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

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SUMMARY

This chapter updates the status of mercury (Hg) and sulfur (S) monitoring in the Everglades region and highlights progress on related research findings. All data presented in this chapter are reported for the calendar year unless otherwise noted. This chapter along with Volume III, Appendices 3-1 and 3-2, fulfills the Everglades Forever Act requirement that the South Florida Water Management District (SFWMD or District) and the Florida Department of Environmental Protection (FDEP) annually issue a peer-reviewed report that summarizes all data and findings of Hg monitoring and research in the Everglades. Additional scientific information is available in the mercury-related chapters of the 1999 Everglades Interim Report, 2000–2004 Everglades Consolidated Reports, and 2005–2012 South Florida Environmental Reports – Volume I (www.sfwmd.gov/sfer).

WHY MERCURY IS A CONCERN

Hg exposure causes human health effects including neurodevelopmental delays in children. Exposure to Hg as methylmercury (MeHg) is particularly hazardous as regards pregnant and breastfeeding women, as well as young children, since MeHg is most harmful in the early stages of human development. Exposure to MeHg occurs primarily from consumption of fish containing MeHg; inorganic Hg is converted to MeHg by naturally occurring sulfate-reducing bacteria in water bodies and then concentrated up the aquatic food chain. MeHg also poses a threat to fish-eating wildlife species and species that prey on them (e.g., egrets, ibis, ospreys, eagles, otters, and panthers), potentially causing reproductive, neurological, and immune system problems.

The Everglades is particularly prone to high MeHg levels in fish due in part to the state’s latitude, meteorology, and atmospheric chemistry, which result in a high rate of Hg deposition from the atmosphere, as well as the Everglades biogeochemistry, which promotes efficient conversion of inorganic Hg from atmospheric deposition to the more toxic and bioaccumulative Hg form, MeHg.

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KEY FINDINGS OF RESEARCH AND MONITORING

Mercury in Everglades Fish and Wildlife

Based on monitoring in the Everglades Protection Area (EPA), MeHg levels in a great majority of game fish targeted by anglers, and fish consumed by wading birds and other wildlife, do not meet U.S. Environmental Protection Agency (USEPA), (USEPA, 1997; 2001) guidance targets for protection of human health or wildlife.

Significant improvements in Hg levels in fish in the Water Conservation Areas (WCAs) in the early to mid-1990s were attributed to effective near-field (South Florida) reductions in atmospheric Hg emissions, though it was hypothesized that a reduction in sulfate (SO$_4^{2-}$) was an additional influencing factor (Axelrad et al., 2005). Subsequent to the reductions in Hg in fish observed until about 2000, the median total mercury (THg) levels in largemouth bass (LMB) (Micropterus salmoides) in the WCAs have remained relatively unchanged [range of yearly medians, 0.30–0.55 milligrams per kilogram (mg/kg)], and are generally above the USEPA MeHg guidance target for protection of human health (0.3 mg/kg), and for protection of fish-eating wildlife [0.346 mg/kg for trophic level (TL) 4 fish]. In contrast, the median THg levels for LMB in Everglades National Park (ENP or Park) did not decline over the 1989–2011 period and continue to be higher and more variable than in the WCAs, with yearly medians ranging from 0.78 to 3.39 mg/kg.

About 70 percent of LMB sampled between 2000 and 2011 from 49 locations within the EPA (2,821 fish sampled) exceeded the USEPA MeHg guidance target for protection of human health. For the 2000–2011 period, 75 percent of TL3 sunfish [bluegill (Lepomis macrochirus), reedar sunfish (L. microlophus), and spotted sunfish (L. punctatus)] sampled from 25 locations in the EPA (1,966 fish sampled) exceeded the USEPA TL3 MeHg wildlife protection guidance target of 0.077 mg/kg. The elevated concentrations of MeHg in fish correlated with elevated concentrations in wildlife. THg concentrations in panther hair, which is representative of body burdens, ranged from 0.092–67 mg/kg. THg has also been measured in great egret (Ardea albus) nestling feathers regularly since 1994 across the central EPA. Similar to the fish data, there has been no distinct trend since 2000 following initial declines in the 1990s.

In 2011, wood stork (Mycteria americana) chicks, a state and federally listed endangered species, were sampled within ENP from three coastal colonies and an inland colony. Coastal ENP colonies showed particularly high levels of feather THg, with means ranging from 5.2 to 10.8 mg/kg.

Mercury Sources to the Everglades

The FDEP has developed a draft statewide Total Maximum Daily Load (TMDL) for Hg, which determined that a reduction in Hg of 86 percent from all nonpoint (atmospheric) anthropogenic Hg sources (from Florida, other U.S. states, and other countries), is necessary to protect public health with respect to fish consumption. Hg inputs to the EPA are overwhelmingly (greater than 95 percent) from atmospheric deposition, and originate predominantly (greater than 95 percent) from sources outside of the U.S.

4 While Hg levels in LMB and sunfish are provided as THg, THg levels can be compared to the MeHg guidance target since more than 95 percent of the THg is in the MeHg form. Similar MeHg/THg ratios are found for bird feathers (e.g., great egrets and wood storks) and mammalian hair (e.g., panthers).
Mercury, Sulfur and Dissolved Organic Matter Biogeochemistry

There are both theoretical and empirical links between SO$_4^{2-}$, dissolved organic matter (DOM), and inorganic Hg methylation, and there is clear evidence that SO$_4^{2-}$ concentrations are enriched anthropogenically throughout much of the Everglades. Because reducing Hg deposition to the Everglades via source control requires international cooperation (potentially requiring decades), other options that could achieve Hg reductions in fish tissue should be considered. Potential options for evaluation include regional reduction in SO$_4^{2-}$ inputs and managing the concentration and character of DOM. However, the role of SO$_4^{2-}$ and DOM in the biogeochemical cycling of Hg within the Everglades is complex and confounded by other variables, and these complexities must be understood and quantified before an effective strategy to reduce MeHg levels through the control/management of SO$_4^{2-}$ or DOM can be designed and implemented.

Although there is ample evidence that S concentrations in the Everglades have increased due to anthropogenic inputs, there is a need to better quantify all sources of S to the system. SO$_4^{2-}$ inputs to the EPA include three primary external sources: (1) inputs from atmospheric deposition, (2) inputs of connate seawater into canals, predominantly from those draining the Everglades Agricultural Area (EAA), and (3) the export of SO$_4^{2-}$ from the EAA, including S that was originally applied as an agricultural soil amendment, SO$_4^{2-}$ released from EAA soil oxidation, and SO$_4^{2-}$ in surface waters released from Lake Okeechobee for agricultural or urban water supply or environmental purposes in the EPA. SO$_4^{2-}$ may also be released from EPA soils through dry out and oxidation. Further investigation is needed to identify the relative contributions of these sources and the feasibility of managing SO$_4^{2-}$ in a manner that would result in a reduction of Hg methylation in the EPA.

Everglades marshes support high rates of organic carbon production (predominantly from calcareous periphyton and vascular plants) via photosynthesis. However, anthropogenic inputs of total phosphorus (TP) have resulted in enhanced production of DOM, with DOM concentrations generally greatest in the northern EPA and lowest further south in ENP. The quality of DOM also changes across the nutrient enrichment gradient, with the DOM characteristic of the northern Everglades being more effective at making inorganic Hg bioavailable for methylation. There is a need to better assess both the effects of DOM on Hg methylation and the sources of DOM to evaluate the potential role of DOM in the state’s restoration efforts.

Research Needs

- **Sulfur Mass Balance Studies**: An accurate S mass balance is critical to better understand S cycling in South Florida and for identifying any opportunities to sufficiently reduce SO$_4^{2-}$ loading to the EPA, lower MeHg levels in Everglades fish, and decrease potential risk to recreational anglers and fish-eating wildlife.

- **Monitoring and Modeling**: Further development of the Everglades Mercury Cycling Model would allow better evaluation of management options for reducing Hg levels. To assess reducing the impacts of possible intrusion of connate seawater, it is recommended that a coupled hydrologic and water chemistry model be developed. The Everglades Landscape Model may be adapted to include S cycling. The District has conducted preliminary data analysis on a SO$_4^{2-}$ budget for Lake Okeechobee. The Lake Okeechobee Environmental Model has a module capable of simulating lake-wide changes in SO$_4^{2-}$ concentrations under various hydrological conditions, which would assist in testing management options.

- **Dissolved Organic Matter**: Research is needed to better understand the importance of the composition and concentrations of DOM that lead to enhanced MeHg production.
• **Effects of Sulfate on Mercury Methylation:** The effects of changing $\text{SO}_4^{2-}$ concentrations on Hg methylation—particularly at low ambient $\text{SO}_4^{2-}$ concentrations—would benefit from further evaluation. Because the Hg methylation rate of $\text{SO}_4^{2-}$ reducing bacteria is increased in the presence of both sulfate and DOM, the interaction of $\text{SO}_4^{2-}$ and DOM loadings on Hg methylation rate would also benefit from more research.

• **Bioaccumulation of Methylmercury in the Food Chain:** MeHg concentrations increase up the food chain and display large variations in Everglades fish that cannot be explained by MeHg concentrations in surface water alone. Further studies are needed to assess seasonal changes in MeHg concentrations in fish at different trophic levels and their relationships with soil, water, and periphyton MeHg concentrations and fish dietary composition.

• **Everglades Bird Habitat Restoration:** Coastal ENP wood storks first sampled in 2011 showed particularly high levels of feather Hg. Ongoing hydrological restoration of the coastal zone is expected to result in an increased prey base there, and consequently, the greatest increase in numbers of wading birds in the Everglades. Therefore, the occurrence of high MeHg exposure to wading birds in this coastal zone area should be considered as part of Everglades habitat restoration planning.

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**MERCURY IN EVERGLADES FISH AND WILDLIFE**

**MERCURY IN LARGEMOUTH BASS**

Ted Lange$^3$, Curtis D. Pollman$^2$, Donald M. Axelrad$^1$ and Barbara Donner$^1$

Mercury (Hg) concentrations in largemouth bass (LMB) (*Micropterus salmoides*) from the Water Conservation Areas (WCAs) were first measured in 1988 in fish from three interior canal locations, and the median total mercury (THg) concentration was 1.75 milligrams per kilogram (mg/kg) (range: 1.2–3.4 mg/kg, n=12). In subsequent years, additional monitoring locations were selected for annual sampling, representing both marsh and canal habitats. As shown in **Figure 3B-1**, eight sites within the Everglades Protection Area (EPA), including six sites within the WCAs and two sites within Shark River Slough in Everglades National Park (ENP or Park) are currently sampled annually. Additionally, LMB and other sport fish are sampled from other locations across the Greater Everglades, including the EPA, for assessing spatial and temporal trends in Hg in fish and potential risk to human health and wildlife.

Axial muscle tissue (fillets) from individual LMB was analyzed for THg to provide a temporally and spatially integrated measure of methylmercury (MeHg) exposure to a long-lived Everglades apex predator (Axelrad et al., 2011). MeHg bioaccumulation by LMB is influenced by several factors, including variations in prey availability and fish growth and movement, but most importantly by ambient MeHg concentrations across the landscape (Gu et al., 2012). While THg concentrations in fish were analyzed in this study, more than 95 percent of the Hg found in top-level predatory fish such as LMB is in the form of MeHg (Grieb et al., 1990; Bloom, 1992) and, as such, THg levels are considered to be a reasonable approximation of MeHg concentrations.

During 2011, 116 LMB were collected from eight sites in the WCAs, a marked reduction from the total of 286 LMB collected in 2010. Fewer samples were due in part to extended periods of low water in the WCAs during summer 2011. Low water levels restricted fish to deepwater refugia (i.e., canals and alligator holes) for extended periods of time, and this resulted in reduced numbers of fish, particularly large-bodied fish (LMB and sunfish) encountered while sampling.
WCA marsh sites. Within Shark River Slough in ENP, a total of 40 LMB were collected from two sites during 2011 and an additional 20 LMB were collected from one site during early 2012. To date, 4,158 LMB from 52 locations have been collected from the EPA and surrounding areas (Figure 3B-1).

Distinctly different trends in LMB THg concentrations are evident between the WCAs and ENP Shark River Slough (Figure 3B-2) over the sampling period. In 2011, the median THg concentration in LMB in the WCAs was 0.46 mg/kg (range: 0.05–1.70 mg/kg, n=116), which represents a 27 percent decrease from 2010 and 66 percent decrease from the year 1989 systemwide median LMB THg of 1.34 mg/kg (range: 0.25–3.90 mg/kg, n=89). LMB THg concentrations declined sharply during the 1990s across the WCAs, possibly due to reductions in South Florida atmospheric emissions from municipal waste combustors and medical waste incinerators (Axelrad et al., 2005). Since 2000, median concentrations have changed little, varying between 0.30 (2001) and 0.55 (2010) mg/kg; the 2011 LMB THg median is within this range. While the region-wide trends in the WCAs show a strong downward trend over time, variations in LMB MeHg bioaccumulation continue to persist across the WCAs as a result of site-specific factors influencing Hg methylation rates (Gu et al., 2012). Current fish consumption advisories from the Florida Department of Health for the WCAs recommend that anglers limit and, in some cases, refrain from consuming LMB (FDOH, 2012).

In Shark River Slough, THg concentrations in LMB were monitored at two locations: (1) L-67 Extension Canal (L67F1) where waters enter ENP from WCA-3, and (2) North Prong Creek (site ENPNP), located in ecotonal habitat situated between the sawgrass marsh of Shark River Slough and the mangrove estuary of the Shark River (Figure 3B-1). In 2011, 40 LMB from Shark River Slough had a median THg concentration of 1.30 mg/kg (range: 0.30–2.35 mg/kg, n=40) representing a decline of 16 percent from 2010 and an increase of 26 percent from the median concentration measured in 1994, the first year LMB were collected from site ENPNP at the south end of Shark River Slough (Figure 3B-2). For 2012, THg in LMB from ENP Shark River Slough (median THg = 0.98 mg/kg; n = 20) includes data from only one site (ENPNP), as sampling has not been completed.

Between 1989 and 2011, the median annual THg concentration in Shark River Slough LMB ranged between 0.78 and 3.39 mg/kg (Figure 3B-2), with no clear trends over the sampling period. However, it is clearly recognizable that all LMB collected from the slough area from 1989 through 2012 (n = 609), with the exception of one fish collected in 1998, have exceeded the 0.3 mg/kg U.S. Environmental Protection Agency (USEPA) (USEPA, 2001) recommended MeHg criterion for the protection of human health, and the annual median THg exceeded 1 mg/kg in 16 of 20 sampling years (i.e., except in 1993, 1998, 1999, and 2008). This has resulted in warnings to anglers to avoid consuming LMB from the freshwater reaches of Shark River Slough (FDOH, 2012).
Figure 3B-1. Largemouth bass (LMB; *Micropterus salmoides*) sampling locations in the Everglades Protection Area (EPA) from 1988 through 2012. Long-term monitoring sites are visited annually in the Water Conservation Areas (WCAs) (●) and Shark River Slough in Everglades National Park (ENP or Park)(●). All others (○) are located in the WCAs and visited periodically to assess trends and potential risk to human health and wildlife from consuming fish.
Figure 3B-2. Annual summaries of total mercury (THg) in muscle tissue of 4,158 LMB collected from canal and marsh sites in the EPA from 1988 through 2012 from regional groupings within WCA-1, WCA-2, and WCA-3 (n=50 sites; 3,549 fish) (top), and Shark River Slough in ENP (n=2 sites; 609 fish; except n=1 site for 2012) (bottom). Box plots represent the median and 25th and 75th percentiles, whiskers represent the 10th and 90th percentiles, and points are outliers. The red line indicates the 0.3 milligrams per kilogram (mg/kg) U.S. Environmental Protection Agency (USEPA) fish tissue methylmercury (MeHg) criterion for protection of human health (USEPA, 2001). The USEPA fish tissue MeHg criterion for protection of wildlife for trophic level (TL) 4 fish is 0.346 mg/kg (USEPA, 1997).
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MERCURY IN EVERGLADES LARGEMOUTH BASS VERSUS STATEWIDE LEVELS

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A total of 703 LMB were collected from the Greater Everglades and analyzed for muscle tissue THg concentrations in 2010 and 2011. Sampling included 38 different locations in 2010 (439 fish collected) and 22 different locations in 2011 (264 fish collected), with 17 sites sampled during both years, and 26 sites sampled during only one of the two years. In aggregate, 40 unique stations were sampled by the Florida Fish and Wildlife Conservation Commission (FWC), including two sites near the northeastern shore of Lake Okeechobee, 11 sites associated with the Everglades Stormwater Treatment Areas (STAs), two sites within the Everglades Agricultural Area (EAA), two sites within Holey Land and Rotenberger wildlife management areas (WMAs), three sites west of the EPA, and two sites immediately to the north and east of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge). The remaining 20 sites are located within the marsh or in canals of the EPA.

LMB THg concentrations were normalized to a 15-inch length to facilitate comparison with LMB concentration data developed for Florida lakes and streams as part of the Florida Department of Environmental Protection (FDEP) statewide Hg Total Maximum Daily Load (TMDL) analysis (also normalized to 15-inch length).5

The normalized Hg concentrations, $H_{LMB15}$, were initially compared across sites sampled in both 2010 and 2011 to assess whether there was a consistent difference in results between the two years. This analysis was conducted using a paired t-test for 14 sites (three of the sites sampled in both years lacked sufficient specimens for at least one of the two years). The comparison showed no consistent difference in paired observations across the two years ($p = 0.2512$, two-tailed test) and, as a result, the data from 2010 and 2011 were combined across sites to estimate the cumulative frequency distribution for $H_{LMB15}$.

The distribution of $H_{LMB15}$ for Everglades sites were compared with the distribution for the same metric for Florida lakes (n = 130) and streams (n = 128) sampled between September 2008 and September 2010 as part of the statewide Hg TMDL analyses conducted by the FDEP (2012a). In this analysis, both sites located within the EAA and other sites associated with the STAs were excluded because these sites are not considered to be representative of the canals and marshes of the EPA. In addition, eight TMDL stream sites located within or near the EPA were included with the FWC Everglades dataset to conduct the distributional analysis. The results from the distributional analysis are shown in Figure 3B-3 as both box plots and cumulative frequency curves. These results, which are unweighted for water body area, indicate that the distribution of fish tissue Hg concentrations in the Everglades is higher compared to that observed in Florida.

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5 The set of lakes and rivers/streams selected for sampling for the statewide mercury TMDL (FDEP, 2012a) was developed using data collected randomly from a matrix of water bodies segregated by key physical and chemical water body characteristics, with the goal of obtaining an even distribution of study sites spanning a wide range of the target variables. Preliminary analyses identified a set of three target variables (pH, color, and chlorophyll $a$ for lakes; pH, color, and nitrate for streams) that were important determinants of the variability of fish tissue Hg concentrations. The selection of lake and stream sites for sampling in turn was based on the joint distribution of these three target variables across five concentration intervals for each variable. This yielded a possible 125 unique variable interval combinations (5x5x5) or sampling bins. Additional lakes and streams were sampled randomly from individual bins to produce a total number of lake and stream reaches or segments of 130 lakes and 128 streams for each water body type. Prospective lakes and streams were selected from the FDEP Status Monitoring Network database (Pollman, 2012a). In both the statewide Hg TMDL study and in this analysis, normalization was conducted using robust regression (StataCorp, 2012) to minimize the influence of outliers on the fitted model parameter estimates. Robust regression was conducted using site location and sample year as categorical variables to develop site-specific slopes for all sites with a minimum of five observations. This latter constraint was imposed to ensure stable output and resulted in excluding data from nine sites (n = 23).
streams and rivers external to the Everglades and substantially higher than concentrations found in Florida lakes. For example, the median $H_{\text{G}_{15}}$ for Everglades sites was 0.689 mg/kg, compared to 0.38 mg/kg and 0.603 mg/kg for the Hg TMDL lakes and streams (excluding Everglades sites), respectively. Differences in mean values for Everglades LMB compared to mean concentrations observed in Florida lakes and streams were evaluated non-parametrically using the Wilcoxon/Kruskal-Wallis test (SAS, 2011). Although the distribution of LMB Hg concentrations in Everglades samples were normal (Shapiro-Wilks test; $p = 0.0626$), the distribution of LMB Hg concentrations in both streams and lake were not, nor did log transforming the data acceptably resolve the non-normality problem. Results from the Wilcoxon test, which was implemented for each possible paired comparison, indicate that mean concentrations of LMB Hg in the Everglades (0.769 mg/kg) are significantly higher than concentrations observed in lakes (mean equals 0.450 mg/kg, $p < 0.001$); but statistically indistinguishable from streams (mean equals 0.644 mg/kg, $p = 0.1660$).

Figure 3B-3. Box plot (left) and cumulative frequency distribution plot (right) comparing standardized LMB (15 inch) THg concentrations measured in the Everglades (averaged across 2010 and 2011 for those sites sampled during both years) with standardized LMB mercury (Hg) concentrations measured in the Florida Department of Environmental Protection (FDEP) statewide Hg Total Maximum Daily Load (TMDL) study from 2008 through 2010. Box plots represent median, and 25th and 75th percentiles; whiskers represent 10th and 90th percentiles; and points are outliers. Sample numbers are as follows: Everglades (including eight Hg TMDL stream sites located within the EPA = 32), Florida lakes = 130, and streams = 120 (external to the EPA).

Figure 3B-4 shows the spatial distribution of $H_{\text{G}_{15}}$ values for the 32 South Florida sites included in the distribution analysis. Within the EPA, the highest concentrations were observed in ENP, followed by sites located in the north central interior of WCA-3A. Lower concentrations were observed for sites in the northern EPA associated with canal waters exiting the EAA or interior stations where the water chemistry is heavily influenced by waters exiting the EAA.
Figure 3B-4. LMB Hg concentrations normalized to 15-inch LMB length. Circle size is proportional to the squared value of the normalized concentration. Squaring the values of normalized Hg concentrations ($Hg_{LMB15}$) was conducted to facilitate visualizing differences in concentration between sites. Data plotted include eight Everglades stream sites sampled as part of the Florida statewide Hg TMDL, plus 24 sites sampled in 2010 and 2011 by the Florida Fish and Wildlife Conservation Commission (FWC) (32 sites total). Range of $Hg_{LMB15}$ is 0.113 to 1.64 mg/kg. [Note: EAA – Everglades Agricultural Area and LNWR – Arthur R. Marshall Loxahatchee National Wildlife Refuge.]
MERCURY IN MOSQUITOFISH AND SUNFISH

Ben Gu, Ted Lange\(^3\) and Donald M. Axelrad\(^1\)

Mosquitofish

Mosquitofish (\textit{Gambusia} spp.) from across the EPA have been analyzed for THg since 1998 (\textbf{Figure 3B-5})\(^6\). During 2011, whole-body concentrations of THg concentrations in mosquitofish from 12 monitoring sites ranged from 0.021 mg/kg at site WCA2F1 to 0.373 mg/kg at site WCA2U3, and levels were higher in 2011 than in 2010 at most sites. However, there was no significant temporal trend in THg in mosquitofish over the period of record (POR) for any of the sites (Spearman Rank Order Correlation, all \(p > 0.05\)).

\textbf{Figure 3B-5.} Annual mean THg concentrations in mosquitofish (\textit{Gambusia} spp.) at monitoring sites from 1998 through 2011. Error bars represent one standard deviation of mosquitofish THg values for multiple sampling sites within each geographic area. The red line represents the 0.077 mg/kg USEPA MeHg criterion for trophic level 3 (TL3) fish for protection of wildlife.\(^6\)

\(^6\) Note that the trophic level (TL) 3 criterion is used for mosquitofish though it is considered to be between TL2 and TL3. MeHg to THg ratio in mosquitofish is lower than that of sunfish or LMB, but its variability and limited data preclude adjustment of mosquitofish THg to MeHg values. Based on available data, the rates of Hg methylation and dietary composition of mosquitofish change seasonally in response to hydrology and food availability and, therefore, the ratio of MeHg to THg in this species also depends on sampling season and locations. Further study is needed to better understand the seasonal changes in MeHg levels in mosquitofish.
In 2011, THg concentrations in mosquitofish exceeded the federal criterion of 0.077 mg/kg MeHg for trophic level (TL) 3 fish for protection of wildlife (USEPA, 1997) at six of the 12 monitoring sites. As noted previously in the Mercury in Largemouth Bass section, it is generally accepted that greater than 95 percent of Hg found in high trophic level fish is in the form of MeHg. This is supported by recent LMB and sunfish surveys by the South Florida Water Management District (SFWMD or District) in the Everglades study area (88–100 percent MeHg; n = 9). However, for lower trophic level fish such as mosquitofish, current Everglades surveys using composite fish samples collected from the STAs (mean MeHg x 100/mean THg = 54 percent; n = 5) and an earlier survey of WCA-2A fish (mean MeHg x 100/mean THg = 73 percent; n = 25) by the District indicate that MeHg as a proportion of THg spans a much wider range (i.e., 13–100 percent).

The highest basinwide THg in mosquitofish concentration (0.201 mg/kg) was found in 1999 and the lowest (0.028 mg/kg) in 2005. Low THg concentrations (i.e., less than 0.077 mg/kg) in mosquitofish were found in wet years (1999, 2001–2006, and 2010), and THg levels greater than 0.077 mg/kg were typically associated with drought years. Drought conditions and dry out have been found to promote sulfate (SO$_4^{2-}$) production and Hg release from sediments and consequently high rates of Hg methylation in the Everglades (Gilmour et al., 2004; Rumbold and Fink, 2006). The annual median THg levels in mosquitofish in WCA-1 (0.058 mg/kg) and WCA-2 (0.052 mg/kg) were less than in WCA-3 (0.075 mg/kg) and at site L67F1 (0.073 mg/kg) in ENP Shark River Slough, but these differences are not statistically significant (Kruskal-Wallis Analysis, p = 0.204).

**Sunfish**

Three TL3 sunfish species—bluegill (*Lepomis macrochirus*), redear sunfish (*L. microlophus*), and spotted sunfish (*L. punctatus*)—have been sampled for THg analysis in the EPA since 1998 (Figure 3B-6). The overall average sunfish whole-body concentration of THg for data pooled from all sites and years is $0.190 \pm 0.176$ mg/kg ($n = 1,879$), with the median value lowest in redear sunfish (0.106 mg/kg), followed by bluegill (0.150 mg/kg) and spotted sunfish (0.257 mg/kg). The median THg level for the POR was highest at the ENP site L67F1 (0.300 mg/kg for all sunfish and 0.396 mg/kg for bluegill). Average THg concentrations for all sunfish and for bluegill at several WCA-3 sites—CA315, CA33ALT, CA35, and CA35ALT—were also above 0.200 mg/kg. During 2011, THg concentrations in the sunfish assemblage from 10 monitoring sites ranged from 0.059 mg/kg at site WCA2F1 to 0.371 mg/kg at site L67F1. Except for two sites, THg levels exceeded the federal MeHg criterion of 0.077 mg/kg for TL3 fish for protection of wildlife. Bluegill is the most common of the sunfish sampled in the EPA, with average THg concentrations ranging from 0.059 mg/kg (site WCA2F1) to 0.394 mg/kg (site L67F1) during 2011.

THg concentrations for the POR varied among sunfish species at each site (Figure 3B-7), with no consistent trends among sites or years. There is a clear north to south trend of increasing THg concentrations in bluegill and redear sunfish in the EPA. Trend analysis (Spearman Rank Order Correlation) on the three sunfish species over time indicates no significant trend for all sites. THg concentration in bluegill displayed a significant upwards trend in WCA-2 ($r = 0.71$, $p = 0.005$, $n = 14$ years) (Figure 3B-7).
Figure 3B-6. Annual mean THg concentrations in sunfish at monitoring sites from 1998 through 2011. Error bars represent one standard deviation of sunfish THg values for multiple sampling sites within each geographic area. The red line represents the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of wildlife.

Figure 3B-7. THg concentrations in three TL3 sunfish species in WCA-1 (site LOXF4), WCA-2 (site U3), WCA-3 (site CA315), and ENP (site L67F1) from 1998 through 2011. Error bars represent one standard deviation of sunfish THg values for multiple sampling sites within each geographic area. The red line represents the 0.077 mg/kg USEPA MeHg criterion for TL3 fish for protection of wildlife.
MERCURY IN PANTHERS

Mark W. Cunningham

The Florida panther (*Puma concolor coryi*) is a federally- and state-listed endangered subspecies, and stressors including environmental contaminants (Roelke et al., 1991; Facemire et al., 1995), infectious diseases (Cunningham et al., 2008), low genetic variability (Johnson et al., 2010), and habitat loss have contributed to the decline of this species. To monitor Hg burdens in the panther population, 136 hair samples from 124 free-ranging Florida panthers sampled in South Florida from 2008 through 2012 were collected at capture or necropsy and analyzed for THg by the FDEP. Areas sampled included public and private lands north of I-75 [including the Florida Panther National Wildlife Refuge and Bear Island and Addition Land Units of Big Cypress National Preserve (BCNP)], Fakahatchee Strand State Preserve, Picayune Strand State Forest, and BCNP south of I-75. The eastern Everglades and ENP were not sampled during this time period. THg concentrations in panther hair ranged from 0.092 to 67 mg/kg.

While detailed analyses are pending, preliminary observations indicate that seven of the 10 panthers with the highest THg concentrations (ranging from 20 to 67 mg/kg) were sampled from BCNP south of I-75. Only one panther north of I-75 (BCNP) was in the top ten, with THg hair concentrations of 20 mg/kg. Roelke et al. (1991) indicated that panthers with hair-THg concentrations greater than 12.57 mg/kg could be at risk.

Brandon (2011), in examining a dataset of THg in panther hair for BCNP for the period 1990 through 2007, noted increases in THg from 2000 through 2007. While the visual trend observed of increasing panther THg was not statistically significant, it corresponded with increased incidence of drying and rewetting cycles in BCNP from 1999 through 2007; such cycles increase MeHg production. The more recent sampling (2008–2012) of BCNP panthers may indicate that their Hg levels remain elevated.

Another possible cause of the apparent recent increase in panther THg in BCNP may be shifts in prey availability. Aerial deer surveys in BCNP recorded a population decline by approximately two thirds from 2001 to 2007. Such declines may have caused a greater dependence by panthers on prey species with higher THg burdens such as raccoons and alligators (Brandon, 2011). A high proportion of the Everglades panther population resides in BCNP, and thus the possible increase in THg in panthers captured in BCNP in recent years deserves further attention.

MERCURY IN GREAT EGRETS AND WOOD STORKS

Peter Frederick

Mercury Levels in Great Egrets

Hg has been sampled in great egret (*Ardea alba*) nestlings regularly since 1994 over much of the central EPA (*Figure 3B-8*). Hg is determined for feathers, which are excellent accumulators and integrators of Hg body burden (Burger, 1993; Furness et al., 1986). Feathers are sampled from great egrets because they are a good representative high trophic level predator, feeding almost exclusively on small to medium sized fishes (McCrimmon et al., 2011). Feathers are from large nestlings (28 to 35 days), which have all of their food harvested from approximately a 25 kilometers (km) radius of the nesting colony; this ensures that the Hg signal is local (McCrimmon et al., 2011). Eight to 15 young are sampled from each colony each year, all from...
different nests. Although Hg was measured as THg, nearly all the Hg in feather tissue is in the methylated form (Frederick et al., 2004).

The broad trend in the data is that THg levels in great egrets fell sharply from a high in 1997 [mean across colonies = 20.68 parts per million (ppm) fresh weight] to a low in 2003 (mean = 2.15 mg/kg or ppm fresh weight) (Figure 3B-9). Since 2003, THg levels have risen somewhat consistently by year, to a mean of 7.79 ppm in 2011. While the trend is robust, it is important to understand that there appears to be relatively high variance in measurements at colonies from year to year, and the colonies sampled have also changed over time, partly due to logistics of sampling and partly because some colonies are no longer active (Figure 3B-10). This results in some uncertainty about the absolute magnitude of change over the years (see standard deviations in Figure 3B-9).

Figure 3B-8. Everglades great egret (Ardea alba) colony locations where feathers from nestlings were sampled from 1994 through 2011.
Figure 3B-9. Mean [± 1 standard deviation (SD)] THg [parts per million (ppm), or mg/kg] in feather tissue of great egret nestlings in the central EPA (1994–2011). Means are of colonies spaced across the EPA.

Figure 3B-10. Mean annual THg in feather tissue (ppm or mg/kg) of great egret nestlings by colony in the central EPA (1994–2011). Different symbols represent different colonies. Lines represent continuous data from individual colonies for three or more continuous years.
Coastal Versus Inland Mercury Levels in Wood Storks

Feathers from wood stork (*Mycteria americana*) chicks have been sampled from inland colonies from 2002 through 2005 using the same methods as previously noted for great egrets. However, colonies in the coastal parts of the Everglades have not been sampled, despite increasing numbers of wading birds nesting in that area. In 2011, a cooperative project was initiated with ENP, and wood stork chicks were sampled in coastal colonies (Paurotis Pond, Cuthbert Lake, and Broad River) as well as at the inland Tamiami West colony. As depicted in **Figure 3B-11**, data suggest that THg contamination in the Tamiami West colony has fluctuated considerably over time, ranging from approximately 2 to 8 mg/kg, even in adjacent years (e.g., 2003 versus 2002, respectively). Coastal ENP colonies in 2011 showed particularly high levels of feather Hg, with means of 10.8 mg/kg (Cuthbert Lake), 8.4 mg/kg (Paurotis Pond), and 5.2 mg/kg (Broad River). These relatively high levels are of particular concern because, with hydrological restoration, the coastal zone area is expected to have the most dramatic restoration of prey base, and consequently the greatest increase in numbers of wading birds in the system. In part because the coastal zone area was historically the area that hosted the greatest nesting numbers, one of the restoration goals for wading birds is to increase the proportion of the population that nests in the estuarine zone. Therefore, the occurrence of high MeHg exposure to wading birds in this coastal zone area should be considered in Everglades habitat restoration.

![Figure 3B-11](image_url)

**Figure 3B-11.** Mean THg (ppm or mg/kg) in wood stork (*Mycteria americana*) nestling feathers (± 1 SD) at the freshwater Tamiami West colony and at coastal locations. Note that coastal locations have been sampled for the first time in 2011. “Coastal ENP” is an average of all samples collected at Paurotis Pond, Cuthbert Lake, and Broad River colonies.
WADING BIRDS TRANSPORT MERCURY FROM MARSHES TO TREE ISLANDS

Ben Gu, Lena Ma, Donny Smoak, Sharon Ewe, Yingjia Zhu, Daniel Irick, Michael Ross and Yuncong Li

The transport of persistent pollutants by seabirds from ocean to land has been documented in recent studies (Blais et al., 2005; Michelutti et al., 2010). Many water birds are top predators in aquatic food chains, accumulating nutrients and pollutants through biomagnification.

High Hg concentrations in fish and other wildlife species from the Everglades have been reported (Frederick et al., 2005). Wading birds are implicated in phosphorus enrichment in tree island soils (Wetzel et al., 2011). Notably in this study, for the first time, wading birds are linked to Hg contamination in the Everglades tree island soil by guano accumulation. The transport of Hg from marsh to upland areas in the Everglades is widespread and has taken place for some time.

In this three-year study, surface soil samples were collected from 26 tree islands across the EPA along with three dated soil cores from two tree islands and samples from a marsh in the central EPA (Figure 3B-12, panel A). Wading birds such as the great egret, white ibis (Eudocimus albus), and wood stork are common predators in the Everglades that consume small fish or crustaceans from the marsh, and roost and breed on selected tree islands. The linkage between wading birds and tree islands was established by measuring THg and stable nitrogen isotopes ($\delta^{15}$N). It is well known that both chemical contaminants and $\delta^{15}$N in consumers display stepwise increases for trophic transfers along food chains (Cabana and Rasmussen, 1994). Unlike marsh soil, upland vegetation, prey fish, and droppings from other wildlife, wading bird guano was enriched with both Hg and $\delta^{15}$N (Table 3B-1).

Table 3B-1. Mean ± standard deviation (SD) of total mercury (THg) concentration in milligrams per kilogram (mg/kg) and stable nitrogen isotope values ($\delta^{15}$N) in tenths of a percent (%) and sample size (n) in soil, biota, and guano samples from the Everglades Protection Area (EPA) (2008–2010).

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>THg ± SD (mg/kg), n</th>
<th>$\delta^{15}$N ± SD (%), n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marsh soil</td>
<td>0.16±0.14, 600</td>
<td>2.6±0.8, 5</td>
</tr>
<tr>
<td>Tree island plants</td>
<td>0.05±0.03, 11</td>
<td>2.3±2.8, 20</td>
</tr>
<tr>
<td>Mammal droppings</td>
<td>0.11±0.10, 8</td>
<td>3.2±2.6, 11</td>
</tr>
<tr>
<td>Wading bird guano$^0$</td>
<td>0.22±0.06, 5</td>
<td>8.4±0.6, 12</td>
</tr>
<tr>
<td>Mosquitofish (Gambusia affinis)</td>
<td>0.08±0.05, 10$^c$</td>
<td>10.1±1.3, 10</td>
</tr>
<tr>
<td>Sunfish (Lepomis spp.)</td>
<td>0.16±0.08, 10$^c$</td>
<td>11.2±2.4, 10</td>
</tr>
<tr>
<td>Great egret (Ardea alba) feather</td>
<td>4.5±4.2, 305$^c$</td>
<td>9.1, 2</td>
</tr>
</tbody>
</table>

a. Cohen et al., 2008.
b. Guano samples are a mix of wading bird species: great egret (Ardea alba), snowy egret (Egretta thula), white ibis (Eudocimus albus), little blue heron (E. caerulea), and tri-colored heron (E. tricolor).
c. SFWMD’s hydrometeorological database, DBHYDRO (www.sfwmd.gov/dbhydro).

9 University of Florida, Soil and Water Science Department, Gainesville, FL
10 University of South Florida, Environmental Science, Policy & Geography, St. Petersburg, FL
11 Ecology and Environment Inc., West Palm Beach, FL
12 Florida International University, Southeast Environmental Research Center, Miami, FL
Figure 3B-12. (A) Location of study sites in the EPA. Solid and open circles indicate sampling sites from surface (short cores) and deep soil (long cores). (B) Soil THg concentrations in mg/kg (mg kg\(^{-1}\)) plotted against soil stable nitrogen isotope values (\(\delta^{15}\)N), a proxy for wading bird influence. (C) Historical changes in soil THg concentrations and (D) \(\delta^{15}\)N values from an unaffected (solid circle) and affected tree island (open diamond), and marsh near the affected island (open circle). [Note: AD – Anno Domini.]
THg concentrations and $\delta^{15}N$ values from 26 tree island soil samples formed two distinct clusters (Figure 3B-12, panel B). Approximately 40 percent of the tree islands investigated had high soil THg concentrations ($0.41 \pm 0.13 \text{ mg/kg}$) and were enriched with $\delta^{15}N$ ($10.2 \pm 1.2\%$), compared to only $0.13 \pm 0.04 \text{ mg/kg}$ THg and $3.9 \pm 1.7\% \delta^{15}N$ from 60 percent of the tree islands, which were similar to the background values in marsh soil (Table 3B-1). These data suggest that wading birds, instead of other wildlife, are biovectors for Hg transport from marshes to tree islands. The proportion of tree islands influenced by wading birds is considerably higher than previously estimated (Wetzel et al., 2011). All tree islands sampled from the Shark River Slough in ENP were Hg hotspots.

Lead $^{210}\text{Pb}$, a natural chemical tracer, was measured from soil organic matter to establish the age of each soil depth interval. Dated soil cores collected from one unaffected tree island, one affected tree island, and its nearby marsh displayed dramatic differences in THg concentrations (Figure 3B-12, panel C) and $\delta^{15}N$ values (Figure 3B-12, panel D) over about the last 150 years. The average THg concentration ($0.54 \pm 0.15 \text{ mg/kg}$) and $\delta^{15}N$ value ($9.6 \pm 0.7\%$) in the affected island soil was fivefold higher than the soil in the unaffected island (THg = $0.11 \pm 0.04 \text{ mg/kg}$; $\delta^{15}N = 1.7 \pm 0.7\%$) and the marsh (THg = $0.11 \pm 0.09 \text{ mg/kg}$; $\delta^{15}N = 3.7 \pm 0.5\%$). The trend of increasing Hg concentrations since 1900 has been closely associated with the increase in atmospheric Hg deposition in South Florida (Rood et al., 1995), as well as enhanced Hg methylation (Gilmour et al., 1998) and MeHg accumulation in food webs resulting from high $\text{SO}_4^{2-}$ loading from the northern EPA (Frederick et al., 2005). A trend of decreasing Hg concentration in all cores after the 1990s (Figure 3B-12, panel C) corresponded with the decreases in Hg bioaccumulation in fish and wading birds possibly due to local reductions in Hg emissions to the atmosphere (Frederick et al., 2005).

Avian transport of contaminants is common in coastal regions (Blais et al., 2005; Michelutti et al., 2010) and has recently been found in inland waters (Cristol et al., 2008) as well as the Everglades. Many wildlife species in the Everglades contain Hg concentrations exceeding federal criteria for animal health (Frederick et al., 2005). The deposition of Hg-laden guano acquired from food in the aquatic ecosystem by migrating birds has contaminated terrestrial soil and food webs (Cristol et al., 2008). On the other hand, considering that 95 percent of Hg in top-level prey fish consists of MeHg and 90 percent of the tree islands have lost their woody vegetation due to major hydrological modifications in the Everglades, dispersal of both new and historical Hg to marshes during the wet season and by soil erosion from the degraded tree islands may contribute to some of the localized hot spots in the Everglades, although this hypothesis warrants further research.
MERCURY AND METHYLMERCURY SOURCES TO THE EVERGLADES

STATEWIDE MERCURY TOTAL MAXIMUM DAILY LOAD PROJECT

Gregory White¹, Curtis D. Pollman² and Donald M. Axelrad¹

As of 2010, all 50 U.S. states had fish consumption advisories in effect due to elevated fish Hg levels, and 81 percent of all advisories nationally were issued, at least in part, because of Hg contamination (USEPA, 2011). Similarly, in 2012 excessive Hg levels in fish were the leading cause of water quality impairment in Florida (FDEP, 2012b). Twenty species of Florida freshwater fish are under some level of advisory (i.e., recommendations of limited consumption or no consumption) including several species in the Everglades. The entire coast of Florida, including over 60 species of marine fish, is also under consumption advisory (FDOH, 2012).

Wet and dry atmospheric deposition of Hg to land and water bodies is the main Hg source to water bodies in Florida as well as the Everglades. Wet atmospheric deposition includes dissolved Hg and particulate Hg scavenged from the atmosphere during rainfall; and dry deposition includes particulate Hg removed from the atmosphere by gravitational settling and particle impaction, and gaseous Hg (predominantly reactive gaseous Hg) reacting with surfaces. For the Everglades, Hg is almost entirely (greater than 95 percent) sourced from wet and dry atmospheric deposition (Guentzel et al., 1998, 2001; Landing et al., 1995; Pollman et al., 1995; Stober et al., 1996, 1998a, 2001).

While a portion of the Hg present in the atmosphere is from natural sources, about 70 percent of the global Hg burden is from human activities that release Hg into the air (FDEP, 2012a). Hg sources to Florida’s water bodies originate from international as well as from U.S. and local sources. Florida’s latitude, geographical setting, and meteorology allow a high rate of Hg deposition from the atmosphere onto Florida’s lands and waters (Gu et al., 2012; FDEP, 2012a). Atmospheric Hg eventually deposits to land and water where a proportion (1–10 percent) is converted in water bodies to MeHg by naturally occurring bacteria and readily bioaccumulates up aquatic food chains reaching high levels in top predator fish (Gu et al., 2012). Almost all human exposure to MeHg results from eating fish (Sunderland, 2007), and there is a higher risk of adverse health effects in children (e.g., neurodevelopmental deficits) from in utero MeHg exposures resulting from women consuming relatively large amounts of fish with elevated MeHg levels (NRC, 2000; USEPA, 2012a).

FDEP rules classify water bodies as impaired for Hg pollution based on Florida Department of Health fish consumption advisories. The federal Clean Water Act requires each state to submit a list of impaired waters to the USEPA and establish TMDLs for these waters. TMDLs define the maximum amount of a pollutant that a water body can assimilate without exceeding water quality standards—in this case, exceedances of the fish tissue MeHg criterion for protection of human health from consumption of fish. As such, development of TMDLs is an important step toward restoring impaired waters. The FDEP has established a draft statewide Hg reduction goal, or TMDL, to address excessive Hg levels found in some Florida fish (FDEP, 2012a). The statewide Hg TMDL project focuses on monitoring and modeling (Figure 3B-13).
Figure 3B-13. Atmospheric monitoring locations for the statewide Hg TMDL project.
Atmospheric monitoring includes wet and dry concentrations of speciated Hg. For 2009, precipitation (wet deposition) was collected daily via the University of Michigan’s Automated Sequential Precipitation Samplers and analyzed for a suite of trace elements, speciated Hg, Hg isotopes, and nutrients. Dry deposition was monitored via the following:

- Continuous bi-hourly sampling for speciated Hg
- Continuous sampling of primary pollutants [ozone (O₃), sulfur dioxide (SO₂), carbon monoxide (CO), nitrogen monoxide (NO), total reactive nitrogen (NOₓ)]
- Filtered particulates less than 2.5 micrometers (PM2.5) and between 2.5 and 10 micrometers (PM10) analyzed for trace elements (i.e., magnesium, aluminum, phosphorus, sulfur (S), titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, rubidium, strontium, molybdenum, cadmium, lanthanum, cerium, samarium, and lead)
- Continuous meteorology

Modeling evaluated two domains: atmospheric and aquatic systems. The dominant atmospheric sources, atmospheric chemistries, transport, and deposition were evaluated from a deterministic approach. The relationships within aquatic systems of water quality, sediment quality (lakes only), and THg in fish tissue were evaluated from an inferential approach. The atmospheric modeling to predict loads of Hg depositing in Florida was conducted at four scales using various public domain modeling software (Table 3B-2). The underlying code for each type of modeling software was enhanced during this project. The modeling effort employed pioneering details on sources and the most spatially and temporally resolved detail in Hg modeling to date.

**Table 3B-2.** Mercury modeling domains and software used for the statewide mercury (Hg) Total Maximum Daily Load (TMDL) project.  
[Note: CMAQ – Community Multi-scale Air Quality Model; ECHMERIT – a global fully coupled mercury-chemistry and transport model; km – kilometers; WRF – Weather Research and Forecasting Model.]

<table>
<thead>
<tr>
<th>Spatial Domain</th>
<th>Mercury Chemistry Model</th>
<th>Meteorological Model</th>
<th>Spatial Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global</td>
<td>ECHMERIT</td>
<td>ECHMERIT &amp; WRF</td>
<td>80 km</td>
</tr>
<tr>
<td>North America</td>
<td>CMAQ</td>
<td>WRF</td>
<td>36 km</td>
</tr>
<tr>
<td>Southeastern U.S.</td>
<td>CMAQ</td>
<td>WRF</td>
<td>12 km</td>
</tr>
<tr>
<td>Florida</td>
<td>CMAQ</td>
<td>CMAQ &amp; WRF</td>
<td>4 km</td>
</tr>
</tbody>
</table>

For the Community Multi-scale Air Quality (CMAQ) modeling, all spatial domains used a pioneering tagging system to track 12 emission categories selected by the FDEP (e.g., coal-fired power plants and natural gas-fired power plants). CMAQ modeling involved using a total of 14 separate tags for evaluating source contributions to total Hg deposition at different locations within the CMAQ model domain. This included five tags explicitly for Florida sources, namely coal-fired electricity generating facilities, oil-fired electricity generating facilities, waste incineration, cement kilns, and all other remaining Florida sources. Six other tags were used to identify all remaining sources within the conterminous U.S. within a given geographical region, namely Georgia, Alabama, Mississippi, Louisiana, Texas, and sources associated with the remaining states in the conterminous U.S. All other remaining sources within the CMAQ model domain (including parts of Canada and Mexico) were also tagged as a source category. In addition, soil emissions of Hg, which are bidirectional, were ascribed a tag, as were...
"background" emissions from sources outside the CMAQ model domain and imported to CMAQ from ECHMERIT, a global fully coupled mercury-chemistry and transport model (S. Sillman, personal communication, January 7, 2012). This allowed for modeled deposition, both wet and dry, as well as Hg species to be identified with a tagged category. The modeling produced some of the most resolute and best evaluated outputs to date, with results showing a greater significance of dry deposition to the total Hg deposition onto Florida. Additionally, a greater variability in deposition spatial patterns was documented, with localized changes in distances of tens of kilometers (km).

The source attribution tagging indicated that the overwhelming fraction of Hg load was from out of state. CMAQ 4-km x 4-km grid predictions for 1,433 lake and stream sites statewide (data provided by Sanford Sillman, University of Michigan, dated May 4, 2012; analyzed by C. Pollman) for soil reemission-corrected estimates of the fractional contribution of Florida atmospheric Hg sources to wet and dry deposition was 2.30 percent as the median, and 7.03 percent for the 90th percentile. The number of Florida sites where sources from within the state exceeded 20 percent of total Hg contribution was less than 1 percent.

Hg loads from other southeastern states were identified as being significant sources and larger than Florida sources in northern Florida. Statewide, sources external to the U.S. dominated the deposition loads. For the Everglades, mean atmospheric Hg deposition for 4-km x 4-km grids in the EPA from global sources (outside of Florida and the U.S.) ranged from 95 to 99 percent for wet deposition and from 88 to 98 percent for dry deposition as a percentage of total atmospheric deposition. For the EPA, dry to wet deposition was about 30:70 (Sanford Sillman, University of Michigan, personal communication). Deposition modeling conducted previously by several researchers produced results that are consistent with the new University of Michigan estimates; these also suggest that sources originating from outside of North America are the dominant sources of atmospheric Hg deposited in the Everglades. For example, Seigneur et al. (2003) suggests that only 17 percent of the total Hg deposition in the Everglades originates from within North America. Subsequent modeling reported by Carlton et al. (2004) using the same model but at a finer scale of spatial resolution (20-km x 20-km versus Seigneur’s 100-km x 100-km grid) yielded North American contributions of 8 percent for the Everglades. More recently, modeling conducted using the Regional Modeling System for Aerosols and Deposition (REMSAD) coupled with inputs averaged from three different global-scale models indicated approximately 90 percent of the Hg deposited in the Everglades originates from outside the REMSAD model domain, which includes the continental U.S. and parts of Mexico and Canada (USEPA, 2008; D. Atkinson, personal communication, May 2009). Clearly, significantly reducing Hg sources to the Everglades will require reduction of global sources via mechanisms such as international treaties, though reductions in mercury in fish will lag behind mercury emissions reductions because of legacy mercury deposits locally and globally from past human activities.

The aquatic modeling applied inferential statistics to the water quality, sediment quality, and fish tissue monitoring data collected from 2008 through 2010. This effort developed relationships between constituents to produce statistical models to better predict THg in fish tissue and models that could be applied to assess necessary load reductions for fish tissue to meet FDEP-identified target values for LMB. A market basket approach—considering the broad variety of fish species consumed in Florida—was used to determine reductions in Hg sources necessary to achieve a 90 percent certainty of humans not exceeding the MeHg reference dose from consuming fish. This analysis determined that Florida fish MeHg levels would need to be reduced by 60 percent to achieve the protective target MeHg level. This reduction in total sources (natural and anthropogenic) is equivalent to an 86 percent reduction in anthropogenic sources given that natural background is assumed to be 30 percent of the total Hg source to the atmosphere. The 86 percent reduction in Hg sources is needed for all nonpoint (atmospheric) Hg sources (from Florida, other U.S. states, and other countries) to protect public health in Florida.
MAJOR SOURCES AND SINKS OF METHYLMERCUFY IN THE EVERGLADES

Yanbin Li\textsuperscript{13} and Yong Cai\textsuperscript{12}

Hg methylation and MeHg demethylation have been found to occur in various compartments of the Everglades, including soils (Gilmour et al., 1998; Vaithy Nathanan et al., 1996), floc (flocculent materials on top of soil) (Marvin-DiPasquale and Oremland, 1998), periphyton (Cleckner et al., 1999), and water (Li et al., 2010). However, it is still unclear which compartment is the major source or sink due to the lack of estimation and comparison of the net MeHg production or degradation in these areas. This information void is partially due to defects in previous models used to estimate the net production of MeHg. This study investigates Hg methylation/demethylation in various compartments of the EPA, assesses the role of these processes in the spatial distribution of MeHg, and identifies major sources and major sinks of MeHg in this ecosystem (Li et al., 2012).

To achieve these objectives, double stable isotope (\textsuperscript{199}Hg\textsuperscript{2+} and Me\textsuperscript{210}Hg) addition experiments were conducted to study methylation/demethylation of Hg in various compartments and areas of the EPA. These isotopes were added to soil, floc, or periphyton samples, and represented newly input Hg species, in contrast to the ambient Hg present in the samples. The net production or degradation rates of ambient and newly input Hg were calculated in soil, periphyton, floc, and water of the EPA using improved calculation models. The previous models for estimating these parameters were improved by taking into account the differences between newly input and ambient Hg in methylation/demethylation efficiency, and correcting the contribution of photodemethylation to Me\textsuperscript{199}Hg concentration when calculating methylation rates in water.

Significant methylation and demethylation of Hg were observed in soil, floc, and periphyton. Methylation and demethylation, which are mediated by sunlight, occur in Everglades waters. However, the rate of Hg photomethylation [1.14 ± 0.02 (×10\textsuperscript{-4} per day \([d^{-1}]\)]) was much slower than that of MeHg photodemet hylation \((k_d = 0.26 ± 0.04 d^{-1})\), indicating that methylation in water plays a minor role in the cycling of MeHg in the Everglades region. Although the newly input Hg\textsuperscript{2+} has a much higher methylation/demethylation efficiency, the net daily produced MeHg from this source was found to account for a very small fraction of MeHg produced (i.e., less than 0.4 percent of that produced from ambient Hg).

Soil was estimated to be the largest source of MeHg in all four areas of the EPA, accounting for 98–100 percent of totally produced MeHg. The net MeHg production rate in soil ranged from 418 to 6,238 nanograms per square meter per day (ng/m\textsuperscript{2}/d), in the order of Refuge < WCA-2 < WCA-3 < ENP (Figure 3B-14). Floc is a major sink of MeHg, with a degradation rate of -9 to -145 ng/m\textsuperscript{2}/d. Water is another sink for MeHg, accounting for approximately 2–10 percent of the total MeHg degradation. Periphyton was found to be a source for MeHg in the northern EPA (Refuge and WCA-2), and a sink in the southern EPA (WCA-3 and ENP).

There is a significant difference between the ambient and newly input Hg species in methylation/demethylation efficiency. The ratio of methylation rate constant of ambient to newly spiked Hg and the ratio of demethylation rate constant of ambient to newly spiked MeHg were estimated to be 0.06 and 0.93 in soil, 0.02 and 0.71 in floc, and 0.53 and 0.50 in periphyton, respectively. If this difference had not been included in the estimation model, then there would have been significant error. For example, the estimated net production (or degradation) rate of MeHg in soil could be overestimated by a factor of 20. The average of the estimated net production (or degradation) rate of MeHg in floc would increase from -70 to 600 ng/m\textsuperscript{2}/d. These

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results indicate that their differences must be considered when estimating the net production of MeHg.

Additionally, statistical analyses indicate that spatial distribution of MeHg in soil and periphyton are mainly related to their in situ methylation. Both methylation and demethylation of Hg in floc are important for controlling MeHg concentration in this compartment, while water MeHg concentration may be controlled by methylation in periphyton and photodemethylation in the water column.

![Net Production or Degradation of MeHg in Various Compartments of the Everglades](image)

**Figure 3B-14.** Net production or degradation of MeHg in soils, floc, periphyton, and water across the EPA.
Between 1995 and 2008, the Aquatic Mercury Cycling in the Everglades (ACME) Project examined in detail the biogeochemical parameters that influence MeHg production at sites across the Everglades. The interdisciplinary ACME team studied Hg cycling in the Everglades through a process-based, biogeochemical lens (Hurley et al., 1998). The ACME database, available at the U.S. Geological Survey (USGS) South Florida Information Access (SOFIA) web page (http://sofia.usgs.gov/exchange/acme/introduction.php), comprises data from all ACME researchers in one central dataset (presently, 61 parameters and 281 sites) to promote its use by interested stakeholders. This website allows downloading of biogeochemical field data from the ACME study. Data are available in tab-delimited or comma-separated value text format, which can be imported into Excel or most spreadsheet and database programs. Data may be selected by station, water quality parameter, or date.

Using the ACME database, Gilmour et al. (2012) provide a detailed biogeochemical evaluation of a set of 10 study sites in the EPA (Figure 3B-15) located across the nutrient, S, and dissolved organic matter (DOM) gradients of the Everglades marsh ecosystem. Spatial and temporal trends in THg and MeHg concentrations in surface water, near-surface sediment (generally 0–4 centimeter sediment depth including the floc or algal mat on top of the peat), and porewater are presented. Biogeochemical information on the study sites is also covered, with a focus on S, DOM, and soil microbiology including microbial metabolic rates and rate constants for Hg methylation. Relationships among inorganic Hg, MeHg, and the other biogeochemical variables across the ecosystem and more than 13 years of data collection are examined.

The ACME study was designed to evaluate the biogeochemical controls on net MeHg in this ecosystem that appear particularly sensitive to Hg inputs. The program sought to determine the importance of Hg methylation in controlling MeHg levels in biota in the Everglades and understand factors such as water chemistry, hydroperiod, and inorganic Hg, nutrient, and S loading that, in turn, control the methylation process in this wetland. Key findings of this study include the following:

- There are large gradients in S, MeHg, and DOM across the Everglades ecosystem, driven in part by agricultural drainage and water management practices.
- SO\textsubscript{4}\textsuperscript{2-} loading to the Everglades increases microbial SO\textsubscript{4}\textsuperscript{2-} reduction in soils, leading to more reducing conditions, greater cycling of nutrients in soils, production of toxic hydrogen sulfide, and enhanced MeHg production and bioaccumulation in some parts of the regional ecosystem.

14 Smithsonian Environmental Research Center, Edgewater, MD
16 Wheaton College, Norton, MA
17 University of Maryland, Chesapeake Biological Laboratory, Solomons, MD
18 U.S. Geological Survey, Reston, VA
19 U.S. Geological Survey, Middleton, WI
- SO$_4^{2-}$ loading and peat degradation are linked processes that lead to increased concentrations and reactivity of DOM in the impacted areas. In turn, this highly reactive DOM also enhances MeHg production.

![Figure 3B-15](image)

**Figure 3B-15.** Location of the 10 Aquatic Mercury Cycling in the Everglades (ACME) study sites in the EPA.

**Figure 3B-16** is an example of analyses conducted in Gilmour et al. (2012) using the ACME database. Across all the sites and dates sampled, MeHg as a percent of THg in surface waters increases with surface water SO$_4^{2-}$ up to a maximum, and then declines. This is suggestive of the “Goldilocks” or unimodal MeHg and SO$_4^{2-}$ response despite the confounding effects of varying water and soil chemistry across the 10 EPA study sites—very low SO$_4^{2-}$ results in low MeHg production as does very high SO$_4^{2-}$ (due to associated high sulfide).
Figure 3B-16. Relationship between MeHg (top) and MeHg as percent of %THg (bottom) and surface water sulfate (SO$_4^{2-}$) across 10 ACME study sites and all dates. [Note: ng/L – nanogram per liter and μM – micromoles.]
MODELING SULFATE AND GAMBUSIA MERCURY RELATIONSHIPS IN THE EVERGLADES

Curtis D. Pollman\(^2\) and Donald M. Axelrad\(^1\)

Hg is problematic because bacteria in aquatic ecosystems convert inorganic Hg to its more bioaccumulative and toxic form, MeHg. MeHg production is governed in part by the activity of sulfate-reducing bacteria (SRB) that use SO\(_4^{2-}\) as the terminal electron acceptor to metabolize organic matter under anaerobic conditions (Gilmour et al., 1992; Branfireun et al., 2001; Jeremiason et al., 2006). In the Everglades, studies conducted using intact soil cores have demonstrated that Hg methylation is enhanced by additions of SO\(_4^{2-}\) into the water column depending upon ambient concentrations (see Gilmour, 2011). Further support for the role of SO\(_4^{2-}\) in the Everglades is indicated by correlation analyses that link long-term dynamics of mosquitofish Hg concentrations to the dynamics of SO\(_4^{2-}\) concentrations in the water column at site 3A-15 within WCA-3A (D. Krabbenhoft, USGS, unpublished data; Axelrad et al., 2005).

Gilmour and Henry (1991) hypothesized that the relationship between SO\(_4^{2-}\) and inorganic Hg methylation rate was nonlinear and essentially unimodal, with a water column SO\(_4^{2-}\) concentration in the range of 200–500 micromolar (µM) [~20–50 milligrams per liter (mg/L)] supporting maximal rates of methylation (Figure 3B-17). According to this paradigm, SO\(_4^{2-}\) availability at concentrations below the optimal concentration limits the activity of SRB, which in

![Figure 3B-17](image-url).

**Figure 3B-17.** Theoretical relationship between water column sulfate (SO\(_4^{2-}\)) and Hg methylation rates in sediments hypothesized by Gilmour and Henry (1991). Figure as redrawn by Langer et al 2001.
turn limits rates of methylation. At concentrations above the optimum, \( \text{SO}_4^{2-} \) reduction produces sulfide at levels inhibitory to inorganic Hg methylation, primarily through the sequestration of labile Hg\(^{2+} \), which is a necessary substrate to support methylation. In a recent review of the literature devoted to studies on the relationship between S and Hg methylation, Gilmour (2011) suggests that the optimal concentration of \( \text{SO}_4^{2-} \) in the water column supporting methylation in freshwater ecosystems is lower (~100 \( \mu \text{M} \) or 10 mg/L), although it can vary depending upon sulfide levels.

Pollman (2012b) recently used data on Gambusia Hg and water column \( \text{SO}_4^{2-} \) concentrations collected from marsh sites throughout the EPA as part the USEPA’s Regional Monitoring and Assessment Program (REMAP; Scheidt et al., 2000; Scheidt and Kalla, 2007) in an effort to identify whether the \( \text{SO}_4^{2-} \) maximum, widely hypothesized (e.g. Gilmour, 2011) exists for the Everglades. Pollman used 90th percentile Gambusia Hg concentrations to define the “maximum methylation potential” as a function of \( \text{SO}_4^{2-} \) concentrations, with \( \text{SO}_4^{2-} \) concentrations divided into intervals for the purposes of determining the 90th percentile Gambusia Hg concentration. As shown in Figure 3B-18, study results indicate a unimodal response similar to that originally hypothesized by Gilmour and Henry (1991). The maxima of the maximum methylation potential

![Figure 3B-18](image.png)

**Figure 3B-18.** Variations in \( \text{SO}_4^{2-} \) methylation potential as determined by changes in Gambusia Hg concentrations as a function of ambient water column \( \text{SO}_4^{2-} \) concentrations. Curves are the result of cubic splines constructed using the 90th percentile Gambusia Hg concentration for In-transformed \( \text{SO}_4^{2-} \) concentration intervals [each interval encompasses 1 In unit change in concentration, with the first interval starting at -6 (0.002 milligrams per liter [mg/L])]. The black curve shows the \( \text{SO}_4^{2-} \) methylation potential resulting from aggregating data from all four regions of the EPA together. Data are from USEPA Regional Monitoring and Assessment Program (REMAP) Cycles 0–6. Analysis from Pollman (2012b). [Note: ng/g – nanograms per gram.]
curves varied between regions sampled by the REMAP and may reflect the amount of sulfide that accumulates as SO$_4^{2-}$ reduction proceeds (Gilmour, 2011). However, it should be noted that Gambusia Hg cannot be predicted by SO$_4^{2-}$ concentrations alone, since other factors such as DOM, Hg availability, and dietary composition of fish are also very important factors in determining Hg in fish. It is also interesting to note that the maxima for all the regions were nearly identical with the exception of WCA-3, and may reflect differences in the nature and concentrations of dissolved organic carbon (DOC), which in turn can influence the bioavailability of Hg$^{2+}$ (Gilmour, 2011). The SO$_4^{2-}$ concentrations corresponding to the maximum methylation potential varied from approximately 1.6 mg/L (1–2.7 mg/L in WCA-3) to 33 mg/L (20–55 mg/L in the Refuge). When the Gambusia data are integrated across all four sampling regions used by the REMAP, the maximum methylation potential occurs at SO$_4^{2-}$ concentrations of approximately 4 to 5 mg/L.

Given both the theoretical and empirical links between SO$_4^{2-}$ and Hg methylation, and given that SO$_4^{2-}$ concentrations throughout much of the Everglades are enriched anthropogenically, one potential option for mitigating high Hg concentrations in fish would be through controlling SO$_4^{2-}$ inputs to the Everglades. However, the role of SO$_4^{2-}$ in the biogeochemical cycling of Hg within the Everglades is complex and confounded by other variables, and these complexities must be understood and quantified before an effective strategy that includes SO$_4^{2-}$ controls for resolving the Hg problem can be designed and implemented. For example, high SO$_4^{2-}$ concentrations can reduce Hg methylation rate through the evolution of high concentrations of sulfide and subsequent precipitation of dissolved Hg$^{2+}$ as metacinnabar (Aiken et al., 2011a)—Hg$^{2+}$ being the necessary precursor for MeHg production. Therefore, the relationship between SO$_4^{2-}$ concentrations and Hg methylation is nonlinear and unimodal (Gilmour and Henry, 1991). Moreover, the influence of other variables—particularly those related to trophic state—can dominate the expression of Hg in the food chain. As a result, simple correlation studies that attempt to link Hg concentrations in Gambusia throughout the Everglades fail to show a clear and meaningful relationship. Restated, Hg biogeochemical cycling is influenced by a number of variables and, as a result, simple models that try to relate biota Hg concentrations to variations in a single variable such as SO$_4^{2-}$ in a system as biogeochemically diverse as the Everglades will be able to capture only a fraction of the variability. It is important to note that these complexities do not negate the importance of SO$_4^{2-}$, but do require that analyses that evaluate the mitigative benefits of controlling SO$_4^{2-}$ on biota Hg concentrations include effects of variations in other key process variables across the landscape as well.

Because the relationship between SO$_4^{2-}$ concentrations and methylation is hypothesized to be unimodal, the effect of management strategies to reduce SO$_4^{2-}$ concentrations across the Everglades may result in decreases in biota Hg concentrations in some locations but increases in other areas. Such results were indicated by preliminary modeling efforts conducted by Pollman (unpublished data) with the USEPA REMAP database$^{20}$ (Scheidt and Kalla, 2007), in which reducing SO$_4^{2-}$ concentrations by a nominal amount (e.g., 50 percent) did not equate to equivalent reductions in Gambusia Hg concentrations and that the expected response (both magnitude and direction) varied spatially.

$^{20}$ The marsh component of the Everglades REMAP was implemented in 1995 by the USEPA to evaluate the health of the Everglades marsh ecosystem. The REMAP utilized a stratified, randomized approach towards sampling that was designed to facilitate quantitative estimates of the areal distribution and variability of a broad suite of key ecosystem metrics, including nutrients, components of major ion chemistry (including SO$_4^{2-}$), and Hg concentrations in biota (including Gambusia), sediments, and surface water. Sampling of the Everglades marsh was conducted in three phases as a series of cycles, with each cycle corresponding to either the dry or wet hydroperiod. Phase I sampling was conducted during both 1995 (Cycles 0 and 1) and 1996 (Cycles 2 and 3), Phase II sampling was conducted during 1999 (Cycles 4 and 5), and Phase III sampling was conducted during 2005 (Cycles 6 and 7).
As a result of the complexities in the $\text{SO}_4^{2-}$–Hg methylation relationship, the key objectives of this study were to:

- Better characterize the nonlinear relationship between $\text{SO}_4^{2-}$ and maximum methylation potential, using REMAP data for Gambusia and $\text{SO}_4^{2-}$ concentrations for all eight cycles of data available.
- Incorporate the algorithm for $\text{SO}_4^{2-}$ effects on methylation potential in a statistical model framework that, when developed in conjunction with other key water column and sediment chemistry variables, can be used to predict variations in Gambusia Hg concentrations across the EPA both spatially and temporally.
- Evaluate and analyze changes in water chemistry and Gambusia Hg concentrations over time at proximally located stations to help identify what factors appear to be driving observed decreases in Gambusia Hg documented in the REMAP datasets between 1995 and 2005.
- Develop a regional conceptual model of $\text{SO}_4^{2-}$ dynamics that predicts how $\text{SO}_4^{2-}$ concentrations will change across the Everglades based on atmospheric deposition, hydrologic inputs and $\text{SO}_4^{2-}$ export from the EAA, and connate seawater intrusion in the major canals.
- Predict changes in the spatial and overall distribution of Gambusia Hg concentrations as a function of specified changes in $\text{SO}_4^{2-}$ export from the EAA with other variables held constant.

**Impacts of Reducing Sulfate Concentrations in Everglades Agricultural Area Discharge Waters**

$\text{SO}_4^{2-}$ inputs to the EPA include three primary sources: (1) direct inputs from atmospheric deposition, (2) likely inputs of connate seawater\(^{21}\) into the canals draining the EAA and routing of water through the EPA, and (3) export of otherwise “excess” $\text{SO}_4^{2-}$ from the EAA derived from other sources, including S that was originally applied as a soil amendment, $\text{SO}_4^{2-}$ released from soil oxidation within the EAA, and elevated $\text{SO}_4^{2-}$ concentrations associated with water pumped from Lake Okeechobee and passing through the EAA.

The objective of this recent study was to evaluate the efficacy of reducing this latter excess or non-marine $\text{SO}_4^{2-}$ exported from the EAA as a means of reducing fish tissue Hg concentrations throughout the Everglades (Pollman, 2012b). Model building, analyses of temporal trends, and impacts of $\text{SO}_4^{2-}$ management scenarios were conducted using Gambusia Hg data coupled with ambient water and sediment chemistry data collected by the USEPA throughout the Everglades as part of REMAP sampling conducted between 1995 and 2005 (Stober et al., 1998b; Scheidt et al., 2000; Scheidt and Kalla, 2007). Four different scenarios of $\text{SO}_4^{2-}$ reductions were simulated using the $\text{SO}_4^{2-}$ dynamics model coupled with the statistical Gambusia Hg model. The scenarios were designed to examine reductions in $\text{SO}_4^{2-}$ exported from the EAA attributable to non-marine sources, with reductions in this “excess” $\text{SO}_4^{2-}$ ranging from 25 to 100 percent.

\(^{21}\)Connate seawater generally refers to groundwater in the surficial aquifer that is marine in origin and was trapped in the interstices of the limestone as the geologic material was deposited. The export of major ions that are ultimately marine in origin may also reflect continued flushing of saline residues present in the muck soils and rock of the EAA (Chen et al., 2006). At this time, it is not possible to distinguish between either pathway. In this report, connate seawater refers a relict marine source that is present either in the surficial aquifer, EAA soils, or both. Estimates of connate seawater contributions of $\text{SO}_4^{2-}$ to surface waters were based on using chloride as a tracer (with the assumption that the chloride is marine in origin) and applying the ion ratio of $\text{SO}_4^{2-}$ to Cl- found in marine waters to estimate the marine component of $\text{SO}_4^{2-}$ concentrations in waters exiting the EAA (Pollman 2012b).
The simulations suggest that eliminating the excess or non-marine $SO_4^{2-}$ will reduce median $SO_4^{2-}$ concentration across the EPA by about two-thirds (from approximately 2.4 mg/L to 0.8 mg/L). However, because of the nonlinear relationship between ambient $SO_4^{2-}$ concentrations and Hg methylation potential, reductions in excess (non-marine) $SO_4^{2-}$, depending upon a site's initial $SO_4^{2-}$ concentrations and the relative influence of waters from the EAA on ambient $SO_4^{2-}$ levels, will result in increases in Gambusia Hg concentrations at some EPA locations and decreases at other areas. In addition, the overall shifts in Gambusia Hg concentrations are expected to be small, regardless of the magnitude in reduction in excess (non-marine) $SO_4^{2-}$. Based on the underlying assumptions of the analysis used to quantify the magnitude of connate seawater input, this is because the overall impact of $SO_4^{2-}$ exiting the EAA not only reflects excess (non-marine) $SO_4^{2-}$ that likely originates in large part from S applied as a soil amendment (including other agricultural inputs draining into the Kissimmee River and Lake Okeechobee) and $SO_4^{2-}$ released from soil oxidation within the EAA, but also $SO_4^{2-}$ derived from connate seawater.

If the role of connate seawater as a source of $SO_4^{2-}$ is indeed as large as suggested by this analysis, then the magnitude of either source alone (connate seawater or non-marine $SO_4^{2-}$ exiting the EAA) is sufficient to elevate concentrations of $SO_4^{2-}$ through much of the EPA by well over an order of magnitude compared to expected background levels. A critical component underlying the $SO_4^{2-}$ reduction scenario analyses was the assumption that chloride (Cl$^-$) concentrations in the major canals draining the EAA primarily reflect marine or connate seawater inputs. Support for this assumption is provided by an in-depth analysis of ion ratios and flow/concentration dynamics in the two major inflows discharging from the EAA into the northern EPA, although this assumption needs to be further tested. For example, whether the use of soil amendments within the EAA have influenced Cl$^-$ concentrations appreciably in excess of connate seawater contributions is not clear but, based on the analyses conducted as part of this study, the likelihood that such amendment use exerts a large influence on Cl$^-$ and sodium (Na$^+$) chemistry in the major canals appears unlikely.

**Scenario Analyses – Results and Discussion**

Four different scenarios of $SO_4^{2-}$ reductions were simulated, corresponding to 25, 50, 75, and 100 percent reductions in excess (non-marine) $SO_4^{2-}$ concentrations exported from the EAA. The effects of two scenarios (50 and 100 percent) on the distribution of $SO_4^{2-}$ across the Everglades landscape are shown in Figure 3B-19. Table 3B-3 indicates that eliminating excess or non-marine $SO_4^{2-}$ from waters exported from the EAA is predicted to reduce the median $SO_4^{2-}$ concentration across the EPA from 2.42 to 0.78 mg/L, and shows predicted negligible changes ($\Delta$) in median Gambusia Hg concentrations for the EPA relative to predicted current levels for the four reduction scenarios for the non-marine $SO_4^{2-}$ signal exported from the EAA.
Figure 3B-19. Observed $\text{SO}_4^{2-}$ concentrations (left) and predicted $\text{SO}_4^{2-}$ concentrations assuming 50 and 100 percent reductions in the excess (non-marine) $\text{SO}_4^{2-}$ component of concentrations exported from the EAA (middle and right, respectively) in the EPA during REMAP Cycles 6 and 7 (May and November 2005, respectively). [Note: These most current data were selected for scenario analyses because Gambusia Hg concentrations have decreased over the time period that REMAP sampling was conducted.]
Table 3B-3. Predicted changes in median sulfate (SO$_4^{2-}$) and Gambusia Hg concentrations across the EPA in response to fractional reductions in the excess non-marine SO$_4^{2-}$ signal exported from the Everglades Agricultural Area (EAA). Current Gambusia Hg concentrations are based on simulations conducted using ambient SO$_4^{2-}$ levels for Regional Monitoring and Assessment Program (REMAP) Cycles 6 and 7. [Note: Δ – changes in, mg/L – milligrams per liter, and ng/g –nanograms per gram.]

<table>
<thead>
<tr>
<th>Metric</th>
<th>Current</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median Gambusia Hg (ng/g)</td>
<td>83.3</td>
<td>83.2</td>
<td>86.1</td>
<td>85.8</td>
<td>85.7</td>
</tr>
<tr>
<td>Median SO$_4^{2-}$ (mg/L)</td>
<td>2.42</td>
<td>2.03</td>
<td>1.62</td>
<td>1.20</td>
<td>0.78</td>
</tr>
<tr>
<td>Median Δ Gambusia Hg (ng/g)</td>
<td>-0.6</td>
<td>-1.5</td>
<td>-3.2</td>
<td>-5.7</td>
<td></td>
</tr>
<tr>
<td>Maximum Gambusia decrease (ng/g)</td>
<td>-4.5</td>
<td>-9.9</td>
<td>-16.2</td>
<td>-27</td>
<td></td>
</tr>
<tr>
<td>Maximum Gambusia increase (ng/g)</td>
<td>7.3</td>
<td>11.4</td>
<td>15.6</td>
<td>19.8</td>
<td></td>
</tr>
</tbody>
</table>

Although the average or median shift in Gambusia Hg concentrations is predicted to be small for the 25 to 100 percent non-marine SO$_4^{2-}$ reduction scenarios, larger reductions in SO$_4^{2-}$ are expected to result in larger shifts—both positive and negative—in regions where the current SO$_4^{2-}$ concentrations are near the maximum methylation potential. From a spatial perspective, the effect of reducing excess EAA SO$_4^{2-}$ inputs is predicted to result in shifting Hg hotspots northward towards the EAA. This is illustrated by Figure 3B-20, which shows the spatial distribution of Δ Gambusia Hg concentrations for the 50 and 100 percent reduction scenarios. Because ambient concentrations of SO$_4^{2-}$ lie on both sides of levels corresponding to the maximum methylation potential, both WCA-3 and WCA-2 are predicted to undergo changes in Gambusia Hg concentrations in both directions. The largest magnitude of change in Gambusia Hg concentrations is predicted to occur in WCA-3, while shifts in WCA-2 are expected to be generally lower because of the larger, direct impact of EAA discharges on WCA-2 Cl$^-$ and SO$_4^{2-}$ concentrations. Hg concentrations in Gambusia throughout ENP are expected to decline in response to reductions in excess (non-marine) SO$_4^{2-}$ exports from the EAA of 50 percent or more. Based on the assumption that Cl$^-$ is a valid tracer for connate seawater, the magnitude of either source alone (connate seawater or non-marine SO$_4^{2-}$ exiting the EAA) is sufficient to elevate concentrations of SO$_4^{2-}$ through much of the EPA by well over an order of magnitude compared to expected background levels. The contributions of both sources to median SO$_4^{2-}$ concentrations in each major hydrologic unit, as well as expected background SO$_4^{2-}$ concentrations are depicted on Figure 3B-21.
**Figure 3B-20.** Predicted changes in *Gambusia* Hg concentrations in response to 50 and 100 percent reductions in excess (non-marine) $\text{SO}_4^{2-}$ exported from the EAA (left and right, respectively) using REMAP Cycles 6 and 7 data.
Figure 3B-21. Contributions from different source categories to median $\text{SO}_4^{2-}$ concentrations in the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), WCA-2, WCA-3, and ENP. Stack bar length shows the median concentration and is the summed contribution from each individual source. Source contribution categories include excess (non-marine) $\text{SO}_4^{2-}$ exported from the EAA (red bar); background contributions (defined as the lower 2.5 percent concentration observed in a given hydrologic unit; green bar); and marine sources, which would be primarily connate seawater (blue bar). WCA-2 is shown separately because of the tenfold scale difference. The analysis for WCA-2 includes both estimates for the apparent background $\text{SO}_4^{2-}$ concentration as defined above, and an "adjusted" background concentration defined by the maximum background concentration (0.031 mg/L) (defined as the lower 2.5 percent concentration) inferred for the other three hydrologic units.
SULFUR AND MERCURY GEOCHEMISTRY IN NORTHWESTERN WATER CONSERVATION AREA 2A

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As a key water quality issue for Everglades restoration and originating in Lake Okeechobee and the EAA from multiple sources (Bates et al., 2002; Orem, et al., 2011), $\text{SO}_4^{2-}$ enters the EPA in discharges from canals or the Everglades STAs. $\text{SO}_4^{2-}$ concentrations in Everglades marshes near discharges may average 60–70 mg/L, compared to background levels of less than 1 mg/L in the ecosystem (Scheidt and Kalla, 2007; Orem et al., 2011) and as low as 0.02–0.03 mg/L (Pollman, 2012b). High $\text{SO}_4^{2-}$ loading stimulates microbial $\text{SO}_4^{2-}$ reduction, causing buildup of sulfide in Everglades anoxic soils. $\text{SO}_4^{2-}$ loading to the ecosystem has also been implicated as a major control on the production and bioaccumulation of toxic MeHg (Orem et al., 2011).

The STAs, designed to remove total phosphorus from surface water through biological uptake, appear to have little effect in reducing $\text{SO}_4^{2-}$ loading to the EPA. Although plants require $\text{SO}_4^{2-}$ in about the same amounts as phosphate, $\text{SO}_4^{2-}$ concentrations in surface waters exceed those for phosphate by more than a factor of 1,000. Therefore, aquatic plants and algae in the STAs that do an efficient job of phosphate removal are unable to significantly reduce $\text{SO}_4^{2-}$ loading from the EAA to the EPA (Pietro et al., 2009).

Northwestern WCA-2A has experienced a dramatic increase in $\text{SO}_4^{2-}$ levels since STA-2 operations began in July 2001 (Garrett and Ivanoff, 2008), though flow from STA-2 has improved WCA-2A hydroperiod, increased water depth, and reduced frequency of dryout. Prior to 2001, this area was rainfall-dominated with $\text{SO}_4^{2-}$ concentrations ranging from 5 to 17 mg/L. Post 2001, the USGS observed $\text{SO}_4^{2-}$ levels of 60 mg/L at sites closest to STA-2 discharges (August 2009 and February 2010), and sulfide levels in porewater ranged from 40 to 6,000 micrograms per liter (μg/L). In surface water, measurable sulfide was present at most sites, with levels up to 300 μg/L. Most sites had surface water sulfide levels that exceed the USEPA National Recommended Criterion of 2 μg/L undissociated hydrogen sulfide (H$_2$S) for protection of fish and other aquatic life (USEPA, 2012b).

Sulfide concentrations in surface water and porewater were correlated with surface water $\text{SO}_4^{2-}$ concentrations. $\text{SO}_4^{2-}$ levels in surface water decreased from sites nearest the STA-2 discharge into northwestern WCA-2A to sites 4 km distant from the discharge at an average rate of 1.64 mg/L per km. $\text{SO}_4^{2-}$ declines across the marsh due to removal by microbial $\text{SO}_4^{2-}$ reduction and dilution. The USGS has observed similar rates of $\text{SO}_4^{2-}$ loss elsewhere in the Everglades.

THg in surface water ranged from 0.8 to 4.3 nanograms per liter (ng/L) in August 2009 and from 0.9 to 2.2 ng/L in February 2010. MeHg concentrations in surface water ranged from 0.04 to 1.1 ng/L in August 2009 (average 0.44 ng/L) and from 0.04 to 0.5 ng/L in February 2010 (average 0.19 ng/L). The decline in MeHg concentrations from August to February is hypothesized to be due to a temperature effect on microbial $\text{SO}_4^{2-}$ reduction and Hg methylation rates. THg and MeHg concentrations in surface waters were highly correlated, and MeHg ranged from 3.9 to 28.3 percent of the total Hg in all surface water samples.

MeHg concentrations in northwestern WCA-2A are elevated relative to areas of the ecosystem far from canal and STA-2 discharges. This may represent stimulation of MeHg production by $\text{SO}_4^{2-}$ entering from STA-2. However, the relationship between $\text{SO}_4^{2-}$ loading and MeHg production is complex, as discussed in detail in Orem et al. (2011). While $\text{SO}_4^{2-}$ loading stimulates microbial $\text{SO}_4^{2-}$ reduction and MeHg production, buildup of sulfide (an end product of
microbial \( \text{SO}_4^{2-} \) reduction) reduces the rate of Hg methylation. In most ecosystems, this results in a unimodal relationship between \( \text{SO}_4^{2-} \) and MeHg, with maximum MeHg produced at some intermediate \( \text{SO}_4^{2-} \) concentration (often referred to as the Goldilocks Zone). This type of relationship between \( \text{SO}_4^{2-} \) and MeHg may exist in northwestern WCA-2A (Figure 3B-22), and the plot of \( \text{SO}_4^{2-} \) versus MeHg has the characteristic bell shape. USGS studies have suggested similar relationships in the ecosystem at other locations along the \( \text{SO}_4^{2-} \) loading gradient (Orem et al., 2011). In northwestern WCA-2A, maximum MeHg concentrations occur at \( \text{SO}_4^{2-} \) concentrations in the range of 40–60 mg/L, which is much higher than observed in other areas. It is hypothesized that this may be due to the high \( \text{SO}_4^{2-} \) loading and the fact that such loading in this case is relatively recent. Sulfide concentrations may not have yet reached levels to effectively inhibit MeHg production except at the highest levels of loading. It is also hypothesized that organic peats and possibly metals may still be effectively reacting with sulfide produced by microbial \( \text{SO}_4^{2-} \) reduction, sequestering the sulfide as metal sulfides or organic S and moderating the amount of free sulfide present. Over time, as sulfide reactive sites on the organic matter and free metals present are reduced by reaction with sulfide, the \( \text{SO}_4^{2-} \) level producing maximum MeHg production is expected to decline. The USGS plans continued monitoring of \( \text{SO}_4^{2-} \) loading and MeHg production at this site to further understand these relationships.

Figure 3B-22. \( \text{SO}_4^{2-} \) concentration plotted against MeHg concentrations for surface waters of northwestern WCA-2A.
DISSOLVED ORGANIC MATTER CONCENTRATION AND CHARACTER IMPACT MERCURY AVAILABILITY FOR METHYLATION

Andrew Graham$^{14}$, Cynthia Gilmour$^{14}$
and George R. Aiken$^{15}$

DOM in the Everglades, originating from degradation of peat and leaching and degradation of algae, periphyton, and macrophyte detritus, varies in concentration and character both spatially (Qualls and Richardson, 2003; Scheidt and Kalla, 2007; Wang et al., 2002) and with hydroperiod (Lu et al., 2003; Scheidt and Kalla, 2007). Chemical characteristics of DOM are influenced by source materials (Qualls and Richardson, 2003) and biogeochemical processes, such as microbial metabolism and photo-oxidation (Aiken et al., 2011a).

Everglades marshes naturally support high rates of organic carbon production via photosynthesis; additionally, the flow of agricultural drainage waters from the EAA to the EPA has resulted in nutrient enrichment of historically oligotrophic wetlands in the WCAs. This nutrient enrichment, including phosphorus addition to the northern EPA, strongly influences the nature of DOM by increasing plant production and altering plant community composition (Davis, 1991), increasing the rate of peat accretion (Craft and Richardson, 1993), causing anaerobic conditions in pore waters in the nutrient-rich areas, and increasing the microbial mineralization rate of organic matter (Amador and Jones, 1995) with the subsequent generation of greater concentrations of DOM (Aiken et al., 2011a).

In general, Everglades DOM concentrations are highest in areas influenced by agricultural drainage waters, lower in more pristine locations, and decrease with distance from northern, eutrophic sites in WCA-2A into WCA-2B, WCA-3A, and further south into ENP (Aiken et al., 2011a) (see Figures 3B-23 and 3B-24). The character of DOM also changes across the nutrient enrichment gradient of the EPA. For instance, SUVA$_{254}$ (specific UV absorbance per meter at wavelength 254 nm divided by DOC concentration) is a strong indicator of the presence of aromatic compounds and is often related to DOM reactivity (Weishaar et al., 2003). Data presented in Figure 3B-24 show that SUVA$_{254}$ decreases from north to south, with impacted sites in the northern EPA consistently having the highest values. The understanding of the role of DOM in Hg methylation is evolving. Hg methylation occurs mainly in mildly sulfidic sediments and soils. New research indicates that nanoparticulate metacinnabar [β-HgS(s)] may be an important, and even the dominant, inorganic Hg species under these conditions (Aiken et al., 2011b; Deonarine and Hsu-Kim, 2009; Gerbig et al., 2011). DOM strongly interacts with β-HgS(s), inhibiting its growth, aggregation, and ordering (Deonarine and Hsu-Kim, 2009; Gerbig et al., 2011; Slowey, 2010). This interaction between DOM and metacinnabar (HgS) has important implications for Hg bioavailability and MeHg production, as nanocolloidal HgS stabilized by DOM has been demonstrated to be highly bioavailable to Hg-methylating SRB (Graham et al., 2012; Zhang et al., 2012).

Both the concentration of DOM and its chemical character impact the bioavailability of Hg for methylation. DOM character varies in space and time (Aiken et al., 2011a), and the nature of DOM may be expected to influence the strength of interactions with HgS and therefore be an important control on Hg bioavailability and methylation (Mitchell and Gilmour, 2008; Aiken et al., 2011a,b). To test this hypothesis, Hg methylation in Hg-DOM-S solutions was evaluated with a wide variety of DOM isolates in the EPA, including from sites 2BS in WCA-2B and F1 in WCA-2A (Gerbig et al., 2011).
Figure 3B-23. Dissolved organic matter (DOM) sampling locations in the EPA. [Note: 1E – 1 East; 1W – 1 West; and STA – Stormwater Treatment Area.]
Figure 3B-24. Seasonal and spatial variability in dissolved organic carbon (DOC) concentration in milligrams carbon per liter (mgC L\(^{-1}\)) (top) and specific ultraviolet absorbance (SUVA\(_{254}\)) (bottom) from select sites (F1, 2BS, 3A15, and TS-7) in the EPA.
Tests on the role of DOM character on Hg bioavailability for methylation were done under controlled conditions in pure cultures of Hg-methylating SRB, Desulfovibrio desulfuricans ND132 (Gilmour et al., 2011; Graham et al., 2012). Results showed that DOM character was an important control on Hg methylation in Hg-DOM-S solutions. DOM with a high degree of aromaticity (reflected in high SUVA254 values) appears to be especially effective at enhancing Hg methylation, consistent with reports that highly aromatic DOM interacts most strongly with HgS and other metal sulfides (Deonarine et al., 2011; Deonarine and Hsu-Kim, 2009; Waples et al., 2005). Therefore, measures of DOM concentration and quality, in addition to SO4²-/sulfide, should be considered in models predicting the sensitivity of ecosystems, including the Everglades, to Hg loads.

Together, these data suggest that DOM in the northern, nutrient-impacted EPA is better able to enhance Hg bioavailability for methylation than DOM in the more pristine marshes. Regional hydrologic restoration is expected to result in changes in the distribution of DOM across the EPA, potentially moving highly aromatic, highly reactive DOM farther south into the ecosystem and, in turn, impacting the production and distribution of MeHg across this area.

**SULFUR SOURCES AND EFFECTS**

**RELATIONSHIPS BETWEEN EMERGENT MACROPHYTE LEAF ELONGATION RATES AND POREWATER SULFIDE LEVELS IN STA-2 CELL 1**

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Li et al. (2009) have suggested that southern cattail (Typha domingensis) has greater tolerance to sulfide toxicity than sawgrass (Cladium jamaicense) and could facilitate Typha’s displacement of Cladium stands in the northern EPA where elevated levels of phosphorus and S co-occur. In that study, species-specific differences in physiology and growth responses of immature, single stem Cladium and Typha plants exposed to various sulfide concentrations in hydroponic culture were evaluated. Compared with controls [0 millimole (mM) sulfide], the net photosynthesis rate for Typha was adversely impacted at a porewater sulfide concentration of 0.92 mM (29.5 mg/L), but only half of that sulfide concentration significantly affected Cladium.

Differences between Typha and Cladium among treatments were also found in final rhizome biomass and total live biomass. Both parameters were reduced at 0.69 mM (22.1 mg/L) sulfide for Cladium, while they were unaffected for Typha. No effects of sulfide on total leaf and root biomass, shoot base biomass, total plant biomass, ratio of live and dead root-supported biomass (leaves, shoot base, and rhizomes) to live and dead root biomass (total RSB/RB ratio), as well as on live RSB/RB ratio (live leaf, shoot base, and rhizome biomass/live root biomass ratio) were detected for either species. Cladium leaf elongation (LE) declined from approximately 0.7 centimeter per day (cm/d) to 0.4 cm/d at 7 mg/L sulfide, whereas Typha LE was not significantly affected until sulfide concentrations reached 22.1 mg/L, where LE declined from 2.4 cm/d to 1.4 cm/d (Li et al., 2009).

To further clarify potential adverse sulfide effects in the Everglades, a study was initiated in which field sites characteristic of low and high sulfide levels were periodically monitored for LE of plants in mature stands of Cladium and Typha. Findings for one of the field study sites (outflow region of STA-2 Cell 1) are briefly discussed here. Since 2000, inflow SO4²− levels to

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STA-2 have been the highest among all the Everglades STAs and WCAs, so this treatment wetland likely represents the most “sulfate-enriched” wetland parcel in South Florida.

Results of the monitoring studies reflected similar LE rates within each species for both 2011 and 2012 (Figure 3B-25). The mean LE rates for Cladium were 0.54 cm/d and 0.63 cm/d during the 2011 and 2012 monitoring periods, respectively. In comparison, mean Typha LE rates for 2011 and 2012 were 1.76 and 2.16 cm/d, respectively. Throughout the combined study period, the Typha LE rate (2.01 cm/d) was consistently higher than the corresponding rate for Cladium (0.59 cm/d). Median ratios of Typha LE to Cladium LE for the 2011 and 2012 monitoring periods were 2.65 and 3.97, with interquartile ranges of 3.26 and 2.95, respectively. These values are substantially lower than the reported LE ratio of 7.1 that was evidence of sulfide toxicity in the laboratory (Li et al., 2009).

Additionally, linear regression analysis of Cladium LE versus sulfide concentration demonstrates the lack of significant relationship (p > 0.05 for the slope of the regression line) between the two variables (Figure 3B-26). Also, no significant correlation was observed between the LE ratio and porewater sulfide concentration. It should be noted that porewater sulfide levels measured in our field study were frequently much higher than the 7 mg/L threshold concentration for Cladium growth inhibition observed in laboratory studies (Li et al., 2009).
While *Typha* has been shown to have a greater capacity than *Cladium* for oxidation of the rhizosphere via radial oxygen loss (ROL) from roots (Chabbi et al., 2000), ROL in *Cladium* is moderately high, reaching 75 percent of ROL rates for *Typha*, for plants grown under long-term (two months) flooded conditions. Development of an oxidized rhizosphere can serve as a buffer against inhibitory effects of reduced compounds such as sulfide (McKee et al., 1988; Chabbi et al., 2000). Indeed, porewater monitoring data of this study indicate that sulfide levels tend to decline in close proximity to the plant stems (Figure 3B-27). This suggests that an oxidized rhizosphere, perhaps due to a greater density of fine roots in soils near the stems, may be inhibiting $\text{SO}_4^{2-}$ reduction or oxidizing sulfide.

It should be noted that these data do not necessarily demonstrate a greater tolerance of *Cladium* to sulfide than observed in laboratory conditions, but rather suggest that the relatively low diffusion rate of sulfide in organic soils, calculated to be 16 percent of that in water, results in dramatically lower delivery rates of sulfide to the oxidized root microenvironment than would be achieved under hydroponic conditions, with the aqueous sulfide levels replenished daily (Li et al., 2009). Regardless of the mechanisms responsible, field-based observations indicate that growth of mature *Cladium* plants as determined by LE rate is not inhibited (relative to *Typha*) by sulfide in one of the most sulfate-enriched Everglades marshes.
SOIL PH, NUTRIENTS AND SULFUR USE IN EVERGLADES AGRICULTURAL AREA

Alan L. Wright\textsuperscript{23} and J. Mabry McCray\textsuperscript{23}

Current University of Florida Institute of Food and Agricultural Services (UF/IFAS) fertilizer recommendations suggest application of 500 pounds elemental S per acre (agricultural S normally contains 90 percent elemental S) once every 3 years—as sugarcane is typically planted only once every 3 years—for sugarcane production on organic soils with a pH 6.6 or higher. Because of environmental concerns regarding the impact of SO\textsubscript{4}\textsuperscript{2-} on conversion of inorganic Hg to more harmful MeHg in the Everglades, providing updated fertilizer recommendations to growers that will be cost-effective and minimize S applications is a priority. Assessment of the fate of applied S fertilizers is important in understanding the contribution of the EAA to S cycling in the Everglades. Field demonstrations at multiple sites in the EAA are established to gauge the effectiveness of elemental S applications.

In this study, fieldwork continues to examine sugarcane response to elemental S on high pH organic soils. For the six study locations, yield responses have ranged from no response to a 33 percent increase in tons of sugar per acre at the rate of 400 pounds elemental S per acre. Results indicate that sugar yield is reduced when pH is greater than or equal to 7.5 as micronutrient availability is decreased. Leaf manganese concentration has generally been a good indicator of potential yield response to S application, with yield reduced with leaf manganese less than 16 mg/kg. An increase in calcium carbonate in the soil results in increased soil pH, and preliminary results indicate that extractable soil calcium may be useful as part of a soil test for predicting sugarcane yield response to S application.

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Figure 3B-27. Concentration of sulfide in soil porewater (6-10 cm depth interval) at distances of 5, 10, 20, 50, and 100 cm from the shoot base of triplicate \textit{Cladium} plants within the STA-2 Cell 1 LE monitoring site. Data points represent means ± standard error (SE) of concentrations measured at each distance during seven sampling events in 2011 and 2012. Therefore, each data point represents the mean of 21 separate porewater sulfide measurements at a 6–10 cm depth in the soil.
Various elemental S-containing materials, such as elemental S, iron sulfate, and aluminum sulfate, were evaluated for leafy greens production to reduce soil pH and increase nutrient availability. All compounds tested performed similarly and tended to produce similar yield responses. Plant-available nutrient concentrations and soil pH were measured several times in the growing season, and amendments enhanced concentrations of plant-available phosphorus. All amendments were effective at increasing leafy greens yield, with the maximum yield occurring at 500 kilograms per hectare (kg/ha). Rates above 500 kg/ha (446 pounds per acre) produced no yield increase. Banded application of amendments was better than broadcast at low rates, but broadcast was better at the higher application rates. At rates below 250 kg/ha, banded application increased yields by 15 percent relative to broadcast application. However, at rates above 250 kg/ha, broadcast application resulted in higher yields than banded. Banded application at high rates had harmful effects on leafy greens growth, as some root burn limited growth resulting in lower yields compared to broadcasting.

In general, soil pH adjustment by S addition has proven temporarily effective, but the large amount required, high cost, and environmental impact may limit its commercial utilization. For short-duration crops, such as leafy greens (10,000–12,000 acres in the EAA), positive benefits in terms of increased nutrient availability and yield have occurred. In contrast, for crops such as sugarcane (450,000 acres in the EAA), which typically remain in the field for 12 months, there was minimal benefit except when soil pH was above 7.5 and the soil contained high calcium carbonate concentrations. The expanded use of fertilizer banding, split application, and foliar application may be viable options to combat the increasing pH.

**FUTURE RESEARCH NEEDS**

As presented in the *Future Research Needs* section of the 2012 South Florida Environmental Report (SFER) – Volume I, Chapter 3B, several recommendations for future research needs related to Hg and S environmental assessment for the Everglades were formulated during the interagency 2011 Workshop on Mercury and Sulfur in South Florida Wetlands (Landing, 2011; final peer-review report is available on the District’s website at [www.sfwmd.gov/library](http://www.sfwmd.gov/library)). Since the June 2011 workshop, coordinated efforts among the District, FDEP, and other stakeholders have continued in order to discuss critical data gaps and refine key recommendations associated with these related research needs, as summarized below.

**SULFUR MASS BALANCE STUDIES**

While there is compelling evidence that SO$_4^{2-}$ promotes conversion of inorganic Hg to MeHg by SRB in the Everglades and that the EAA is a key source of SO$_4^{2-}$ to the EPA, relatively little is known about specific sulfur sources and sinks. An accurate S mass balance is critical for identifying any opportunities to sufficiently reduce SO$_4^{2-}$ loading to the EPA, potentially lower MeHg levels in Everglades fish, and decrease risk to recreational anglers and fish-eating wildlife.

The District’s Sulfur Action Plan includes S mass balance as a key research goal (SFWMD, 2011). There are large uncertainties regarding the rate of agricultural application of S in the EAA, rate of S release from oxidation of EAA soils, and source(s) of the high S levels in EAA soils. Additional research on EAA soil S dynamics is needed to estimate soil S content and character and the time required for soils to reach natural S levels in the absence of agricultural application of S. The S mass balance should include analyzing the effects of backpumping sulfate-enriched waters from the EAA on SO$_4^{2-}$ concentrations in Lake Okeechobee, as well the effects of other sources, including internal supply of SO$_4^{2-}$ resulting from soil oxidation and agricultural inputs entering Lake Okeechobee through the Kissimme River. Further study is also warranted to evaluate recent modeling that hypothesized that connate seawater is a significant source of SO$_4^{2-}$ to the EPA, to quantify atmospheric depositional S contributions and the contribution and
proximate sources of $\text{SO}_4^{2-}$ inputs from Lake Okeechobee to the EAA, and investigate the viability of $S$ removal options in the EAA.

**MONITORING AND MODELING**

Comprehensive, long-term monitoring in Everglades media has provided a valuable database to help examine trends and enhance understanding of various processes in the regional system. Importantly, there is a continued need to monitor atmospheric $\text{Hg}$ deposition, Me$\text{Hg}$ accumulation in fish and other biota, and water quality, especially $\text{SO}_4^{2-}$ concentrations. Currently, these monitoring activities are conducted by the District under the Everglades Forever Act mandates and reported in the annual SFER. Also, the USGS and University of Florida continue to conduct field studies to assess the relationships of DOC, $\text{SO}_4^{2-}$, and Me$\text{Hg}$ in biota.

It is widely 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 various rate equations covering the important $\text{Hg}$ cycling processes in the Everglades. Further efforts are necessary to develop this model to be applicable to widely varying conditions found throughout the system, including the EAA, STAs, WCAs, and ENP.

To assess the effects of possible intrusion of connate seawater, it is recommended that a coupled hydrologic and water chemistry model be developed that includes both $\text{Cl}^-$ and $\text{SO}_4^{2-}$ dynamics and incorporates explicit representations for groundwater interactions with overlying water across the Everglades landscape. It is desirable that such a model also be capable of simulating how the hydrologic alterations imposed by the Comprehensive Everglades Restoration Plan (CERP) will influence surface water $\text{Cl}^-$ and $\text{SO}_4^{2-}$ concentrations, and enable computations of the effect of changing EAA inputs of agricultural and connate seawater $\text{SO}_4^{2-}$ as well as the effect of changes in the $\text{SO}_4^{2-}$ anthropogenic component of atmospheric deposition.

Additionally, the Everglades Landscape Model (ELM) may be adapted to include $S$ cycling. It is important for some of these models to include a detailed account of the current movement of water throughout the system as well as associated environmental variables (e.g., dissolved oxygen, DOC, and pH) monitored by the District.

The District has conducted preliminary data analysis on a $\text{SO}_4^{2-}$ budget for Lake Okeechobee. The Lake Okeechobee Environmental Model (LOEM) has a module capable of simulating lake-wide changes in $\text{SO}_4^{2-}$ concentrations under various hydrological conditions. There is also interest in conducting data analyses using historical water quality data ($\text{SO}_4^{2-}$, DOC, color, etc.) from the District’s monitoring network to document historical trends of $\text{SO}_4^{2-}$ concentrations and the relationships among $\text{SO}_4^{2-}$, DOC, and TH$\text{g}$ in fish. Such analyses are also expected to be useful for modeling efforts in a hindcasting perspective.

**DISSOLVED ORGANIC MATTER**

DOM has been shown to influence the bioavailability of inorganic $\text{Hg}$ to SRB, influence the binding of $\text{Hg}^{2+}$ to sediments, and be involved in the photochemical reduction of $\text{Hg}^{2+}$ and the photochemical breakdown of Me$\text{Hg}$. DOC, which is a subset of DOM, is included in the District’s water quality monitoring network for selected sites. Historical data for DOC are also available in the District’s hydrometeorological database, DBHYDRO (www.sfwmd.gov/dbhydro). While the role of DOC on Hg methylation in the Everglades has been initially evaluated, more research is needed to better understand the importance of the composition and level of DOM on Me$\text{Hg}$ production. Also, because higher DOM concentrations and greater levels of aromatic DOM—which is most effective in making $\text{Hg}^{2+}$ bioavailable for
methylation by SRB—are present in the northern, nutrient-impacted EPA, it is key to examine the causes for the elevated DOM to determine possible opportunities to reduce such levels.

**EFFECTS OF SULFATE ON MERCURY METHYLATION AND DEMETHYLATION**

Available research indicates that the relationship between $\text{SO}_4^{2-}$ concentration and Hg methylation rate is nonlinear and unimodal, and that the maximum methylation potential associated with $\text{SO}_4^{2-}$ varies across the Everglades. Because the magnitude and direction of the effect of $\text{SO}_4^{2-}$ reductions is so sensitive to the shape of relationship and the locus of the $\text{SO}_4^{2-}$ maximum, the effects of changing $\text{SO}_4^{2-}$ on Hg methylation—particularly at low ambient concentrations (i.e., from ~ detection limit to 5 mg/L)—would benefit from further evaluation. Because the growth of SRB is stimulated in the presence of both $\text{SO}_4^{2-}$ and DOM, the interaction of $\text{SO}_4^{2-}$ and DOM loadings on Hg methylation rate also requires more research.

Previous and current studies indicate that demethylating bacteria can significantly reduce MeHg concentrations in the Everglades. However, little is known about the factors that promote demethylation. An understanding of the role of demethylation in the MeHg mass balance may help clarify the variations of MeHg in wildlife in different marsh areas that cannot be explained by $\text{SO}_4^{2-}$ concentration and Hg methylation potential and lead to management alternatives that promote activity of demethylating bacteria.

**BIOACCUMULATION OF METHYLMERCURY IN THE FOOD CHAIN**

MeHg concentrations increase up the food chain and display large variations in Everglades fish that cannot be explained by MeHg concentrations in surface water alone. Limited available data show that the percentage of MeHg relative to total Hg in fish, especially in low trophic level fish (e.g., *G. holbrooki*), change seasonally in response to diet (i.e., detritus versus periphyton). There are also large variations in Hg in high trophic level fish. Initial assessments suggest that these variations might be associated with fish trophic position as affected by prey types (i.e., grass shrimp versus sunfish for LMB). Further studies are needed to assess seasonal changes in MeHg concentrations in fish at different trophic levels and their relationships with soil, water, and periphyton MeHg concentrations and fish dietary composition.

**LITERATURE CITED**


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