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Distribution of total and methylmercury in different ecosystem compartments in the Everglades: Implications for mercury bioaccumulation

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Mercury bioaccumulation in Florida Everglades is related to the distribution patterns of mercury species among ecosystem compartments.

Abstract

We analyzed Hg species distribution patterns among ecosystem compartments in the Everglades at the landscape level in order to explore the implications of Hg distribution for Hg bioaccumulation and to investigate major biogeochemical processes that are pertinent to the observed Hg distribution patterns. At an Everglade-wide scale, THg concentrations were significantly increased in the following order: periphyton < flocculent material (floc) < soil, while relatively high MeHg concentrations were observed in floc and periphyton. Differences in the methylation potential, THg concentration, and MeHg retention capacity could explain the relatively high MeHg concentrations in floc and periphyton. The MeHg/THg ratio was higher for water than for soil, floc, or periphyton probably due to high dissolved organic carbon (DOC) concentrations present in the Everglades. Mosquitofish THg positively correlated with periphyton MeHg and DOC-normalized water MeHg. The relative THg and MeHg distribution patterns among ecosystem compartments favor Hg bioaccumulation in the Everglades.

Keywords: Mercury; Methylmercury; Everglades; Distribution; Bioaccumulation

1. Introduction

The Florida Everglades is a subtropical wetland ecosystem that mainly receives mercury (Hg) input from atmospheric deposition (Stober et al., 2001). Monitoring data show that total Hg (THg) concentrations in Everglades surface water and soil are typically within background levels (<10 ng/L for water and <500 ng/g for soil) (Arfstrom et al., 2000; Stober et al., 2001). However, elevated Hg levels (up to 3 mg/kg), comparable with those observed at highly contaminated sites, were detected in Everglades wildlife and have led to the issue of a fish consumption advisory for almost the entire Everglades (Schaefer et al., 2004; Ware et al., 1990). The unexpectedly high Hg levels in Everglades wildlife must therefore be driven by biogeochemical controls that make Hg available for bioaccumulation, rather than by high Hg loading (Arfstrom et al., 2000; Gilmour et al., 1998). The elevated Hg levels in wildlife could be related to high methylmercury (MeHg) production rate in Everglades soil, which is a critical factor in Hg bioaccumulation (Gilmour et al., 1998). However, there are a number of biogeochemical processes, such as partitioning and

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methylation/demethylation of Hg, intermittent drying and rewetting, the sulfur cycling and phosphorus biogeochemistry, controlling Hg cycling in the Everglades (Axelrad et al., 2006; Cleckner et al., 1998, 1999; Krabbenhoft et al., 1998; Marvin-DiPasquale and Oremland, 1998; Zhang and Lindberg, 2000). The relative distribution pattern of Hg species, among various ecosystem compartments, is an overall consequence of biogeochemical cycling of Hg species and other relevant processes (e.g. sulfur cycling).

The distribution of Hg species among different ecosystem compartments critically influences Hg fate and bioaccumulation in the food web. Methylmercury is the most bioavailable and toxic Hg species (Ullrich et al., 2001) and can be bioaccumulated in the food web leading to elevated Hg concentrations in predatory fish (Mason and Benoit, 2003). Once formed in the environment, MeHg must be present in bioavailable forms for bioaccumulation to occur. In different ecosystem compartments, MeHg has different bioavailability and thus has varying contributions to Hg bioaccumulation. For example, MeHg in sediment, especially deep sediment, has decreased bioavailability (Ullrich et al., 2001). Methylmercury dissolved in water is generally considered to be mobile and bioavailable, but this availability is debatable, when the interactions of Hg with other factors (e.g. dissolved organic carbon, DOC) are considered (Ravichandran, 2004). Methylmercury present in periphyton could enter higher trophic level zooplankton and fish through digestion as a direct food source (Cleckner et al., 1999; Loftus, 2000). The accumulation of Hg in periphyton has been observed in Boreal Canadian Shield lakes, suggesting that periphyton may play a role in Hg methylation and serve as an important vector of MeHg to higher organisms (Desrosiers et al., 2006a,b). This could also be the case for the Everglades, although lakes and wetlands are different in ecosystem characteristics. Mercury species distribution among compartments in the Everglades and the implications of this distribution on Hg fate are not fully understood, especially on a large scale throughout the entire Everglades ecosystem (National Research Council Committee on Restoration of Greater Everglades Ecosystem, 2005).

In this paper we analyzed Hg species distribution patterns among ecosystem compartments at the landscape level. Our objective was to explore the implications of Hg distribution for Hg bioaccumulation and to investigate major biogeochemical processes that are pertinent to the observed Hg distribution patterns. Although intensive studies conducted in localized areas or toward specific processes exist (Cleckner et al., 1998; Gilmour et al., 1998; Hurley et al., 1998; Krabbenhoft et al., 1998; Rumbold and Fink, 2006), a large-scale perspective is required to address Hg issue in the Everglades. This landscape-scale study, providing an overview of Hg distribution among ecosystem compartments and linking Hg distribution patterns to bioaccumulation, enhances our understanding toward Hg biogeochemical cycling and bioaccumulation in the Everglades. This study is useful for adaptive management of the Comprehensive Everglades Restoration Program (CERP), since the patterns of Hg species distribution among ecosystem compartments are dynamic and may be influenced by human activities, such as restoration practices (Rumbold and Fink, 2006). Additionally, Hg cycling in wetland systems has been the focus of Hg studies due to observations of unexpectedly high Hg concentrations in wildlife of wetlands (Driscoll et al., 1998; King et al., 2002; Lacerda and Fitzgerald, 2001; Mehrotra and Sedlak, 2005; Zhang et al., 2004). Although efforts have been made to understand Hg cycling in wetlands (Garcia et al., 2006; O'Driscoll et al., 2005; St Louis et al., 1996), it is not fully understood how elevated levels of Hg in wildlife accumulated from background levels of THg in environmental media. The findings of this study may be applicable for other wetlands and shed new light on interpreting Hg cycling and bioaccumulation in wetland ecosystems.

2. Materials and methods

2.1. Sampling

The Everglades currently includes four management units – Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR), two Water Conservation Areas (WCA-2 and WCA-3), and the Everglades National Park (ENP), encompassing a total area of about 5500 km^2 (Stober et al., 2001). The US Environmental Protection Agency (EPA) Region 4 Regional Environmental Monitoring and Assessment Program (R-EMAP) integrates research, monitoring, and assessment by using a probability sampling design to sample the entire Everglades freshwater marsh, excluding tree islands and shrubby sawgrass strands (Stober et al., 2001). In 2005 EPA Region 4 conducted R-EMAP Phase III sampling at approximately 250 randomly located stations (Fig. 1), half in May (the dry season) and half in November (the wet season).

Surface water, soil, flocculent material (floc), periphyton, and Eastern mosquitofish (*Gambusia Holbrooki*) were sampled at each site, if possible. Water

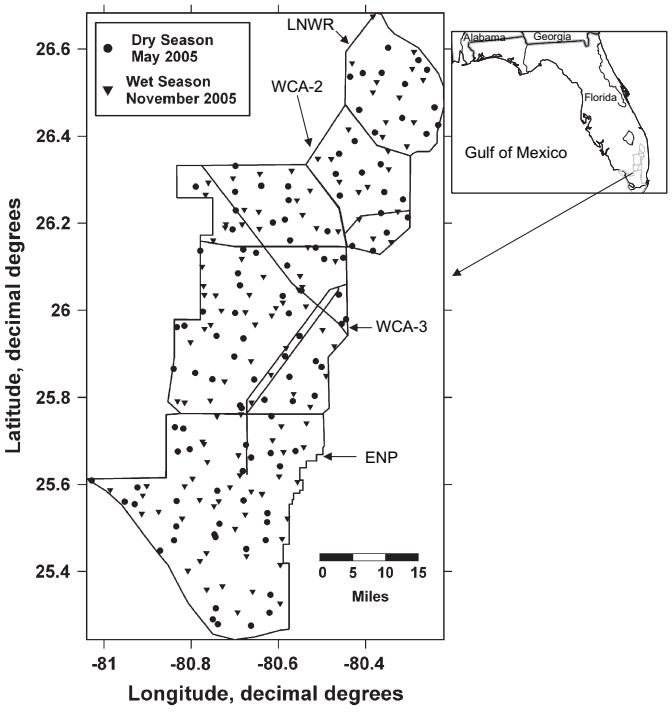

Fig. 1. A map showing sampling sites in the Florida Everglades during the dry (May) and wet season (November). LNWR: Arthur R. Marshall Loxahatchee National Wildlife Refuge; WCA-2 and WCA-3: Water Conservation Areas; ENP: Everglades National Park.

samples were passed through a Nylon screen (105 μm) to remove large particles in the field and analyzed for THg and MeHg in the laboratory without further filtration. Floc was collected on top of soil, consisting of suspended organic material containing mostly detritus from plants and algal inputs from periphyton (Neto et al., 2006). Three types of periphyton, floating mat (floating), soil mat (lying on the soil surface), and epiphytic (associated with macrophyte), were collected in the field and the combined results were reported. Clean technique was followed during sample collection, shipment, storage, and analysis phases. Detailed sampling procedures, including apparatus and QA/QC, were reported previously (Stober et al., 2001).

2.2. Hg determination

Total Hg concentrations in soil, floc, periphyton, and mosquitofish were determined by cold vapor atomic fluorescence spectrometry (CVAFS) (Merlin 10.035, PS Analytical, UK) following standard operating procedures (SOPs), modified after the EPA method 7474 (Jones et al., 1995; USEPA, 1998). Water THg was analyzed by gold amalgamation with CVAFS following the EPA Method 1631E (USEPA, 2002). Methylmercury analyses in soil, floc, and periphyton samples were conducted using a Brooks Rand MeHg system following SOPs modified after EPA method 1630 (USEPA, 2001) and literature (Qian et al., 2000). Methylmercury in water was determined according to EPA Method 1630 (USEPA, 2001). Total Hg and MeHg concentrations in soil, floc, and periphyton were calculated based on dry weight, while THg concentrations in mosquitofish were based on wet weight. Total Hg concentration in mosquitofish reported for a given sampling station was an average for all mosquitofish (up to 7) analyzed for that site. Mosquitofish MeHg was not determined since over 95% of Hg present in mosquitofish is in the form of MeHg (Stober et al., 2001).

For THg analysis in soil, floc, and periphyton, samples were homogenized and digested with concentrated HNO_3, in closed ampoules, at 121 °C, for 1 h using an autoclave (Jones et al., 1995). To determine THg in mosquitofish, the entire fish was digested using the same closed-ampoule acid digestion procedure. MeHg in soil, floc, and periphyton samples were extracted with acidic $KBr/CuSO_4/CH_2Cl_2$, followed by pipetting 2 ml of CH_2Cl_2 extract into 40 ml of distilled deionized water (DIW) and purging this solution, leaving MeHg in the aqueous solution (Cai et al., 1997; Qian et al., 2000).

2.3. Determination of ancillary parameters

An extensive list of physical and chemical variables, such as water DOC and soil ash free dry weight (AFDW), was included in this study. The procedures for determining these ancillary parameters can be found elsewhere (Stober et al., 2001). Select variables were reported in Table 1.

2.4. Quality assurance of sample analysis

Two method blanks, a pair of matrix spikes and/or two certified reference materials (CRM) accompanied each sample batch (up to 20 samples). A sediment CRM (MESS-3, 91 ng/g Hg) and a tissue CRM (DORM-2, 4600 ng/g Hg in dogfish muscle) were used for THg analysis, while IAEA-405 (5.49 ng/g of MeHg as Hg in sediment) was used for MeHg analysis. In all method blanks, total Hg or MeHg concentrations were below 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]). Recoveries for matrix spikes or CRMs were within the acceptable ranges (70–130% for THg and 65–135% for MeHg). The instrument performance was checked by running an intermediate calibration standard at regular intervals (usually every 10 samples) and all were within the acceptable range (85–115% for THg and 67–133% for MeHg compared to initial readings). Although some low-level contamination was noted in the THg analysis of aqueous system blanks, results were appropriately qualified to minimize the impact of false positive results during data interpretation.

Table 1
Select characteristics of Everglades compartments

Compartments	Parameters	Values, median (range)	
		Dry season	Wet season
Water	DOC (mg/L)	21 (11–50)	16 (4.6–45)
Soil	Mineral content (g/g)	0.34 (0.04–0.95)	0.37 (0.04–1.00)
	Bulk density (g/ml)	0.12 (0.04–0.79)	0.12 (0.05–0.75)
	Ash free dry weight (g/g)	0.66 (0.05–0.96)	0.64 (0.09–0.96)
Floc	Mineral content (g/g)	0.20 (0.05–0.68)	0.26 (0.05–1.00)
	Bulk density (g/ml)	0.02 (0.01–0.05)	0.02 (0.01–0.79)
	Ash free dry weight (g/g)	0.80 (0.32–0.95)	0.75 (0.30–0.95)

2.5. Statistical analysis

Differences in Hg concentrations (THg or MeHg) among different ecosystem compartments were compared using the Wilcoxon signed rank test. Correlation analysis was conducted on log-transformed THg and MeHg concentrations in the various compartments. The reason for log-transformation was that Hg concentrations, which were originally deviated from the normal distribution, generally followed the normal distribution after transformation. We conducted sampling in two different seasons and processed the data set for each season separately. Comparisons across seasons were not made, to avoid confounding influences from seasonal variations in Hg concentrations. As part of a series of manuscripts interpreting the data obtained in this comprehensive project, we focused on Hg distribution across ecosystem compartments in this paper. Other important aspects of Hg cycling, such as the seasonality and spatial heterogeneity, are being reported elsewhere. All plotting and statistical tests were performed on S-PLUS (Insightful Corp., Version 6.2) or SigmaPlot (Systat software, Inc., Version 9.01).

3. Results and discussion

3.1. Distributions of THg

Differences in THg concentrations among different ecosystem compartments (water, soil, floc and periphyton) were observed (Table 2). As generally observed in natural environments, Everglades water contained low THg, with a median of around 2.2 ng/L. Significant differences, as revealed by the Wilcoxon signed rank test, in THg concentrations were observed for particulate phases (soil, floc and periphyton). Soil contained the highest THg, followed by floc and periphyton, in decreasing order. All comparisons were significant at $p < 0.01$, except the difference between mosquitofish and floc which was significant at $p = 0.02$.

Atmospheric Hg deposition (wet and dry fall) is the primary and uniform source of Hg in the Everglades, with inorganic Hg as the main form deposited (Axelrad et al., 2006). After deposition, Hg undergoes a series of transport and transformation processes, including adsorption, sedimentation, evasion, oxidation/reduction, and methylation/demethylation. The distribution patterns of Hg species among various ecosystem compartments would be the result of all these processes. For soil and floc, adsorption should be the main process entrapping Hg. Higher THg in soil, compared with floc, could be related to the differences in compositional characteristics between these two compartments. Soil is higher in mineral content and bulk density while lower in organic matter (OM),

Table 2
Total Hg concentrations in various ecosystem compartments in the Everglades (ng/L for water and ng/g for other compartments)

Sampling event	Compartment	Range	Median	Mean	SD[a]	LCL[b] (95%)	UCL[c] (95%)
Dry season (May 2005)	Water	0.91–7.0	2.3	2.6	1.3	2.3	2.9
	Soil	9.3–270	110	120	53	100	130
	Floc	19–260	89	96	47	85	110
	Periphyton	2.4–80	11	16	14	12	20
	Mosquitofish	4.8–270	52	68	54	54	81
Wet season (November 2005)	Water	1.1–8.3	2.2	2.6	1.3	2.3	2.8
	Soil	17–350	140	140	72	130	160
	Floc	34–300	130	130	54	120	150
	Periphyton	3.5–92	21	23	16	20	27
	Mosquitofish	4.8–320	87	100	69	90	120

[a] Standard deviation.
[b] Lower confidence limit of mean.
[c] Upper confidence limit of mean.

compared with floc (Table 1). Although both OM and oxide minerals show strong affinity to bind Hg, inorganic Hg is preferentially bound with minerals while MeHg is predominantly associated with OM in solid compartments (Ullrich et al., 2001). The major form of Hg in Everglades soil and floc is inorganic Hg. Higher THg in soil, than in floc, is likely due to higher mineral content in soil. Although treated as a particulate compartment, periphyton is virtually an assemblage of autotrophic microalgae, heterotrophic bacteria and associated macrophyte plants and detritus (Smith, 2004). Different from soil and floc, uptake by living cells could be an important process retaining Hg in periphyton, which could contribute to the differences in THg between periphyton and soil or floc.

3.2. Distributions of MeHg

Methylmercury distribution patterns were different from THg. Floc was higher in MeHg concentrations ($p < 0.01$) than soil and periphyton (Table 3). Methylmercury concentrations in soil and periphyton were not significantly different ($p = 0.43$) for the dry season; while significantly higher MeHg concentrations in periphyton ($p < 0.01$), as compared to soil, were observed during the wet season. The relative MeHg (MeHg to THg ratios) concentrations (Fig. 2) decreased in the following order: water > periphyton ($p < 0.05$) > floc ($p < 0.001$) > soil ($p < 0.001$).

In various compartments, MeHg concentration is influenced by a number of processes, particularly by MeHg production in one compartment, followed by the transport of MeHg into different compartments. Strong correlations between THg and MeHg were observed for soil, floc, and periphyton in our study (Table 4), indicating likely in situ Hg methylation in these three compartments. This agrees with previous studies (Cleckner et al., 1999; Gilmour et al., 1998). After production, MeHg will be released from these particulate compartments into water. Support for this came from our observation that water MeHg was not only correlated with soil MeHg + floc MeHg + periphyton MeHg ($R = 0.50$, $p < 0.001$, data not shown), but also correlated independently with each of them (Table 4). In addition to transport to water, MeHg could be relocated among particulate compartments, as evidenced by correlations among soil, floc and periphyton MeHg. During these transport processes, floc acts as a linkage between periphyton and soil. Methylmercury produced in periphyton may move into floc accompanying the algae decay. Methylmercury present in floc can be buried in deeper soil during sedimentation.

Higher relative MeHg in periphyton and floc than in soil were likely due to the differences in methylation potential, THg concentrations, and MeHg retention capacity among

Table 3
Methylmercury concentrations in various ecosystem compartments in the Everglades (ng/L for water and ng/g for other compartments)

Sampling event	Compartment	Range	Median	Mean	SD[a]	LCL[b] (95%)	UCL[c] (95%)
Dry season (May 2005)	Water	0.035–3.8	0.29	0.48	0.61	0.34	0.63
	Soil	0.11–11	1.2	2.0	2.2	1.6	2.5
	Floc	0.28–36	3.3	5.3	6.5	3.8	6.9
	Periphyton	0.052–6.1	0.67	1.1	1.2	0.76	1.4
Wet season (November 2005)	Water	0.038–2.8	0.21	0.29	0.32	0.23	0.34
	Soil	0.04–12	0.49	0.87	1.4	0.61	1.1
	Floc	0.24–13	3.0	3.6	2.8	3.1	4.2
	Periphyton	0.04–9.4	1.5	2.0	1.8	1.6	2.3

[a] Standard deviation.
[b] Lower confidence limit of mean.
[c] Upper confidence limit of mean.

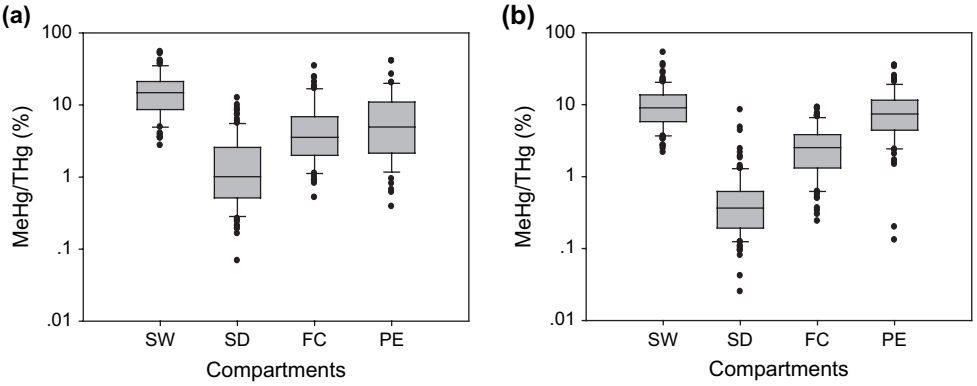

Fig. 2. Boxplots of MeHg/THg ratios in different compartments in the Everglades. SW: surface water; SD: soil; FC: floc; PE: periphyton. (a) Dry season and (b) wet season.

these three compartments. First, compared with soil, floc and periphyton are believed to be more favorable for MeHg production because they are richer in microbial communities and OM (Neto et al., 2006; Smith, 2004). Although no attempt was made in this study to measure microbial activities of sulfate-reducing bacteria (SRB), that are known as primary producers of MeHg (Ullrich et al., 2001), higher levels of carbon dioxide and methane were observed in floc and periphyton compared with soil in our previous sampling events (Stober et al., 2001). This could indicate higher microbial activities in floc and periphyton, as the higher OM content provides sufficient carbon sources for microbes. In a laboratory incubation of intact sediment cores collected from the Everglades, Gilmour et al. (1998) found high Hg methylation rates in surficial sediments that are primarily layers of floc and/or periphyton. Comparative tests also confirmed that the net Hg methylation potentials measured in periphyton, particularly macrophyte-associated periphyton, are significantly higher than in any other matrix (Cleckner et al., 1999; Mauro et al., 2002). Secondly, floc and periphyton may have stronger affinities to bind MeHg because of their higher OM content. Thirdly, living algae and other organisms are present in floc and periphyton (Smith, 2004). These organisms can take up MeHg from water through pertinent biological activity (Loftus, 2000).

The relative MeHg concentrations in water were observed to be higher than those in soil, floc, and periphyton (Fig. 2). Since MeHg is not likely to be produced in Everglades water (Mauro et al., 2002), this indicates that MeHg had higher potential to be redistributed into water than THg during compartmentalization process of Hg species. Possible reasons accountable for high relative MeHg in water include water chemistry and characteristics of the particulate compartments in the Everglades, among which DOC plays an important role. Everglades water is typically rich in DOC, with medians of 21 and 16 mg/L for the dry and wet season in this study (Table 1). We observed significant correlations ($R = 0.51$, $p < 0.001$) between Hg (THg and MeHg) and DOC (Fig. 3), as observed in other studies (Babiarz et al., 1998; Watras et al., 1998). Moreover, the MeHg/THg ratio also correlated positively with DOC concentrations in the water, suggesting Everglades DOC has stronger binding capability with MeHg than with THg. This result agrees with a laboratory study using ultrafiltration (Cai et al., 1999). The stronger binding capability of DOC with MeHg compared with THg means that a larger MeHg fraction is complexed with DOC and therefore remains in the water. This leads to higher MeHg/THg ratio, in comparison to other environmental compartments.

Table 4
Correlation matrix (Pearson correlation coefficients between log-transformed concentrations and sample number) for Hg species in various ecosystem compartments

		Surface water		Soil		Floc		Periphyton		Mosquitofish
		THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg	THg
Surface water	THg	1								
	MeHg	**0.57**[a] (191)	1							
Soil	THg	0.19 (190)	0.15 (190)	1						
	MeHg	0.24 (190)	**0.25** (190)	**0.34** (226)	1					
Floc	THg	0.10 (161)	−0.10 (161)	**0.52** (161)	0.05 (161)	1				
	MeHg	0.24 (161)	**0.34** (161)	0.13 (161)	**0.63** (161)	**0.39** (161)	1			
Periphyton	THg	0.19 (116)	0.25 (116)	**0.44** (136)	0.07 (136)	**0.51** (90)	0.15 (90)	1		
	MeHg	0.14 (116)	**0.56** (116)	**0.63** (136)	**0.38** (136)	0.22 (90)	**0.34** (90)	**0.55** (138)	1	
Mosquitofish	THg	0.08 (167)	0.19 (167)	0.20 (170)	0.05 (170)	0.11 (140)	0.16 (140)	0.19 (110)	**0.52** (110)	1

[a] Numbers in bold indicate significant correlations at $p < 0.001$ level.

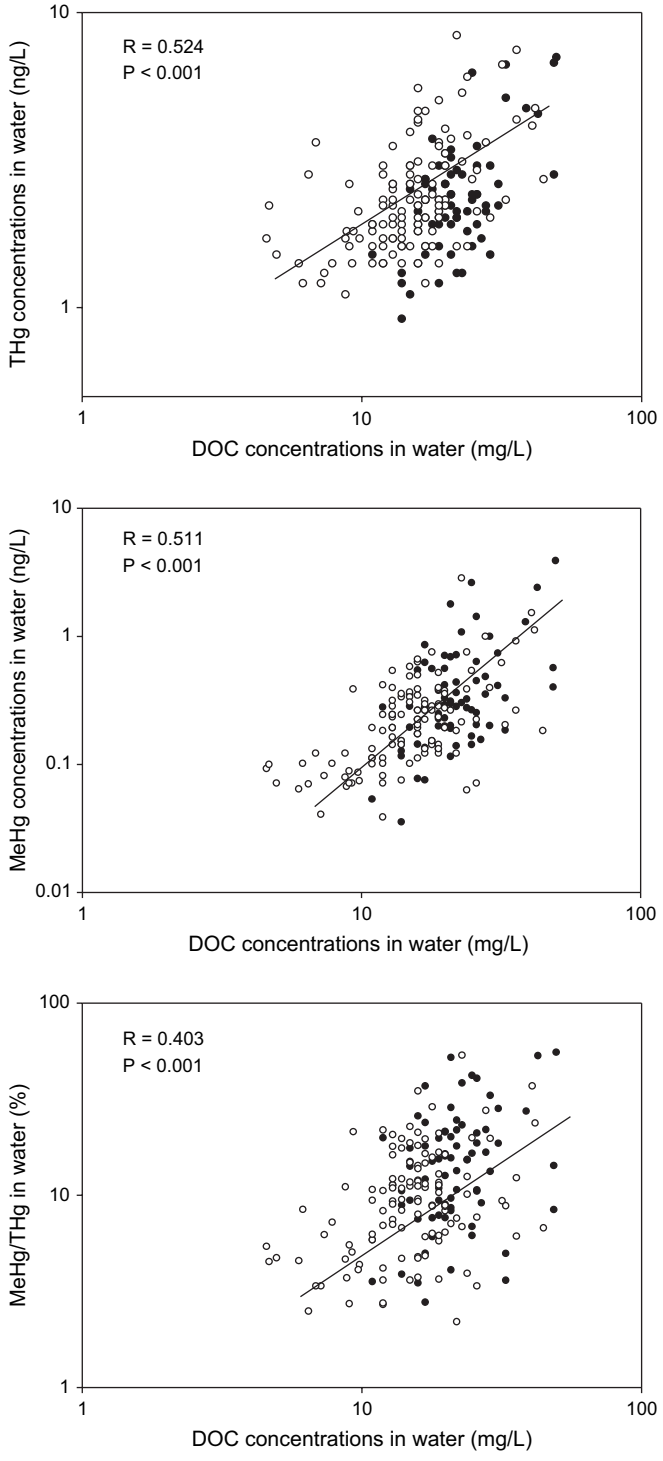

Fig. 3. Correlations between Hg (THg, MeHg, and MeHg/THg ratio) and DOC in Everglades water. Closed and open circles are data obtained in the dry and wet season, respectively.

We also compared the MeHg/THg ratios in Everglades water with those in other waters (Table 5). The MeHg/THg ratios in Everglades water are the highest among all these studies. This could be ascribed to the high Hg methylation potential in the Everglades and the strong binding of MeHg to DOC, which allows MeHg to remain in the water column.

3.3. Implications for Hg bioaccumulation

Mercury in mosquitofish comes from MeHg present either in the water or transferred through the food web. Total Hg concentrations in mosquitofish correlated strongly (Fig. 4b) with MeHg in periphyton, which is a major food supply for mosquitofish (Browder et al., 1994), suggesting bioaccumulation of MeHg through the food web (Cleckner et al., 1998; Loftus, 2000). Water MeHg and mosquitofish THg were not correlated (Fig. 4a). There are two reasons for this lack of correlation. First, Hg in fish is primarily bioaccumulated through the diet, rather than directly taken up from the water (Morel et al., 1998). Second, bulk MeHg concentration in water is probably unable to represent the bioavailable fraction of MeHg for uptake. Studies show that DOC has a high capacity for binding MeHg and plays a critical role in controlling the bioavailability of water MeHg (Babiarz et al., 2001; Cai et al., 1999; Watras et al., 1998). When mosquitofish THg was correlated with DOC-normalized water MeHg concentration (expressed as ng of MeHg per mg of C), a significant positive correlation was found (Fig. 4c). The negative correlation between bioaccumulation factor (BAF) for MeHg in mosquitofish and water DOC was also strong (Fig. 4d). These results confirmed the effect that DOC has on decreasing bioavailability of MeHg in the water. Similar results have been reported elsewhere (Driscoll et al., 1995; Ravichandran, 2004; Watras et al., 1998). It should be noted that uptake through the food web is likely the primary pathway even if direct uptake from water makes a contribution to Hg bioaccumulation in mosquitofish.

Since diet and water represent two major pathways for Hg bioaccumulation, the Hg distribution patterns among environmental compartments observed here, i.e. high relative MeHg in water and periphyton, are favorable for Hg bioaccumulation. This could account, at least in part, for the elevated Hg concentrations in fish and wildlife in the Everglades (Axelrad et al., 2006).

Periphyton is an important base component of the Everglades food web, serving as a primary food source for numerous species of invertebrates, small fishes and amphibians (Smith, 2004). Relatively high MeHg concentrations in a primary food source would enhance the bioavailability of Hg in the Everglades. Mercury accumulation in the upper trophic levels has been ascribed to periphyton, which can act as an indicator of fish Hg levels (Cleckner et al., 1998). Periphyton can be reasonably considered as a major pathway for Hg methylation, uptake, and bioaccumulation in this ecosystem. However, the role periphyton plays in Hg bioaccumulation should be evaluated carefully. Everglades periphyton, as well as food web structure, varies between different sites and seasons (Smith, 2004). Depending on the available food source and periphyton types, diet shift do occur in the Everglades. For example, mosquitofish are opportunistic in food habits and will feed on other food sources, such as zooplankton, in addition to periphyton (Browder et al., 1994; Loftus, 2000).

High relative MeHg concentrations in water are also probably related to Hg bioaccumulation in the Everglades.

Table 5
MeHg/THg ratios in water reported in the literature

Water type	Geographic location	MeHg/THg ratio (%), range (median)	Reference
Wetland	Florida Everglades	2–52 (11)	This study
Wetland	Florida Everglades	4.4–14 (7.2)[a]	Babiarz et al. (2001)
Wetland	New York	6–16	Driscoll et al. (1998)
Surface ocean		1–5	Morel et al. (1998)
River	New Jersey	0.01–1.3 (0.2)[a]	Schaefer et al. (2004)
River	Wisconsin	0.9–7.8 (4.4)[a]	Babiarz et al. (1998)
Lakes	Remote	1–20	Morel et al. (1998)
Lakes	New Jersey	2–34 (5)[a]	Schaefer et al. (2004)
Lakes	Wisconsin	6–30 (5.8)[a]	Watras et al. (1998)
Freshwaters	Michigan, Minnesota, Wisconsin, Georgia	0.4–36 (3.2)[a]	Babiarz et al. (2001)
Estuarine waters	Florida Bay	<0.03–52 (10)	Kannan et al. (1998)

[a] Calculated from data reported in the original literature.

Although fish Hg cannot always be correlated with water MeHg (Cleckner et al., 1998), dissolved MeHg, even in the form of complexes with DOC, is still bioavailable to a certain extent (Ravichandran, 2004). The positive correlation between mosquitofish THg and DOC-normalized water MeHg, observed in this study, suggests that dissolved MeHg could be partially bioavailable for uptake by mosquitofish. Supports for this notion also comes from that MeHg in Everglades water is mainly associated with low molecular-weight DOC (<3 kDa) (Cai et al., 1999) for which passive diffusion through mosquitofish gill may be possible (Ravichandran, 2004). Additionally, complexation with DOC will increase the solubility of MeHg and facilitate its transport from the particulate compartment to water (Mason and Benoit, 2003; Ravichandran, 2004). This could increase the MeHg pool potentially available for bioaccumulation (Ravichandran, 2004).

Despite the absence of correlation between mosquitofish THg and floc MeHg, the floc layer could contribute to Hg bioaccumulation by increasing MeHg production and mobility of THg and MeHg. High THg levels were present in floc, which had comparable ranges to soil in terms of THg concentrations (Table 2). The combination of high THg levels and high methylation potential would result in high MeHg production in floc, as evidenced by highest MeHg in floc among soil, floc and

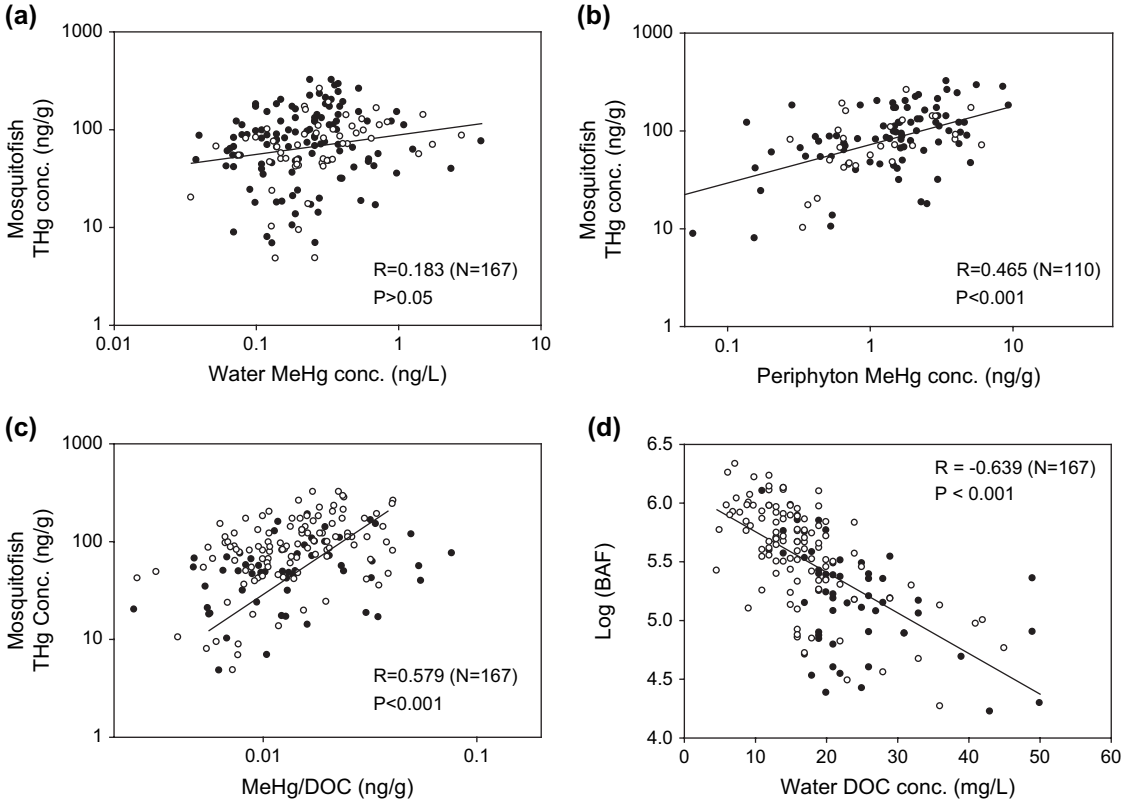

Fig. 4. Mercury bioaccumulation in mosquitofish from water and periphyton in the Everglades. (a) Mosquitofish THg versus water MeHg; (b) mosquitofish THg versus periphyton MeHg; (c) mosquitofish THg versus DOC-normalized water MeHg; (d) bioaccumulation factor (BAF) as a function of DOC. Closed and open circles are data obtained in the dry and wet season, respectively.

periphyton. Floc generally has a low bulk density and can be easily transported by water flow. Consequently, both THg and MeHg present in the floc layer may be transported to wherever the floc is transported by water flow. Additionally, floc appears to act as a boundary layer preventing periphyton from becoming directly incorporated into the soil during decay of algae. Simultaneously, this process prevents MeHg produced in periphyton from being sequestered into the soil and thus makes MeHg more mobile and bioavailable.

4. Conclusions

At the landscape level, the relative MeHg concentrations (MeHg to THg ratios) decreased in the following order: water -> periphyton > floc > soil in the Everglades. The Hg distribution patterns were related to a series of compartmentalization processes (including adsorption, absorption and Hg methylation), which are influenced by compositional characteristics of environmental compartments (e.g. soil and floc OM and mineral content, water DOC). Mosquitofish THg positively correlated with periphyton MeHg and DOC-normalized water MeHg. Hg bioaccumulation occurs mainly through food web and through possible uptake from water. Since periphyton and water represent two important pathways of Hg bioaccumulation, the observed Hg distribution patterns in the Everglades are plausibly favorable for Hg bioaccumulation.

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