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# Air–Surface Exchange of Gaseous Mercury over A Mixed Sawgrass–Cattail Stand within the Florida Everglades

FRANK J. MARSIK\* AND  
GERALD J. KEELER

University of Michigan Air Quality Laboratory,  
Ann Arbor, Michigan 48109

STEVE E. LINDBERG

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

HONG ZHANG

Tennessee Technological University,  
Cookeville, Tennessee 38505

The Florida Everglades Dry Deposition Study (FEDDS) was conducted to test newly developed measurement techniques used to quantify the dry-deposition of speciated mercury to the Florida Everglades ecosystem. One component of FEDDS employed micrometeorological and dynamic flux chamber techniques to study the air–surface exchange of gaseous elemental mercury over a mixed sawgrass/cattail marsh within Water Conservation Area 3. These measurements provided information related to the magnitudes of, and processes associated with, the bi-directional flux of gaseous elemental mercury within this ecosystem for use in the development of a canopy-scale mercury dry deposition model. During the 2000 FEDDS study period, on average elemental gaseous mercury was emitted from the ecosystem during the daytime ( $16 \pm 30 \text{ ng m}^{-2} \text{ h}^{-1}$ ), with deposition observed at night ( $-1 \pm 4 \text{ ng m}^{-2} \text{ h}^{-1}$ ). The measured fluxes followed a diurnal pattern and were positively correlated with ambient temperature, solar radiation, and water vapor fluxes and negatively correlated with carbon dioxide fluxes. Our study results suggest that while flux-gradient techniques currently used in many mercury air–surface exchange studies can provide useful information on the general nature of mercury fluxes and the environmental parameters that influence them, there is sufficient uncertainty in the measurement of vertical gradients of gaseous elemental mercury to warrant caution in the interpretation of such measurements, especially during periods typically characterized as having small gradients (day/night transition periods and well-mixed conditions).

## Introduction

The biogeochemical cycling of mercury within freshwater ecosystems in the State of Florida has been of interest since 1989, when elevated ( $>0.5 \text{ ppm}$ ) levels of mercury were detected in largemouth bass taken from the Florida Everglades (1). The continued observance of elevated levels of toxic methylmercury (MeHg) in fish and other wildlife within

the Florida Everglades and other freshwater ecosystems within the state has led the Florida Department of Health to maintain limited consumption advisories for several species of sport fish from these ecosystems due to potential health risks to consumers (2). Having both natural and anthropogenic sources (3–7), mercury can be found in the atmosphere as elemental gaseous mercury [ $\text{Hg}(0)$ ] ( $>95\%$ ), reactive (divalent) gaseous mercury [ $\text{Hg}(\text{II})$ ], and particulate mercury [ $\text{Hg}(\text{p})$ ] (8, 9). Mercury may experience exchanges with the environment via wet deposition, particle deposition, as well as the air–soil (10–13), air–vegetation (14–18), and/or air–water exchange (19–21) of its gaseous forms. Within the Florida Everglades, deposited mercury can participate in a number of competing processes, including sedimentation, methylation via naturally occurring bacteria (22, 23), bacterial degradation of methylmercury (24), as well as conversion to dissolved gaseous  $\text{Hg}(0)$  [DGM] within Everglades surface waters and sediments (25, 26) via photoinduced and bacterial processes.

Both long- and short-term measurement studies have suggested that wet deposition is the predominant pathway for mercury deposition to South Florida and the Everglades, with annual wet-deposition estimates ranging from 20 to  $30 \mu\text{g m}^{-2} \text{ yr}^{-1}$  (27, 28). A number of measurement and modeling studies have suggested the dry-deposition of mercury species is also likely to be an important contributor to the total loading of atmospheric mercury to the Everglades (7, 29–31), with estimates generally in the range of  $10\text{--}20 \mu\text{g m}^{-2} \text{ yr}^{-1}$ .

The Florida Everglades Dry Deposition Study (FEDDS) was designed to directly address the issue of mercury dry-deposition to this sensitive ecosystem by: (1) testing the ability of newly developed measurement techniques to quantify ambient concentrations of speciated mercury within the Everglades, (2) testing the ability of a newly developed surrogate sampling surface to directly measure oxidized mercury dry deposition to the Everglades, and (3) developing an ecosystem-level, process-based model for use in the estimation of the dry-deposition of mercury to the Everglades as part of regional transport and fate models.

Measurements associated with the FEDDS project were conducted over a mixed sawgrass (*Cladium jamaicense*) and cattail (*Typha domingensis*) marsh located within the South Florida Water Management District's Water Conservation Area 3 (WCA3). The dry-deposition measurement and modeling results from the study will be presented in a forthcoming manuscript. This paper focuses on one important component of the dry-deposition process, the bi-directional exchange of gaseous  $\text{Hg}(0)$ . Micrometeorological and dynamic flux chamber techniques were used to characterize this exchange over the vegetation and open water between the vegetation, respectively. While measurements of air–surface exchange of gaseous  $\text{Hg}(0)$  have been performed in the Everglades previously (18), those measurements were conducted within the Everglades Nutrient Removal (ENR) project, which is a constructed wetland and Water Conservation Area 2A (WCA2A), which is a managed wetland that has been significantly impacted by agricultural runoff from the Everglades Agricultural Area (EAA) (32). In contrast, the FEDDS measurements site within WCA3 was relatively pristine with respect to direct discharges or runoff, although this site has been directly impacted by atmospheric deposition from local mercury emission sources (28).

## Experimental Section

**Site Description.** The Florida Everglades covers approximately 903 900 hectares in South Florida and is the largest

\* Corresponding author e-mail: marsik@umich.edu.

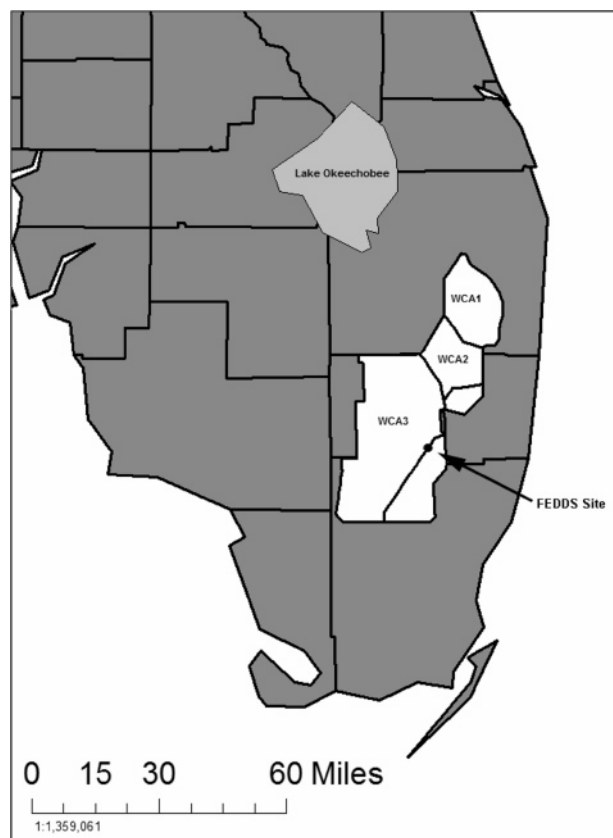


FIGURE 1. Location of the FEDDS measurement site.

subtropical wetland in the United States. The present day Everglades consists of the Everglades National Park and a series of Water Conservation Areas (WCAs). The largest of these WCAs, WCA3, covers an area of 234 913 hectares in western Broward and Dade counties. The vegetation within WCA3 is primarily comprised of sawgrass marshes (141 095 hectares, 60%), wetland prairies (64 470 hectares, ~28%), and cattail marshes (11 750 hectares, 5%) (Kenneth Rutchev, personal communication). The FEDDS measurement site was located in the eastern portion of WCA3, near the South Florida Water Management District's S-151 pumping station (Figure 1). Measurements were conducted from a 4 m by 4 m wooden platform that extended 30 m into the marsh from the canal road leading to the S-151 station. The vegetation surrounding the platform was primarily sawgrass, with an intrusion of cattail in the immediate vicinity of the platform. Measurements were performed during two distinct climatological periods: 24 February–04 March 1999 (dry season) and 05–21 June 2000 (wet season). Unfortunately, meteorological conditions were not favorable during the 1999 FEDDS study, and thus a very limited dataset was obtained, making it difficult to draw any scientifically credible conclusions. For this reason, this paper presents the data from the 2000 FEDDS study period only.

**Determination of Gaseous Hg(0) Fluxes (Micrometeorological Method).** Thirty-minute average fluxes of gaseous Hg(0) were obtained using the gradient transport theory, which describes the vertical flux of a given species using the relation:

$$F_C = -K_z \frac{\Delta C}{\Delta Z} \quad (1)$$

where  $F_C$  is the flux of some quantity,  $C$ ,  $K_z$  is the vertical eddy-transfer coefficient, and  $\Delta C/\Delta Z$  is the time-averaged vertical gradient of species  $C$ , which in this case was gaseous

Hg(0). During the 2000 FEDDS study, the average canopy height was 280 cm and gaseous Hg(0) gradients were obtained by making measurements at 20 and 220 cm above the canopy [i.e., at 300 and 500 cm above water level (AWL)].

Using the assumption that all scalar quantities are mixed in a similar fashion within the surface layer, the vertical eddy-transfer coefficient for heat,  $K_H$ , can be used to compute the flux of other passive scalar species such as water vapor or, in our case, gaseous Hg(0), for which concentration gradients can be obtained (33). The vertical eddy-transfer coefficient for heat was obtained using the following relation and Monin–Obukhov similarity theory:

$$K_H = \frac{k(z-d)u_*}{\phi_H} \quad (2)$$

where  $k$  is the von Karman constant (0.4),  $z$  is the geometric mean height of the two levels over which the gaseous Hg(0) gradient was obtained,  $u_*$  is the friction velocity,  $d$  is the displacement height (a measure of the effective height of the canopy), and  $\phi_H$  is the similarity function for the dimensionless potential temperature gradient in the surface layer (which accounts for the effects of atmospheric stability). Here, we assume that  $d = 0.7h$ , where  $h$  is the average height of the vegetation canopy (34). Values of  $\phi_H$  were determined using the following relations (35).

For stable conditions ( $z/L \geq 0$ ):

$$\phi_H = 1 + 5 \frac{z}{L} \quad (3)$$

For unstable conditions ( $z/L < 0$ ):

$$\phi_H = \left(1 - 15 \frac{z}{L}\right)^{-1/2} \quad (4)$$

$L$  is the Monin–Obukhov length, as determined by ref 36:

$$L = - \frac{\bar{\theta}_v u_*^3}{kgw'\theta'_v} \quad (5)$$

where  $g$  is the acceleration due to gravity and  $\bar{\theta}_v$  and  $\overline{w'\theta'_v}$  are the absolute mean and vertical turbulent fluxes of the virtual potential temperature, respectively.

The vertical turbulent fluxes of momentum, sensible heat, water vapor, and carbon dioxide were determined via eddy-correlation using a Solent Research Ultrasonic Anemometer (Gill Instruments Ltd.) and an infrared gas analyzer (IRGA, NOAA-ATDD). These measurements were used to calculate turbulent transfer coefficients used in the estimation of gaseous Hg(0) fluxes to and from the canopy, and to investigate potential relations between the obtained gaseous Hg(0) fluxes and other environmental variables. These quantities were measured with a sampling frequency of 10 Hz, with the 30-min average fluxes determined using the following equation:

$$F_C = \overline{w'c'} = \frac{\sum_{i=1}^n (w - \langle w \rangle)(c - \langle c \rangle)}{n} \quad (6)$$

where  $w$  and  $c$  are the instantaneous values of the vertical velocity and scalar quantity, respectively, and the angle-bracketed quantities are the associated running means. The fluxes were computed in real-time using a digital recursive filter (400 s time constant) to calculate the running mean quantities. The coordinate system of the sonic anemometer is mathematically rotated to obtain a zero vertical mean and transverse velocity ( $\bar{w} = \bar{v} = 0$ ). The friction velocity,  $u_*$ , used in the calculation eddy-transfer coefficient, was determined

using the standard formulation of  $u_* = (-u'w')^{1/2}$ . The run-to-run variability in flux quantities obtained using eddy-correlation is typically on the order of 10% (37). Using this estimate, and assuming that these uncertainties are random over time, the relative uncertainties in  $u_*$  and  $\phi_H$  were estimated to be 5% and 20%, respectively, resulting in a relative uncertainty for  $K_H$  of approximately 20%.

The use of gradient transport theory requires that the atmospheric turbulence field reaching the sensors is horizontally homogeneous and stationary (i.e., statistical properties do not change over the averaging period). These conditions are typically achieved if the turbulent air being sampled has traveled for an adequate upwind distance (or fetch) over which the underlying surface characteristics do not change. At our measurement site, adequate fetch was observed for periods during which the wind direction was from a sector ranging from 40° to 210°, and thus the summary statistics presented within this paper are confined to periods when the flow was from this sector. Additionally, significant and rapid changes in the thermodynamic and chemical structure within the atmospheric surface layer took place near sunrise and sunset, resulting in rapid changes in the turbulence levels at the site. During such rapid changes, time-averaged thermodynamic and chemical gradients may not be in equilibrium with their respective fluxes within the surface layer, and thus the use of gradient transport theory is not valid due to the lack of stationarity in the turbulence field. For this reason, data from these periods of transition, representing approximately 10% of the overall FEDDS measurement period, were not used in the statistical results presented in this paper. The data presented was separated into daytime and nighttime periods, defined as follows: daytime (0700 to 1900 EDT) and nighttime (2000 to 0600 EDT).

**Determination of 30-min Average gaseous Hg(0) Gradients.** Thirty-minute average gradients of gaseous Hg(0) over the canopy were measured using a Tekran model 2537A Mercury Vapor Analyzer and Tekran model 1110 Synchronized Two-Port Sampling Unit. Teflon sampling lines were used to minimize scavenging of mercury vapor during the measurements. Combined, these two units allowed for measurement of the gaseous Hg(0) concentration at two levels above the Everglades vegetation by automatically switching between these levels at 10-min intervals. During each 10-min interval, the Tekran model 2537A Mercury Vapor Analyzer obtained two 5-min average concentrations of gaseous Hg(0) by using two alternating gold amalgamation traps and cold-vapor atomic fluorescence spectrometry (CVAFS). During any given 5-min period, one trap was being sampled upon while the other was being analyzed. For a given 30-min interval, the average of all measurements at the lower level was subtracted from the average of all measurements at the upper level to obtain the 30-min average gradient of gaseous Hg(0). A series of line-bias test (500 cm-level sample line minus 300 cm-level sample line) were performed prior to and through the study. Adjustments to the obtained gradients were made using this information. An average line bias ( $N = 142$  bias pairs) of  $0.01 \pm 0.06$  ng  $m^{-3}$  was observed during the 2000 study, with line biases ranging from  $-0.06$  ng  $m^{-3}$  at the start of the study to  $0.03$  ng  $m^{-3}$  at the completion of the study. We feel confident in our characterization of the gaseous Hg(0) gradients with these biases applied, given that the variation from the start to the end of the study was slow, consistent, and we were able to characterize the variation given our frequent ( $N = 5$ ) bias checks during the study. However, this occurrence underscores the importance of performing a number of bias checks throughout a given study, as performing a single bias determination either at the start or at the end of a given study may misrepresent the true bias in the gradient

measurements. Additionally, the use of a single instrument to measure the Hg(0) concentration at both levels eliminates potential biases which may be introduced through the use of two instruments, for which the performance could vary differently over the course of a given study. The two traps used within our single instrument were carefully matched, so as to limit any bias between traps. The Tekran model 2537 Mercury Vapor Analyzer was calibrated on site using an internal permeation source.

Overall uncertainty in the gaseous Hg(0) gradient measurement was determined through a series of laboratory injection experiments that were performed to determine the overall precision of the Tekran model 2537 Mercury Vapor Analyzer for a given concentration. These tests suggested that the relative uncertainty in a given 5-min average Hg(0) concentration measurement was on the order of 1%. During the FEDDS 2000 measurement study, average Hg(0) concentrations were approximately  $1.6$  ng  $m^{-3}$ . Assuming the error is random over time, an estimated error in a given measured concentration difference would be  $\pm 0.02$  ng  $m^{-3}$ , which translates to an uncertainty in the midday fluxes on the order of  $\pm 35\%$ .

**Determination of gaseous Hg(0) Fluxes (Dynamic Flux Chamber Method).** During the 2000 FEDDS measurement study, a limited number of measurements were made of the evasion of gaseous Hg(0) from the water surface at our site using a polycarbonate dynamic flux chamber (DFC). The details to this method have been presented in a previous manuscript (21). In brief, flushing air was drawn by vacuum through the DFC at a constant flow rate (1.5 LPM). Concentrations of gaseous Hg(0) were measured at both the inlet and the outlet of the DFC using a Tekran model 2537A Mercury Vapor Analyzer and a Tekran model 1110 Synchronized Two-Port Sampling Unit. The steady-state flux was calculated using the equation:

$$F = (C_o - C_i)Q/A \quad (7)$$

where  $F$  is the mercury emission flux (ng  $m^{-2} h^{-1}$ ),  $C_o$  and  $C_i$  are the outlet and inlet mercury concentrations (ng  $m^{-3}$ ), respectively,  $Q$  is the flushing flow rate ( $m^3 h^{-1}$ ), and  $A$  is the emission area ( $m^2$ ) covered by the chamber. DFC blanks were obtained at the start and completion of the study by placing the DFC over a clean, inert foil surface. The average of the pre- and post-study DFC blanks was determined to be  $0.25$  ng  $m^{-2} h^{-1}$ . Measured fluxes were corrected for this bias.

**Meteorological Measurements.** In addition to the turbulent flux measurements described above, simultaneous measurements of solar radiation (Li-Cor LI-200X Pyranometer), net radiation (REBS Q\*7.1), air temperature/relative humidity (Campbell Scientific CS-500 Temperature/Relative Humidity Probe), wind speed and direction (R.M. Young Wind Monitor-RE), surface water temperature (Campbell Scientific 107 Temperature Probe), and vertical profiles of temperature (Omega fine-wire thermocouples) and wind speed (C.W. Thornthwaite sensitive three-cup anemometers) were made at the site. Laboratory tests showed that 30-min average temperatures using the fine-wire thermocouples agreed to within  $\pm 0.03$  °C. The C.W. Thornthwaite sensitive three-cup anemometers were compared against each other using a wind tunnel at the University of Michigan and were found to agree within 3% at wind speeds near 300 cm/s.

**Statistical Analyses.** SPSS V11.0 (Chicago, IL) was used for the data analyses presented within this paper. Measures of skewness and kurtosis were obtained for the distributions of daytime and nighttime gaseous Hg(0) gradients and fluxes. These distributions were found to approximate the normal distribution, and thus One Sample T-Tests were used to compare distributions against the null hypothesis that the mean gradients and fluxes were equal to zero. Finally, relations between the estimated gaseous Hg(0) fluxes and



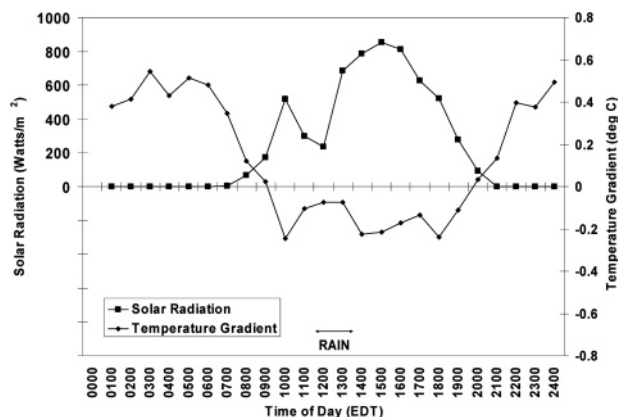


FIGURE 2. Temporal variation of hourly average global solar radiation and vertical temperature gradient ( $T_{500\text{CM}} - T_{300\text{CM}}$ ) over vegetation at the FEDDS site on 18 June 2000.

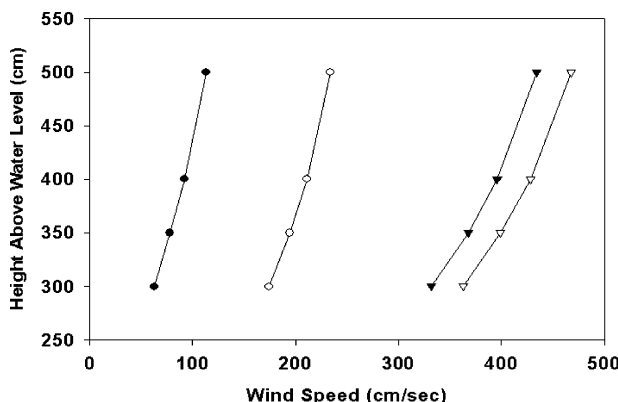


FIGURE 3. Temporal variation of the 30-min average vertical wind speed profiles over vegetation at the FEDDS site on 18 June 2000 [0600 EDT, ●; 0900 EDT, ○; 1200 EDT, ▼; 1500 EDT, ▽].

environmental variables were investigated using Pearson correlation coefficients.

## Results and Discussion

**Air–Surface Exchange of gaseous Hg(0) over Sawgrass/Cattail Canopy.** While the behavior of gaseous Hg(0) gradients and fluxes varied with the meteorological conditions observed during the 2000 FEDDS, the general trends observed on 18 June 2000 are representative of the majority of the 2000 FEDDS measurement period and are presented in Figures 2–6. During the pre-dawn hours of 18 June, a positive temperature gradient, here defined as  $T_{500\text{CM}} - T_{300\text{CM}} > 0^\circ\text{C}$ , formed over the canopy, resulting in a thermally stable environment over the canopy (Figure 2). This thermal stability helped to suppress the transport of momentum toward the surface, leading to light winds that exhibited very little variation with height (Figure 3). During this time, a significant positive gradient in gaseous Hg(0), here defined as  $[\text{Hg}(0)]_{500\text{CM}} - [\text{Hg}(0)]_{300\text{CM}} > 0 \text{ ng m}^{-3}$ , developed within the stable surface layer above the canopy, suggesting that the surface was acting as a sink for gaseous Hg(0) (Figure 4). The stable thermal environment and light winds resulted in low turbulence levels within this layer (as inferred from the friction velocity), leading to relatively small ( $< 10 \text{ ng m}^{-2} \text{ h}^{-1}$ ) fluxes of gaseous Hg(0) to the canopy (Figure 5). It should be noted that our calculations suggest that average nighttime eddy-transfer coefficient was on the order of  $0.05 \text{ m}^2/\text{s}$ , while the diffusion coefficient for gaseous Hg(0) in air is believed to be considerably smaller ( $\sim 0.09 \text{ cm}^2/\text{s}$ ). For this reason, we believe that turbulent exchange and not laminar diffusion at the vegetation surface was the primary contributor to the nocturnal loss of Hg(0) in the layer measured.

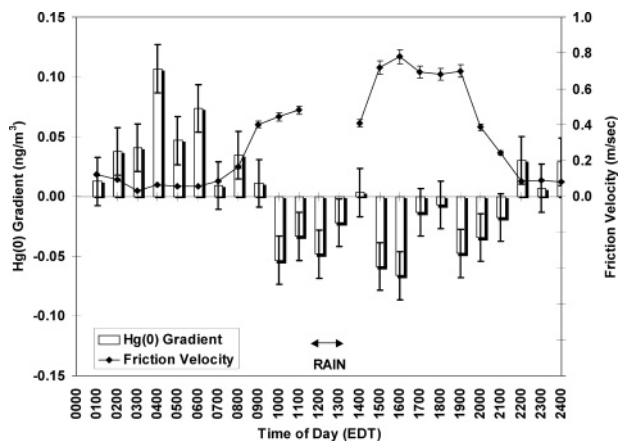


FIGURE 4. Temporal variation of the hourly average friction velocity and gaseous Hg(0) gradient ( $[\text{Hg}(0)]_{500\text{CM}} - [\text{Hg}(0)]_{300\text{CM}}$ ) on 18 June 2000.

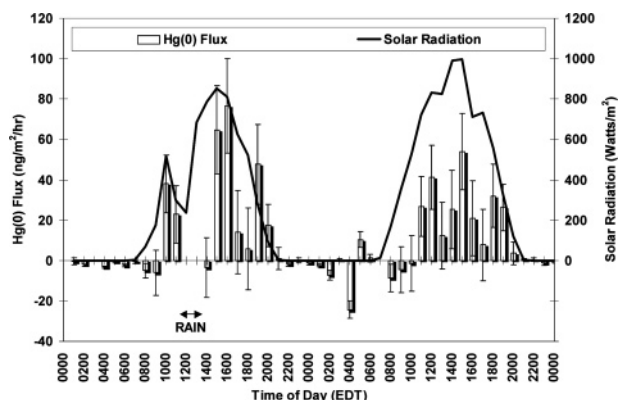


FIGURE 5. Temporal variation of the hourly average surface Hg(0) flux (bars) and incoming solar radiation (line) for the period of 18–19 June 2000. Missing data represent periods during which inadequate fetch was reported and/or rainfall was reported.

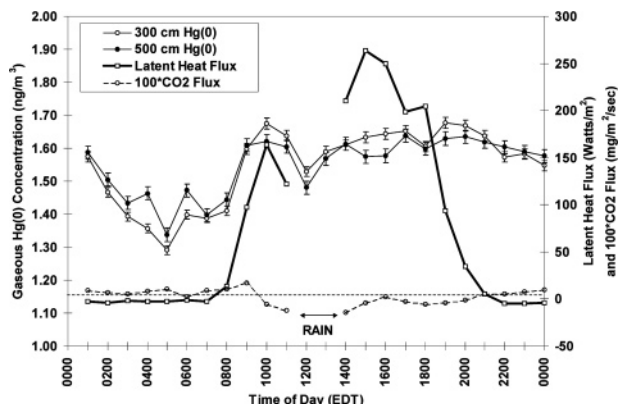


FIGURE 6. Temporal variation of hourly average ambient gaseous Hg(0) concentrations at 300 and 500 cm, and latent heat and  $\text{CO}_2$  fluxes above the vegetation canopy on 18 June 2000.

Following sunrise ( $\sim 0630$  EDT), the incident solar radiation warmed the canopy and thus the surrounding air, leading to the establishment of a negative temperature gradient and thermally unstable conditions (Figure 2). With momentum now more easily transported to the surface, the overall wind speeds and the vertical shear in wind speed increased, leading to an increase in the production of turbulence through both thermal and mechanical processes (Figure 3). During this transitional period, the measurements indicated that gaseous Hg(0) was being deposited to the canopy until 1000 EDT, at which time a significant negative gradient of gaseous Hg(0)

developed and the canopy became a source of gaseous Hg(0) to the atmosphere ( $\sim 40 \text{ ng m}^{-2} \text{ h}^{-1}$ ) (Figures 4 and 5, respectively). Following this initial period of gaseous Hg(0) emission, an area of clouds and rainshowers moved over the site resulting in a reduction of incoming solar radiation and gaseous Hg(0) emission from the canopy (Figure 5). Because the presence of rain drops within the volume of air sampled by the sonic anemometer contaminates the measured turbulence data, the determination of eddy-transfer coefficients (and thus gaseous Hg(0) fluxes) was not possible during this period. Immediately following the precipitation, the measurements presented in Figure 4 suggest that gaseous Hg(0) was initially deposited to the wetted canopy for a short period, before solar radiation dried the canopy and the canopy became a source of mercury to the atmosphere once again. Inspection of Figure 5 indicates that the peak emissions of gaseous Hg(0) occurred during the period of maximum solar radiation, with decreasing gaseous Hg(0) fluxes observed as solar radiation decreased during the late afternoon. In the evening, a positive gradient of gaseous Hg(0) was re-established shortly after sunset as a result of the redevelopment of the stable nocturnal surface layer and consequent reduction in turbulence (Figures 2–4). Figure 5 indicates that during this latter period, the canopy ceased to be a source of mercury and predominantly small, and generally insignificant, deposition fluxes of gaseous Hg(0) were subsequently observed for the balance of the night of 18 June.

Figure 5 also suggests that, in general, the trends that were observed on 19 June were consistent with those observed on 18 June. One exception, however, occurred during the pre-dawn hours (0400 and 0500 EDT) on 19 June when there was a short-term increase in the turbulence levels. The occurrence of enhanced intermittent turbulence within the nocturnal boundary layer is a well-documented, although still somewhat poorly understood, phenomenon (38). These intermittent events can lead to large amounts of mass exchange over short periods of time ( $\sim$ minutes), during which the fluxes of a given scalar are not necessarily in equilibrium with the time-averaged gradients. While it was beyond the scope of our study to determine if the 0400–0500 EDT period was impacted by the type of mesoscale phenomena which can lead to intermittent breakdowns of the nocturnal boundary layer (e.g., internal gravity waves), this does represent a period for which the “stationarity” requirement for use of gradient transport theory was likely violated and thus underscores why nighttime flux-gradient measurements must be carefully interpreted.

**Environmental Influences on Observed gaseous Hg(0) Gradients and Fluxes.** Figure 6 provides a more detailed view of the processes linked to our observed gradients and fluxes of gaseous Hg(0) on 18 June. The data suggest that the hourly average gaseous Hg(0) gradient (calculated using the available measurements at each level during a given hour) that developed on the morning of the 18th was not due to a loss of gaseous Hg(0) within a shallow layer next to the canopy, but rather from a layer that likely extended to several meters above the canopy. Similar losses were observed on many nights during the study when overnight winds were light and dew was present on the vegetation canopy. Despite the fact that gaseous Hg(0) is relatively insoluble and thus not expected to deposit to wetted surfaces, it is likely that reactive gases (such as ozone) and particulate matter that had deposited to the canopy earlier in the day may have led to a rather complex chemical makeup of the dew droplets, which acted to enhance the uptake of gaseous Hg(0) by the canopy surface (14). We believe that this surface loss was not merely an artifact resulting from the loss of the gaseous Hg(II) fraction of total gaseous mercury to the vegetation, because our sample inlets were not heated and gaseous Hg(II) would likely

have been scavenged by the inlet filters and sample lines at both levels. Also, measurements of the ambient concentrations of Hg(II) at our site during both the 1999 and the 2000 FEDDS intensives indicated that ambient levels of Hg(II) decrease rapidly with the onset of dew on the canopy vegetation during the early evening (39). In contrast, the observed rate of loss of gaseous Hg(0) from the surface layer on 18 June was relatively slow.

Following sunrise ( $\sim$ 0630 EDT), an increase in the ambient concentrations of gaseous Hg(0) within the surface layer was observed at the same time as the observed increase in the water vapor (or latent heat) flux. These coincident increases suggest that one potential source of the gaseous Hg(0) was evaporation of the dew from the canopy surface. If this was indeed the process observed, it would suggest that the gaseous Hg(0) that deposited to the canopy at night quickly fluxed back to the atmosphere within a few hours of sunrise, and thus the gaseous Hg(0) emitted later in the day was not simply the re-emission of gaseous Hg(0) deposited overnight. An alternate explanation for the observed morning increase in gaseous Hg(0) is the downward mixing/transport of higher concentrations of gaseous Hg(0) from a height within the boundary layer that had not been depleted during the previous night. In reality, we were likely seeing a combination of these two processes. If the sole source of the gaseous Hg(0) had been the dew, we would have expected to see gradients suggesting that the canopy was a source of mercury. Instead, we observed gradients that continued to suggest deposition to the canopy, which would suggest that the source of gaseous Hg(0) during this period was from above the canopy. Unfortunately, this was a period for which the observed gradients of gaseous Hg(0) were within the range of uncertainty for the measurement ( $\pm 0.02 \text{ ng m}^{-3}$ ), indicating that the measurement technique was greatly challenged during this transitional period, thus limiting our ability to confidently attribute the observed increase in gaseous Hg(0) concentration to either of our proposed mechanisms.

Figure 6 also indicates that the onset of the emission of gaseous Hg(0) from the canopy environment most closely followed the timing of the start of  $\text{CO}_2$  uptake by the canopy, providing evidence that the net emission of gaseous Hg(0) from the canopy was controlled by stomatal exchange processes, as opposed to solely emission from the water column or evaporation of the dew-wetted vegetation surface. Gaseous Hg(0) gradients and fluxes peaked in the mid- to late-afternoon, coincident with the peaks in both water vapor (latent heat) flux and  $\text{CO}_2$  uptake by the canopy. Emission of gaseous Hg(0) from the canopy ceased following sunset, when  $\text{CO}_2$  uptake from the canopy and water vapor release from the canopy decreased, suggesting a closing of the stomata.

The overall diurnal trends observed during the 2000 FEDDS study were consistent with chamber study results of observed diurnal trends in the emission of gaseous Hg(0) from aquatic vegetation (*Pragmites communis*) in Lake Onondaga, NY, with the relative magnitudes of these latter emissions correlated with total mercury content of the sediments within which the plants were rooted. During that study, a lack of emission at night, as well as the maximum emissions at the time of maximum light and transpiration rate, suggested a link between gaseous Hg(0) emission from the plants and transpiration and/or photosynthesis (40). Similar results were obtained during a study of the air–surface exchange of gaseous Hg(0) within the northern Everglades (ENR and WCA2), which observed that both sawgrass and cattail species had the capacity to emit gaseous Hg(0) (17, 18). The observed emissions also exhibited a diurnal pattern with strong correlations with solar radiation, water vapor flux, and  $\text{CO}_2$  flux, again suggesting a link between gaseous Hg(0) emissions and transpiration and/or photosynthesis. A

lack of gaseous Hg(0) emission from an uprooted cattail marsh during one period of that study underscored the role of the aquatic sediment as the likely source of the gaseous Hg(0) that was emitted from the vegetation. A number of studies have also observed diurnal gaseous Hg(0) emissions from terrestrial vegetation, but the relation with soil mercury concentrations was not conclusive (41–44). The results of the 2000 FEDDS study were consistent with these previous studies, in that the observed trends in Hg(0) fluxes were also highly correlated with ambient temperature ( $r = 0.44$ ,  $p < 0.01$ ), water vapor or latent heat flux ( $r = 0.40$ ,  $p < 0.01$ ), friction velocity ( $r = 0.40$ ,  $p < 0.01$ ), solar radiation ( $r = 0.39$ ,  $p < 0.01$ ), and CO<sub>2</sub> flux ( $r = -0.27$ ,  $p < 0.01$ ).

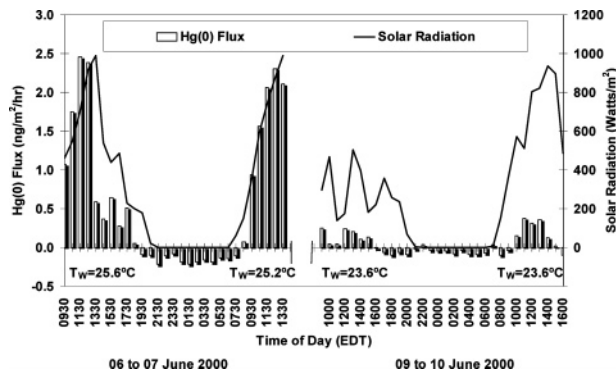
As described earlier, the timing of the onset of gaseous Hg(0) emissions/deposition during our study underscored the likely role of stomatal control on the observed Hg(0) emissions. Despite the overall significant correlation of our observed gaseous Hg(0) fluxes with water vapor and CO<sub>2</sub> fluxes, significant hour-to-hour variability was observed during the study, which was not directly correlated with changes in water vapor and CO<sub>2</sub> fluxes associated with the canopy. There are a number of plant-related processes that could have contributed to the observed variability, especially when one considers that gaseous Hg(0) exchange is the net difference of both emission and deposition processes that are likely occurring simultaneously. First, while previous research has shown that gaseous Hg(0) emission rates from emergent aquatic vegetation were linked to sediment mercury concentrations (40), little is known about the relation between gaseous Hg(0) production rates within sediments and/or movement within the sediments and whether these processes might be rate limiting with respect to maintaining a supply of dissolved gaseous Hg(0) to plant roots for uptake and emission.

Above the water surface, the uptake of gaseous species such as gaseous Hg(0) by vegetation is subject to atmospheric, leaf boundary layer, and canopy-level controls. These canopy level controls involve resistances to sorption at the leaf surface, transport via stomata, and biochemical regulation within the leaf cavity (45, 46). Sorption at the leaf surface will be impacted by the chemical nature of the mercury and other species present on the vegetation. Stomatal conductances will be influenced by the time-varying influences of solar radiation, humidity, water stress, and temperature (47, 48). While the relative importance of these factors is not known with respect to the sawgrass and cattail species found at our site, it is likely that each of these factors plays a role in the air–surface exchange of mercury. The rate at which they respond to changes in solar radiation and other environmental influences likely varies, as will their influence on the exchange of gaseous Hg(0) with the canopy at any given time.

#### Dynamic Flux Chamber Measurement of Hg(0) Fluxes.

A limited number of measurements of the water surface evasion of gaseous Hg(0) were made during the 2000 FEDDS intensive during the periods of 05–07 June and 09–10 June 2000 using a dynamic flux chamber (DFC). These measurements were performed in areas of open water among the vegetation near our measurement platform to quantify the relative contribution of the water surface to the overall emission of gaseous Hg(0) from the ecosystem. At the WCA3 site, water surface fluxes of gaseous Hg(0) ranged from  $-0.28$  to  $2.84 \text{ ng m}^{-2} \text{ h}^{-1}$  ( $N = 219$  20 min averages), with an average flux of  $0.25 \pm 0.66 \text{ ng m}^{-2} \text{ h}^{-1}$ . These magnitudes are similar to those previously observed over surface waters within WCA2 and ENR in the Florida Everglades (21), and for flooded soils in a northern wetland ecosystem (49).

The DFC measurements showed a strong diurnal trend with emissions occurring during the day and weak deposition at night (Figure 7). Hourly average evasion fluxes of gaseous



**FIGURE 7.** Temporal variation of solar radiation and gaseous Hg(0) evasion at the water surface on 06, 07, 09, and 10 June 2000.

Hg(0) ( $N = 60$ ) were highly correlated with solar radiation ( $r = 0.78$ ,  $p < 0.01$ ), but poorly correlated with water temperatures ( $r = -0.08$ , not significant). This former result was not unexpected, as previous studies of the evasion of gaseous Hg(0) from water surfaces have shown that peak evasion of gaseous Hg(0) typically occurs at the time of peak solar radiation, as a result of the link between photoinduced production of dissolved gaseous Hg(0) from Hg(II) species within the water column (21, 49, 50) and its subsequent evasion from the water surface. For our study, the peak gaseous Hg(0) emissions occurred prior to solar noon, but this observation is likely the result of the shading of surface waters due to the presence of the emergent vegetation. While our measured evasion of gaseous Hg(0) was poorly correlated with water temperature (peak water temperature occurred during the late afternoon), Figure 7 shows that daily average water temperature appeared to be an important factor in influencing the magnitude of the peak emission at the site. Despite the fact that the observed levels of solar radiation on 10 June were similar to those observed on 06 and 07 June, the water surface fluxes of gaseous Hg(0) were more similar to those observed on 09 June. This observation suggests that the water temperature may have influenced the overall magnitude of water surface evasion of Hg(0), potentially through its impact on the solubility of dissolved gaseous Hg(0) within the water column (21). Overall, these evasion fluxes were significantly lower than those observed over the Everglades vegetation, underscoring the important role of aquatic emergent vegetation in the air–surface exchange of gaseous Hg(0) within the Everglades ecosystem.

**Implications.** On average, the 2000 FEDDS study results suggest that gaseous Hg(0) was emitted from the ecosystem during the daytime ( $16 \pm 30 \text{ ng m}^{-2} \text{ h}^{-1}$ ), with deposition observed at night ( $-1 \pm 4 \text{ ng m}^{-2} \text{ h}^{-1}$ ). Using a One-Sample T-Test, the daytime and nighttime mean gradients and fluxes of gaseous Hg(0) were found to be statistically different from zero ( $P < 0.01$ ). In Table 1, the gaseous Hg(0) flux estimates obtained during the 2000 FEDDS study are compared with data obtained during previously discussed work within the Everglades Nutrient Removal (ENR) Project and Water Conservation Area 2 (WCA2) (17). In the previous study, gaseous Hg(0) emissions from cattail exceeded that from sawgrass, with the greater relative stomatal conductance associated with cattail presented as a possible explanation for the differences in emission from the two species. It can be seen that the daytime gaseous Hg(0) fluxes observed during 2000 FEDDS study were quite similar to those observed over a sawgrass canopy at the WCA2 study site ( $17 \pm 29 \text{ ng m}^{-2} \text{ h}^{-1}$ ).

Despite the similarity of observed daytime gaseous Hg(0) fluxes during the 2000 FEDDS and WCA2 studies, one should exercise caution before using these results to scale-up gaseous Hg(0) emission estimates to the entire fraction of the Everglades covered by this vegetation type. As noted, earlier



**TABLE 1. Summary of Observed Gaseous Hg(0) Fluxes during Recent Studies Conducted within the Florida Everglades**

data set	mean Hg flux $\pm$ std dev (ng m <sup>-2</sup> h <sup>-1</sup> )	N	ref
<b>Summer 2000</b>			
FEDDS <i>Cladium/Typha</i> , daytime	16 $\pm$ 30	214	this study
FEDDS <i>Cladium/Typha</i> , nighttime	-1 $\pm$ 4	134	this study
<b>All Seasons (1997–1998)</b>			
ENR <i>Typha</i> , daytime	31 $\pm$ 50	185	ref 17
ENR <i>Typha</i> , nighttime	0.2 $\pm$ 15	241	ref 17
<b>Summer 1997</b>			
WCA2A, <i>Cladium</i> , daytime	17 $\pm$ 29	96	ref 17

work suggested that the magnitudes of gaseous Hg(0) emissions were correlated with sediment Hg concentrations (40), with a later study observing gaseous Hg(0) emissions that were very low for a cattail stand which had been uprooted from the sediments (18). Additional studies within the Everglades have shown that the depth of sawgrass rhizomes and root zones has been found to vary from 1 to 15 cm below the surface in marl soils, to up to 30 cm deep for peat soils (51), and that sediment mercury is mobile and varies in concentration with depth (52). Therefore, the magnitude of plant-mediated gaseous Hg(0) emissions for a given area is likely to be a complex function of plant species, environmental parameters, mercury concentration profile within the sediment, and plant rhizome depth. A recent paper describes the relationship between production of gaseous Hg(0) in sediments and the emission of gaseous Hg(0) from aquatic macrophytes and concludes that the emitted gaseous Hg(0) must originate within the rhizosphere (53). Understanding the interaction of these factors may provide important information regarding how quickly the emergent aquatic vegetation within the Everglades can respond to ongoing mercury emission reductions that are occurring across South Florida (31).

Finally, one of the overall goals of the FEDDS project was to determine the feasibility of using newly developed measurement techniques for the quantification of speciated mercury dry deposition to the Florida Everglades. This paper addressed the use of an automated mercury analyzer for the determination of vertical gradients of gaseous Hg(0) and the fluxes that result from them. As noted in the methodology section, the precision of the automated mercury analyzer used in this study was excellent with respect to the measurement of absolute ambient gaseous Hg(0) concentrations. The challenge in extending the use of this and similar automated systems to the measurement of gaseous Hg(0) gradients is that one is dealing with a classical measurement problem of accurately obtaining a measurement of a small difference between two large numbers. As seen in Figures 4–6, the precision of the measurement is sufficient for the characterization of the overall trends in gaseous Hg(0) air–surface exchange. However, there are a number of periods during which the measurement of the gaseous Hg(0) gradients was quite challenging. For our study, these periods were: (1) when both the thermodynamic and the chemical structures of the surface layer were in transition (near sunrise and sunset), (2) when solar radiation levels were reduced by clouds and/or precipitation, and (3) during some afternoon periods when turbulence levels were at a maximum. If one assumes that this uncertainty/error in the gradient measurement is random over the course of the study, then mean gradients and fluxes can be characterized. However, individual esti-

mates of the gaseous Hg(0) gradient and resulting flux should be viewed with caution when measured gradients are small.

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## Supporting Information Available

Summary of observed daily mean meteorological conditions during the 2000 FEDDS study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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