultural Best Management Practices) may be the most practical means of lowering MeHg levels in Everglades fish in the foreseeable future (Orem et al., 2011). The Hg–DOC–sulfate reaction mediated by SRB and producing MeHg is shown in **Figure 3B-7**.

Recent efforts have attempted to determine an EAA sulfur mass balance to quantify sources and sinks, and identify opportunities to reduce sulfur input to and MeHg levels in the Everglades. As shown in **Table 3B-3**, three different estimates are presented although none of these are considered adequate for managing Everglades MeHg levels by means of identifying opportunities for reducing sulfur inputs. Information is lacking on the proportion of the EAA represented by highly organic soils, sulfur levels in EAA soils, the agricultural sulfur application rate, the proportion of sulfur in EAA soils that originated from agricultural application, and sources of sulfur to Lake Okeechobee, among others. Research to produce accurate estimates of EAA, Lake Okeechobee, and Everglades sulfur mass balances is the first step toward determining if reducing sulfur loading is feasible for reducing MeHg levels in the Everglades.



Production of Toxic and Bioaccumulative Methyl Mercury in the Everglades by Sulfate Reducing Bacteria (SRB)

$$2\,CH_2O + SO_4^{2-} \xrightarrow{SRB} H_2S + 2\,HCO_3^-$$

Reactants and Products	Sources	Input Reduction
CH_2O = organic carbon	From wetland plants	Not feasible
SO_4^{2-} = sulfate	EAA, Lake Okeechobee	SO_4^{2-} mass balance / BMPs
Hg^{2+} = inorganic mercury	Atmospheric deposition	International Hg treaties
SRB = sulfate reducing bacteria	Naturally occurring	N/A
MeHg = methyl mercury	SRB metabolism	N/A
H_2S = hydrogen sulfide	SRB metabolism	N/A
HCO_3^- = bicarbonate	SRB metabolism	N/A

Adapted by D. Axelrad from figures from W. Orem and D. Krabbenhoft, USGS

Figure 3B-7. Sulfate-reducing bacteria (SRB) mediated methylmercury (MeHg) production in the Everglades.

Table 3B-3. Three estimates of annual sulfur inputs to and outputs from Everglades Agricultural Area (EAA) canals.

Reference	Schueneman, 2001; Wright et al., 2008	Corrales et al., 2011	Gabriel et al. 2010		
			Moderate Year	Wet Year	Dry Year
EAA area (hectares)	222,582	290,600	280,466	280,466	280,466
Soil oxidation rate (centimeter per year)	1.3	1.4	1.3	1.3	1.3
Sulfur concentration in EAA soils (percent)	0.55	0.35	0.37	0.37	0.37
Sulfur input to EAA metric tons per year (mt/yr)					
EAA soil oxidation	54,127	49,169	30,646	30,646	30,646
Agricultural sulfur applications[1]	3,561	11,775	6,286	6,286	6,286
Lake Okeechobee	26,689	35,217	31,057	40,626	28,494
Levees		5,858			
Groundwater		4,055			
Atmospheric deposition, wet	1,621	4,229	3,864	2,861	3,295
Atmospheric deposition, dry			529	487	508
Total Sulfur input to the EAA (mt/yr)	**85,998**	**110,303**	**72,382**	**80,906**	**69,229**
Sulfur Loss					
EAA crop harvest (mt/yr)	24,341	23,182	25,500	25,500	25,500
Sulfur output to EAA canals and input to EPA (mt/yr)	**61,657**	**87,121**	**46,882**	**55,406**	**43,729**

[1] Assumed agricultural sulfur application rate: Schueneman and Wright 16.0; Corrales et al. 37.0; Gabriel et al. 22.4 kg/hectare/yr

Table from B. Donner and D. Axelrad, FDEP

INFORMATION NEEDS AND RECOMMENDATIONS

- Accurate estimate of EAA, Lake Okeechobee, and Everglades sulfur mass balances, including quantification of agricultural application of sulfur to soils in the EAA and applications previously not measured [e.g., addition of gypsum ($CaSO_4$) for EAA soil erosion control].
- Oxidation rate of EAA soil organic sulfur for dry and submerged soil conditions.
- Relative contributions of natural and agricultural sulfur to organic sulfur in EAA soils.
- Time for sulfur release from EAA soils to reach a steady-state value after cessation of agricultural applications of sulfur.
- Sulfur concentration and soil depths assessment across the EAA.
- Groundwater (connate seawater) sulfur inputs to the EAA and EPA.
- High-resolution spatial sampling framework implementation over various time periods to capture particular meteorological conditions (i.e., dry, wet, and intermediate seasons) with more frequent measurement of sulfur flux occurring at water structures in the Everglades to better determine sulfur inputs to various areas of the ecosystem (Gabriel, 2009).

- Modeled sulfate concentrations across the EPA as a function of (1) reduced sulfate loading and (2) the response of Hg levels in Everglades fish to sulfate concentration, which will enable an estimation of sulfate load reduction to the ecosystem necessary to achieve desired fish Hg reductions.
- Review options for Everglades hydropattern restoration to minimize sulfur effects:
    - Delivery of sulfate-contaminated water through the Everglades canal system to protected areas such as the ENP and WCA-1 (areas that previously did not have elevated levels of sulfur) may cause environmental harm. In contrast to transporting water though the canal system, moving water as sheetflow over expansive marsh areas may allow for sequestration of reduced sulfur in soils and thus reduce the sulfate loads delivered to these protected areas (Orem, 2007).
    - Current management practices have altered the Everglades natural drying and rewetting cycles. Soil drying results in the oxidation of reduced sulfur to sulfate. Upon rewetting, pulses of sulfate reduction and MeHg production occurs (Orem, 2007).
- Review potential effects of Aquifer Storage and Recovery on Everglades sulfur loading (Krabbenhoft et al., 2007).
- Estimate the effectiveness and cost of sulfur Best Management Practices for the EAA and the Lake Okeechobee Watershed.
- Continue to evaluate effectiveness of agricultural sulfur application for enhancing sugarcane and vegetable crop production.
- Research alternatives to sulfur application to EAA crops so as to maintain adequate crop production rates while minimizing environmental impact (e.g., alternative means of lowering soil pH).

RESEARCH IN PROGRESS

MERCURY WET DEPOSITION TO THE EVERGLADES

Dry deposition of Hg is very difficult to collect and measure, so routine monitoring of the flux of atmospheric Hg in the environment has almost exclusively focused on wet deposition. The most extensive network for monitoring the wet deposition of Hg both in the Everglades, and across the United States is the Mercury Deposition Network (MDN; http://nadp.sws.uiuc.edu/mdn). Results from the MDN show that wet deposition fluxes in the Everglades consistently rank among the highest in the continental United States. This is illustrated by conducting an analysis of annual Hg wet deposition fluxes for all MDN sites (analysis restricted to sites and years with valid observations exceeding 46 weeks/year out of the possible 52).

These data indicate that wet deposition Hg flux to one of the four Everglades MDN sites (FL04, FL11, FL34, FL97 – see **Figure 3B-8**) was the highest recorded for any MDN sites nationally for 11 of the 14 sampling years between 1997 and 2010 (**Table 3B-4**). Further, for the 3 years out of 14 where Everglades MDN sites did not have the highest Hg deposition nationally, only one of the four Everglades MDN sites had been operational, and that one site was ranked either second or third highest in Hg deposition nationally.

Site FL11 located at the Beard Research Center in Everglades National Park has among the longest periods of record in the MDN network. Hg wet deposition at this Everglades National Park site ranked highest nationally in 7 of the 14 consecutive MDN sampling years to 2010, and it has never ranked below third. In only one year did any of the four Everglades sites rank below ninth (site FL97 in 2009; rank = 11).

Table 3B-4. Ranking of Everglades Mercury Deposition Network (MDN) sites with respect to annual THg deposition fluxes (wet only) for all MDN sites within a given year, with valid data reported for 47 or more weeks (see **Figure 3B-8** for station locations). A ranking of "1" indicates highest measured THg flux in the national MDN network. Absence of ranking indicates the MDN site was not operational or data were inadequate.

Year/Site	Total Number of U.S. MDN Sites	FL04	FL11	FL34	FL97
1997	15		1		
1998	21		1		
1999	24		1		
2000	33	2	1	6	
2001	43		2		
2002	41	1	2		
2003	57	1	3	9	
2004	55		3		
2005	68		3		
2006	70		1		
2007	72		1	8	2
2008	85		2	5	1
2009	97		1	8	11
2010	87		3	1	2

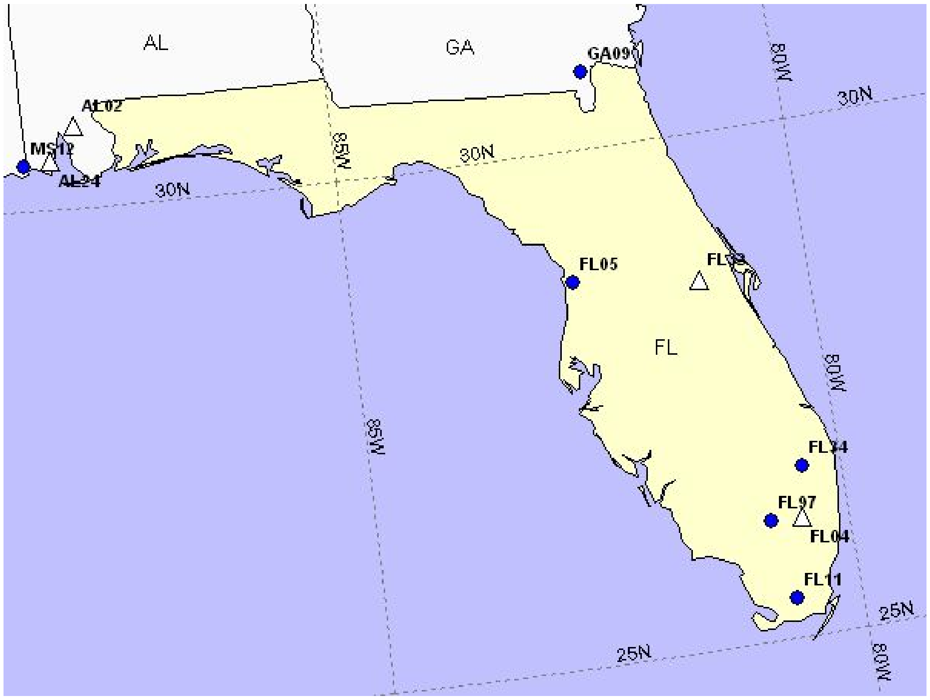


Figure 3B-8. Location of MDN sites in Florida.

As first noted by Guentzel et al. (2001), the large wet-deposition THg fluxes in South Florida reflect the combination of relatively high volume-weighted mean (VWM) Hg concentrations in rainfall, coupled with the relatively high rainfall totals characteristic of South Florida (see **Figures 3B-9** and **3B-10** for spatial plots of VWM concentrations and wet deposition fluxes respectively across the continental U.S. in 2010).

Guentzel et al. (2001) suggested that local (within Florida) emission sources of reactive gaseous mercury (RGM) and particulate mercury could account for only 30 to 46 percent of the summertime Hg wet deposition fluxes, which is the period when the largest fraction (70-90 percent) of Hg wet deposition occurs throughout Florida. The question thus arises why wet deposition fluxes of Hg in South Florida are so high.

Guentzel et al. (2001) further suggested that the tall convective storms characteristic of South Florida during the summer may be responsible. These tall convective storms can access and scavenge comparatively high concentrations of RGM in the free troposphere, thereby producing summertime rain Hg concentrations that are elevated compared to other regions in the U.S. where convective storms are of lesser height and thus do not penetrate into the free troposphere to the same extent. Subsequent aircraft measurements conducted in the vicinity of South Florida by Sillman et al. (2007) demonstrated that concentrations of RGM increase with altitude from 10 picograms per cubic meter (pg/m^3, near ground) to 250 pg/m^3 (approximately 3 km altitude), thus substantiating the Guentzel et al. (2001) hypothesis. Selin and Jacob (2008) have also suggested deep scavenging of the free troposphere by convective storms as explaining high wet deposition fluxes of Hg during the summer in the southeast U.S.

Latitudinal and seasonal variations in key oxidants involved in the conversion of gaseous elemental mercury (Hg^0) to RGM may also be important (Selin and Jacob, 2008), although the role is less clear. This is relevant in that Hg^0, the dominant mercury species in the atmosphere (>95 percent), has a half-life of approximately 6–12 months in the atmosphere whereas RGM deposits to land or water in a matter of days.

Modeling of RGM dynamics in the marine boundary layer (MBL) conducted by Holmes et al. (2009) suggests that 35 to 60 percent of the RGM present in the MBL derives from oxidation of Hg^0 with bromine (Br). More recent modeling was conducted by Holmes et al. (2010) with the global transport and deposition model GEOS-Chem to compare the roles of the hydroxyl radical (OH) and ozone (O_3) versus bromine (Br) as oxidants for Hg^0.

The results show that while modeling with both suites of oxidants can reproduce overall Hg deposition patterns observed at northern latitudes, inclusion of Br is necessary to simulate polar atmospheric Hg depletion events. On the other hand, because Br concentrations are lower at subtropical altitudes, modeling with Br alone is not capable of reproducing the elevated wet deposition fluxes of Hg observed in the southeast.

Overall, these results suggest that the high wet deposition fluxes of Hg observed in the southeast U.S. and in particular in South Florida, are driven by tall convective storm scavenging of RGM from the free troposphere, and possibly as a secondary factor by latitudinal variations in the Hg^0 oxidants, OH and O_3.

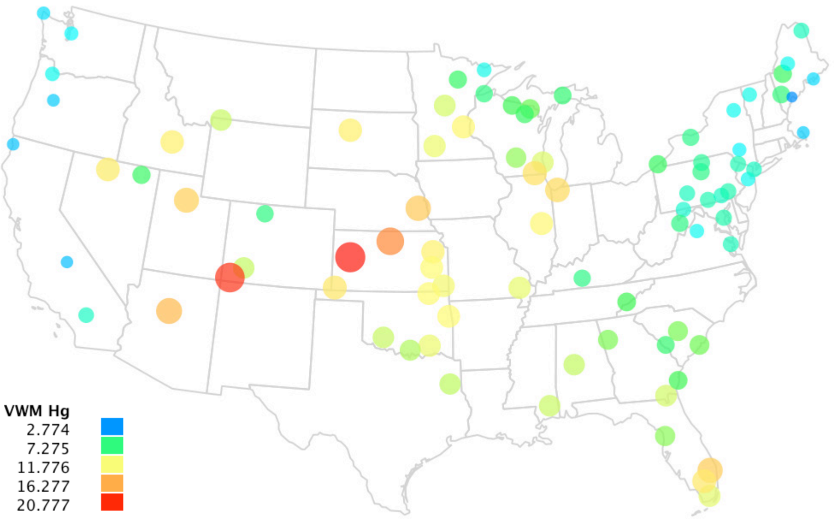


Figure 3B-9. Annual volume weighted mean concentrations for THg in wet deposition for sites monitored by the MDN in 2010. Only sites with valid observations for 50 or more weeks were included in the analysis. Concentrations in nanograms per liter (ng/L).

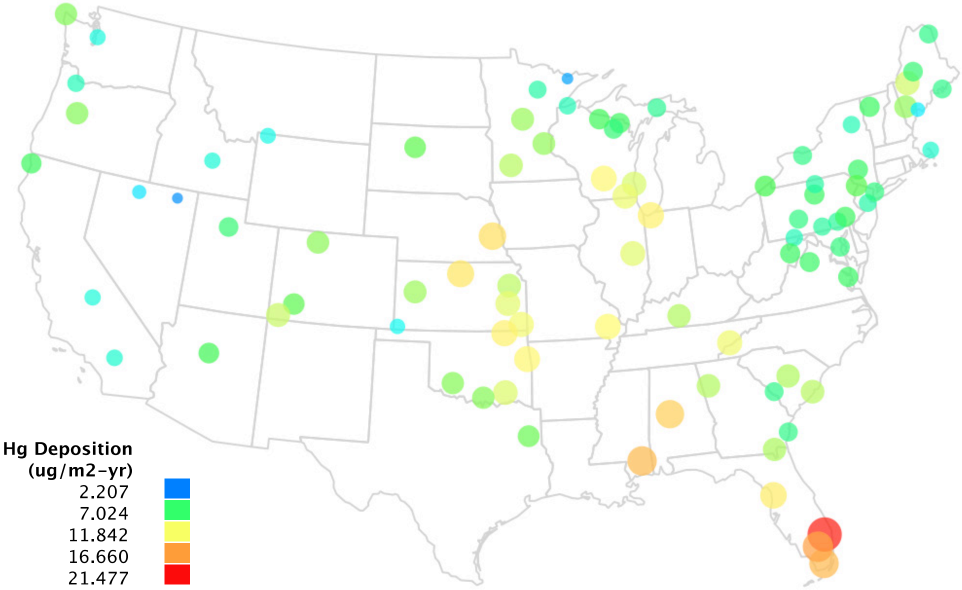


Figure 3B-10. Annual wet deposition fluxes of THg in wet deposition sites monitored by the MDN in 2010. Only sites with valid observations for 50 or more weeks were included in the analysis. Fluxes are in micrograms per square meter per year (µg/m^2-yr).

IMPACTS OF SULFATE-ENRICHED STA-2 WATER DISCHARGED INTO WCA-2A

Studies have demonstrated that sulfate is entering the EPA in concentrations that greatly exceed background levels (2007 SFER – Volume I, Appendix 3B-3; Bates et al., 2001; Orem et al., 2010; Scheidt and Kalla, 2007). The highest average surface water sulfate concentrations in the EPA are observed in canal water in and just downstream of the EAA.

As part of restoration efforts to reduce phosphorus loading to the EPA while increasing water flow, EAA canal water is routed through STAs prior to being discharged into the Everglades. While STAs were designed to significantly reduce phosphorus loading to the EPA, they remove very little sulfate. STA removal efficiency for phosphorus is about 70 percent, but only about 10 percent for sulfate (Pietro et al., 2009).

Prior to the opening of STA-2 in July 2001, rainfall was the primary source of water to WCA-2A. After the completion of STA-2, treated water was released into the northwest corner of WCA-2A. This new discharge from STA-2 to WCA-2A resulted in an increase in mean WCA-2A water depth of 20 centimeters (cm), and an increase in WCA 2A hydroperiod from under five months to almost ten months per year. A preliminary study of the effects of this hydropattern restoration on northwestern WCA-2 showed positive effects of the STA-2 water discharge to WCA-2A including decreased soil loss due to oxidation, decreased surface water total phosphorus, increased relative abundances of low nutrient indicator species, and decreased relative abundances of high nutrient indicator species (Garrett and Ivanoff, 2008).

However, large increases in surface water conductivity and major ions, including sulfate, in northwestern WCA-2A were recorded as a result of STA-2 water discharges (Scheidt and Kalla, 2007; Garrett and Ivanoff, 2008). Prior to the opening of STA-2, sulfate concentrations ranged from 5 to 17 mg/L. The post-discharge average sulfate concentration in northwestern WCA-2A was 60.8 ± 1.0 mg/L which was consistent with sulfate levels found in the STA-2 discharge water. In addition, surface water ammonium and DOC concentrations increased significantly after STA-2 began discharging, while dissolved oxygen levels decreased at most monitoring stations (Garrett and Ivanoff, 2008). Porewater concentrations of sulfate, sulfide, total dissolved phosphorus, ammonium, and total dissolved Kjeldahl nitrogen in WCA-2A also increased at nearly all monitoring stations, while nitrate + nitrite concentrations decreased (Garrett and Ivanoff, 2008).

The USGS conducted studies of the impacts of the sulfate release into northwestern WCA-2A in August 2009 and February 2010. Sulfate levels of 60–80 mg/L at sites closest to STA-2 discharges were observed. Sulfide levels in porewater ranged up to 3,000 micrograms per liter (µg/L). These sulfide levels are insufficiently high at present to be toxic to sawgrass (*Cladium jamaicence*) (Li et al., 2009), but sulfide levels may increase over time if current levels of sulfate loading from STA-2 are sustained. In surface water, measurable sulfide (S^{-2} + HS^{-2} + H_2S) was present at most sites, with levels up to 300 µg/L (**Figure 3B-11**). At pH values of about 7, this translates to undissociated hydrogen sulfide (H_2S) levels of up to approximately 150 µg/L, which greatly exceeds the USEPA standard of 2 µg/L for surface water.

Other reduced sulfur species such as sulfite and thiosulfate were also present at high concentrations in surface water and porewater in northwestern WCA-2A. Nutrient (phosphate and ammonium) levels in porewater are elevated in the most sulfate enriched sites, suggesting the possibility of sulfate-induced nutrient remobilization via internal eutrophication. MeHg distributions in northwestern WCA-2A reflect a balance between stimulation of Hg methylation by sulfate and inhibition by sulfide. Overall, northwestern WCA-2A is similar geochemically to site F1 in eastern WCA-2A during the 1990s, except for much lower levels of total phosphorus in northwestern WCA-2A. Northwestern WCA-2A represents an important natural laboratory for examining the impacts of high sulfate loading on the Everglades.

Continued monitoring of northwestern WCA-2A will be of considerable interest to assist in understanding the costs and benefits of restoring the Everglades hydropattern using STA-derived water containing a myriad chemical species, including sulfate. Monitoring should be designed to test hypotheses, such as the effects of post-hydropattern restoration water quality and quantity on biogeochemical processes and aquatic plants and animals.

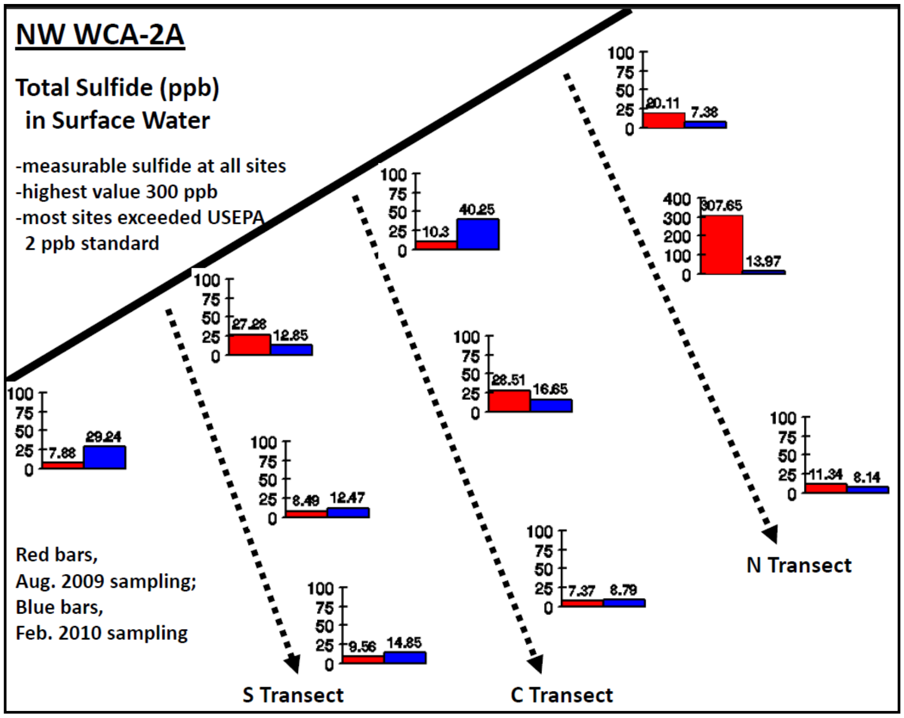


Figure 3B-11. Total sulfide in parts per billion (ppb) in surface waters of northwestern WCA-2A**.**

MERCURY AND METHYLMERCURY DISTRIBUTIONS IN EVERGLADES NATIONAL PARK

Beginning in 2008, the USGS and the National Park Service have collaborated to annually sample 76 sites across the ENP for sulfur, Hg, MeHg, and DOC (Krabbenhoft et al., 2010) (**Figure 3B-12**). The objective was to examine whether linkages exist between water quality changes in the ENP and canal water releases from the S-12 canal and the L-67 terminus along the northern ENP boundary. Since surface water releases generally follow Shark River Slough, the hypothesis was that several water quality indicators would be correlated with canal water releases.

At each site, surface water and mosquitofish (*Gambusia holbrooki*) were collected. Water samples were analyzed for general water quality parameters, THg, MeHg, sulfate, DOC, and specific ultraviolet adsorption. Fish were analyzed for THg and MeHg. Compared to the other surface water analytes, THg concentrations exhibited little variability across the ENP (**Figure 3B-13**, left panel). This low THg variability is likely due to the relatively uniform deposition pattern of atmospheric Hg that occurs across the Everglades, as evidenced by the MDN data (Krabbenhoft et al., 2008).

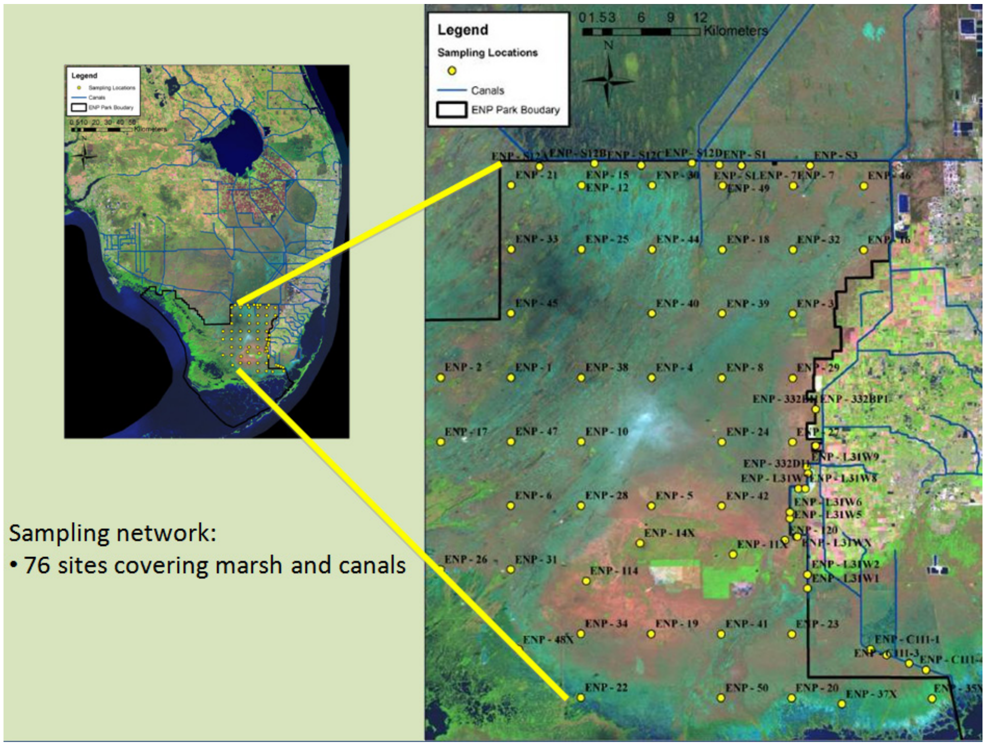


Figure 3B-12. ENP sampling network (figure from D. Krabbenhoft, USGS).

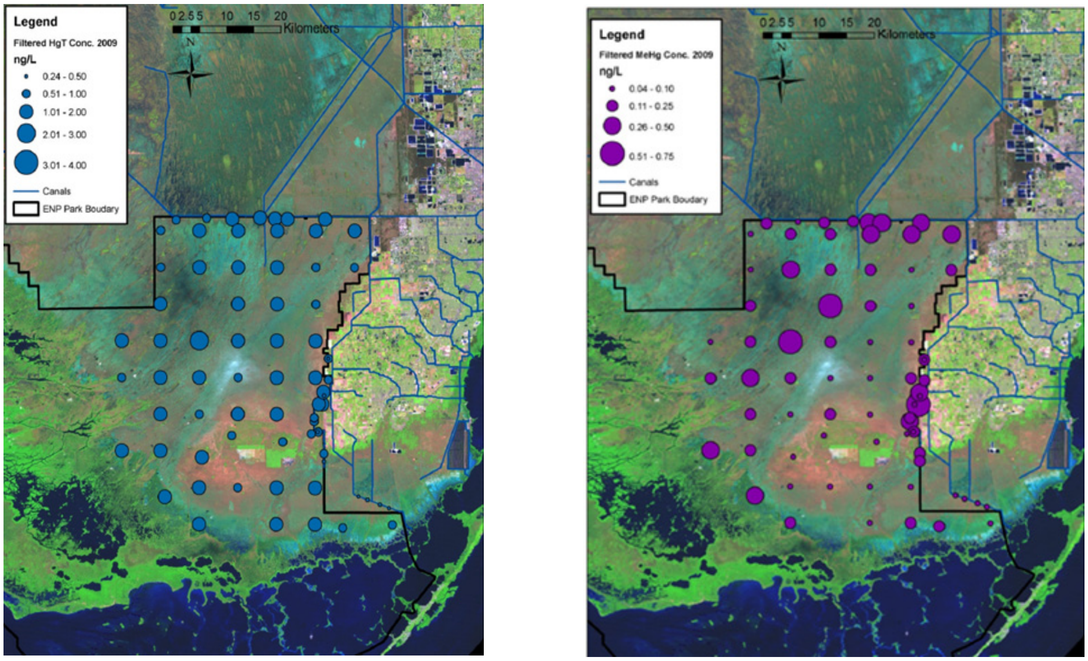


Figure 3B-13. ENP water column filtered THg (left panel) and filtered MeHg (right panel) from 2009 sampling (figures from D. Krabbenhoft, USGS).

Surface water MeHg concentrations showed a different pattern from THg (**Figure 3B-13**, right panel), with elevated levels [0.25–0.75 nanograms per liter (ng/L)] generally observed in Shark River Slough. Much lower MeHg concentrations (generally less than 0.1 ng/L) are seen in areas of the ENP where the presence of canal water is not apparent (determined by sulfate and fluoride markers), such as the Rocky Glade area. Samples collected from the S-12/L-31W region generally show MeHg concentrations between levels from Shark River Slough and Rocky Glade. Much like the results from northwestern WCA-2A, there is an optimum sulfate concentration at which maximal MeHg levels occur. However, the optimal sulfate level for the ENP appears to be much lower that what is observed for WCA-2.

For the ENP dataset, low sulfate concentrations (less than 1 mg/L) were associated with a substrate limitation response, which means Hg methylation by SRB was limited by the amount of available sulfate. High sulfate concentrations (greater than about 5 mg/L) were associated with an inhibition effect, presumably due to sulfide accumulation in porewater causing reduced Hg bioavailability. At mid-level sulfate concentrations (1–5 mg/L), MeHg production appears to be maximal in the ENP.

As observed elsewhere in the Everglades, MeHg in mosquitofish tissue exhibited a spatial pattern that agreed very closely with the aqueous MeHg results. Further, DOC concentrations also affected Hg methylation, possibly due to inorganic Hg being partitioned into DOC and made bioavailable for methylation. The effects of both sulfate and DOC concentrations on MeHg production in the ENP are shown in **Figure 3B-14**.

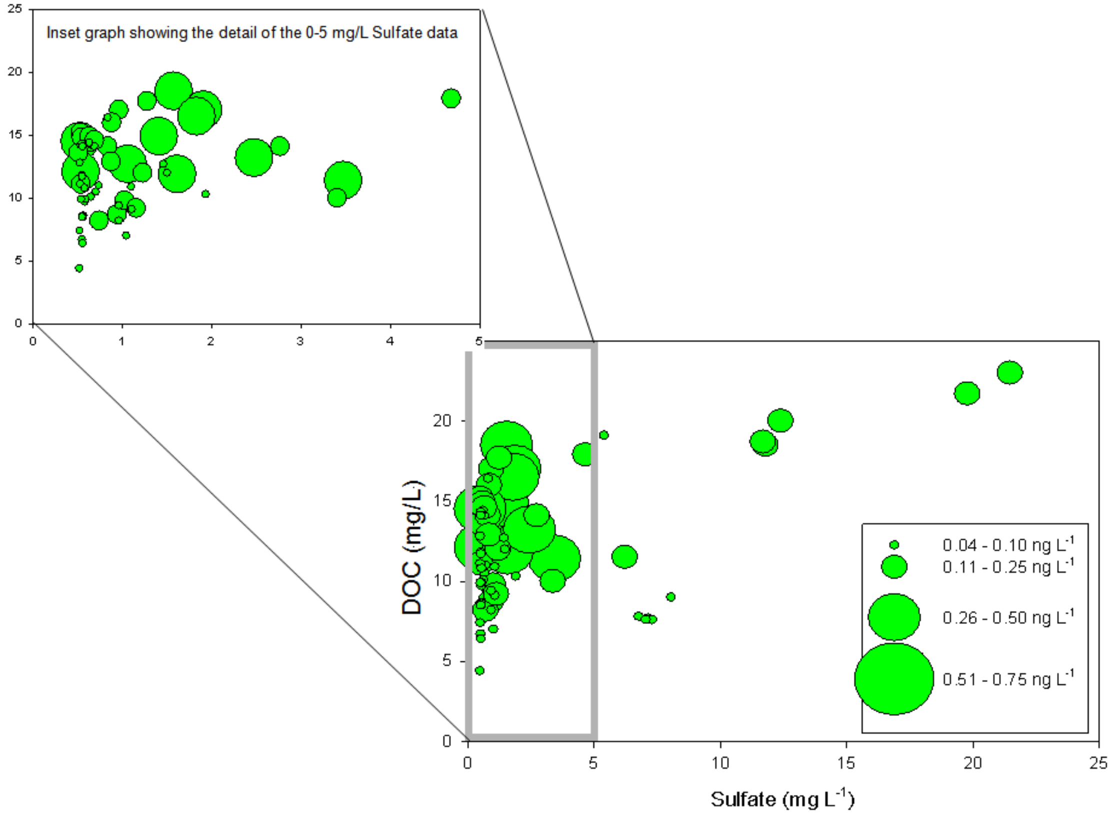


Figure 3B-14. Distribution of surface water MeHg versus sulfate and dissolved organic carbon (DOC) in the ENP (figure from D. Krabbenhoft, USGS).

Results from this study suggest that MeHg production in the ENP reacts to the loading and distribution of sulfate similarly to previously studied regions of the Everglades, but with a different range of optimum sulfate concentrations (compared with WCA-1, WCA-2, WCA-3, and Big Cypress National Preserve). The delivery of sulfate and DOC from the EAA and Northern Everglades by canals to the ENP has a profound effect on MeHg production; most of Shark River Slough shows elevated levels of MeHg compared to "background" (areas unaffected by canal water). Restoring water flow to the southern portions of the Everglades is a key goal of the restoration effort in South Florida, but environmental effects of surface water quality also need to be considered when making decisions regarding Everglades restoration.

SOIL pH, NUTRIENTS AND SULFUR USE IN EVERGLADES AGRICULTURAL AREA

When soils of the EAA were initially drained in the early 1900s to support crop production, soil pH values were much lower than at present. Most EAA organic soils historically had pH values ranging from 4.5 to 5.5. In contrast, although pH is spatially variable, the current typical pH range for the shallow muck soils of the EAA is 6.5 to 7.5.

EAA organic soils are underlain by hard limestone bedrock. With decreasing soil depth as a result of subsidence of drained soil, tillage operations for bed preparation, weed control, incorporation of fertilizers, and planting, there is increased transport of particles of calcium carbonate from the subsurface into the root zone of the surface soil. Additionally, carbonates dissolved in water can move up in the soil profile due to evapotranspiration, and are often deposited at or near the soil surface. Evidence of this effect can be observed by the white crust formed on the soil surface during dry weather conditions (Wright and Snyder, 2009).

The result of these factors is that EAA soil pH has increased through time, which exerts a negative effect on nutrient availability to crops, particularly for micronutrients (e.g., iron, manganese). Therefore, micronutrient availability to crops during the growing season is a concern. In addition, phosphorus availability to plants is strongly influenced by soil pH, and its availability is maximized when pH is between 5.5 and 7.5 (Wright and Snyder, 2009). Elemental sulfur (S) application to soils has the potential to reduce soil pH and increase nutrient availability and is often applied to crops for this purpose.

The University of Florida developed recommendations for elemental S use for sugarcane in the 1980s, which calls for application of S at a rate of 500 pounds per acre for sugarcane when soil pH exceeds 6.6. This does not, however, imply all growers are using elemental S, and application rates are often below the recommended 500 pounds per acre. Instead, higher micronutrient application or perhaps foliar applications are made. The trend of increasing EAA soil pH has renewed interest in investigating the efficacy of elemental S and to update the University of Florida's recommendations for sugarcane. Currently, recommendations of S use on vegetable crops are not available, but efforts are under way to investigate the efficacy of S amendments for leafy greens.

Numerous research trials are being conducted at different sites across the EAA to determine effectiveness of elemental S on increasing nutrient availability to crops and on enhancing yield. In general, no consistent response of sugarcane yield to elemental S is evident, although in a few cases yields were increased due to S application. Most of these sites, however, had soils with pH below 7.4. A more consistent response of enhanced crop yield to S addition is evident for soils having a pH greater than 7.4. These higher pH soils also had relatively higher extractable calcium levels. These sites are being investigated further to define measured responses in terms of soil test variables, and extractable calcium concentration may need to be included along with soil pH in a revised S recommendation.

For leafy greens crops, addition of elemental S at a rate above 500 pounds per acre failed to show any yield benefit, but lower rates did produce a significant yield response. Elemental S addition has been shown to increase nutrient availability in the short term (less than two months after application), which coincides with the shorter growing season of leafy greens. This increase in nutrient availability, including phosphorus and micronutrients (Ye et al., in press, 2010a, 2010b), by S application stimulated the growth and increased yields of romaine and iceberg lettuce.

In certain circumstances, a benefit may exist for elemental S use to enhance sugarcane and vegetable crop yield in the EAA. However, due to its relatively high cost, the economic viability of S additions is currently unclear.

EVALUATION OF SULFUR IMPACTS IN SOUTH FLORIDA MARSHES

Sulfate enrichments have been found to cause phosphorus release or internal eutrophication in aquatic ecosystems (Lamers et al., 2002; Smolders et al., 2006). A preliminary study suggested that elevated levels of sulfate may promote phosphate release from Everglades sediments (Axelrad et al., 2008). A three-year laboratory and field evaluation of sulfur impacts in South Florida marshes has recently been completed (DB Environmental, 2011; Dierberg et al., 2011). The principal objectives were to determine the effects of elevated water column sulfate levels on phosphorus cycling and vegetation health in natural wetlands and STAs. This study is detailed in the 2010 SFER – Volume 1, Appendix 3B-2, with results of the first set of lab incubations on soil slurries amended with sulfate. The porewater concentrations and phosphorus release from intact soil cores of STAs were presented in the 2011 SFER – Volume I, Chapter 3B. Three field mesocosm platforms were also introduced in the 2011 SFER. WY2012 results are presented here, including the results of chemical gradient analyses in Cell 1 of STA-2 and field-scale mesocosm experiments performed to assess the effects of elevated water column sulfate levels on phosphorus release from soils collected from unimpacted and impacted (with respect to S) South Florida wetlands.

Drought-Induced Effects on Surface Water and Porewater Chemistry in STA-2, Cell 2

The porewater soluble reactive phosphorus (SRP) concentrations were significantly elevated ($p \leq 0.05$) at all three regions (inflow, mid, and outflow) of the cell immediately after rehydration from the drought during June 2–19, 2009, as shown on **Figure 3B-15**. Correlations between SRP and total sulfide (TS) porewater concentrations were not significant ($p > 0.05$) for most of the station/deployment combinations, indicating sulfate reduction was not associated with the phosphorus mobilization during any of the three deployment periods. It is concluded that drought-induced effects, such as increased organic matter decomposition under aerobic conditions, were more important factors in mobilizing soil phosphorus than sulfate reduction.

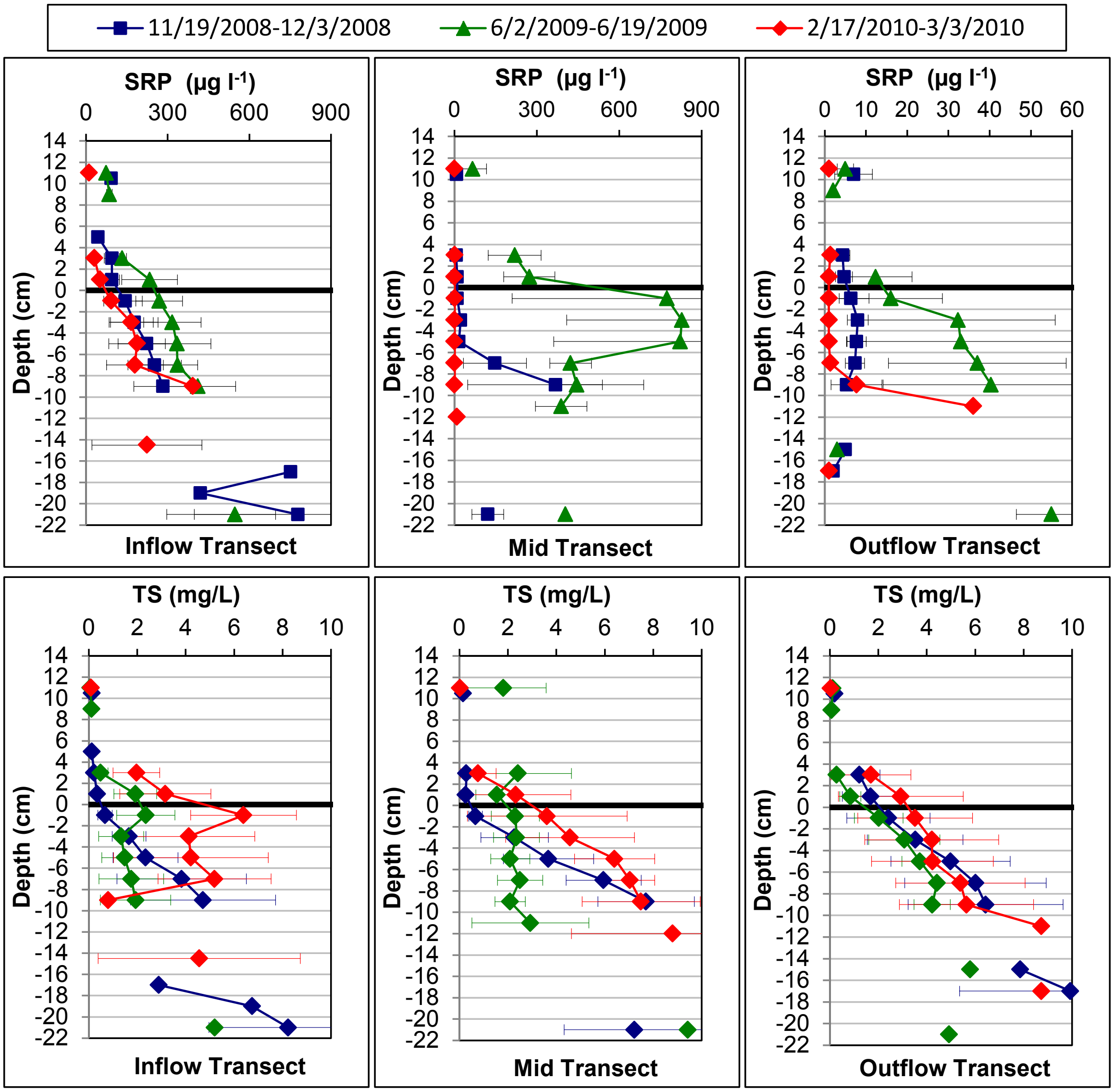


Figure 3B-15. Vertical profiles of soluble reactive phosphorus (SRP) and total sulfide (TS) concentrations from the bottom waters and soil porewaters at three transects in STA-2 Cell 1 on three occasions. Error bars represent ± 1 standard error of the mean of three stations along each transect. Note the different scale on the x-axis for SRP.

STA Mesocosms at Port Mayaca

A mesocosm platform at Port Mayaca has been deployed to test the effects of sulfate on P mobilization under a typical STA configuration [i.e., front-end emergent (cattail, *Typha* spp.) followed by back-end submerged (water nymphs, *Najas* spp.) communities]. An additional treatment of increasing the calcium and alkalinity concentrations in conjunction with sulfate amendments, is also being evaluated. Although porewater sulfide levels in the sulfate-amended mesocosms have gradually increased over time, to date the sulfate amendments (about 90 mg/L) to Lake Okeechobee source water have not impaired phosphorus removal performance of the STA process trains (**Figure 3B-16**). The addition of calcium and alkalinity slightly decreased the initial phosphorus concentration of the Lake Okeechobee raw water, but appears not to have further phosphorus removal effects within the treatment train.

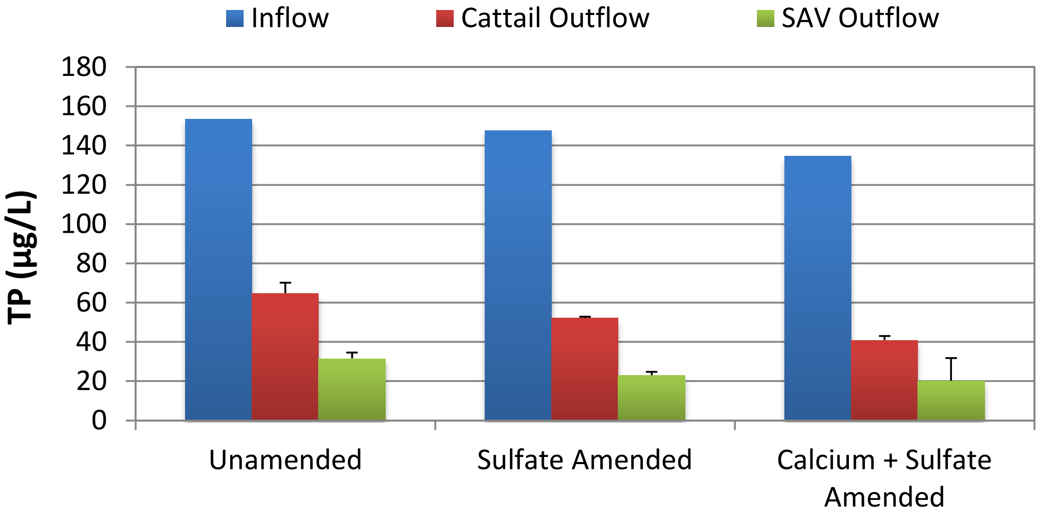


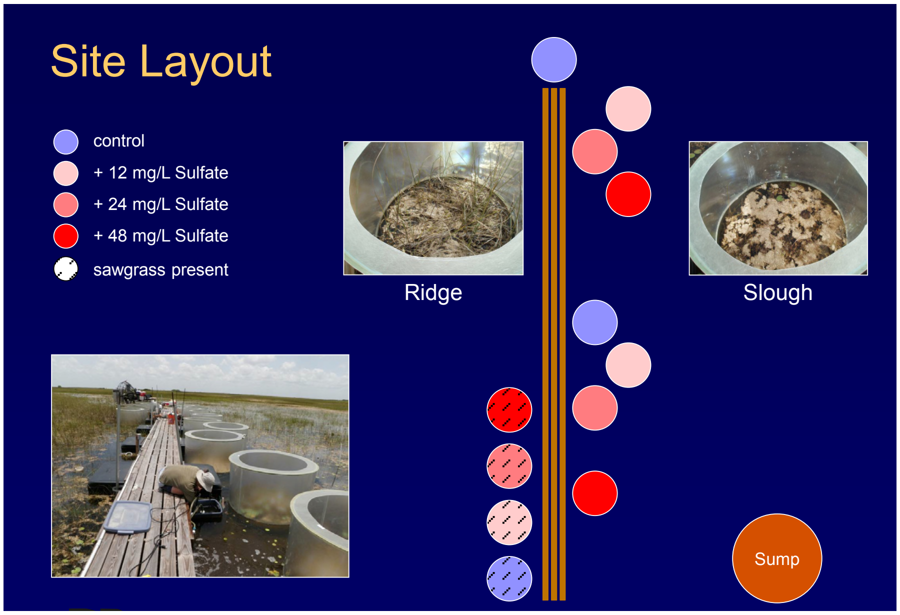
Figure 3B-16. Total phosphorus (TP) concentrations in the unamended and amended surface water of emergent (cattail) and submerged aquatic vegetation (SAV) mesocosms in the "STA" platform at Port Mayaca (May 15, 2009–May 18, 2011).

Mesocosm Enclosures within WCA-3A

An enclosure platform also has been deployed in a relatively "pristine" (low phosphorus, low sulfate) area of WCA-3A (**Figure 3B-17**). The enclosures are operated in a batch mode where outside surface water is exchanged with the inside water on a biweekly basis. A system of underwater ports and valves facilitate the water exchange and also minimize the hydrostatic "head" difference between the inside and outside of the enclosures.

After each water exchange, selected treatments received sulfate amendments to final concentrations of 12, 24, and 48 mg/L. The remaining triplicate set of enclosures was unamended (controls), but still received water exchanges. Amendments and water exchanges were initiated in July 2010. They were discontinued after March 3, 2011, due to low water levels, but were resumed in July 2011 after rehydration of the site at the beginning of the wet season.

Relative to the control enclosures, sulfate amendments have not caused an increase in surface (**Figure 3B-18**) or porewater (**Figure 3B-19**) phosphorus concentrations within any of the sulfate-amended enclosures during the first wet season, even though microbial sulfate reduction has resulted in an increase in porewater sulfide levels (**Figure 3B-19**). The platform will continue to be used to test for phosphorus mobilization and sulfide toxicity on the plant communities for a second wet season in 2011–2012.



Site Layout

● control

● + 12 mg/L Sulfate

● + 24 mg/L Sulfate

● + 48 mg/L Sulfate

▨ sawgrass present

Ridge

Slough

Sump

Figure 3B-17. Layout of the enclosures in WCA-3A receiving various sulfate amendments. Also shown are typical slough (floating periphyton) and ridge (floating periphyton interspersed with sawgrass and spike rush) vegetation communities.

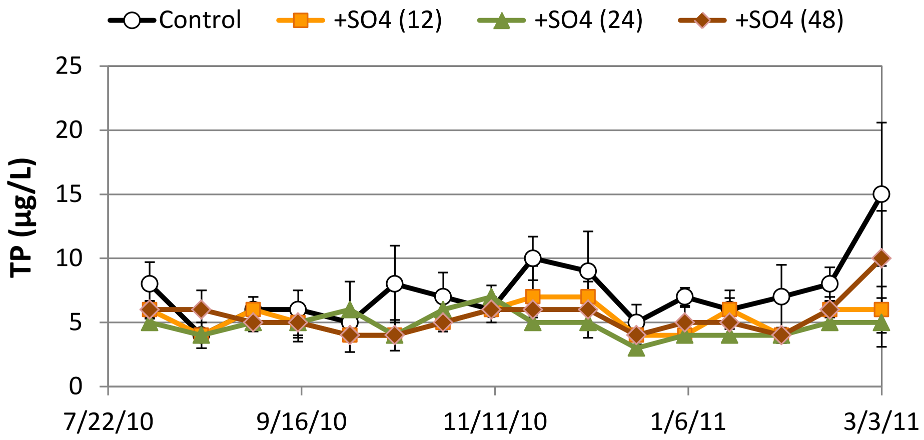


Figure 3B-18. TP concentrations in the surface waters of sulfate-amended and unamended enclosures during the first wet season in WCA-3A. Each data point represents the mean (± 1 standard error) of three replicate enclosures.

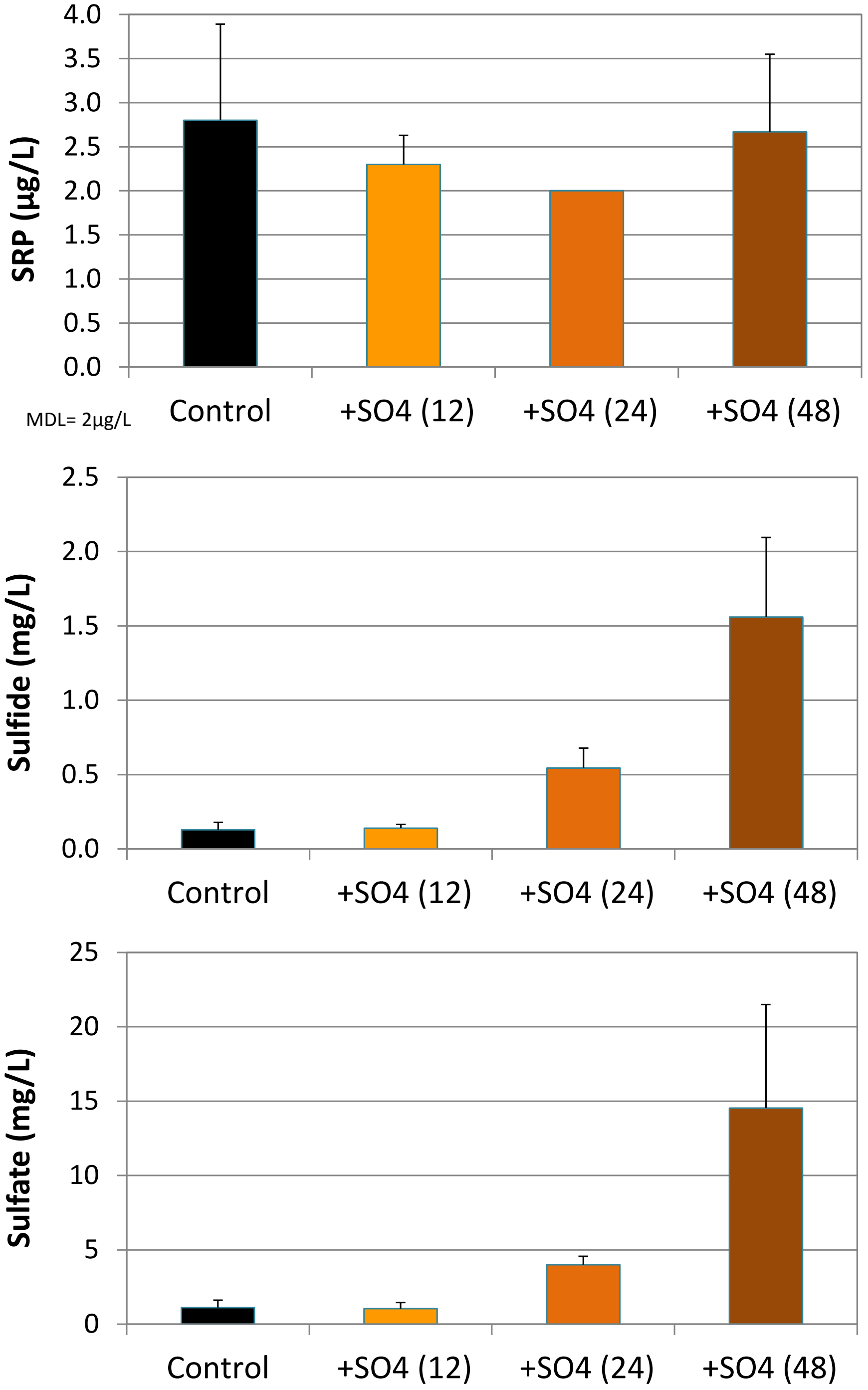


Figure 3B-19. Soluble reactive phosphorus (SRP), sulfide and sulfate concentrations in the porewaters of sulfate-amended and unamended enclosures after the first wet season in WCA-3A on March 3, 2011. The enclosures received biweekly exchanges with the outside water and amendments since July 22, 2010. Each data point represents the mean (± 1 standard error) of three replicate enclosures.

MERCURY MASS BUDGET AND EFFECT OF PHOTODEMETHYLATION

Studies on ecosystem-level Hg cycling (e.g., Hg mass budgets) are useful not only for understanding the magnitude of legacy Hg contamination, but also for predicting the fate of new Hg. By combining multiple datasets, two Hg mass budgets were constructed, with one for the newly deposited Hg during the 2005 wet season (loosely referred to as new Hg) and the other for the Hg present in the system (referred to as old Hg).

Mass Budget of New Mercury

The results of mass budget estimation for the newly deposited THg during the 2005 wet season (**Figure 3B-20**) suggest that soil is the largest sink for retaining THg, with around 80 percent of seasonally deposited Hg being retained in soil in all four management units (WCA-1, WCA-2, WCA-3, and ENP) (Liu et al., 2008, 2009). After deposition, THg redistribution into other ecosystem components was relatively small (e.g., 3.0 to 6.5 percent for floc in WCAs). Evasion and soil loss are two important pathways of Hg removal from the system, with 10 and 8 percent of the seasonally deposited THg being removed through these two pathways, respectively. Compared to evasion and soil loss, water outflow is a minor pathway of THg removal for all four management units, accounting for less than one percent of the THg deposited (Liu et al., 2011).

Mass Budget of Current Mercury

The mass budgets for the Hg present in the ecosystem at the time of sampling (November 2005) and for Hg inputs and outputs during the 2005 wet season suggest that a significant amount of THg has been stored in the Everglades, in particular in soil and floc (**Figure 3B-21**). The Everglades soil (top 10 cm layer) stored from 784 kilograms (kg) THg for WCA-1 to 7,381 kg THg for ENP, while the THg masses in floc can be up to 10–15 percent of soil THg amounts. The mass storage of THg in periphyton, macrophyte, and mosquitofish was small (1 percent or less). THg storage in soil greatly exceeded THg mass in any other component as well as any THg input or output (Liu et al., 2011).

The mass budget estimate for both new and current Hg carries a certain degree of uncertainty (Liu et al., 2011). For the newly deposited Hg during the 2005 wet season, the uncertainties associated with the predicated THg masses entering each ecosystem component after being deposited were about 20–30 percent, but could be higher (50–60 percent) for WCA-2. The uncertainties associated with the calculated mass storage of THg currently present in the ecosystem components were usually less than 30 percent for water and soil, but could be higher for the other ecosystem components (e.g., about 30–60 percent for floc). It is difficult to estimate uncertainty for Hg masses in periphyton and macrophyte as well as for Hg inputs (e.g., atmospheric deposition and water inflows) and outputs (e.g., water outflows, evasion, and soil loss) due to lack of data.

Effect of Photodemethylation on Methylmercury Mass Balance

Photodegradation of MeHg in water is one of the most important processes to the cycling of MeHg. Previous studies have shown that the reduction in MeHg caused by photodegradation could be as high as 80–83 percent of total MeHg discharged into downstream waters (Sellers et al., 1996). There is a lack of quantitative estimates for the role of photodemethylation in the cycling of MeHg in the Everglades.

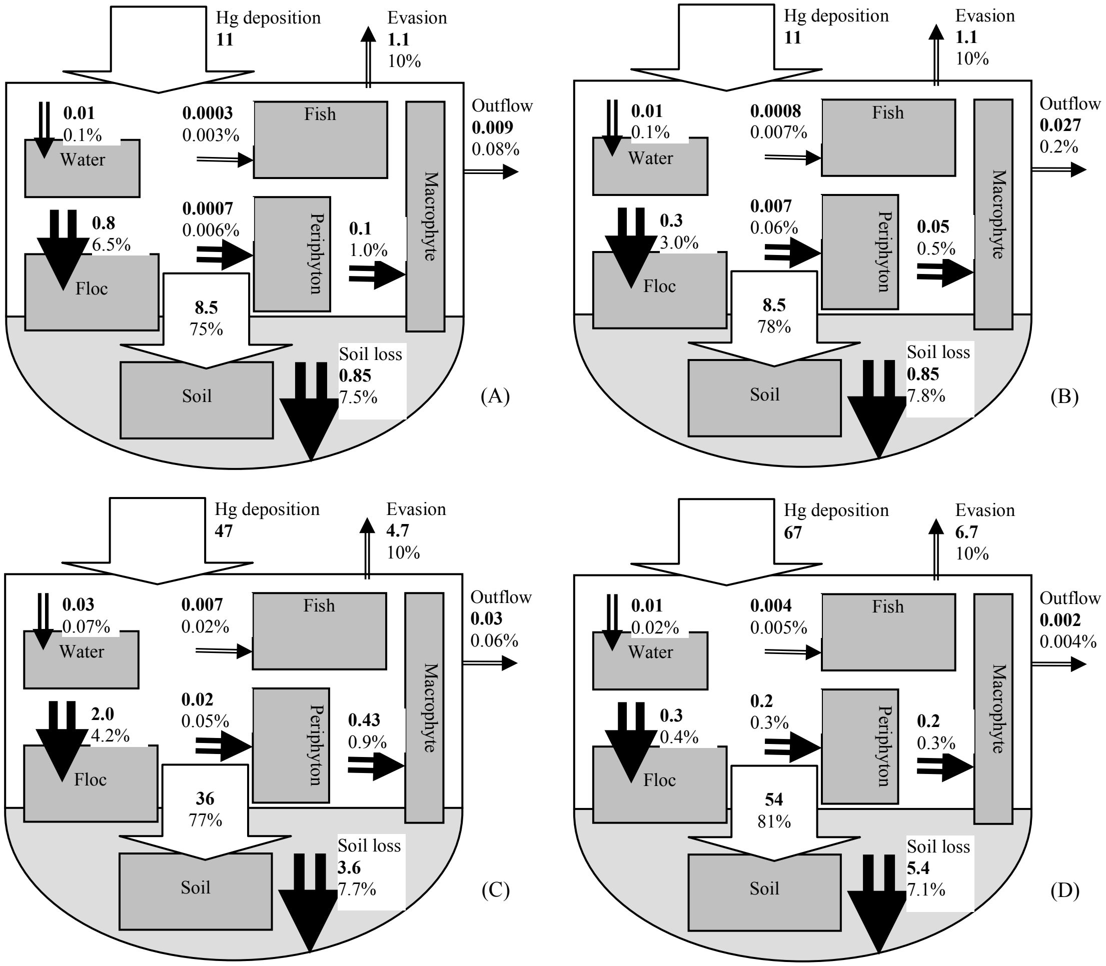


Figure 3B-20. Mass (kg) and fraction (%) of THg entering each ecosystem component or leaving the system after being deposited into the Everglades in the 2005 wet season for (A) WCA-1, (B) WCA-2, (C) WCA-3, and (D) ENP. [Note: Arrows do not project the actual transport pathways; mosquitofish was abbreviated to fish in the figure.]

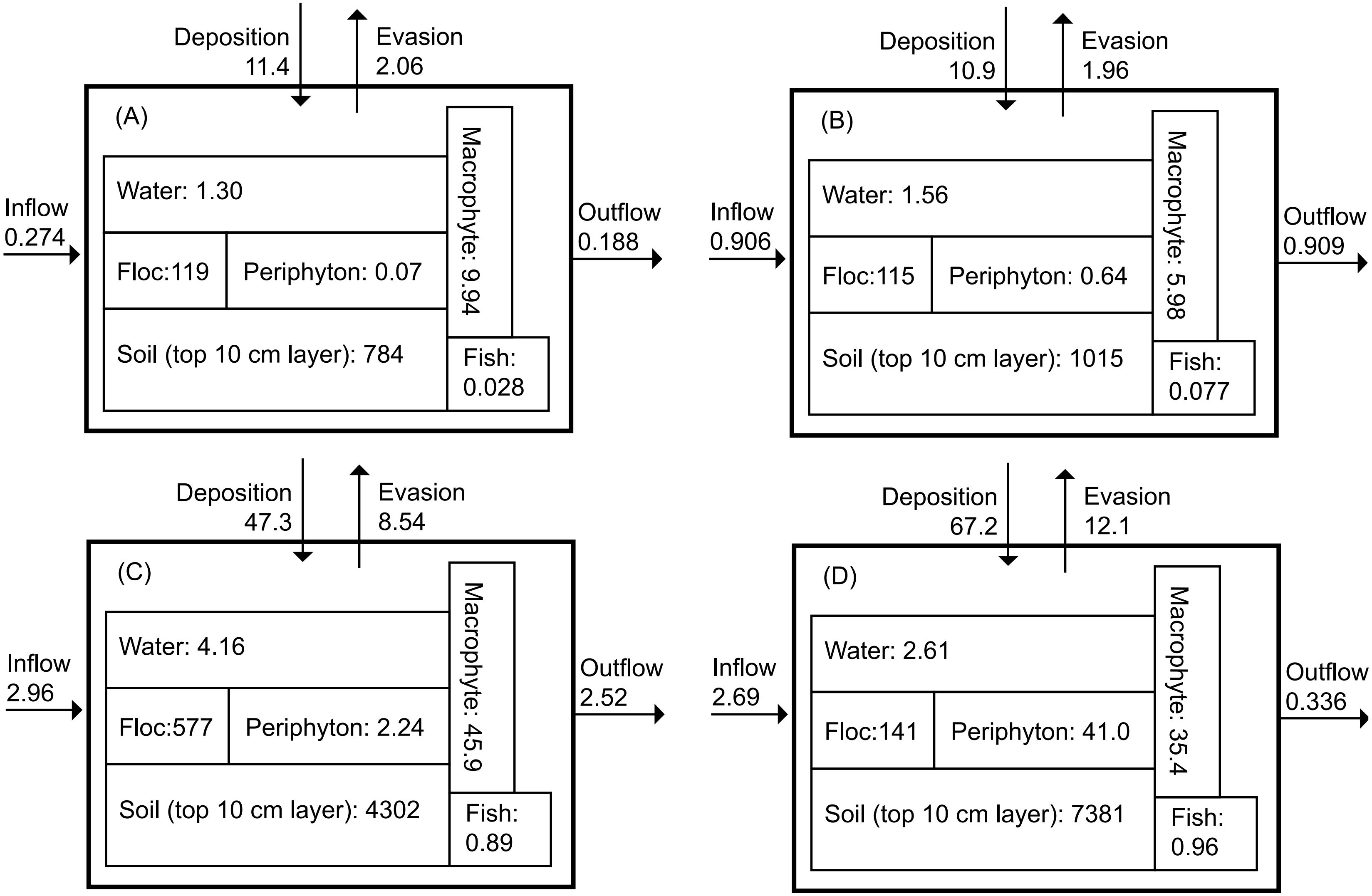


Figure 3B-21. Mass budget of THg present in (A) WCA-1, (B) WCA-2, (C) WCA-3, and (D) ENP. Values (kg) accompanying arrows depict THg inputs and outputs during the 2005 wet season. [Note: Numbers (kg) inside ecosystem components illustrate instantaneous THg mass storage at sampling (November 2005); mosquitofish was abbreviated to fish.]

A stable isotope (Me^{201}Hg) addition method was implemented to investigate the degradation of MeHg in Everglades surface waters. It was found that, while degradation of MeHg was not observed under dark conditions, the spiked Me^{201}Hg decreased quickly in Everglades water exposed to sunlight, with second-order photodegradation rate constants (k_D) being 9.45 ± 0.23 [$\times 10^{-3}$ square meters per Einstein (m^2 E^{-1})] for sterilized water and 10.87 ± 0.86 ($\times 10^{-3}$ m^2 E^{-1}) in unsterilized Everglades water. These results suggest that photodegradation is the key pathway of MeHg degradation in Everglades water.

To quantify the importance of photodemethylation in MeHg cycling, a model was developed to calculate the mass budget of MeHg in the Everglades (Li et al., 2010). As shown in **Figure 3B-22**, most of the MeHg produced from the newly deposited Hg during 2005 was compartmentalized to soil (63.2 percent). The photodegradation of MeHg represented a loss of 6.1 percent of the MeHg produced annually and, more significantly, the reduction of MeHg by this process accounted for about 31.4 percent of the MeHg diffused into the water column. These results indicate the importance of photodegradation in the biogeochemical cycling of MeHg in the Everglades. It should be noted that MeHg photodegradation is strongly influenced by the concentration and composition of dissolved organic matter (DOM). In addition to affecting light attenuation, DOM may control the cycling of such free radicals as hydroxyl radicals. Both processes are important in the photodegradation of MeHg. Since DOM concentration and composition in the Everglades vary spatially and temporally, photodemethylation could contribute more water MeHg reduction in some areas or during some seasons.

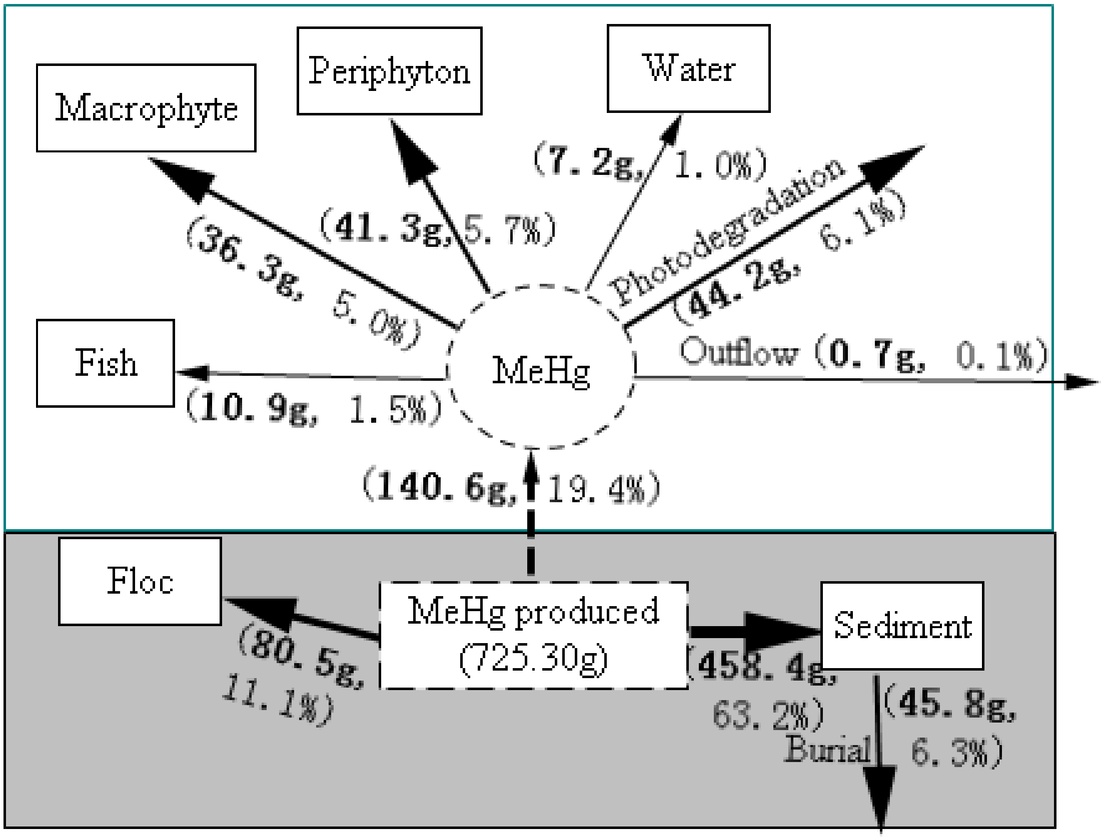


Figure 3B-22. Annual mass (g) and fraction (%) budget of MeHg produced from annually deposited Hg in the Everglades. The sum of MeHg produced from annually deposited Hg in sediment, floc, and periphyton was used.

LITERATURE REVIEW ON THE IMPACT OF SULFUR ON METHYLMERCURY IN AQUATIC ECOSYSTEMS

MeHg became a compound of concern in the 1950s and 1960s following several disasters (Minamata, Niigata) where the compound was inadvertently released to the environment. By the late 1960s and early 1970s, research had demonstrated that MeHg could be produced from inorganic Hg contamination in situ in freshwater and estuarine sediments. By the 1980s, further research found that MeHg production occurs most rapidly in sediments and soils, and under anoxic conditions. Radioisotopic methods were developed for the direct measurements of Hg methylation and demethylation rates in natural samples. Using those methods and seasonal observation it became apparent that MeHg production is largely microbial, since it is temperature dependant, related to levels of microbial activity, and blocked by bacterial inhibitors.

The complex relationship between sulfur and MeHg was also apparent early on in the study of methylation. One of the earliest studies of Hg methylation in sediments reported very low rates of Hg methylation from mercury sulfide. Some of the seminal work on MeHg distributions in sediments was in English estuaries, where an inverse relationship between MeHg and sulfide in sediments was observed. Even in early culture experiments it was clear that sulfide interfered with MeHg production.

Given the inhibition of MeHg production by sulfide, it was surprising in the mid-1980s to find that dissimilatory SRB are important as mediators of metal methylation in estuarine sediment. In studying tin methylation, co-occurrence of tin methylation rates with sulfate reduction rates in Chesapeake Bay bottom sediments was observed; tin-methylating SRB from those horizons was later isolated. The same observation for Hg, and isolated Hg-methylating dissimilatory SRB were made. In both systems, inhibition of sulfate reduction also inhibited Hg or tin methylation, while inhibition of other anaerobic metabolic groups did not. Nevertheless, while dissimilatory SRB produced MeHg and methyltins in estuarine sediments, the sulfide produced through their respiration back-inhibited the process. Compeau and Bartha (1985) hypothesized that SRB are the principal Hg methylators in estuarine sediments.

The importance of sulfate-reducing bacteria in MeHg production in fresh water was also something of a surprise. The activity of these bacteria is generally limited by sulfate concentration in fresh water. In freshwater sediments, sulfate reduction is not usually the dominant terminal bacterial degradation process, as it often is in saline systems. In the 1980s, observations of elevated Hg levels in freshwater fish from “uncontaminated” lakes and reservoirs prompted renewed study of MeHg production in freshwater ecosystems. By that time, agencies in North America and Europe were starting to notice that MeHg contamination of freshwater fish was more widespread than were the known Hg point sources.

Because of the widespread nature of the problem, atmospheric deposition was suspected. This deposition could include anthropogenically increased deposition rates for Hg, acid, or other chemicals. For example, researchers in Sweden recognized that fish Hg levels were higher in southern Sweden than in the north, and that this might be a function of higher atmospheric deposition of Hg or acid in the south. The emerging spatial patterns of Hg in fish were similar to the newly developed spatial models of acid deposition in both the United States and Europe. The roles of pH, sulfuric acid, and nitric acid in MeHg production and bioaccumulation began to be explored.

Several experiments in the 1980s showed that acidification of freshwater sediments by sulfuric or other acids depresses MeHg production. It is not the acidity per se that inhibits MeHg production, rather than sulfate or chloride. Concomitantly, a number of researchers showed that sediments in moderately acidified lakes often maintain near-neutral pH through the generation of alkalinity by SRB. Therefore, it seemed unlikely that acid deposition was impacting Hg methylation rates via alterations of pH in the habitats where MeHg is produced. However, field research on lakes affected by acid deposition showed that sulfuric acid deposition leads to increased sulfate reduction in lake sediments. SRB had been identified as Hg methylators by that time, so research on MeHg in fresh water began to examine the role of sulfate.

Now, almost 30 years since the link between sulfate-reduction and Hg methylation was made, a web search on MeHg and sulfate yields more than 200 references. The body of research on the role of sulfur in MeHg cycling includes studies in many types of ecosystems, and at multiple scales and time frames. These include biogeochemical surveys as well as manipulative experiments on scales from microcosms to ecosystems. Studies of methylation by bacteria in culture also have yielded information on potential mechanisms of methylation and demethylation. The literature was synthesized for each of these types of studies by Gilmour (2011).

Almost two dozen experimental manipulations of sulfate concentration or load have provided information about the response of MeHg to changes in sulfate, ranging from small-scale laboratory studies to ecosystem-level field studies. Across these studies, the sulfate concentration at which MeHg production or accumulation was optimal was generally between 70 and 150 micromoles (µM) (approximately 7–14 mg/L sulfate). **Figure 3B-23** provides an overview of those studies.

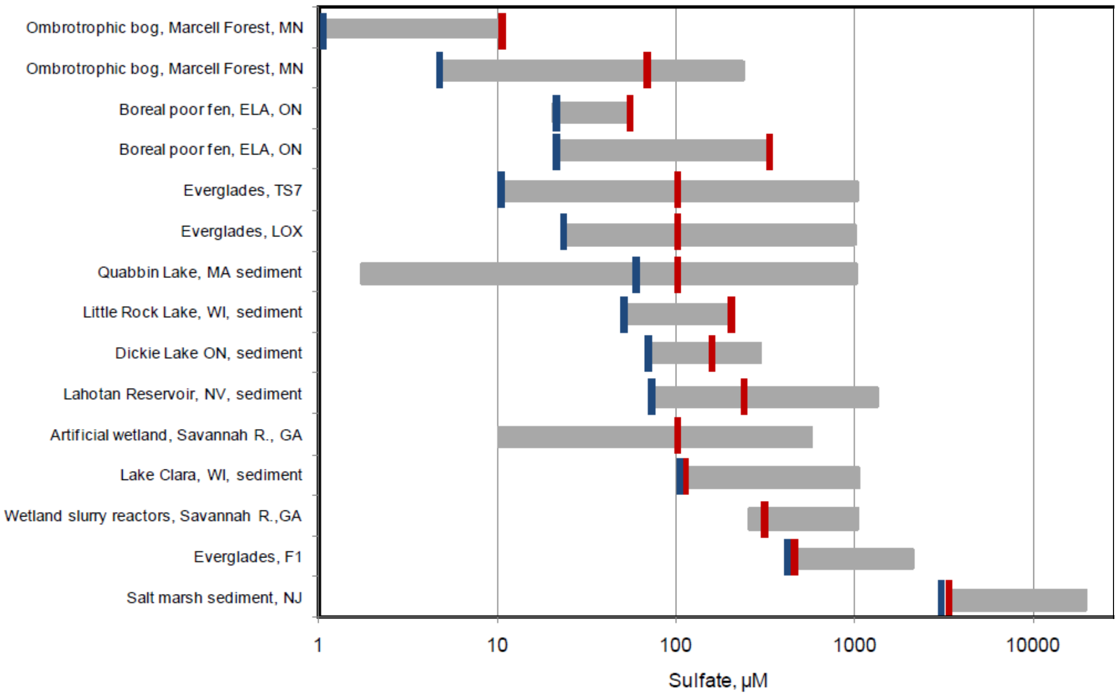


Figure 3B-23. Summary of literature reports of the effect of experimental sulfate amendments on MeHg production in sediments and soils. Blue lines are ambient sulfate concentrations in surface waters of the systems examined. Grey bars show the range of sulfate concentrations achieved by sulfate amendments in the experiments. Red lines show the sulfate concentration at which MeHg concentration or production was highest; MeHg production declined at sulfate concentrations above and below the red line. In some cases the red line represents the average of a range of optimal concentrations.

Taken together, the literature shows that net MeHg production is most favored under biogeochemical conditions where sulfate is sufficient to support significant rates of microbial sulfate reduction, without much accumulation of aqueous sulfide. **Figure 3B-24** provides a conceptualization of how biogeochemical controls on sulfide and DOM impact MeHg production.

In summary, Gilmour (2011) demonstrates that anthropogenic sulfate contamination of freshwater ecosystems from sources like acid deposition, acid-mine drainage, agriculture, and eutrophication have the potential to increase MeHg levels in freshwater ecosystems.

Studies at various ecological scales show that MeHg production is intimately linked to the sulfur and iron cycles. Many studies have demonstrated that Hg methylation occurs most readily in anaerobic sediments, soils and bottom waters, and decaying periphyton mats, in zones of microbial sulfate or ferric iron reduction. All the Hg-methylating organisms identified in the last 20 years are dissimilatory sulfate-reducing and iron-reducing bacteria in the Deltaproteobacteria (Gilmour, 2011).

In regard to the Everglades, assays for microbial iron reduction in soils have yielded low or undetectable rates. As for many other ecosystems, MeHg production in Everglades soils is most favored under biogeochemical conditions where sulfate is sufficient to support significant rates of microbial sulfate reduction, without excess accumulation of sulfide (see 2007 SFER – Volume I, Appendix 3B-2 and Appendix 3B-3).

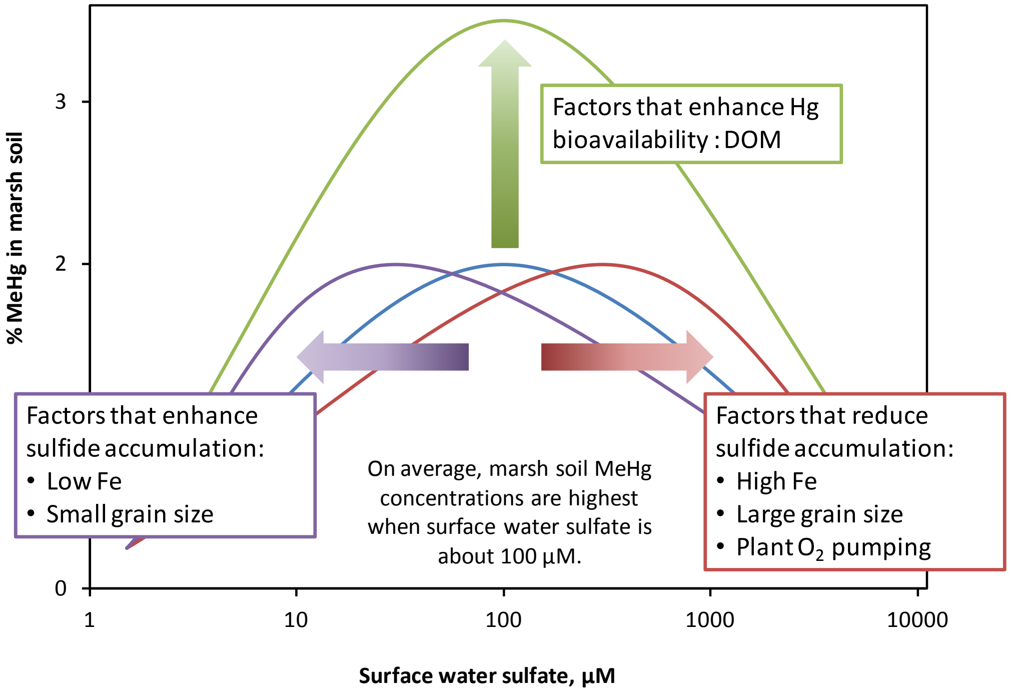


Figure 3B-24. MeHg production is favored under biogeochemical conditions where sulfate is sufficient to support significant rates of microbial sulfate reduction, without much accumulation of aqueous sulfide. Across the suite of published sulfate amendment studies, the average surface water sulfate concentration at which marsh soil MeHg was highest was around 100 micromoles (µM)[10 milligrams per liter (mg/L)]. Factors that influence the amount of sulfide that accumulates in response to sulfate reduction can shift that optimum left or right (horizontal arrows). Additionally, the magnitude of net MeHg production (vertical arrow) changes with dissolved organic material (DOM)-driven bioavailability of Hg for uptake and methylation by bacteria (Note: Fe = iron and O_2 = oxygen).

FUTURE RESEARCH NEEDS

Organized by the SFWMD, FDEP, and USGS, the 2011 Workshop on Mercury and Sulfur in South Florida Wetlands was held in West Palm Beach, Florida on June 21–22, 2011. In addition to participants from the three organizations, representatives from the Smithsonian Institute, Aqua Lux Lucis, Inc., Tetra Tech, Inc, Florida Gulf Coast University, Florida Atlantic University, Florida State University, University of Florida, DB Environmental, Inc., U.S. Department of Interior Everglades Program, and FWC also participated. The workshop's purpose was to discuss research conducted since the last annual workshop related to Hg and sulfur biogeochemistry, and ecological effects in South Florida wetlands. This workshop was intended to support activities under the SFWMD's Sulfur Action Plan, the USGS South Florida Ecosystem Program, and the FDEP South Florida Mercury Science Program. Through these programs, the three agencies investigate the effects of elevated Hg and sulfur levels throughout the Greater Everglades, with research emphasis placed on Hg and sulfur interactions, internal eutrophication (sulfate-induced nutrient release from sediments), sulfide toxicity, agricultural applications of sulfur, and sulfur mass balance.

Five recommendations for future research needs were formulated during the workshop, as summarized in the Peer-Review Report on the 2011 Workshop on Mercury and Sulfur in South Florida Wetlands (Landing, 2011), which is available on the SFWMD's website at www.sfwmd.gov/library. The following sections summarize the recommendations, as well as current and possible future research activities associated with these topics.

Recommendation 1: Sulfur Mass Balance Studies

There is compelling evidence that elevated levels of sulfate can trigger the production of MeHg by SRB in Everglades ecosystems and the EAA is a key source of sulfate to the EPA (see 2011 SFER – Volume I, Chapter 3B). An accurate mass balance of sulfur is critical to the understanding of sulfur cycling in South Florida. The SFWMD's Sulfur Action Plan includes sulfur mass balance as a prime research goal. Results on a large-scale sulfur budget for EAA during a wet, a dry, and a moderate year of precipitation were reported in the 2011 SFER (Volume I, Chapter 3B). The SFWMD is also planning to initiate a study on small-scale sulfur mass balance in the Everglades. There are large uncertainties regarding agricultural application of sulfur and a lack of knowledge of sulfur levels in EAA soils, and sulfur release from oxidation of EAA soils. Ye et al. (2010b) conducted a survey on sulfur distribution in the EAA as influenced by agricultural application of sulfur. Orem et al. (2011) provided an estimate of the net flux of sulfate from the Lake Okeechobee to the EAA. Corrales et al. (2011) also provide a sulfur budget including flow over levees and a groundwater flux. Recently, the FDEP has indicated it will play a more active role for the research on sulfur mass balance for South Florida wetlands.

Recommendation 2: Modeling Studies

It is accepted that the ability to reliably predict how any system will respond to changes in inputs or outputs or internal cycling rates requires the use of models. The Everglades Mercury Cycling Model (E-MCM) is a dynamic model that includes a wide variety of rate equations covering the important Hg cycling processes in the Everglades (2010 SFER – Volume I, Chapter 3B). It could be further developed to be applicable to the variety of conditions found throughout the system, including the EAA, STAs, WCAs, and ENP. An effort to construct a predictive model for water quality, sulfate, MeHg, and Hg levels in mosquitofish is being undertaken by Aqua Lux Lucis, Inc., under contract to the FDEP, with a report due in fall 2011. The Everglades Landscape Model (ELM) (see http://www.sfwmd.gov/portal/page/portal/xweb - release 2/elm) also could be adapted to include sulfur cycling. It is important for some of these models to include a detailed accounting of the current movement of water throughout the system, and associated environmental variables such as dissolved oxygen, DOC, and pH, which can be provided by the SFWMD.

The District has conducted preliminary data analysis on a sulfate budget for Lake Okeechobee. The Lake Okeechobee Environmental Model (LOEM) consists of a module that is capable of simulating lake-wide changes in sulfate concentration under various hydrological conditions. District scientists are also interested in conducting data analysis using the historic water quality data (sulfate, DOC, color, etc.) from the SFWMD monitoring network to document the historic trends of sulfate concentration and the relationships between sulfate, DOC, and THg in fish. Such analyses are also extremely useful to modeling efforts in a hind-casting sense.

Recommendation 3: Monitoring

Long-term monitoring in various media have provided an extremely useful database to help examine trends and to understand a wide variety of processes. The workshop participants recognized the importance of continued monitoring of atmospheric Hg deposition, Hg accumulation in fish and other biota, and water quality, especially sulfate concentration. These monitoring activities are conducted by the District under the mandates of the Everglades Forever Act. Findings are reported in each year's SFER. In addition, scientists from USGS and the University of Florida system have conducted various field studies to assess the relationships of DOC, sulfate, MeHg, and Hg in biota (see 2010 SFER – Volume I, Appendix 3B-3; Aiken et al., 2011; Li et al., 2009, 2010; Orem et al., 2011).

Recommendation 4: Dissolved Organic Matter

DOM has been shown to influence the bioavailability of Hg to SRB, to influence the binding of Hg^{2+} to sediments, and is involved in the photochemical reduction of Hg^{2+} and the photochemical breakdown of MeHg. Dissolved organic carbon (DOC, a substitute for DOM) is included in the district water quality monitoring network for selected sites. Historic data for DOC are also available in the District's DBHYDRO database. The role of DOC on Hg methylation in the Everglades has been evaluated (see recent review by Aiken et al., 2011; Krabbenhoft et al., 2010, and this chapter). More research is needed to understand the importance of the composition and level of DOM to MeHg production.

Recommendation 5: Mercury Methylation and Demethylation

The impacts of sulfate additions on the formation of MeHg and its impacts on biota in the Everglades ecosystems were summarized in the 2011 SFER – Volume I, Chapter 3B. Studies on the relationship between sulfate concentration and Hg methylation in the Everglades marsh have been conducted (2010 SFER – Volume I, Appendix 3B-2; Orem et al., 2011). A recent review of the literature on the impact of sulfate on MeHg in sediments and soils was conducted by Cynthia Gilmour, via a contract with FDEP (Gilmour, 2011). This review shows that net MeHg production is most favored under biogeochemical conditions where sulfate is sufficient to support significant rates of microbial sulfate reduction, without much accumulation of aqueous sulfide. Research on rates of demethylation of MeHg (biological, abiotic, and photochemical) in the Everglades is very limited (Li et al., 2010).

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