

## Diel variability of mercury phase and species distributions in the Florida Everglades<sup>\*</sup>

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**Abstract.** Preliminary studies of mercury (Hg) cycling in the Everglades revealed that dissolved gaseous mercury (DGM), total mercury (Hg<sub>T</sub>), and reactive mercury (Hg<sub>R</sub>) show reproducible, diel trends. Peak water-column DGM concentrations were observed on or about noon, with a 3 to 7 fold increase over night-time concentrations. Production of DGM appears to cease during dark periods, with nearly constant water column concentrations that were at or near saturation with respect to the overlying air. A simple mass balance shows that the flux of Hg to the atmosphere from diel DGM production and evasion represents about 10% of the annual input from atmospheric deposition. Production of DGM is likely the result of an indirect photolysis reaction that involves the production of reductive species and/or reduction by electron transfer. Diel variability in Hg<sub>T</sub> and Hg<sub>R</sub> appears to be controlled by two factors: inputs from rainfall and photolytic sorption/desorption processes. A possible mechanism involves photolysis of chromophores on the surface of a solid substrate (e.g., the periphyton mat) giving rise to destabilization of sorbed mercury and net desorption during daylight. At night, the sorption reactions predominate and the water-column Hg<sub>T</sub> decreases. Methylmercury (MeHg) also showed diel trends in concentration but were not clearly linked to the solar cycle or rainfall at the study site.

### Background

The issuance of fish consumption advisories statewide in Florida, due to elevated levels ( $\geq 0.5 \mu\text{g g}^{-1}$ , muscle tissue) of Hg (Ware et al. 1990), has stimulated considerable monitoring and research activity on the sources, transport, and fate of Hg in Florida (Dvonch et al. 1995; Guentzel et al. 1995; Stober et al. 1995; Vaithyanathan et al. 1996). Mercury concentrations in game fish from the Everglades are of particular concern, where Hg concentrations exceed  $1.5 \mu\text{g g}^{-1}$ . This observation has resulted in a “do not consume”

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advisory for about 90% of the remaining Everglades (excluding Big Cypress National Preserve). In addition to human-health concerns, Hg has possibly adversely affected the reproductive patterns of fish-eating birds from this region (Spalding et al. 1994; Sundlof et al. 1994), and been identified as a principal factor in the death of at least one Florida panther which had a liver mercury concentration of  $110 \mu\text{g g}^{-1}$  (Jordan 1990), and is strongly implicated in the deaths of two other panthers (Roelke et al. 1991).

Recently, there has been a growing body of evidence linking photochemical processes to mercury speciation in the atmosphere (Schroeder et al. 1991), the aquatic environment (Amyot et al. 1994, 1997; Lindberg et al. 1995; Sellers et al. 1996), and terrestrial systems (Sexaver-Gustin & Taylor 1996). More direct evidence comes from observations of diel production and accumulation of  $\text{Hg}^0$  in the epilimnion of lakes and much lower  $\text{Hg}^0$  concentrations in hypolimnetic waters where light levels are very low (Amyot et al. 1994; Lindberg et al. 1995). Although most photochemical studies involving mercury have focused on reduction reactions that produce  $\text{Hg}^0$ , photodegradation of methylmercury (MeHg) has recently been shown to be an important process in temperate lakes (Sellers et al. 1996). In the present study, we investigated the diel variability of  $\text{Hg}_\text{T}$ ,  $\text{Hg}_\text{R}$ , DGM, and MeHg in the Everglades.

In response to Hg contamination in the Everglades, the U.S. Geological Survey initiated the Aquatic Cycling of Mercury in the Everglades (ACME) project (Krabbenhoft 1996). The overall objective of the ACME project is to provide information on the hydrologic, biologic and geochemical processes controlling Hg cycling in the Everglades. Here, we present results on short-term (diel) variability of Hg speciation and phase distributions, propose mechanistic models of the processes controlling the diel variability, and evaluate the importance of these processes in the overall Hg cycle.

### Site description

This study was conducted at Rubber Tree Head (Figure 1), a tree island located near the center of Water Conservation Area 2A (WCA2A) ( $80^\circ 23' \text{ W}$ ,  $26^\circ 18' \text{ N}$ ), a  $547 \text{ km}^2$  conservation area managed by the South Florida Water Management District. A small, privately owned structure on stilts (historic fishing and hunting camp) located at the north end of the island was used as a staging area. A wooden dock extends from the structure into an adjacent open-water slough where water samples were taken. Rubber Tree Head is situated in an area of WCA2A that is predominantly sawgrass (*Cladium jamaicense*) intermixed by a complex mosaic of sloughs that are dominated by water lilies (*Nymphaea* sp.), floating hearts (*Nymphoides aquatica*), spatter-

dock (*Nuphar advena*), and periphyton mats (McCormick et al. 1996). The mat is an assemblage of green, golden-brown, and blue-green algae that can be floating, submerged, or attached to macrophytes. The periphyton mat, phytoplankton and detrital products are vital food resources. Additionally, these algae influence oxygen levels in the water, affect nutrient cycling and sediment accumulation, and likely are an important factor in the Hg cycle and biotic uptake of mercury (Cleckner et al. this issue). Soils in this area of the Everglades are about 1 to 3 m of organic sediments (Histosols), specifically named Everglades peat (Davis 1943).

### Materials and methods

Sampling procedures for this study employed low-level trace metal clean techniques (Hurley et al. this issue; Olson et al. 1997). Samples were acquired using a peristaltic pump, a 30 cm length of C-flex pump-head tubing, and a precleaned Teflon<sup>1</sup> sampling line. The inlet end of the sampling line was positioned at mid-water column depth at the beginning of each sampling period. The pump was left running at a slow rate (about 50 ml min<sup>-1</sup>) during the entire period of each study (24–30 hr). Samples were taken about every 90 minutes during the December 1995, March 1996, and June 1996 diel samplings, while a less frequent sampling schedule was used on the first diel study (July 1995) when samples were taken nine times over 24-hours.

Samples were obtained for Hg<sub>T</sub>, Hg<sub>R</sub>, DGM, and MeHg, except during the initial sampling period (July, 1995) when Hg<sub>R</sub> was not sampled. Duplicate or triplicate samples were taken at least 10% of the time. While it is assumed the majority of DGM in our samples is Hg<sup>0</sup>, our sampling and analytical methods do not distinguish between Hg<sup>0</sup> and other volatile mercury species possibly present. Total mercury and MeHg samples were filtered with an in-line 0.45 µm Calyx capsule filter (precleaned by filling with 50% HNO<sub>3</sub> for two days, rinsing with deionized water, filling with 50% HCl, rinsing, and filling with deionized water until use), whereas unfiltered water samples were taken for Hg<sub>R</sub> and DGM. Upon collection MeHg samples were placed in a darkened cooler with dry ice. Total Hg and Hg<sub>R</sub> samples were immediately acidified using 10 ml and 1 ml, respectively, of 6 N HCl and kept in a darkened cooler. In this study, Hg<sub>R</sub> is defined as that fraction of total Hg pool that is labile enough for reduction by SnCl<sub>2</sub> after acidification. For DGM samples, about 1.5 to 1.8 liters of water were pumped into a 2-liter, two-port Teflon vessel and the DGM was collected immediately using purge and trap. One port served as

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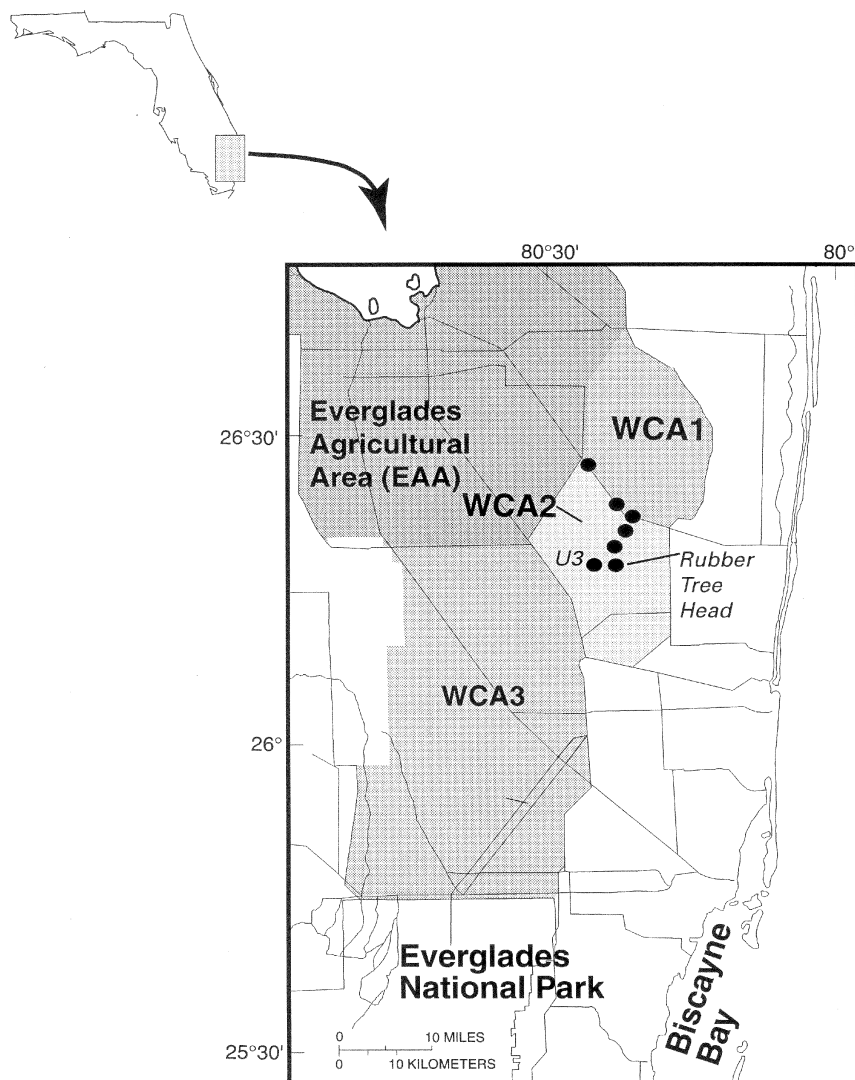


Figure 1. Site location map of the Rubber Tree Head in Water Conservation Area 2A (WCA2A). Site U3 is the location where the 4-day incubation experiment was conducted. Unlabeled sites are sampling locations of the ACME project.

the inlet for the purge gas ( $N_2$ , precleaned using a gold trap) and connected to a 20 cm long borosilicate glass frit through which the  $N_2$  is bubbled, and the other port serves as an outlet for the gas train. A soda-lime trap and gold trap are connected in series downstream of the outlet port. DGM samples were purged for 1 hour at  $500 \text{ ml min}^{-1}$ .

Samples collected for this study were shipped to Madison, Wisconsin and analyzed as follows. Total mercury and  $\text{Hg}_\text{R}$  were analyzed using the methods of Bloom & Fitzgerald (1987), and methylmercury by the distillation/ethylation method of Horvat et al. (1993). A more complete description of our analytical methods and precautions we have taken to circumvent matrix interference can be found in Olson et al. (1997).

In addition to Hg sampling, several other measurements were made during each sampling period. Incident solar radiation was measured about 1 m above the water surface using a LiCOR quantum sensor, which responds to photosynthetically active radiation (PAR, 400–700 nm). Temperatures of the surface water, air, and sediments (20 cm depth) were monitored using copper-constantan thermocouples. Temperature and PAR ( $\text{Watt m}^{-2}$ ) measurements were made every 10 seconds and averaged over 15 minute intervals using a datalogger. A water-quality monitor equipped with pH, temperature, dissolved oxygen, specific conductance, and redox probes was deployed during each sampling trip, and measurements were made at least hourly.

## Results and discussion

*Diel variability and production of DGM.* During each sampling period, a reproducible diel pattern in DGM was evident (Figure 2). DGM sample replicates show good agreement, with less than 10% difference generally observed. Peak DGM concentrations occur on or about solar noon, with maximum values 3 to 7 times greater than the minimum levels, which were observed just before sunrise. If the controlling process leading to the accumulation of  $\text{Hg}^0$  in the surface water of the Everglades is a photoreduction, then the maximum observed  $\text{Hg}^0$  concentration for a given day should relate to solar intensity. A linear regression of the average PAR for the two-hour period preceding the observed peak DGM concentration versus peak concentration shows that this relation is significant at less than the 0.01 level, and yields a coefficient of determination of ( $r^2$ ) = 0.93, and an intercept of  $0.008 \text{ ng l}^{-1}$  (Table 1, Figure 3). Considerably lower  $r^2$  values are calculated for linear regressions of peak DGM versus average water temperature and water column depth (Table 1). These results are different than those of Amyot et al. (1997) who found a nonlinear relation between DGM production and radiation intensity in northern temperate lakes. The poor correlation of DGM with temperature suggests that production and evasion are not significantly affected in the range of water temperatures observed for this study (about 20 to 35 °C), and that sunlight and wind speed are more important in determining concentration and flux of DGM from Everglades surface waters. Accumulation of DGM in the water column is the net effect of reduction, evasion, and oxidation. Additional

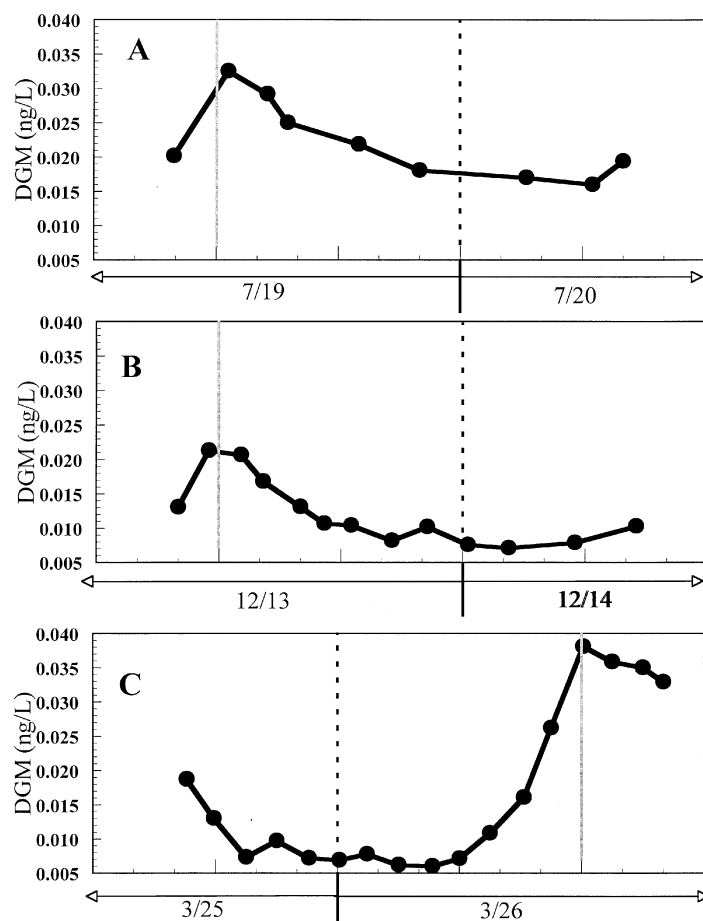


Figure 2. Results of the diel sampling results for dissolved gaseous mercury (DGM) for the July, 1995 (panel A); December, 1995 (panel B); and March, 1996 (panel C) sampling trips. Each data point represents a single analysis, although replicate samples show variability is less than 10% for this sampling procedure. Vertical gray lines are drawn at noon and dashed black lines indicate midnight for each sampling period.

corroborating evidence that photoreduction is the process controlling DGM production is the observation that night-time minimum DGM concentrations for three of the four sampling trips are very similar to the calculated intercept of the regression analysis (Figure 3). Using the average ambient air  $\text{Hg}^0$  concentration for the Everglades of  $1.5 \text{ ng m}^{-3}$  (Gill et al. 1995), and the Henry's Law coefficient of 0.32 (Schroeder et al. 1991), the equilibrium  $\text{Hg}^0$  water concentration at  $25^\circ\text{C}$  is about  $0.005 \text{ ng l}^{-1}$ . Such close agreement with our observed night time minimum DGM concentrations suggests that little or no DGM production occurs at night.

Table 1. Results of linear correlation analysis of Peak DGM against average PAR for the two hour period preceding peak DGM, average water temperature during sampling period, and water depth.

	Peak DGM (ng L <sup>-1</sup> )	Ave. PAR (Watt m <sup>-2</sup> )	Ave. water temp. (°C)	Water depth (cm)
July '95	0.033	599	33	45
Dec. '95	0.022	504	22	35
March '96	0.039	875	25	10
June '96	0.033	695	29	38
( <i>r</i> <sup>2</sup> , <i>m</i> , <i>b</i> ) <sup>1</sup>		(0.93, 3.5 × 10 <sup>-5</sup> , 0.008)	(0.19, 6.5 × 10 <sup>-4</sup> , 0.014)	(0.23, -1.6 × 10 <sup>-4</sup> , 0.035)

<sup>1</sup> Descriptive statistics of a linear regression analysis between DGM and PAR, average water temperature, and water depth. The coefficient of determination (*r*<sup>2</sup>), slope (*m*), and intercept (*b*) are given for each regression.

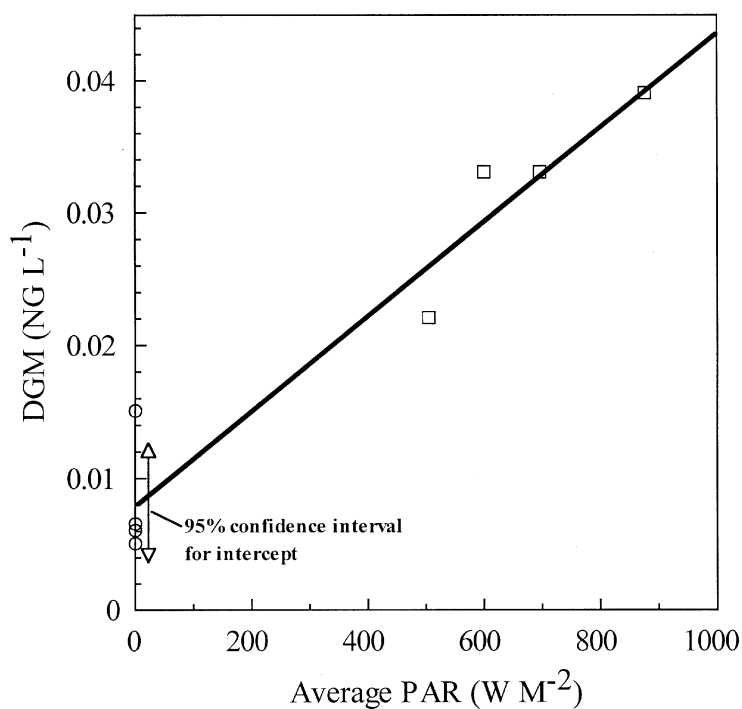
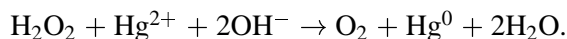


Figure 3. Plot of maximum observed DGM concentration versus average PAR for the two hour period preceding the observed maximum DGM concentration. Squares are the maximum observed DGM concentrations, and circles are the night time minimums observed for each diel sampling. Regression statistics for this data show an *r*<sup>2</sup>, slope, and intercept values of 0.93, 3.5 × 10<sup>-5</sup>, 0.008, respectively. The 95% confidence interval for the intercept, which is a predictor of night-time (no sunlight) DGM concentration, is also shown.

Using diel DGM accumulation profiles and assuming that the patterns are a result of production and evasion (assuming no reoxidation), we calculate an average annual mass flux of Hg from surface water. Our average daily DGM accumulation is about  $0.020 \text{ ng l}^{-1} \text{ d}^{-1}$ , and using our measured average water depth at the Rubber Tree Head of 0.3 m, we calculate an annual evasion rate of Hg from the system of  $2.2 \mu\text{g m}^{-2} \text{ y}^{-1}$ . Although this flux is only about 10% of the estimated flux from atmospheric deposition (Guentzel et al. 1995), it is still an important consideration for mass balance considerations. We performed this calculation assuming a static system, whereas in the environment evasion is continually occurring process during the buildup of DGM. Therefore, our flux rate probably represents a minimum value.

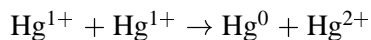
The precise mechanism that results in the production of DGM in the Everglades is not known. From a theoretical standpoint, at pH levels greater than about 5.5, Hg(II) can be reduced to  $\text{Hg}^0$  by reacting with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Schroeder et al. 1991), which is a known product of photolysis reactions involving humic substances (Schwarzenbach et al. 1993):



At pH less than 5.5, however, oxidation of  $\text{Hg}^0$  by  $\text{H}_2\text{O}_2$  can occur:



Given that Everglades surface waters are high in dissolved humic matter (ranging from 29 to 41 mg/L in WCA2A during the study; Hurley et al. this issue), and the pH of surface water at the Rubber Tree Head is about 7.2, the peroxide reductive reaction is plausible. Amyot et al. (1994), however, showed that addition of peroxide to incubated lake samples with circum-neutral pH had no effect on net DGM production, suggesting the peroxide driven oxidation or reduction was not important. A second possible photolysis reaction involves the reduction of  $\text{Hg}^{2+}$  by electron transfer from a chromophore in an excited state after absorbing a photon. The chromophore could be attached to the  $\text{Hg}^{2+}$  ion as a ligand, or could be sorbed to the surface of a suspended particle or fixed substrate where  $\text{Hg}^{2+}$  ions are sorbed (Zafiriou et al. 1984). For electron transfer to be the only process seems unlikely, since this would require a nearly simultaneous transfer of two electrons to reduce  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ . The product of a one electron transfer,  $\text{Hg}^{1+}$ , is a relatively unstable species in oxic waters, and likely would produce  $\text{Hg}^0$  through the following disproportionation reaction (Schroeder et al. 1991):



Two experiments conducted during the diel sampling efforts lend insight into the photoreduction process. In the first experiment, six two-liter, purge



and trap vessels were filled with 0.22  $\mu\text{m}$  filtered surface water from the Rubber Tree Head at 0430 on March 26, 1996 (when the minimum DGM level was observed, Figure 2) and left on the dock exposed to sunlight until 1730. Sealed vessels allow quantification of DGM production rates, since the measured accumulation rate of DGM in the water column is potentially a minimum rate due to evasion. Filtered water was used to test whether the photoreduction process is mediated by particle-associated chromophores, or possibly algal cells. Both Teflon and borosilicate glass vessels (three of each) were used to test the possible effects of light attenuation by vessel walls. After incubation, accumulated DGM in the samples was purged as described above. The second experiment was conducted during the December 1995 diel sampling, at a nearby site, U3 (see Figure 1), to test the stability of  $\text{Hg}_\text{T}$  and MeHg to sunlight exposure. For this experiment, 84 replicate 0.22  $\mu\text{m}$  filtered surface water samples (28 each for  $\text{Hg}_\text{T}$ ,  $\text{Hg}_\text{R}$ , and MeHg) were collected in Teflon bottles and placed just below the surface of the water and incubated for up to four days.

Results from the first experiment indicate the concentration of DGM in the six two-liter vessels at the end of the 1-day experiment were very similar (average =  $0.064 \text{ ng l}^{-1}$ , range =  $0.061\text{--}0.067 \text{ ng l}^{-1}$ ), with no statistical difference between glass and Teflon vessels. Since the vessels were exposed to sunlight for about 11 hours and started with an initial concentration of  $0.006 \text{ ng l}^{-1}$ , the mass accumulation rate of DGM for this solar cycle was  $0.058 \text{ ng l}^{-1} \text{ d}^{-1}$ , or  $0.005 \text{ ng l}^{-1} \text{ hr}^{-1}$ , which is identical to the rate we observed for the water column at the Rubber Tree Head (Figure 2c).

Results from the second experiment showed a steady declining concentration trend in  $\text{Hg}_\text{T}$  (Figure 4). A linear regression of  $\text{Hg}_\text{T}$  versus time yields a  $r^2 = 0.84$  and a slope of  $-0.062 \text{ ng Hg}_\text{T} \text{ l}^{-1} \text{ d}^{-1}$ . The only loss mechanism of  $\text{Hg}_\text{T}$  from the incubated bottles is by reduction and evasion into the small headspace in each bottle. Similar rates of  $\text{Hg}_\text{T}$  loss and DGM production lead us to conclude that the pool of Hg available for photoreduction is in dissolved  $\text{Hg}_\text{T}$ , and not particulate Hg. Samples analyzed for MeHg showed no apparent change over the 4 day incubation period. This observation suggests the MeHg photodegradation process observed by Sellers et al. (1996) in Canadian lakes is not a dominant process in the water column at this site. This disparity is likely due to the much higher DOC levels in the Everglades, which limits UV light penetration beyond a depth of a few cm (J. Grimshaw, unpublished data), and is probably a contributing factor as to why Everglades waters are high in MeHg. Further experiments will be conducted to determine the limiting factors of this process.

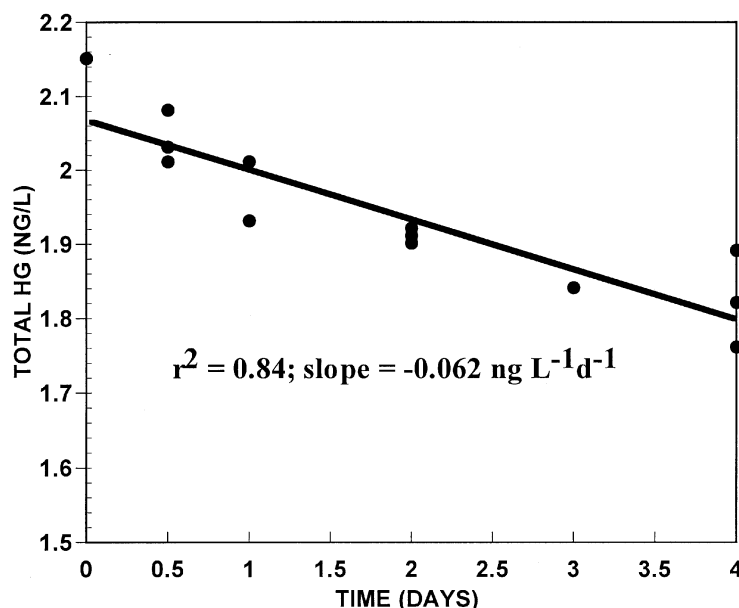


Figure 4. Results of the 4-day incubation experiment for total mercury. Replicate, 0.22  $\mu\text{m}$  filtered water samples were collected at  $t = 0, 0.5, 1, 2, 3,$  and 4 days. Except for  $t = 0$  and 3 days, triplicate samples were collected at each time interval. The regression line for these data have a coefficient of variation ( $r^2$ ) = 0.81, and slope =  $-0.068 \text{ ng Hg}_T \text{ l}^{-1} \text{ d}^{-1}$ .

*Diel variability of  $\text{Hg}_T$ ,  $\text{Hg}_R$ , and MeHg and controlling processes.* While the diel response of  $\text{Hg}^0$  was somewhat anticipated, surprisingly  $\text{Hg}_T$ ,  $\text{Hg}_R$ , and MeHg also showed substantial, short-term variability during diel sampling (Figures 5a–5h). After the initial sampling effort (July, 1995), during which an afternoon thunderstorm contributed a considerable amount of rainfall (Figure 5a–b), we attributed the variability in  $\text{Hg}_T$  to a combination of a pulse input of  $\text{Hg}_T$  from rainfall (which is known to be high in mercury, up to  $100 \text{ ng l}^{-1}$ ; Dvonch et al. 1995) followed by an equilibration period with  $\text{Hg(II)}$  partitioning to sediment, periphyton, and plant surfaces. Variability of MeHg did not appear to be linked with the rainfall, although there appeared to be a net accumulation of MeHg during darkness.

Climatic conditions during the December, 1995 sampling were different in three regards. Although it rained twice, rainfall amounts were much less than that observed during the July, 1995 sampling, and solar intensity and average water temperature were lower (Table 1). Similar to the first diel sampling,  $\text{Hg}_T$  showed a marked increase in concentration following the two rain events (Figure 5c). More striking, however, is the steady decline in  $\text{Hg}_T$  from noon on 12/13 until sunrise on 12/14, and the similar response of  $\text{Hg}_R$  (Figure 5c

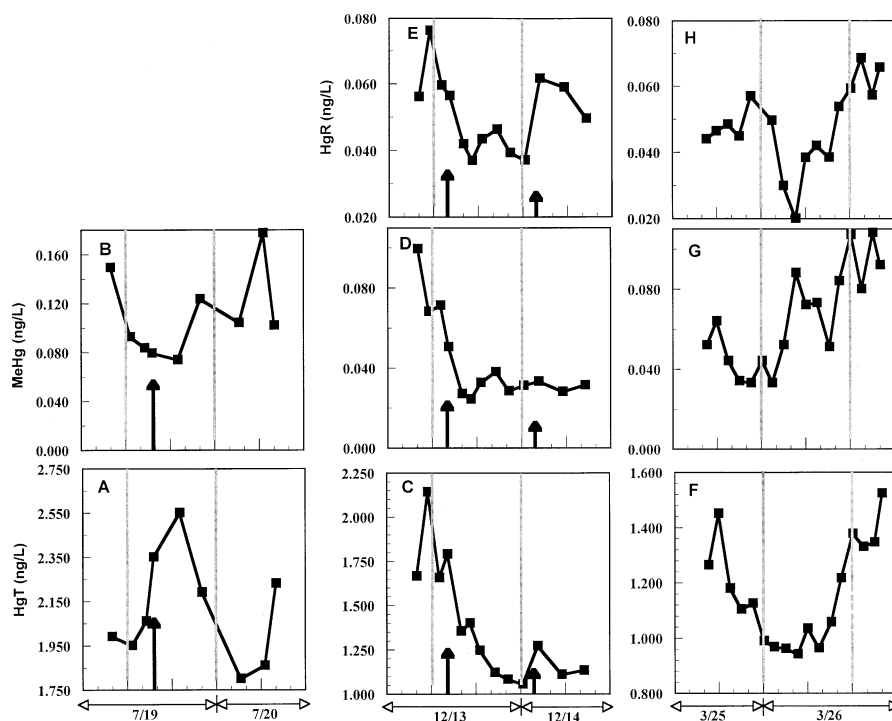


Figure 5. Results of the diel sampling results for Hg<sub>T</sub>, Hg<sub>R</sub>, and MeHg for the July, 1995; December, 1995; and March, 1996 sampling trips. Vertical gray lines are drawn at noon and midnight for each sampling period. Vertical arrows indicate the occurrence of rainfall, and the length of the arrow is an estimate of the relative magnitude (amount of water) of individual storms.

and e). Methylmercury also followed a very similar trend, with the exception of no apparent response to rain events.

No rain events occurred during the March, 1996 sampling, which precluded the complicating signal from rainfall. In addition, solar intensity was notably greater (due to comparatively little cloud cover) and water depth was substantially less than the two previous diel sampling efforts (Table 1). This sampling trip was also logistically different in that sampling started mid-afternoon on the first day and carried through until the evening of the second day, to further test the hypothesis that the rise in Hg<sub>T</sub> concentration at sunrise would follow the solar cycle. Without the complicating effect of rainfall, the diel patterns of Hg<sub>T</sub> and Hg<sub>R</sub> were more clear. Both species showed nearly identical trends, and similar to DGM, track the solar cycle closely in a sinusoidal manner (Figure 5f and h). Methylmercury, on the other hand showed no discernible trend during the first 8 hours of sampling (Figure 5g), but showed a general trend of increasing concentration after that point. The lack of a diel

trend in MeHg concentrations suggests that it is not the dominant precursor Hg species to DGM.

In addition to the diel Hg patterns observed during individual trips, a seasonal trend in  $\text{Hg}_T$  concentration is also evident by comparing our data among trips (Figures 5a, c, and f). A decrease in the maximum observed  $\text{Hg}_T$  concentration for each diel sampling is a reflection of the transition from the rainy summer season, with the associated greater inputs of Hg, to the drier winter and spring seasons. A similar seasonal trend has also been noted over a much wider area of the northern Everglades by Hurley et al. (this issue).

Preliminary observations from diel samplings in the Florida Everglades indicate that the total mass of Hg in the water column follows a diel pattern at this site in the Everglades. We attribute this phenomenon to photochemically driven sorption and desorption. A photochemical model that invokes heterogeneous energy transfer (Miller & Zepp 1979), could explain these observations. During daylight hours, chromophores (most likely carotenoids, porphyrins and quinoid type compounds) sorbed to or part of the surface of a solid substrate (e.g., sediments, macrophytes, periphyton mat) become excited by adsorbing photons. Alternatively, the  $\text{Hg(II)}$  atom itself may become excited by energy transfer from an nearby excited chromophore, which shifts the outer electrons of the Hg atom from bonding to non-bonding orbitals. At the higher energy level, the reaction rate of  $\text{Hg(II)}$  desorption is elevated, and thus a net accumulation of  $\text{Hg(II)}$  in the water occurs during the day. Under dark conditions, the reverse reaction (sorption) predominates, and a net loss of  $\text{Hg(II)}$  from the water column results. Although the diel  $\text{Hg}_T$  trend shown here is novel, other researchers have shown that chromophores on the surfaces of algae cells perform photolytic transformations regardless of whether the algae is living dead, suggesting it is an extracellular process and not directly involved in intercellular metabolic processes (Zepp & Wolfe 1987). Macrophytes and periphyton mats, which float at the surface of the water, and thus would not be shielded by the light screening effects of the high DOC water, are in an optimal position to facilitate photochemical sorption/desorption of Hg.

## Conclusions

Diel variability of all major Hg species is clearly evident at this site in the Everglades. A reproducible diel pattern in DGM was observed, with peak concentrations always occurring on or about solar noon, and 3 to 7 fold greater than night-time concentrations. Production of DGM appears to cease at night, since water column DGM concentrations during darkness are very stable and at or near saturation with respect to the overlying air. The peak

DGM concentration during the diel cycle correlated well with the average solar intensity ( $r^2 = 0.93$ ). The calculated annual mass flux of mercury leaving Everglades water column as a result of DGM production is  $2.2 \mu\text{g m}^{-2} \text{y}^{-1}$ , about 10% of atmospheric deposition. An indirect photolysis reaction that involves the production of other constituents capable of reducing  $\text{Hg(II)}$ , or reduction of  $\text{Hg(II)}$  to  $\text{Hg(I)}$  by electron transfer, followed by a disproportionation reaction to produce  $\text{Hg}^0$  are likely the DGM production mechanisms. Photo-incubation experiments carried out in the field suggest that this process occurs in the water column, and the source of the Hg for this process is the dissolved  $\text{Hg}_\text{T}$  pool. These experiments also showed that photodegradation of MeHg does not appear to occur at depth in the Everglades, and is perhaps a contributing factor to the generally high levels of MeHg observed in Everglades water.

Variability in  $\text{Hg}_\text{T}$  and  $\text{Hg}_\text{R}$  appear to be controlled by two factors: inputs from rainfall and a process that is tied to the solar cycle. Inputs from rainfall result in “spike” increases of water-column  $\text{Hg}_\text{T}$  concentrations and to a lesser degree  $\text{Hg}_\text{R}$ . Overlain on this incremental signal from rainfall is a nearly sinusoidal trend that appears to be related to solar intensity. The observed trend in  $\text{Hg}_\text{T}$  (filtered and unfiltered) indicates the total mass of Hg in the water column is changing on a diel basis, with greater concentrations observed during daylight. This observation leads us to conclude that a portion of the total mass of Hg in the water column at this study site is moving into and out of solution on a diel basis. A model that can possibly explain this observation is photochemically driven sorption and desorption, which has been shown for other trace metals. Future research efforts will seek to reveal the details of this process. Diel variability in MeHg concentrations, although substantial, did not appear to be directly linked to photolysis reactions nor rainfall.

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