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Mercury Mass Budget Estimates and Cycling Seasonality in the Florida Everglades

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We estimated the mass budget for mercury (Hg) seasonally deposited into the Florida Everglades and investigated seasonality of Hg cycling by analyzing data obtained for water, soil, flocculent detrital material (floc), periphyton, and mosquitofish collected throughout the Everglades freshwater marshes in the 2005 dry and wet seasons. Higher wet season total Hg (THg) in soil, floc, and periphyton agreed with greater Hg amounts entering these compartments during the wet season, probably owing to substantially greater Hg deposition in the wet season than in the dry season. Seasonal differences were absent for THg in surface water. Methylmercury (MeHg) showed mixed seasonal patterns, with higher water and soil MeHg and lower periphyton MeHg in the dry season but no seasonality for floc MeHg. Seasonal variations in Hg deposition, MeHg production and transport, and mass of ecosystem compartments could be responsible for the seasonality of MeHg cycling. Higher mosquitofish THg, higher bioaccumulation factors, and higher biomagnification factors from periphyton to mosquitofish were observed in the wet season than in the dry season, indicating that the wet season is more favorable for Hg bioaccumulation. The mass budget estimation agreed with this result.

Introduction

Elevated levels of mercury (Hg) have been found in fishes, wading birds, and large predators in the Florida Everglades (*1*). Efforts have been made to investigate the scope and magnitude of Hg contamination and to understand Hg biogeochemical cycling in this subtropical wetland ecosystem (*2, 3*). Several important aspects in Hg biogeochemical cycling, including source (*4*), transport (*5, 6*), transformation (especially methylation/demethylation) (*7–10*), and bioaccumulation (*11, 12*) have been investigated to various degrees. However, Hg cycling and the corresponding biogeochemical controls in this complicated ecosystem, particularly at the landscape level, are not fully understood. A mass budget for Hg cycling in the Everglades remains lacking, which hampers predicting the fate of Hg in this system after deposition.

Precipitation in the Everglades reflects the subtropical climate of south Florida, with a rainy wet season (May−October) and a dry season (November−April) (*2, 13*). Following this precipitation pattern are characteristic hydropatterns, involving seasonal variations in water distribution, flooding duration, and freshwater flows (*2*). The distinct wet–dry season periodicity in rainfall and hydrology controls Hg deposition as well as the physical, chemical, and biological characteristics of the marsh, leading to seasonality of Hg cycling in the Everglades (*2*). Strong seasonal patterns have been observed for surface water methylmercury (MeHg), production of dissolved gaseous Hg, and Hg methylation in Water Conservation Area (WCA) 2A in the northern Everglades (*9, 10, 14*). However, the seasonality of Hg distribution and cycling has not been extensively investigated, especially on the landscape scale including the entire Everglades. Exploring the seasonal variation in Hg cycling will help elucidate biogeochemical processes that control Hg cycling across ecosystem compartments and bioaccumulation in the food web.

In 1993 the U.S. Environmental Protection Agency (EPA) Region 4 launched the Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP), which employed a probability-based sampling design to sample the entire freshwater Everglades both in the dry and wet season. This sampling design allows us to investigate seasonality in Hg cycling and to estimate Hg mass budget on the Everglades-wide scale. In this paper we analyze the data obtained in the R-EMAP phase III sampling event that was conducted in 2005. Our objective was to further the understanding of Hg cycling in the Everglades by providing a mass budget estimation for Hg seasonally deposited into this ecosystem and examining the seasonality of Hg cycling and bioaccumulation influenced by hydropatterns. To our best knowledge, this is the first study attempting to estimate mass budget for Hg deposited into the Everglades.

Materials and Methods

Sampling and Sample Analysis. Sampling was conducted throughout the freshwater Everglades, including Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR), WCA-2, WCA-3, and Everglades National Park (ENP). Surface water, pore water, soil, flocculent detrital material (floc), periphyton, and Eastern mosquitofish (*Gambusia holbrooki*) were collected at 228 randomly located stations; 109 in May (the dry season) and 119 in November (the wet season) (Figure S1 in the Supporting Information). A variety of physical and chemical variables, including total Hg (THg) and MeHg, were measured for the collected samples. Detailed sampling and analytical procedures can be found in the Supporting Information and references cited therein.

Quality Assurance of Hg Analysis. All participating laboratories for Hg analysis are accredited by the National Environmental Laboratory Accreditation Conference (NELAC). Strict quality assurance and control procedures were followed during sample analysis. For each sample batch (up to 20

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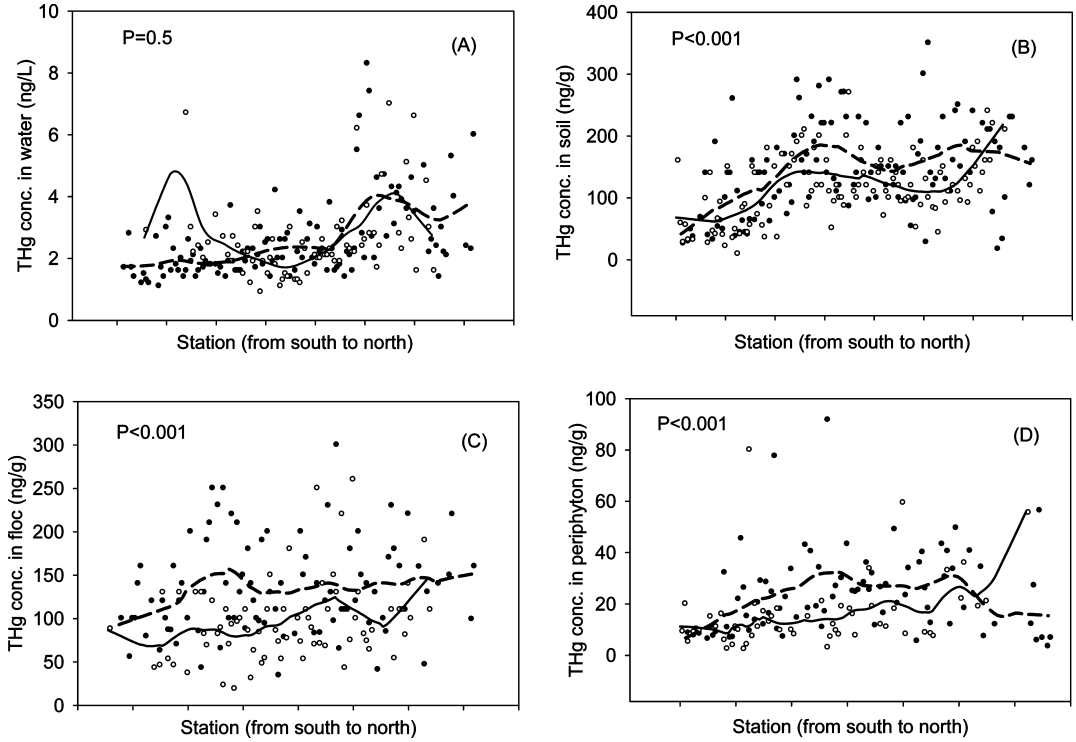

FIGURE 1. Seasonal differences of THg concentrations in (A) surface water, (B) soil, (C) floc, and (D) periphyton in the Everglades. Open and closed circles are data obtained in the dry and wet season, respectively. Solid and dashed lines are fitted by locally weighted regression (LOESS) for the dry and wet season data, respectively. The P value denotes the statistical significance of seasonal differences.

samples), at least two method blanks, a pair of matrix spikes, and/or two certified reference materials (CRMs) were included. All method blanks were observed to be below corresponding detection limits (THg: 0.2 ng/L [water], 2.4 ng/g [soil, floc, and periphyton], 3.2 ng/g [mosquitofish]; MeHg: 0.02 ng/L [water], 0.04 ng/g [soil, floc, and periphyton]). Acceptable recoveries were obtained for all matrix spikes or CRMs (70–130% for THg and 65–135% for MeHg). Only 2 individual analytical results were rejected as not meeting the data quality objectives.

Data Analysis. The differences in THg and MeHg in each environmental matrix between the dry and wet seasons were evaluated by plotting the spatial series of corresponding Hg concentrations along the sampling stations. The data series was smoothed by using locally weighted regression (LOESS) on SigmaPlot (Systat software, Inc., Version 9.01). Wilcoxon rank sum tests were performed on S-PLUS (Insightful Corp., Version 6.2) to test the statistical significance of differences in Hg concentrations between seasons.

Seasonal variation in Hg cycling was investigated through estimating the mass budget of Hg seasonally deposited into the Everglades via wet and dry deposition. Our sampling events took place at the end of each season and thus we estimated the fraction of Hg entering into each ecosystem compartment (e.g., water, soil, etc.), among total seasonally deposited Hg, after a whole season's compartmentalization processes (see Supporting Information). For each season, the mass balance of THg follows:

$$M_{BD}^{THg} = \Delta C_{SW}^{THg} V_{SW} + \Delta C_{SD}^{THg} M_{SD} + \Delta C_{FC}^{THg} M_{FC} + \Delta C_{PE}^{THg} M_{PE} + \Delta C_{PK}^{THg} M_{PK} + \Delta C_{FS}^{THg} M_{FS} + \Delta C_{SW}^{THg} V_{OF}^{THg} + M_{EV}^{THg} + M_{BU}^{THg} \quad (1)$$

where M, ΔC, and V refer to mass, change in concentration resulted from seasonally deposited Hg, and volume, respectively. For each parameter, the subscript denotes the ecosystem compartment, while the superscript denotes the Hg species. Table S1 defines the input parameters used to estimate the Hg mass budget (see Supporting Information). The distribution ratio (R) of Hg between water and other compartments (R = [Hg in solid or biological matrix] / [Hg in water], L/g) was defined and used to relate water Hg to Hg in the other compartments (see Supporting Information). Taking into account the relationship between water Hg, solid or biotic phase Hg, and R, the equation could be written as

$$M_{BD}^{THg} = \Delta C_{SW}^{THg} \times \left(V_{SW} + R_{SD}^{THg} M_{SD} + R_{FC}^{THg} M_{FC} + R_{PE}^{THg} M_{PE} + R_{PK}^{THg} M_{PK} + BAF_{FS}^{THg} M_{FS} + V_{OF}\right) + M_{EV}^{THg} + M_{BU}^{THg} \quad (2)$$

For MeHg, a similar mass balance was calculated as denoted below:

$$M_{PD}^{MeHg} = \Delta C_{SW}^{MeHg} \times \left(V_{SW} + R_{SD}^{MeHg} M_{SD} + R_{FC}^{MeHg} M_{FC} + R_{PE}^{MeHg} M_{PE} + R_{PK}^{MeHg} M_{PK} + BAF_{FS}^{MeHg} M_{FS} + V_{OF}\right) + M_{BU}^{MeHg} \quad (3)$$

In contrast to THg, the source of MeHg is not atmospheric deposition but methylation of seasonally deposited inorganic Hg in the ecosystem (Table S1) (*15*). The details in calculating the concentration changes in each compartment are described in the Supporting Information.

Results and Discussion

Seasonal Variation in THg Cycling. THg concentrations in soil, floc, and periphyton varied seasonally, with higher concentrations in the wet season for all 3 matrices ($p < 0.001$) (Figure 1). Seasonal differences in THg ($p = 0.5$) were not found for surface water.

Our results of THg budget estimation suggest that soil is the largest sink for Hg with about 80% of seasonally deposited THg being entrapped in this compartment (Figure 2), in

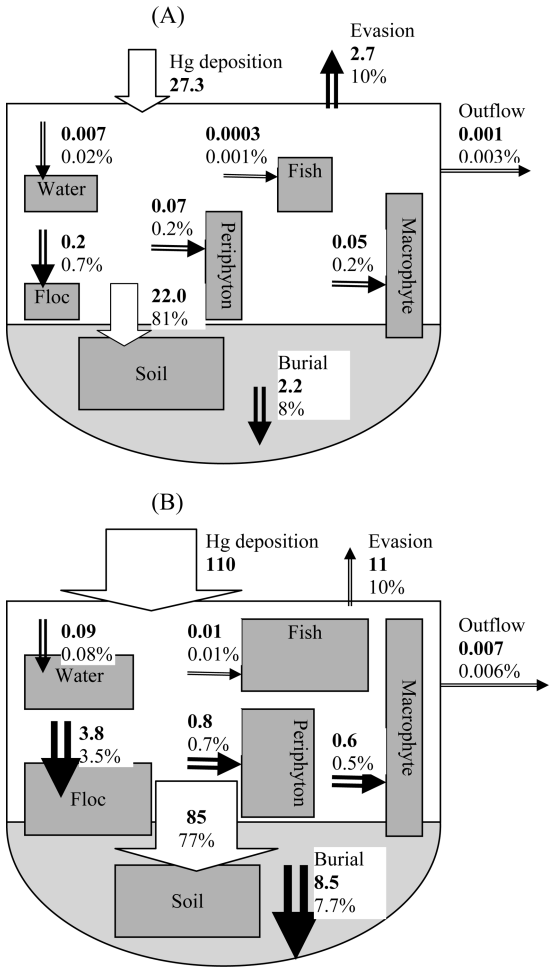

FIGURE 2. Mass (in bold, kg) and fraction (%) budget of THg deposited to the Everglades in (A) dry and (B) wet season in 2005. Arrow and rectangle sizes show seasonal variation in Hg amounts entering ecosystem compartments and in compartment mass, respectively. Arrows do not project the actual transport pathways.

agreement with previous studies (*2, 15*). Floc retains 0.7 and 3.5% of THg deposited into the Everglades during the dry and wet season, respectively. During redistribution after deposition, only a small proportion of THg deposited is retained in the water. Evasion (from water and in particular transpiration through macrophyte) represents an important pathway of Hg removal, with 10% of seasonally deposited THg being evaded out of this ecosystem according to the literature (*14, 16, 17*). Mercury removal with outflow to Florida Bay and the Keys accounts for a very small proportion of THg deposited, probably due to the slow movement of water in this wetland (*2*). The proportion of THg accumulated in mosquitofish is also low, possibly due in part to low biomass estimates used to represent the standing stock.

The mass budget estimation revealed that Hg cycling in the Everglades has a distinct seasonal pattern (Figure 2). Our results suggest that 22.0, 0.2, and 0.07 kg of Hg entered into Everglades soil, floc, and periphyton, respectively, during the 2005 dry season. These amounts were significantly lower than the 85, 3.8, and 0.8 kg found in these compartments in the wet season. Elevated THg in soil, floc, and periphyton in the wet season is therefore expected, as a result of substantially increased Hg amounts entering these compartments.

The observed seasonality in Hg cycling results primarily from the seasonal variations in Hg deposition. Atmospheric deposition (wet and dry), with the dominant Hg form being inorganic Hg, contributes over 95% of the Hg input to the Everglades (*3, 18, 19*). Both dry and, in particular, wet Hg deposition are substantially higher in the wet season as compared to the dry season (*4, 20, 21*). We estimated that 110 kg of Hg was deposited into the Everglades during the 2005 wet season, while only 27.3 kg of Hg was deposited during the dry season (see Table S1, Supporting Information). Such an increase in Hg deposition in the wet season led to the seasonal differences in Hg amounts entering ecosystem compartments.

In addition to seasonal variations in Hg deposition, transport processes, such as adsorption and biological uptake, may exhibit seasonal variability as a result of seasonal changes in physicochemical characteristics of the Everglades ecosystem. These variations in transport could also contribute to the observed seasonality in THg concentrations in soil, floc, and periphyton. We examined the difference between the dry and wet season in the THg distribution ratio (R), a parameter defined to characterize Hg compartmentalization. R was higher in the wet season for floc and periphyton ($P < 0.01$), while this ratio exhibited no seasonal difference for soil ($P = 0.5$) (Figure S2). Higher R suggests that THg is more likely to be redistributed into floc and periphyton, instead of being retained in the water column, in the wet season than in the dry season. Such redistribution could contribute to the higher THg observed in floc and periphyton in the wet season. Higher R in the wet season could be related to lower DOM and turbidity in surface water (Table S2). Most Hg present in Everglades water is complexed with DOM or adsorbed to suspended particulates (*15, 22*). The lower wet season DOM and turbidity would result in a correspondingly lower association between Hg and DOM or suspended particles, which would produce an expectedly higher R.

We did not observe seasonal differences in water THg, which is probably due to the fact that our sampling events occurred at the end of each season. Our results (Figure 2) and previous studies have shown that a very small fraction of the seasonally deposited Hg is retained in the water column after a whole season's compartmentalization. This small fraction of Hg could be insufficient to significantly change water THg concentration, even in the wet season.

Seasonal Variability in MeHg Cycling. The results of the LOESS-smoothed spatial series plots (Figure 3) and Wilcoxon rank sum test suggest that seasonal variations in MeHg were present for water, soil, and periphyton, but absent for floc. For water and soil, significantly higher MeHg concentrations ($p < 0.001$) were detected in the dry season. MeHg was higher in the wet season than in the dry season for periphyton ($p < 0.001$).

For MeHg cycling, atmospheric deposition is not an important direct source due to extremely low MeHg concentrations in atmospheric deposition (*23*), but instead contributes an inorganic Hg pool for MeHg production. A number of postdepositional processes, in particular MeHg production and transport, play an important role in MeHg cycling and influence MeHg concentrations in various compartments. In the Everglades, MeHg is produced primarily in soil, floc, and periphyton (*8, 9, 24*). MeHg produced in these compartments can then be transported into the water column and/or transferred to the food web.

Seasonal patterns in soil, floc, and periphyton MeHg are ascribed to seasonal variations in MeHg production and transport and in the mass of ecosystem compartments. The wet season is more favorable for Hg methylation than the dry season (*2, 25*). Our budget estimation for MeHg produced from seasonally deposited Hg suggests that MeHg production increased significantly in the wet season for soil, and particularly, floc and periphyton (Figure 4). The seasonal variability in MeHg transport during the compartmentalization processes, characterized by R, showed mixed patterns for soil, floc, and periphyton (Figure S2). No seasonal

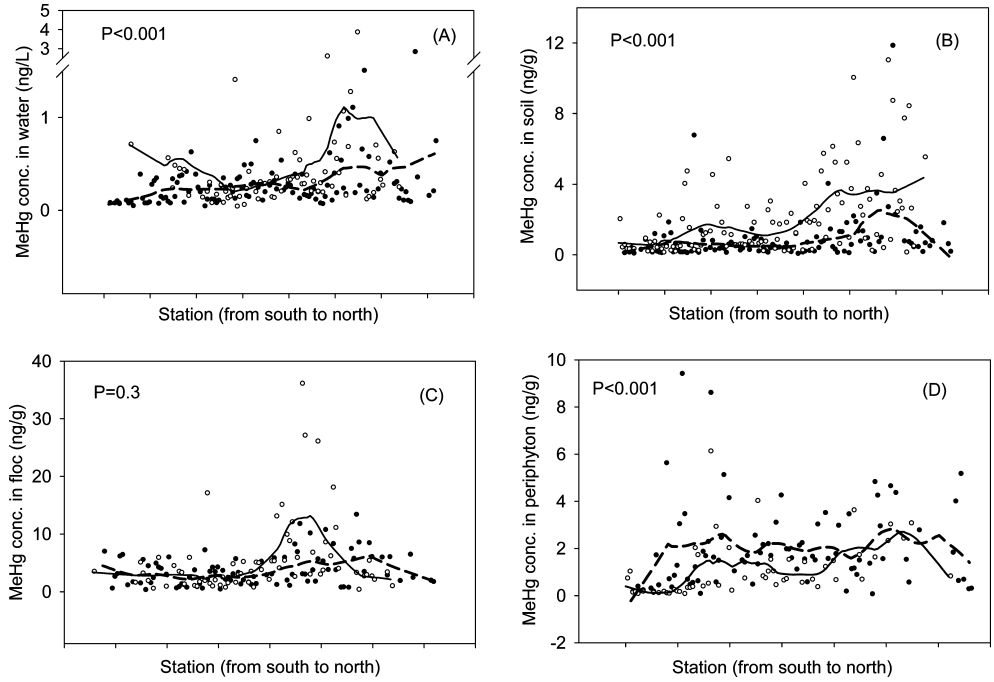

FIGURE 3. Seasonal differences of MeHg concentrations in (A) surface water, (B) soil, (C) floc, and (D) periphyton in the Everglades. Open and closed circles are data obtained in the dry and wet season, respectively. Solid and dashed lines are fitted by locally weighted regression (LOESS) for the dry and wet season data, respectively. The P value denotes the statistical significance of seasonal differences.

differences in MeHg *R* were observed for floc. Lower *R* for soil and higher *R* for periphyton were observed in the wet season than in the dry season. It appears that soil is less capable of retaining MeHg during the wet season than during the dry season and that periphyton formed in the wet season has stronger capability to retain MeHg. The absence of seasonality in floc MeHg could be accounted for by the parallel increase in MeHg production and in floc mass in the wet season as both are increased dramatically. It should be noted that the mean, instead of median, of floc thickness was used to estimate floc dry mass in the dry season because the median was zero (i.e., many dry season sites were devoid of floc). This potentially results in a considerable overestimation of floc mass. For periphyton, the increase in MeHg production and retention may be sufficient to offset the higher biomass and create higher MeHg concentration in the wet season, as we observed. Lower soil MeHg in the wet season could be related to MeHg transport. As we estimated, only 58% of MeHg produced from Hg deposited in the 2005 wet season was retained in the soil, remarkably lower than the 86% retained in the dry season.

There are several reasons for the enhanced MeHg production in the wet season. First, periphyton biomass and primary productivity peaks during the wet season (*13*) causing increased activity and accumulation of floc. As the coverage of floc and periphyton on Everglades soil increases, the potential area for Hg methylation becomes proportionally larger as well. Second, the Hg pool available for methylation is greater in the wet season than in the dry season. Previous studies have shown that MeHg is likely synthesized primarily from new inorganic Hg supplied by atmospheric deposition and not from legacy Hg released from soil (*25, 26*). Substantially greater Hg deposition in the wet season provides a larger inorganic Hg pool available for methylation, compared with the dry season. Third, seasonal alterations in physicochemical parameters are favorable for MeHg production in the wet season. The elevated water level could change dry season aerobic conditions of surficial soil into anaerobic conditions during the wet season. This change is important for Hg methylation since the primary Hg methylator, sulfate-reducing bacteria, is more active under anaerobic conditions (*25*). Additionally, sulfate produced from sulfide oxidation in surficial soils following the dry season drawdown, the substrate of methylation process, will become available accompanying reinundation of oxidized soils when the wet season returns. Previous studies have shown that a first-flush release of nutrients, including sulfate, and Hg usually occurred during the first postdryout sampling (*26*). We did not observe higher sulfate in surface and pore water in the wet season, probably because our wet season sampling was conducted at the end of wet season.

Lower water MeHg in the wet season is likely caused by the dilution effect of abundant rainfall. Rainwater is typically low in MeHg, with inorganic Hg as the dominant form (*23*). Everglades MeHg is unlikely to be produced in the water column (*24*), although Hg methylation has been observed in some waters (*27, 28*). It is true that more MeHg is produced in soil, floc, and periphyton, and that subsequently more MeHg is transported into water column in the wet season (Figure 4). However, the MeHg seasonally transported to water (0.6 and 6.6 g for dry and wet season in 2005) is small, compared to the legacy MeHg pool in water, which was estimated to be about 1000–2000 g (*2*). Therefore, the abundant rainfall in the wet season, which results in a 2-fold increase in water volume (Table S1), is sufficient to lower water MeHg by dilution.

Seasonal Variability in Hg Bioaccumulation. Mosquitofish are ubiquitous in the Everglades and have a lifespan of only a few months (*12*). Thanks to the short lifespan, mosquitofish are suitable for studying seasonality in Hg bioaccumulation as Hg levels found in a mosquitofish sample will be the result of recent accumulation (*12*). Significantly higher weight-adjusted THg (the average THg without weight-adjustment showed the same pattern and is not shown) was observed for mosquitofish in the wet season than in the dry season ($p < 0.001$) (Figure 5). The bioaccumulation factor for Hg in mosquitofish and biomagnifications factor (BMF = [mosquitofish THg]/[periphyton MeHg]) between mosquitofish and periphyton were significantly higher in the wet

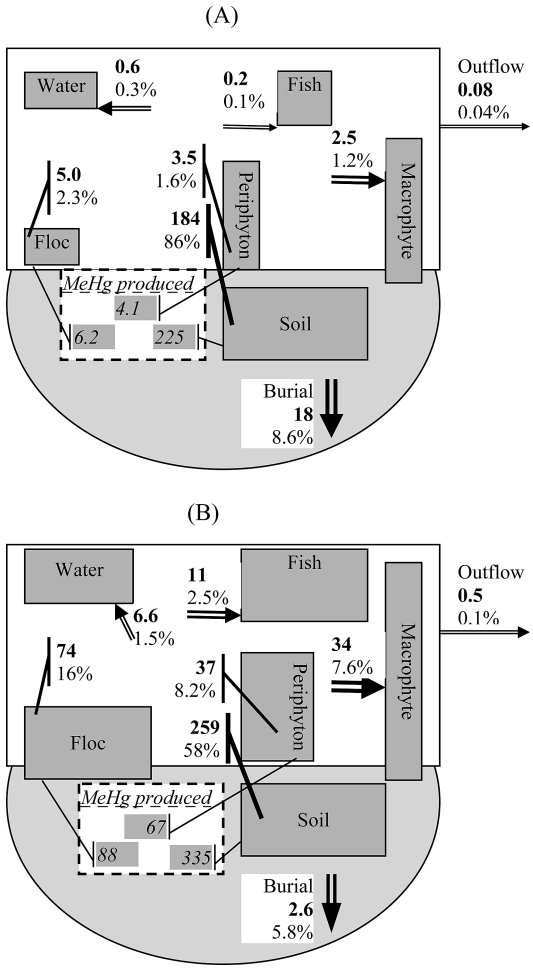

FIGURE 4. Mass (in bold, g) and fraction (%) budget of MeHg produced (from seasonally deposited Hg) in the Everglades during (A) dry and (B) wet season in 2005. Rectangle size shows seasonal variation in compartment mass. MeHg produced is shown in a rectangle with dashed line, with filled callouts linked to respective compartments. MeHg retained in soil, floc, or periphyton after redistribution is shown by line callouts. Arrows do not project the actual transport pathways.

season than in the dry season ($P < 0.001$), indicating stronger bioaccumulation of Hg in the wet season.

The results of mass budget estimates for MeHg revealed that the wet season is favorable for Hg bioaccumulation (Figure 5). Budget estimates suggested that 2.5% (11 g) of MeHg produced from Hg deposited in the 2005 wet season was accumulated into mosquitofish, substantially exceeding 0.1% (0.2 g) in the dry season. The increase in MeHg amount accumulated in fish during the wet season exceeds the increase in estimated mosquitofish biomass (Figure 4 and Table S1), indicating enhanced bioaccumulation. Mercury bioaccumulation can occur through either direct uptake from the water or via diet through the food web, with the latter being the more important pathway for aquatic organisms to accumulate MeHg (*12, 25*). Our estimates showed not only more MeHg is produced in the wet season, but also more MeHg is redistributed into water, floc, and periphyton instead of being retained by soil (Figure 4). MeHg in water could be accumulated through the uptake pathway, while floc and periphyton represent major diet pathways for Hg bioaccumulation since both are important food web components in the Everglades (*12, 25, 29*).

In addition to MeHg production, a variety of biotic and abiotic factors can influence Hg bioaccumulation. Biotic factors, such as trophic position and food web structure,

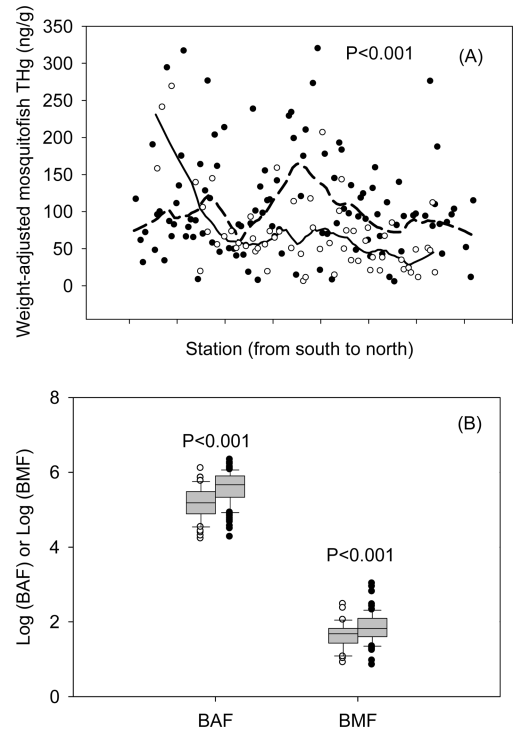

FIGURE 5. Stronger Hg bioaccumulation in the wet season (closed circles and dashed lines) than in the dry season (open circles and solid lines) in the Everglades, as shown by (A) weight-adjusted mosquitofish THg and (B) bioaccumulation factor (BAF) and biomagnification factor from periphyton to mosquitofish (BMF). The P value denotes the statistical significance of seasonal differences.

significantly affect Hg bioaccumulation through the diet pathway (*15*). Higher Hg bioaccumulation in the wet season is likely related to seasonal food web structure changes. Everglades mosquitofish are at varying trophic levels, 2.0−3.0 (*12*) or 4.0−4.5 (*30*), depending on specific environmental conditions. Mosquitofish were observed to eat less algae and more invertebrates in the wet season compared to the dry season (*15*), indicating an upward shift in trophic position in the wet season (*12*). As expected, the upward trophic position in the wet season would result in more Hg uptake and bioaccumulation, as MeHg concentrations generally increase by a factor of 3−10 from one trophic level to the next one up (*31*).

Abiotic factors, such as physical and chemical characteristics of water (depth, temperature, pH, turbidity, DOM, etc.), can influence Hg bioaccumulation through changing food web structure. Abiotic factors could also influence Hg bioaccumulation by affecting MeHg availability. The seasonality in Hg bioaccumulation in the Everglades could also be related to the seasonal variation in abiotic factors, e.g., DOM. MeHg is known to be present mainly as complexes with DOM in waters (*22, 28, 32, 33*). Once complexed with DOM, MeHg exhibits limited bioavailability for uptake by aquatic organisms. Everglades water is higher in DOM in the dry season than in the wet season, suggesting more MeHg could be complexed by DOM in the dry season. Therefore, MeHg in Everglades water could be less favorable for bioaccumulation through direct uptake in the dry season, compared with the wet season.

Implications and Uncertainty of Mass Budget Estimation. The mass budget model, agreeing with results of field sample analysis, reveals distinct seasonal patterns in Hg cycling and bioaccumulation in the Everglades. The seasonality in Hg cycling results from the seasonal variations in Hg inputs and in biogeochemical conditions. The seasonality

in Hg cycling could vary with year, particularly when extreme weather conditions are present for that year. For example, among the past 3 phases of REMAP, a significant increase in soil THg in the wet season, compared to the dry season, was observed for phases II (1999) and III (2005), but not for phase I (1995–1996). This is probably due to the fact that the 1995–1996 dry seasons were relatively wet in comparison to the 1999 and 2005 dry seasons. Apart from the Everglades, Hg cycling seasonality is likely expected for other aquatic ecosystems because seasonal climate change occurs naturally. In fact, seasonality of Hg cycling has been documented for other aquatic and wetland ecosystems (*34*–*36*).

It should be noted that a large uncertainty could exist for THg and MeHg fluxes estimated here. The sources of uncertainty include atmospheric Hg deposition (in particular dry deposition for which limited information is available), calculations in *R* values, estimation of Hg outputs (e.g., evasion and outflow), and estimation of ecosystem mass. For Hg mass budget in the entire Everglades, as is the case of this study, the uncertainty could be exaggerated because some items were estimated based on studies in a localized area (e.g., Hg evasion). We would particularly point out that many median or mean values (e.g., *R*, water depth, and floc thickness) were used in the model, which would inevitably lead to the uncertainty in model output because the Everglades is highly spatial in terms of ecological conditions. Only from the uncertainty in *R* (±1 SE), we estimated an uncertainty on the Hg fluxes of 30–40%.

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Supporting Information Available

A table listing input parameters for estimating the mass budget of Hg seasonally deposited into the Everglades, a table listing ancillary parameters, a figure showing the seasonal differences in *R* values, and a sampling map. This material is available free of charge via the Internet at http://pubs.acs.org.

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