Degradation of Methylmercury and Its Effects on Mercury Distribution and Cycling in the Florida Everglades

7 AUTHORS, INCLUDING:

Yanbin Li
Ocean University of China
18 PUBLICATIONS **178** CITATIONS

SEE PROFILE

Georgio Tachiev
consultant
11 PUBLICATIONS **389** CITATIONS

SEE PROFILE

Xinbin Feng
Institute of Geochemistry, Chinese Acade…
341 PUBLICATIONS **7,021** CITATIONS

SEE PROFILE

Yong Cai
Florida International University
78 PUBLICATIONS **1,944** CITATIONS

SEE PROFILE

Degradation of Methylmercury and Its Effects on Mercury Distribution and Cycling in the Florida Everglades

YANBIN LI,[†,‡] YUXIANG MAO,[†,⊥]
GUANGLIANG LIU,[†,‡]
GEORGIO TACHIEV,[§] DAVID ROELANT,[§]
XINBIN FENG,[‖] AND YONG CAI*,[†,‡]

*Department of Chemistry & Biochemistry,
Florida International University, Miami, Florida 33199,
Southeast Environmental Research Center,
Florida International University, Miami, Florida 33199,
Applied Research Center, Florida International University,
Miami, Florida 33174, State Key Laboratory of Environmental
Geochemistry, Institute of Geochemistry, Chinese Academy of
Science, 46 Guanshui Road, Guiyang 550002, China, and
Henan Polytechnic University, Jiaozuo 454000, China*

Methylmercury (MeHg) is recognized as one of the major water quality concerns in the Florida Everglades. Degradation of MeHg in the water is thought to be one of the most important processes to the cycling of MeHg, but there is a lack of quantitative estimations of its effect on the distribution and cycling of MeHg in this ecosystem. Stable isotope (Me[201]Hg) addition method was implemented to investigate the degradation of MeHg in the Everglades. By combining these results with the field monitoring data, effects of photodegradation on MeHg distribution and its contribution to MeHg cycling were estimated. The results indicate that degradation of MeHg in Everglades water is mediated by sunlight and that UV-A and UV-B radiations are the principal driver. The spatial pattern of MeHg photodegradation potential (P_{PD}) generally illustrated an increasing trend from north to south in the Everglades, which was opposite to the distribution of MeHg in water column. Correlation analysis shows that MeHg concentration in the water had a significant negative relation to P_{PD}, suggesting that photodegradation could play an important role in controlling the distribution of MeHg in Everglades water. Furthermore, about 31.4% of MeHg input into the water body was removed by photodegradation, indicating its importance in the biogeochemical cycling of MeHg in the Everglades. This percent reduction is much lower than that reported for other ecosystems, which could be caused by the higher concentration of DOC in the Everglades.

* Corresponding author phone: (305)348-6210; fax: (305)348-3772; e-mail: cai@fiu.edu.
† Department of Chemistry & Biochemistry, Florida International University.
‡ Southeast Environmental Research Center, Florida International University.
⊥ Henan Polytechnic University.
§ Applied Research Center, Florida International University.
‖ Chinese Academy of Science.

The relatively slower degradation of MeHg could be one of the main reasons for the high ratio of MeHg to total mercury (THg) in this ecosystem.

Introduction

Methylmercury (MeHg), a potent neurotoxin, is among the most widespread contaminants that are posing a potential threat to both humans and wildlife (*1*). As a major sink of MeHg, degradation of MeHg plays an important role in the biogeochemical cycling of mercury in aquatic ecosystems (*2, 3*). This process may be determined by a number of abiotic and biotic pathways in nature. Although microbial demethylation of MeHg was observed both in sediment (*4*) and in water column (*5*–*7*), photodegradation was commonly thought to be the most important process in clear and oligotrophic lakes (*2, 3, 8*). Both ultraviolet (UV) and visible (Vis) radiations hold the capacity to degrade MeHg, either via direct UV radiation (*9*) or indirect photolysis by reactive oxygen species (e.g., ·OH, $^1O_2$) (*10*). Different opinions were reported on whether UV or visible light was the primary driver for photodegradation of MeHg in natural waters (*2, 3, 6, 8, 11*). These inconsistent results suggest that the pathways of MeHg degradation in natural waters may vary in different ecosystems.

Hg is recognized as one of the major water quality concerns in the Florida Everglades because elevated mercury (Hg) levels were found in fish, wading birds, and other wildlife (*12*). Bioaccumulation is the major route for MeHg entering aquatic food webs. Hence, key processes (production, degradation, and bioaccumulation) controlling the biogeochemical cycling of MeHg are vital in determining the final concentration of Hg in fish. Great efforts have been made to investigate the production (*13, 14*) and bioaccumulation of MeHg (*15, 16*) in the Everglades, but few studies (*17*) have focused on another important process, the degradation of MeHg in Everglades water. A mass balance model was previously developed and used to estimate the mass budget of MeHg in the Everglades (*18*). However, the photodegradation of MeHg was absent from that model because of the lack of data. As MeHg degradation, especially the photoinduced degradation, could contribute a large extent to the cycling of MeHg, the absence of MeHg degradation would underestimate the mass of MeHg diffusing into the water. MeHg photodegradation was found to account for about 80% of the MeHg mobilized annually from sediments in the Toolik Lake water (*2*), and about 83% of MeHg flowing into the lake was found to be removed by photodegradation in the Lake 240 of northwestern Ontario (*3*). As a subtropical wetland, the intensity of sunlight in the Everglades is high (with an average photosynthetically active radiation (*PAR*) of 327 μmol m^{-2} d^{-1} (*19*)), and the sunshine duration is long (average (1977–1987) 3218 h per year (*20*)). Hence, the photodegradation of MeHg in the water is expected to play an important role in the biogeochemical cycling of MeHg in the Everglades.

The objectives of this study were to investigate the degradation of MeHg in Everglades water and to assess the role of this process in spatial distribution and cycling of MeHg in the Everglades. Stable isotope (Me[201]Hg) spiked incubation experiments were conducted to study the effects of microorganisms and different spectra of sunlight (UV-A, UV-B, and visible light) on the degradation of MeHg. Based on the measurement of the degradation rate in Everglades water, the annual MeHg degradation flux was calculated to estimate its contribution to the cycling of MeHg in this ecosystem. In

addition, the spatial distribution pattern of MeHg degradation potential was derived from these experimental results to evaluate its effect on the distribution of MeHg in Everglades water.

Methods

Materials and Chemicals. MeHg standard was purchased from Ultra Scientific (N. Kingstown, RI, USA). Enriched [201]HgO (atomic percentage, 96.17 ± 0.56) was purchased from Oak Ridge National Laboratory (Oak Ridge, Tennessee). Other reagents used were of reagent grade or higher. Cellulose nitrate membranes (0.22 μm) in Corning Sterile Filter Systems were purchased from Corning Life Sciences (Corning, New York). Five kinds of films were used (UV block film1 and 2, UV-B block film, transparent film, and aluminum foil); detailed information about these films was provided in the Supporting Information.

Collection of Waters. Water samples were collected from the Everglades by using gloved hands to fill precleaned 2-L Teflon bottles. The samples were kept in a cooler and transported to the laboratory within 3 h. MeHg degradation experiments were conducted immediately upon arrival at the laboratory. Two batches of samples were collected at site FL3 (Figure S2) on July 22 (Exp 1) and September 16, 2009 (Exp 2) to study the degradation of MeHg in Everglades water and the effects of light quality. The water chemistry in the Everglades varies from north to south. For instance, total phosphorus, sulfate, and dissolved organic matter (DOC) concentrations generally bear a decreasing gradient from north to south (12). Therefore, waters at the other four sites (sites FL1, FL2, FL4, and FL5, see Figure S2) located from north to south were additionally collected in October 2009 for the purpose of measuring the average rate constant of MeHg degradation. The trace-metal clean techniques were followed during sample collection, shipment, and analysis (21).

Effects of Sterilization and Sunlight Quality on MeHg Degradation. Stable isotope (Me[201]Hg) addition method was employed to study the degradation of MeHg. The experiments were performed under ambient temperature (28.5 ± 0.8 °C) and light conditions at Florida International University (FIU, Figure S2), which is within 10 km of the Everglades. Upon arrival at the laboratory, waters were divided into two aliquots. One aliquot was sterilized by filtration using a 0.22 μm cellulose nitrate membrane. The sterilized and unsterilized waters (200 mL) were transferred to 0.5-L FEP (fluorinated ethylene-propylene) Teflon bottles. Me[201]Hg, synthesized from isotope-enriched [201]HgO using methylcobalamin (22), was then spiked to each bottle to form a final concentration of about 0.6 ng L^{-1} as Hg, which was within the range of MeHg (0.035−3.8 ng/L) in Everglades water. Bottles with sterilized waters were incubated under ambient temperature and light conditions for 6 days. Bottles with unsterilized waters were further divided into two groups. One group was also incubated under ambient temperature and light conditions, while the other group was incubated under dark condition by wrapping bottles with aluminum foil. During the experiment, intensity of ambient *PAR* was measured at 15 min intervals routinely using LI-192 Quantum Sensor (LI-COR Biosciences, Lincoln, Nebrasks). Triplicates (three separate bottles) were employed for each trial, and Me[201]Hg in the incubated samples was determined after 0, 2, 4, and 6 days of incubation. The preparation and sampling of the sterilization trials were conducted in a laminar flow cabinet with UV light to maintain sterile conditions. Water samples were stored by adding HCl (conc.) to form a final concentration of 1% (v/v) and were kept at 4 °C until analysis.

Another set of experiments was performed to study the effects of sunlight quality on MeHg degradation. Five trials with different sunlight levels were performed by wrapping the FEP Teflon bottles with different films: (1) full ambient sunlight (not wrapped), (2) around 80% of ambient sunlight (wrapped with transparent film), (3) UV-A+Vis (wrapped with UV-B block film), (4) Vis (wrapped with UV block film 1 or 2), and (5) dark (wrapped with aluminum foil). The other experimental procedures and storage method were the same to those aforementioned.

Rate Constant of MeHg Degradation. Waters (200 mL) were collected at each site, transferred to 0.5-L FEP Teflon bottles, and then spiked with isotope-enriched Me[201]Hg to the average concentration of MeHg (0.38 ng L^{-1}) in the Everglades. Nine independent samples were prepared, among which three were collected after 0, 3, and 6 days of incubation, respectively.

Sample Analysis. Me[201]Hg in the water samples was analyzed by aqueous phenylation and purge-and-trap preconcentration followed by gas chromatography inductively coupled plasma mass spectroscopy (GC-ICP-MS) (23). Analytical details and QA/QC procedures are provided in the Supporting Information.

Data Analysis. A model based on the second-order chemical kinetics was used to describe the degradation of MeHg in the water (eq 1) (2, 8). After integration of eq 1, $\ln(C_{MeHg})_t$ could be simulated by $\ln(C_{MeHg})_0$ and cumulative *PAR* photon flux (*J*) (8), as described in eq 2. The rate constant of MeHg degradation, k_D, was then obtained by linear regression of $\ln(C_{MeHg})_t$ on *J*, using Origin (Version 6.0 for Windows, OriginLab Corp., Northampton, MA). The square of correlation coefficient (r^2) and probability (p) were employed to evaluate the quality of the fit. *t* test was then employed to determine whether a significant difference existed between two treatments with SPSS (version 12 for Windows, SPSS Inc., Chicago, IL)

$$\frac{dC_{MeHg}}{dt} = -k_D \times C_{MeHg} \times PAR \qquad (1)$$

$$\ln(C_{MeHg})_t = \ln(C_{MeHg})_0 - k_D \times J \qquad (2)$$

where C_{MeHg} is the concentration of MeHg (ng L^{-1}); k_D is the rate constant of MeHg photodegradation (m^2 E^{-1}); *PAR* is the photosynthetically active radiation (E m^{-2} d^{-1}); and *J* is cumulative *PAR* photon flux (E m^{-2}).

Results and Discussion

MeHg Degradation in Everglades Water and Effects of Light Quality. Figure 1A illustrates the effects of sterilization and light on the degradation of MeHg in Everglades water. The concentration of spiked Me[201]Hg decreased from 0.6 to around 0.2 ng L^{-1} after 6 days of exposure to the sunlight ($p < 0.05$) with or without sterilization, while degradation of MeHg was not observed in the dark ($p > 0.1$) (Figure 1A, Figure S3C). To further validate the effect of microorganisms on the MeHg degradation, k_D values at trials with and without sterilization (Table 1) were calculated according to eq 2. The MeHg in unsterilized water had a $k_D = 9.45 \pm 0.23$ ($\times 10^{-3}$ m^2 E^{-1}), while the filter-sterilized samples had a $k_D = 10.87 \pm 0.86$ ($\times 10^{-3}$ m^2 E^{-1}) (Table 1). *t* test analysis showed that removing microorganisms had no significant effect on the degradation of MeHg ($p > 0.05$). These results suggest that photodegradation is the key pathway of MeHg degradation in Everglades water. This conclusion is consistent with some previous studies, most of which were conducted in clear and oligotrophic lakes (2, 3, 8). However, some contrary evidence also exists. MeHg demethylation was found to be primarily driven by microorganisms in five small forest lakes (7), and microbial or no light-mediated chemical pathways were reported to be contributed to MeHg degradation in the waters of Mediterranean Sea (6). These debatable results suggest
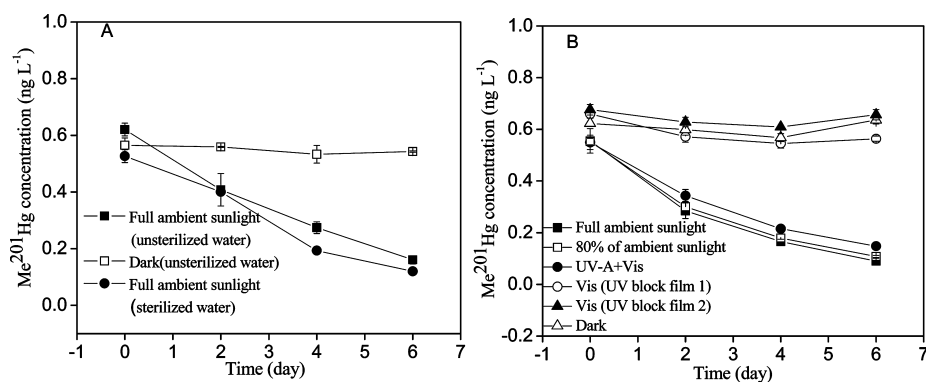
FIGURE 1. Degradation of MeHg in Everglades water. A, experiment conducted in July 2009 (Exp 1); B, experiments conducted in September 2009 (Exp 2). Exp 1 was designed to test the effects of microorganisms and sunlight on MeHg degradation. Exp 2 was designed to test the effect of sunlight quality on MeHg photodegradation. Error bars represent the standard deviation for triplicate sample analysis.

TABLE 1. Measured Rate Constants of MeHg Photodegradation under Various Experimental Treatments

	k_D (10^{-3} m^2 E^{-1})					
	full ambient sunlight (unsterilized)	80% of ambient sunlight (unsterilized)	UV-A +Vis (unsterilized)	Vis[a] (unsterilized)	dark (unsterilized)	full ambient sunlight (sterilized)
Exp1[b]	9.45 ± 0.23	N/A	N/A	N/A	0[c]	10.87 ± 0.86
Exp2[b]	10.39 ± 0.96	9.35 ± 0.49	7.59 ± 0.39	0[c]	0[c]	N/A

[a] Two kinds of UV block films (1 and 2) with different visible light transmission percentage were used for the purpose of comparison. [b] Exp 1 was designed to test the effects of microorganism and sunlight on MeHg degradation. Exp 2 was designed to test the effect of sunlight quality on MeHg photodegradation. The k_D was measured both in Exp 1 and 2 for full ambient sunlight, and both of these rates are reported. These rates are not statistically different (t test, $p > 0.1$). [c] In calculating k_D by linear regression, zero means the p value was greater than 0.1.

that the pathways of MeHg degradation in natural water may vary in different ecosystems.

Effects of sunlight quality on the degradation of MeHg are shown in Figure 1B. In samples exposed to dark or visible light, no significant MeHg degradation occurred ($p > 0.1$) (Figure 1B, Figure S3I, G, H), while significant degradation of MeHg was observed in waters exposed to full ambient sunlight, 80% of ambient sunlight and "UV-A+Vis" (Figure 1B). The k_D values were calculated to further estimate the contribution of different spectra of sunlight on MeHg photodegradation (Table 1). The k_D values obtained from the trials blocking UV-B were significantly lower than those under full ambient sunlight ($p < 0.05$), decreasing from 10.39×10^{-3} to 7.59×10^{-3} m^2 E^{-1} (27%). However, this decrease in k_D could be attributed to the decrease in UV-A radiation because UV-B block film also blocked about 21% of UV-A. Therefore, the transparent film, which blocked 23% of UV-A radiation (similar to UV-B block film) and 24% of UV-B (much lower than UV-B block film), was employed to validate the effect of UV-B. The k_D values for this treatment, 9.35×10^{-3} m^2 E^{-1}, was significantly different from that (7.59×10^{-3} m^2 E^{-1}) obtained by wrapping the bottle with the UV-B block film ($p < 0.05$), confirming the effect of UV-B on MeHg photodegradation. Finally, the proportion of k_D derived from different spectra of sunlight relative to the global k_D (P(UV-B), P(UV-A), P(Vis)) were calculated. P(Vis) was calculated as the division of k_D obtained under Vis by k_D obtained under full sunlight. P(UV-B) was calculated as division of the difference between k_D obtained by blocking with transparent film and UV-B block film by k_D obtained under full sunlight. Then P(UV-A) was determined using the function of "1- P(UV-B)-P(Vis)". The values of P(UV-B), P(UV-A), and P(Vis) were found to be 15, 85, and 0%, respectively, suggesting that photoinduced degradation of MeHg in the Everglades was principally driven by UV-A and UV-B radiation. Similar studies have been conducted to study the effect of light spectra on MeHg photodegradation in a lake ecosystem (8).

UV-A and UV-B radiation were also found to be the primary driver in that ecosystem. The consistent conclusions obtained from the two different ecosystems indicate that it may also apply in other ecosystems.

Average k_D Values in the Everglades. Figure S4 shows the rate constant of MeHg degradation at the five studied sites in the Everglades. The k_D values ranged from 9.92×10^{-3} to 13.17×10^{-3} m^2 E^{-1}, with a mean value of $(10.82 \pm 1.33) \times 10^{-3}$ m^2 E^{-1}. By implementing the values of P(UV-B) and P(UV-A) obtained above, the average rates of MeHg degradation derived from UV-B (k_D(UV-B)) and UV-A(k_D(UV-A)) were estimated to be 1.62×10^{-3} and 9.20×10^{-3} m^2 E^{-1}, respectively. As Teflon bottles are not completely transparent to UV radiation, values of k_D obtained using Teflon bottles will underestimate the true values (8). Therefore, values of k_D(UV-B) and k_D(UV-A) obtained with Teflon bottles were amended by using the literature reported transmittance of UV-B (66%) and UV-A (82%) through Teflon bottles (24). This amendment resulted in a k_D(UV-B) value of 2.45×10^{-3} m^2 E^{-1}, a k_D(UV-A) value of 11.22×10^{-3} m^2 E^{-1}, and a global k_D value of 13.67×10^{-3} m^2 E^{-1} in Everglades water.

Although the chemical parameters were different at the five studied sites (Table S1), the k_D values at these sites were comparable (Figure S4). There were no significant differences ($p > 0.05$) in k_D values at the studied sites except for site FL5 where k_D was statistically higher ($p < 0.05$) than the other sites. Nevertheless, the RSD of the k_D values obtained from all of these studied sites was 12.3%, suggesting that the spatial variability of k_D in the Everglades is low. Compared with previous studies (2, 8), the k_D values for the Everglades were higher, which could be related to the different environmental conditions of the ecosystems studied.

Since k_D did not vary dramatically with site, the factors influencing UV transmittance through the water likely play a dominant role in MeHg degradation in Everglades water. As UV light attenuation in waters with moderate to high DOC was primarily determined by DOC concentration (25−28),

DOC should be one of the key factors controlling the degradation of MeHg in the Everglades, a wetland with high DOC. It should be noted that, in addition to affect light attenuation, DOC may influence MeHg degradation through other processes. For instance, laboratory studies have shown that reactive oxygen species, especially hydroxyl radical ($\cdot$OH), may play a major role in the photolysis of MeHg (10). If this is the case, parameters related to the production and scavenging of $\cdot$OH could affect the amount of reactive oxygen in the water and subsequently affect the degradation of MeHg. DOC (29, 30), among other factors (e.g., nitrate, iron, and carbonate) (30−32), is important in regulating the cycling of $\cdot$OH in the water. Further studies are necessary to clarify the mechanisms of MeHg photodegradation in the natural water and to screen the controlling factors that result in the different k_D values among different ecosystems.

The Influence of MeHg Photodegradation on Spatial Distribution of MeHg in Everglades Water. In order to examine the spatial patterns of MeHg degradation in the Everglades, the depth integrated rate and potential of MeHg photodegradation were calculated. Sunlight mediated MeHg degradation resulting from UV-B and UV-A radiation was evaluated and integrated separately. The light intensity for X type of radiation at Z depth ($I(X,Z)$) is calculated from the light intensity in the surface water ($I(X,0)$) by exponentially decreasing it with depth according to the Beer−Lambert equation (eq 3). Combined with the calculation of the photodegradation rate in the surface water, the photodegradation rate at Z depth can be described (8) as eq 4 (a detailed derivation of this equation is provided in the Supporting Information). Light attenuation coefficients (k_X) for UV-B and UV-A are estimated from DOC concentrations using the equations (eq 7) provided in the literature (26, 27). MeHg concentration at any depth was assumed to be equal to $C_{MeHg}(0)$. Then MeHg degradation is integrated with respect to water column depth to obtain the photodegradation rate within the entire water column ($G_{PD}(X)$). The sum of G_{PD} derived from different spectra of sunlight results in the MeHg photodegradation rate within the entire water column (G_{PD}). G_{PD} is an important parameter for evaluating the photodegradation of MeHg. However, as it is dependent on the concentration of MeHg in the water, it is not suitable for use in evaluating the potential of photodegradation. Hence, another parameter, the photodegradation potential within the entire water column (P_{PD}), is defined in order to describe the potential of photodegradation. This parameter is defined as the division of G_{PD} by average concentration of MeHg in the water column ($\bar{C}_{MeHg}$) (eq 6) and is independent of concentration of MeHg in the water.

$$I(X,Z) = I(X,0) \times e^{(-k_x Z)} \tag{3}$$

$$\frac{dC_{MeHg}(Z)}{dt} = -k_D(X) \times C_{MeHg}(Z) \times PAR(0) \times e^{(-k_x Z)} \tag{4}$$

$$G_{PD}(X) = \int_0^D \left(-\frac{dC_{MeHg}(Z)}{dt} \times 10^3 \right) dZ = $$
$$k_D(X) \times C_{MeHg}(0) \times PAR(0) \times \frac{(1 - e^{(-k_x D)})}{k_x} \times 10^3 \tag{5}$$

$$P_{PD} = \frac{G_{PD}}{\bar{C}_{MeHg}} \times 10^{-3} \tag{6}$$

$$k_{UV\text{-}B} = 0.415 DOC^{1.86} \quad k_{UV\text{-}A} = 0.299 DOC^{1.53} \tag{7}$$

where X is the type of sunlight (UV-A, UV-B, or Vis); Z is a specific depth of water (m); $I(X, 0)$ is the intensity of X type of sunlight above the surface of the water (E m^{-2} d^{-1}); $I(X, Z)$ is the intensity of X type of sunlight at Z depth (E m^{-2} d^{-1});
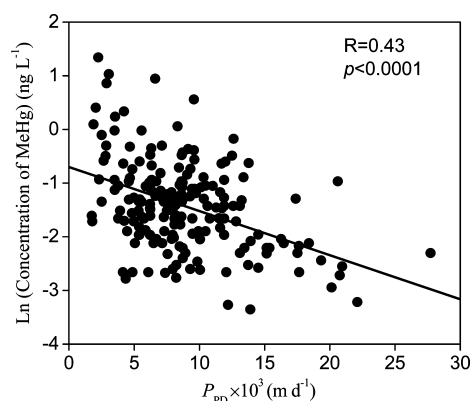

FIGURE 2. Relation of MeHg concentration to MeHg photodegradation potential (P_{PD}). Data obtained from both the dry season and wet season were employed here to conduct correlation analysis.

$C_{MeHg}(Z)$ is the concentration of MeHg at a specific depth Z (ng L^{-1}); $\bar{C}_{MeHg}$ is the average concentration of MeHg in the water column; $PAR(0)$ is the PAR above the surface of the water (E m^{-2} d^{-1}); $k_D(X)$ is the photodegradation constant of X type of sunlight with respect to $PAR(0)$ (E^{-1} m^2); k_X is the light attenuation coefficient of X type of sunlight (m^{-1}); G_{PD} is the MeHg photodegradation rate within the entire water column (ng m^{-2} d^{-1}); P_{PD} is the photodegradation potential within the entire water column (m d^{-1}); and D is the water depth (m).

Among these aforementioned parameters, DOC, D, and $C_{MeHg}(0)$ were obtained from our monitoring results in 2005 (18). From north to south, DOC generally showed a decreasing trend, both in the dry and wet seasons (Figure S6D, d). The concentration of DOC in the dry season (range 11.0−50.0 mg L^{-1}, average 22.9 mg L^{-1}) was higher than that in the wet season (range 4.6−45.0 mg L^{-1}, average 16.5 mg L^{-1}). The average concentration of DOC at the five studied sites in the wet season was 12.0 mg L^{-1} in 2005 (Figure S6d) and was 15.6 mg L^{-1} in 2010 (Table S1). This means that concentration of DOC in the Everglades was relatively stable over the time. Daily $PAR(0)$ data in 2005 were estimated by linear regression of measured daily PAR during these incubation experiments on corresponding NOAA satellite radiation data (Figure S5) (33). Then the G_{PD} and P_{PD} were calculated, both in the dry and wet seasons, and shown in contour maps illustrated in Figure S6. The spatial pattern of G_{PD} was complicated, with several "hot spot" and "cold spot" areas, widely distributed in the Everglades in both dry and wet seasons (Figure S6A, a). The P_{PD}, which takes into consideration MeHg concentration, showed a different distribution pattern from G_{PD}. In the dry season, P_{PD} generally presented an increasing trend from north to south, with a "hot spot" between 25.85° N and 26.05° N and a "cold spot" between 26.25° N and 26.37° N (Figure S6B). In the wet season, from north to south, P_{PD} also generally presented an increasing trend (Figure S6b).

The distribution of MeHg (Figure S6C, c) was in general negatively related to that of P_{PD} in Everglades water. For example, from north to south, MeHg generally showed a decreasing trend, both in the dry and wet seasons. At the location of the "hot spot" or "cold spot" of P_{PD} in the dry season, there was a corresponding "cold spot" or "hot spot" of MeHg. Correlation analysis indicate that MeHg and P_{PD} were significantly related (Figure 2). These results suggest that the spatial variation of photodegradation, which is a function of DOC, could play an important role in controlling the distribution of MeHg in the Everglades. Significant positive correlations between MeHg and DOC in Everglades water was observed in previous studies (21). It was previously attributed to the possible stabilization of MeHg after binding with DOC (21), but this hypothesis was not validated either

by direct experimental or field data. From the results of the current study, the strong correlations between MeHg and DOC could be at least partially explained by the DOC-induced decrease in MeHg photodegradation potential within the water column, which is a result of DOC-induced reduction in UV transmittance through the water.

Contribution of MeHg Photodegradation to the Cycling of MeHg in the Everglades. The importance of photodegradation to the cycling of MeHg in the Everglades was estimated using the results obtained in this study. A mass balance model was previously developed and used to estimate the mass budget of MeHg produced from annual deposited Hg in the Everglades (*18*). However, the photodegradation of MeHg was absent from that model, which could underestimate the mass of MeHg input into the water. The mass balance model was improved by adding photodegradation of MeHg to the balance equation (eq 9). According to the aforementioned definition of MeHg photodegradation potential within the entire water column (P_{PD}), photodegradation of MeHg resulting from seasonally deposited Hg can be estimated from the system-averaged P_{PD}, as described in eq 8. Finally, a new balance equation was derived to calculate the mass budget of MeHg in the Everglades (eq 10)

$$M_{PD}^{MeHg} = \Delta C_{SW}^{MeHg} \times \overline{P_{PD}} \times S \times d*10^3 \qquad (8)$$

$$M_{TP}^{MeHg} = \Delta C_{SW}^{MeHg}(V_{SW} + R_{SD}^{MeHg}M_{SD} + R_{FC}^{MeHg}M_{FC} + \\ R_{PE}^{MeHg}M_{PE} + R_{PK}^{MeHg}M_{PK} + BAF_{FS}^{MeHg}M_{FS} + V_{OF}) + \\ M_{BU}^{MeHg} + M_{PD}^{MeHg} \qquad (9)$$

$$M_{TP}^{MeHg} = \Delta C_{SW}^{MeHg}(V_{SW} + \overline{P_{PD}} \times S \times d*10^3 + \\ R_{SD}^{MeHg}M_{SD} + R_{FC}^{MeHg}M_{FC} + \\ R_{PE}^{MeHg}M_{PE} + R_{PK}^{MeHg}M_{PK} + BAF_{FS}^{MeHg}M_{FS} + V_{OF}) + \\ M_{BU}^{MeHg} \qquad (10)$$

where M_{TP}^{MeHg} is the annual MeHg produced from annual deposited Hg in sediment, floc, and periphyton (ng) (*18*), ΔC_{SW}^{MeHg} is change in concentration of MeHg resulting from seasonally deposited Hg (ng L^{-1}); M_{PD}^{MeHg} is the mass of MeHg photodegradation (ng); the $\bar{P}_{PD}$ is the system-averaged P_{PD} (m d^{-1}); S is the Everglades area (m^2); and d is the number of days in the season. Meanings of the other symbols are the same as in ref *18* and are listed in Table S2.

From the aforementioned results of P_{PD} in the Everglades, the system-averaged P_{PD} was calculated to be 6.6×10^{-3} m d^{-1} in the dry season and 18.8×10^{-3} m d^{-1} in the wet season. Values of other parameters and variables in eq 10 were the same as those used in the preceding paper (*18*). Finally, MeHg mass budget in the dry and wet seasons was obtained, and the sum of them resulted in the annual mass budget in the Everglades. The annual MeHg diffused into water column from the benthic layer (floc and sediment) was then calculated as the sum of annually produced MeHg distributed into all compartments in the water column (fish, macrophyte, periphyton, water, photodegradation, and outflow) (Figure 3). As shown in Figure 3, most of annually produced MeHg was compartmentalized to sediment (69.5%). About 19.4% was distributed to the compartments in water column, including fish, macrophyte, periphyton, water, photodegradation, and outflow. Although photodegradation of MeHg represented a small fraction of the annually produced MeHg (6.1%), reduction of MeHg by this process accounted for about 31.4% of the MeHg diffused into the water column. These results indicate the importance of photodegradation in the biogeochemical cycling of MeHg in the Everglades. This percent reduction in MeHg caused by photodegradation
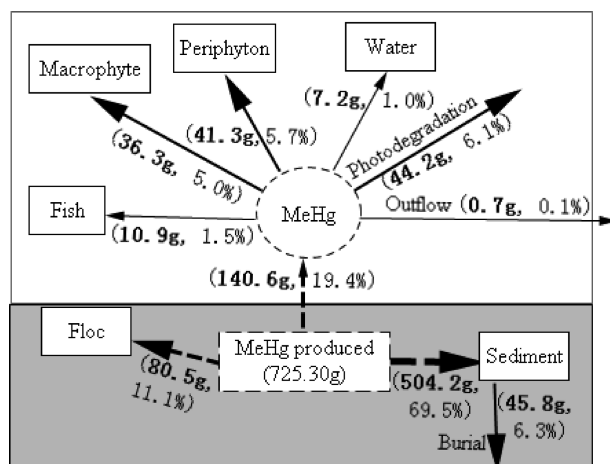

FIGURE 3. Annual mass (in bold, g) and fraction (%) budget of MeHg (produced from annual deposited Hg) in the Everglades. Annual MeHg produced from annual deposited Hg was the sum of MeHg produced from sediment, floc, and periphyton (*18*). The fraction of MeHg distributed to each compartment was related to the annual produced MeHg. The benthic layer-water diffusing flux of MeHg was calculated as the sum of the compartmentalization of produced MeHg to the compartments in the water column (fish, macrophyte, periphyton, water, photodegradation, and outflow).

in the Everglades is much lower than that reported for other ecosystems. Photodegradation accounted for about 80% of the MeHg mobilized from sediment into water in Toolik Lake (*2*), and about 83% of MeHg flowing into the Lake 240 was removed by photodegradation (*3*). The relatively lower percent reduction in MeHg in the Everglades could be attributed to its higher DOC concentration (20 mg L^{-1}), which can decrease the transmittance of UV through water. Indeed, if the average DOC concentration in Everglades water is decreased to 4.4 mg L^{-1} (average concentration in Toolik Lake), the average P_{PD} will increase to 39.6×10^{-3} m d^{-1} in the dry season and 113.5×10^{-3} m d^{-1} in the wet season. If these hypothetical $\bar{P}_{PD}$ values are used to calculate the MeHg mass budget in the Everglades, photodegradation will account for about 74% of the annual MeHg input into water column. It was reported that the ratio of MeHg to THg in Everglades water (~11%) is higher than that reported in other ecosystems (*21*). From the aforementioned analysis, the higher MeHg/THg ratio could be partially explained by the lower photodegradation rate, which is the result of high DOC concentration in the Everglades.

Moreover, the annual average value of MeHg photodegradation rate within the entire water column (G_{PD}) was calculated to be 3.4 ng m^{-2} d^{-1} with the data shown in Figure S6. If elemental mercury (Hg^0) is the major product of MeHg photodegradation as suggested in the literature (*10*), the photodegradation process would contribute a large extent to the evasion of Hg^0 in the Everglades (6.0 ng m^{-2} d^{-1} (*34*)). This possible contribution of MeHg photodegradation to the evasion of Hg^0 was also found in other ecosystems (*2, 3*), indicating the importance of this process on the elimination of Hg from aquatic ecosystems.

Acknowledgments

Supporting Information Available

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Mergler, D.; Anderson, H. A.; Chan, L. H. M.; Mahaffey, K. R.; Murray, M.; Sakamoto, M.; Stern, A. H. Methylmercury Exposure and Health Effects in Humans: A Worldwide Concern. *Ambio* **2007**, *36*, 3–11.

(2) Hammerschmidt, C. R.; Fitzgerald, W. F. Photodecomposition of Methylmercury in an Arctic Alaskan Lake. *Environ. Sci. Technol.* **2006**, *40*, 1212–1216.

(3) Sellers, P.; Kelly, C. A.; Rudd, J. W. M.; MacHutchon, A. R. Photodegradation of Methylmercury in Lakes. *Nature* **1996**, *380*, 694–697.

(4) Marvin-Dipasquale, M. C.; Oremland, R. S. Bacterial Methylmercury Degradation in Florida Everglades Peat Sediment. *Environ. Sci. Technol.* **1998**, *32*, 2556–2563.

(5) Schaefer, J. K.; Yagi, J.; Reinfelder, J. R.; Cardona, T.; Ellickson, K. M.; Tel-Or, S.; Barkay, T. Role of the Bacterial Organomercury Lyase (Merb) in Controlling Methylmercury Accumulation in Mercury-Contaminated Natural Waters. *Environ. Sci. Technol.* **2004**, *38*, 4304–4311.

(6) Monperrus, M.; Tessier, E.; Amouroux, D.; Leynaert, A.; Huonnic, P.; Donard, O. F. X. Mercury Methylation, Demethylation and Reduction Rates in Coastal and Marine Surface Waters of the Mediterranean Sea. *Mar. Chem.* **2007**, *107*, 49–63.

(7) Matilainen, T.; Verta, M. Mercury Methylation and Demethylation Waters. *Can. J. Fish. Aquat. Sci.* **1995**, *52*, 1597–1608.

(8) Lehnherr, I.; St. Louis, V. L. Importance of Ultraviolet Radiation in the Photodemethylation of Methylmercury in Freshwater Ecosystems. *Environ. Sci. Technol.* **2009**, *43*, 5692–5698.

(9) Inoko, M. Studies on the Photochemical Decomposition of Organomercurials-Methylmercury (II) Chloride. *Environ. Pollut.* **1981**, *2*, 3–10.

(10) Chen, J.; Pehkonen, S. O.; Lin, C. J. Degradation of Monomethylmercury Chloride by Hydroxyl Radicals in Simulated Natural Waters. *Water Res.* **2003**, *37*, 2496–2504.

(11) Sellers, P.; Kelly, C. A.; Rudd, J. W. M. Fluxes of Methylmercury to the Water Column of a Drainage Lake: The Relative Importance of Internal and External Sources. *Limnol. Oceanogr.* **2001**, *46*, 623–631.

(12) Stober, Q. J.; Thornton, K.; Jones, R.; Richards, J.; Ivey, C.; Welch, R.; Madden, M.; Trexler, J.; Gaiser, E.; Scheidt, D.; Rathbun, S. *South Florida Ecosystem Assessment: Phase I/II (Technical Report)-Everglades Stressor Interactions: Hydropatterns, Eutrophication, Habitat Alteration, and Mercury Contamination*; U.S. EPA Region 4: Athens, GA, 2001.

(13) Cleckner, L. B.; Gilmour, C. C.; Hurley, J. P.; Krabbenhoft, D. P. Mercury Methylation in Periphyton of the Florida Everglades. *Limnol. Oceanogr.* **1999**, *44*, 1815–1825.

(14) Gilmour, C. C.; Riedel, G. S.; Ederington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. A.; Stordal, M. C. Methylmercury Concentrations and Production Rates across a Trophic Gradient in the Northern Everglades. *Biogeochemistry* **1998**, *40*, 327–345.

(15) Cleckner, L. B.; Garrison, P. J.; Hurley, J. P.; Olson, M. L.; Krabbenhoft, D. P. Trophic Transfer of Methyl Mercury in the Northern Florida Everglades. *Biogeochemistry* **1998**, *40*, 347–361.

(16) Duvall, S. E.; Barron, M. G. A Screening Level Probabilistic Risk Assessment of Mercury in Florida Everglades Food Webs. *Ecotoxicol. Environ. Saf.* **2000**, *47*, 298–305.

(17) Krabbenhoft, D. P.; Hurley, J. P. The Sun's Detoxifying Effects on Mercury in the Everglades. In *U.S. Geological Survey Program on the South Florida Ecosystem-Proceedings of the South Florida Restoration Science Forum*; U.S. Geological Survey Open-File Report 99-181; Gerould, S., Higer, A., Eds.; Boca Raton, FL, 1999.

(18) Liu, G. L.; Cai, Y.; Kalla, P.; Scheidt, D.; Richards, J.; Scinto, L. J.; Gaiser, E.; Appleby, C. Mercury Mass Budget Estimates and Cycling Seasonality in the Florida Everglades. *Environ. Sci. Technol.* **2008**, *42*, 1954–1960.

(19) Gu, B. H.; Chimney, M. J.; Newman, J.; Nungesser, M. K. Limnological Characteristics of a Subtropical Constructed Wetland in South Florida (USA). *Ecol. Eng.* **2006**, *27*, 345–360.

(20) Doehring, F.; Karl, T. *A History of Sunshine Data in the United States 1891–1980*; National Climatic Center: Asheville, NC, 1981.

(21) Liu, G. L.; Cai, Y.; Philippi, T.; Kalla, P.; Scheidt, D.; Richards, J.; Scinto, L.; Appleby, C. Distribution of Total and Methylmercury in Different Ecosystem Compartments in the Everglades: Implications for Mercury Bioaccumulation. *Environ. Pollut.* **2008**, *153*, 257–265.

(22) Martin-Doimeadios, R. C. R.; Stoichev, T.; Krupp, E.; Amouroux, D.; Holeman, M.; Donard, O. F. X. Micro-Scale Preparation and Characterization of Isotopically Enriched Monomethylmercury. *Appl. Organomet. Chem.* **2002**, *16*, 610–615.

(23) Mao, Y. X.; Liu, G. L.; Meichel, G.; Cai, Y.; Jiang, G. B. Simultaneous Speciation of Monomethylmercury and Monoethylmercury by Aqueous Phenylation and Purge-and-Trap Preconcentration Followed by Atomic Spectrometry Detection. *Anal. Chem.* **2008**, *80*, 7163–7168.

(24) Amyot, M.; Lean, D.; Mierle, G. Photochemical Formation of Volatile Mercury in High Arctic Lakes. *Environ. Toxicol. Chem.* **1997**, *16*, 2054–2063.

(25) Kirk, J. T. O. Optics of UV-B Radiation in Natural Waters. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* **1994**, *43*, 1–16.

(26) Scully, N. M.; Lean, D. R. S. The Attenuation of Ultraviolet Radiation in Temperate Lakes. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* **1994**, *43*, 135–144.

(27) Donahue, W. F.; Turner, M. A.; Findlay, D. L.; Leavitt, P. R. The Role of Solar Radiation in Structuring the Shallow Benthic Communities of Boreal Forest Lakes. *Limnol. Oceanogr.* **2003**, *48*, 31–47.

(28) Huovinen, P. S.; Penttila, H.; Soimasuo, M. R. Spectral Attenuation of Solar Ultraviolet Radiation in Humic Lakes in Central Finland. *Chemosphere* **2003**, *51*, 205–214.

(29) Mopper, K.; Zhou, X. L. Hydroxyl Radical Photoproduction in the Sea and Its Potential Impact on Marine Processes. *Science* **1990**, *250*, 661–664.

(30) Brezonik, P. L.; Fulkerson-Brekken, J. Nitrate-Induced Photolysis in Natural Waters: Controls on Concentrations of Hydroxyl Radical Photo-Intermediates by Natural Scavenging Agents. *Environ. Sci. Technol.* **1998**, *32*, 3004–3010.

(31) Liao, C. H.; Kang, S. F.; Wu, F. A. Hydroxyl Radical Scavenging Role of Chloride and Bicarbonate Ions in the H_2O_2/UV Process. *Chemosphere* **2001**, *44*, 1193–1200.

(32) Zepp, R. G.; Faust, B. C.; Hoigne, J. Hydroxyl Radical Formation in Aqueous Reactions (pH 3–8) of Iron(II) with Hydrogen-Peroxide - the Photo-Fenton Reaction. *Environ. Sci. Technol.* **1992**, *26*, 313–319.

(33) Kalnay, E.; Kanamitsu, M.; Kistler, R.; Collins, W.; Deaven, D.; Gandin, L.; Iredell, M.; Saha, S.; White, G.; Woollen, J.; Zhu, Y.; Chelliah, M.; Ebisuzaki, W.; Higgins, W.; Janowiak, J.; Mo, K. C.; Ropelewski, C.; Wang, J.; Leetmaa, A.; Reynolds, R.; Jenne, R.; Joseph, D. The NCEP/NCAR 40-Year Reanalysis Project. *Bull. Am. Meteorol. Soc.* **1996**, *77*, 437–471.

(34) Krabbenhoft, D. P.; Hurley, J. P.; Olson, M. L.; Cleckner, L. B. Diel Variability of Mercury Phase and Species Distributions in the Florida Everglades. *Biogeochemistry* **1998**, *40*, 311–325.