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Total gaseous mercury concentration and flux over a coastal saltmarsh vegetation in Connecticut, USA

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Abstract

The objective of this study is to characterize the ambient total gaseous mercury (TGM) concentration (C) at a coastal salt marsh and the TGM flux (F) between the marsh and the atmosphere using data collected on a near-continuous basis from 5 Jun to 8 July, 1997 and from 8 March to 23 July, 1998. In general, C was lower in the afternoon than at night, which is believed to be a result of diurnal variation in the mixing efficiency of the atmospheric boundary layer. The lack of a significant upward trend from March to July 1998 implies that TGM was removed from the boundary layer at a rate equal or greater than the surface emission. Three episodes of low C (0–1 ng m^{-3}) occurred in July 1998, each lasting about 3 h. The TGM flux, F, was determined with the micrometeorological aerodynamic method. An episodic event of large positive F (emission) occurred in early spring of 1998 and appears to have been triggered by ice melting. It is proposed that three competing mechanisms – Hg vaporization, oxygen transport via roots, and diffusion into plants via stomata – may have played a role in the Hg exchange over other periods, resulting in bi-directional exchange of Hg with the atmosphere. Extrapolation of the 1998 data to the whole year suggests a weak sink removing 4 ± 7μg Hg m^{-2} yr^{-1} from the atmosphere, a rate similar in magnitude to wet or particulate deposition to the site but much smaller than the rate of Hg accumulation in the sediment.

Keywords: Gaseous mercury; Mercury cycle; Wetland; S. *patens*; Long Island sound; Micrometeorology; Evapotranspiration

1. Introduction

There are three pathways of air-surface exchange of mercury (Hg): wet deposition, particulate deposition and gaseous exchange (Lindqvist and Rodhe, 1985; Fitzgerald, 1989). Of these, the least understood pathway is via the gaseous phase. The need for accurate assessment of local Hg balances (Fitzgerald et al., 1991; Xiao et al., 1991; Lindberg et al., 1992) and of anthropogenic and natural contributions to the atmospheric Hg (Lindberg et al., 1998; Mason et al., 1994) has motivated a number of studies on the controls on total gaseous mercury (TGM) flux in upland ecosystems (Lindberg et al., 1998,1992, 1995; Gustin et al., 1997; Leonard et al., 1998a,b; Kim et al., 1995), rivers and lakes (Xiao et al., 1991; Schroeder et al., 1992) and open oceans (Kim and Fitzgerald, 1986). Studies on wetland ecosystems are scanty. Our work appears to be the first that focuses on a salt marsh. While they are not a significant Hg source or sink on the global scale, salt marshes are important habitats for numerous marine and bird species, and hence Hg cycling is of particular concern in these habitats.

This paper reports the results of the experiments we conducted at the Farm River salt marsh (Fig. 1) from 5 June to 8 July, 1997 and from 8 March to 23 July, 1998. Our first objective is to characterize the ambient TGM concentration (C) monitored on a near-continuous basis. This is justified because only a few studies have reported continuous measurements of C at fine (5–10-min) time steps in the past. It is understood that variations in C reflect mechanisms such as boundary layer mixing and chemical reactions at scales much larger than the salt

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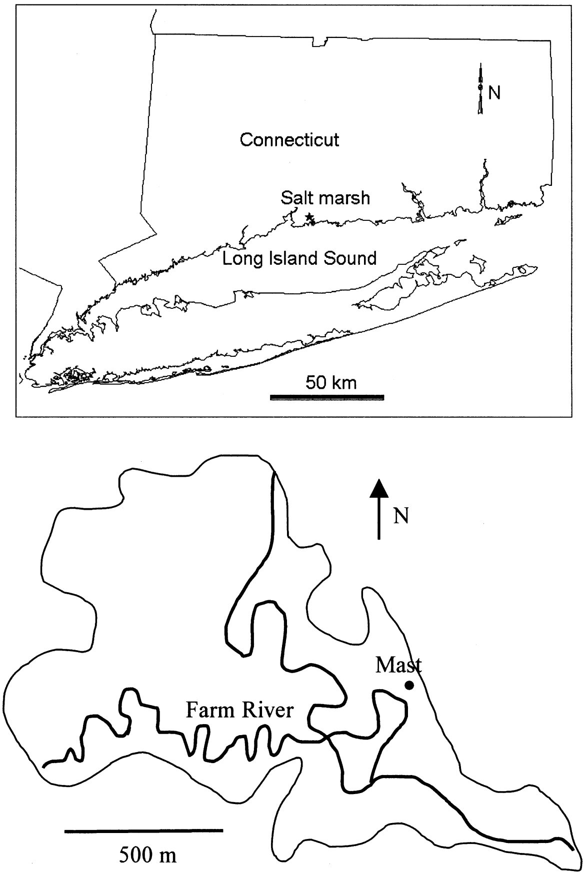

Fig. 1. Top: Map showing the location of the Farm River salt marsh; Bottom: Map of the marsh.

marsh and hence the influence of the salt marsh itself is minimal, particularly with north winds (Fig. 1). We did not have the logistics to measure boundary layer parameters and other chemical species in the atmosphere, which would have helped to further refine our interpretation of the results. Despite this, examination of the TGM data suggests several processes that may play a role in atmospheric Hg cycling.

Our second objective is to examine the behavior of the TGM exchange between the marsh and the atmosphere and to estimate the magnitude of this pathway over the full year. Unlike C, the TGM flux, F, measured with the micrometeorological aerodynamic method has a footprint several hectares in size in the upwind direction. Salt marshes are challenging systems for gas exchange studies; In addition to the usual microclimatic variables (temperature, humidity, solar radiation, turbulence, air stability), variations in the redox potential and salinity due to regular tidal flooding, and the role of plants in various stages of growth are among the possible variables controlling the TGM exchange.

2. Experimental methods

2.1. Site

Our site was the Farm River salt marsh near New Haven, Connecticut (72°52′W, 41°16′N; Fig. 1). The vegetation was a typical high-marsh species, S. *patens*. The dead above-ground plant tissues of the previous year's growth was 0.3 m tall at the beginning of the field experiments. In 1998, new leaves started to emerge on Day 106 (16 April), which was at least 15 d earlier than in a normal year owing to an El Nino warm winter and spring (January–April temperature 2.6°C higher than the norm). The plants reached a height of 0.6 m in July in both 1997 and 1998. There was excellent fetch (160–600 m) over the wind direction sector 150–300°, and therefore the discussion of F will be restricted to this sector.

The tidal channels running through the marsh carry freshwater runoff from a $66\ \mathrm{km}^2$ watershed (McCaffrey and Thomson, 1980). At the micrometeorological mast 30 m away from the edge, tidal water was present twice a day except 1–2 d of each month during the lowest tide, with each inudation event lasting on average 3.7 h. Salinity of the surface water ranged from 14 to 24 PSU, a variation attributed in part to evapotranspirative water loss (He, 1998). Hg concentration was $200\text{–}470\ \mathrm{ng\,g^{-1}}$ (dry weight) in the top 20-cm sediment layer, which was higher than those of background soils ($10\text{–}50\ \mathrm{ng\,g^{-1}}$, Gustin et al., 1994; Lindqvist et al., 1991), and $30\text{–}90\ \mathrm{ng\,g^{-1}}$ in the deep layer below 35 cm. Analysis of the Hg concentration of two sediment cores shows the onset of Hg pollution in about 1820 (Varekamp, 1998).

2.2. Instrumentation

Ambient TGM concentration was sampled sequentially at heights of 0.88 and 2.76 m above the sediment surface, which were within the internal boundary layer of the marsh surface. Air was drawn at $1.5\ \mathrm{l\,min^{-1}}$ through one of the two inlets via a short tubing (2.1 m, OD 0.64 cm, FEP) to a Teflon solenoid valve and then through 30-m tubing of the same type to a Hg analyzer (model 2537A, Tekran, Toronto, Canada) for on-line detection of concentration. A data logger (model CR10, Campbell Scientific, Logan, Utah) was used to switch the valve every 5 and 10 min during the 1997 and 1998 experiments, respectively. Over each of these short intervals the analyzer provided two sequential concentration values, one with each of the two Hg cartridges. The clock of the Hg analyzer was delayed by 22 s to account for the travel of air through the tubing. The concentration values were sorted by heights and were averaged over 90-min intervals, using the Sympson's averaging method (Press et al., 1992), to give the concentration gradient. The Hg analyzer was calibrated daily at 1:00 EDT against an internal permeation source certified to an accuracy of 5%. The inlet particulate filters (0.2 μm PTFE membrane) were replaced every 2 weeks.

An eddy covariance system (sonic anemometer/thermometer model 1012R2A, Lymington, UK; hygrometer model K20, Campbell Scientific) was used to monitor the evapotranspiration rate and other turbulence parameters. The TGM flux, F, was computed as

$$F = g(C_1 - C_2), \tag{1}$$

where g is an aerodynamic conductance which is related to the eddy diffusivity K

$$g = 1 \bigg/ \int_{z1}^{z2} \frac{1}{K}\,\mathrm{d}z, \tag{2}$$

and C_1 and C_2 are TGM concentrations at heights $z_1 (= 0.88$ m) and z_2 ($= 2.76$ m), respectively. Here K was determined with the eddy covariance data with correction for air stability following the functions of Businger and Dyer (Panofsky and Dutton, 1984). The computed flux follows the sign convention that a positive value indicates emission of Hg from the surface, and a negative value indicates deposition. Additional micrometeorological measurements included air temperature and gradient, humidity, net radiation, 1-cm sediment temperature, global radiation, leaf wetness and time of inudation.

2.3. *Quality of flux data*

An advantage of the micrometeorological technique over chamber methods is that it does not alter the microenvironment of the system under investigation. We should, however, bear in mind that the vertical C gradient is small and potential biases must be treated with care. Four factors can introduce uncertainties to the gradient data with the sequential sampling method: repeatability, memory or blanking effect, inlet bias, and stationarity. The sensitivity of the Hg analyzer was stable, varying by $< 0.5\%$ between two calibrations 24 h apart, so the short-term repeatability was excellent. The second factor, memory effect of the sampling lines/Hg cartridges, may smear the C gradient between the two heights. Two pieces of evidence show that this was not a problem. First, the analyzer was able to accurately measure the ambient C (about 2 ng m^{-3}) immediately after switching from the permeation source which had a very high concentration (16.3 ng m^{-3}). Second, when an inlet filter that had been exposed to the laboratory air of elevated concentrations was connected to one of the inlets, C would increase slightly (by about 0.05 ng m^{-3}) for 2–3 samples through that inlet, while C of the air coming from the other inlet remained unchanged.

To assess the inlet bias, we positioned the two inlets next to one another for 2–48 h after each inlet filter change. The difference in the 90-min concentration, C_1–C_2, was 0.0018 ± 0.0203 ng m^{-3} ($n = 27$, mean ± one standard deviation) in 1997 and 0.0028 ± 0.015 ng m^{-3} ($n = 102$) in 1998. Given an averaged aerodynamic conductance g of 0.06 m s^{-1}, this corresponds to a flux bias of 0.4 ± 4.4 and 0.6 ± 3.2 ng m^{-2} h^{-1} for 1997 and 1998, respectively.

It is a common practice in micrometeorology to use a single analyzer to resolve small concentration gradients which otherwise would not be possible with multiple analyzers due to sensor biases. The tradeoff is that gradient data with sequential sampling by a single analyzer may be subject to a large random scatter at times when the background concentration is highly variable or non-stationary. To investigate this scatter, we simulated the sequential sampling using the thermocouples and compared the resulting temperature gradient (y, °C) with the true gradient (that from simultaneous sampling, x). As expected, little systematic bias existed, as shown by the regression equation $y = 0.002 + 1.01\,x$ ($n = 144$, $R^2 = 0.99$), and the overall scatter was quite small, with a residual error of 0.05°C or 5% of the observed standard deviation. This provides an order of magnitude estimate for the uncertainty in the C gradient due to non-stationarity.

To test the performance of the aerodynamic method, we computed the sensible heat flux using $H_\mathrm{a} = \rho c_p g(T_1 - T_2)$, where T_1 and T_2 are air temperatures at heights z_1 and z_2, respectively, ρ is air density, c_p is specific heat of air at constant pressure, and H_a is expressed in W m^{-2}. The aerodynamic method was biased high by 6% as shown by the regression equation, $H_a = -3.6 + 1.06\,H$ ($n = 146$, $R^2 = 0.89$), where H is the sensible heat flux measured with the eddy covariance. In the following, no correction was made to the Hg flux data, so the reader should keep in mind the accuracy of the aerodynamic method.

3. Results and discussion

3.1. *TGM concentration*

In this section, we describe the data from the 1998 experiment to characterize the ambient TGM concentration, because the record was much longer and was interrupted by fewer power failures than the 1997 data. About 95% of all the 10-min data lay below 2.6 ng m^{-3} and 5% below 1.3 ng m^{-3}, with a maximum of 10.1 ng m^{-3} recorded on midnight, 19 May during a heavy rain event. The mean value over the period 23 March–23 July was 1.85 ng m^{-3} (standard deviation 0.46 ng m^{-3}, $n = 15280$), very similar to previous observations near Long Island Sound (Fitzgerald et al., 1983).

Fig. 2 shows the diurnal variation in C for three wind sectors. The landscape within 50-km upwind of the sector 300–90° is mainly natural vegetation. Over this wind direction range, only 11% of measurements exceeded

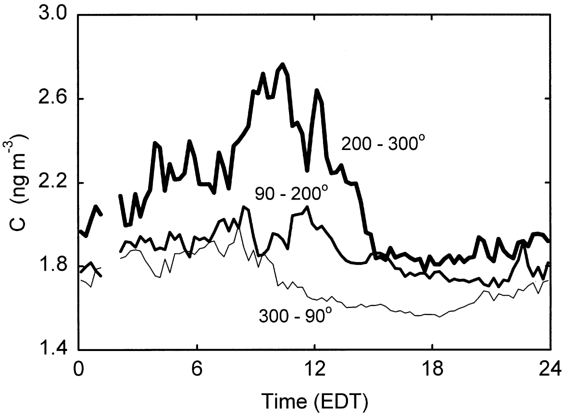

Fig. 2. Diurnal variations in TGM concentration over three wind sectors: 200–300° (under the influence of local anthropogenic sources), 300–90° (clean land sector), 90–200° (Long Island Sound) over the 1998 experimental period. The corresponding mean concentrations were 2.11 ± 0.59, 1.74 ± 0.36, and 1.85 ± 0.40 ng m^{-3}.

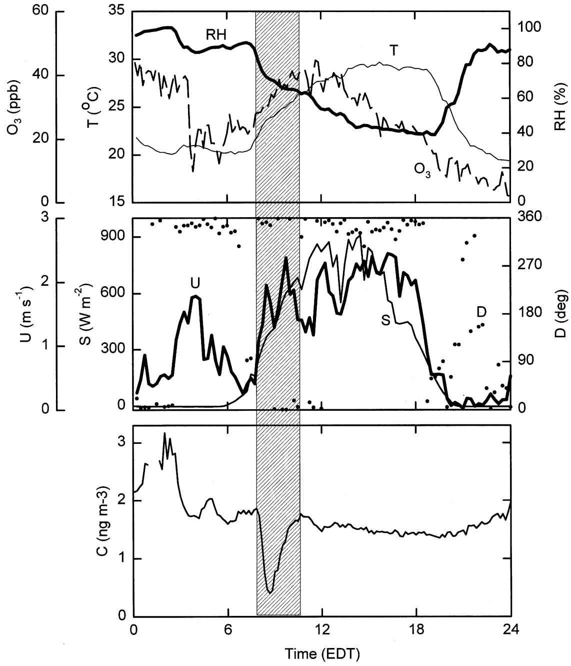

Fig. 3. An example of episodic low TGM concentration on Day 199 (18 July) 1998. Also shown are ozone concentration (O_3), air temperature (T), relative humidity (RH), wind speed (U), global radiation (S), and wind direction (D). Ozone concentration was observed 10 km NW of the site at a local air quality monitoring station (Ecosystem Assessment Unit, 1998).

2.0 ng m^{-3}, a mean value for the mid-latitude background air (Slemr et al., 1985), suggesting that any upwind anthropengic sources in this sector had negligible influence on C. The lower afternoon concentration is unlikely to be a result of photochemical transformations of the gaseous Hg to Hg of particulate form involving O_3. A laboratory study of the gas phase reaction (Hall, 1995) suggests that the rate of decrease in C by O_3 oxidation is no greater than 0.01 ng m^{-3} over a 12-h period, too small to explain the day–night difference in Fig. 2. A more plausible explanation is that the air was more diluted in the daytime owing to more vigorous turbulent mixing and a deeper mixed layer. This is analogous to CO_2 in mid-latitude deciduous forests in the winter where the CO_2 concentration is lower in the daytime as a result of the turbulent mixing, even though the surface is a source throughout the 24-h cycle.

The regression of the daily minimum C, or "background" concentration, with time over the 1998 experimental period shows no significant upward trend ($C = 1.62 - 0.0008x$, $r = -0.16$, $n = 107$, where x is day of year), implying that gaseous Hg was removed from the boundary layer at a rate equal to or greater than the surface emission. We postulate that oxidation of Hg in the aqueous phase in clouds, including those formed by convection (boundary layer clouds) and in synoptic weather systems, maintains a C gradient across the boundary layer inversion, which in turn drives an entrainment flux from the boundary layer to the free atmosphere at a rate comparable to the surface flux. A similar process is known for water vapor. The entrainment mechanism moves water vapor from the boundary layer to the air layer above where it is converted to liquid water by cloud formation. The entrainment flux is of equal magnitude to the surface evapotranspiration rate (Barr and Betts, 1997) so that water vapor does not build up in the boundary layer over periods of weeks to months. If for the sake of discussion we assume that the surface was a source emitting Hg at a rate of 20 ng m^{-2} h^{-1} (Lindberg et al., 1998; Leonard et al., 1998b; Xiao et al., 1991) and was balanced by the entrainment flux across the boundary layer top, and given a mean C of 2 ng m^{-3} and a typical boundary layer depth of 1 km, we estimate the residence time of TGM in the boundary layer to be 4 d. The actual residence time should be shorter than this since the anthropogenic contributions to the boundary layer are not included in the estimate.

Three episodes of exceedingly low C (0–1 ng m^{-3}) were recorded in July 1998, all in relatively clean air (ozone concentration 30–40 ppb, monitored at an air quality station 10 km NW of the site) in the morning hours under cloudy conditions, with two associated with north wind and one with south wind. An example is shown in Fig. 3. The patch size of the clean air was 11 km given a typical wind speed of 1 m s^{-1} and duration of 3 h. The relatively smooth leading edge of the time series suggests that the air masses had undergone sufficient mixing prior to their arrival and hence were not generated locally. Unusually, low concentrations were observed in the arctic after the polar sunrise (Schroeder et al., 1998). Concentrations below 1 ng m^{-3} were also seen at other mid-latitude sites but their validity was suspected because of cartridge passivation arising from interference with the gold traps by other compounds after weeks of operation. It is relatively easy to determine when passivation is occurring since one cartridge is usually affected before the other (Schaedlich, 1997). In our case, both cartridges started to give low readings at the same time. Additionally, a calibration cycle in the middle of one event, which would have cured the problem temporarily had it been passivation (Schaedlich, 1997), did not bring the readings back to "normal". We believe our low values are genuine, but obviously further tests, such as those with addition of a standard concentration to the sampling line (Schroeder et al., 1995), are needed to rule out the possibility of passivation completely.

The cause of these episodes is not known. The significant positive correlation of TGM with ozone in the arctic region suggested chemical transformation of the elemental Hg to the particulate phase or reactive gaseous Hg (Schroeder et al., 1998). A positive correlation also existed between the two species in the mid-latitude continental air and was interpreted as evidence for the influence of anthropogenic pollution (Poissant, 1997; Lamborg et al., 1995). We suggest that the low concentrations of this study may have been caused by the intrusion of the free atmosphere from above the boundary layer where the gaseous elemental Hg had undergone chemical transformation in the clouds. The clean patch size was comparable with horizontal roll vortices or mesoscale cellular convection known to exist in the daytime convective boundary layer (Stull, 1988).

3.2. TGM flux

Fig. 4 shows all 90-min flux data, with key statistics given in Table 1. To facilitate discussions, data of 1998 are divided into four periods: episodic release (Day 83–94, 24 March–4 April), period before complete leaf-out (Day 95–129, 5 April–9 May), early growth (Day 130–179, 10 May–28 June), and full foliage (Day 180–200, 29 June–19 July). The 1997 experiment was in the period of early growth transition, noting that the growing season was at least 15 d later than in 1998. The flux at our site was characterized by an episodic release and by the influences of soil temperature and plant biological activities. These are discussed below.

The episodic release started at the time when the daily minimum temperature increased above the freezing point (Fig. 4) and appears to have been triggered by ice melting during this unusually warm event in early spring. It was not an instrumental artifact because tests immediately before and after the episode showed no inlet bias. The 90-min flux during this episode was significantly correlated with solar radiation, but not with sediment temperature (Table 1). The average flux was much higher than during any other period.

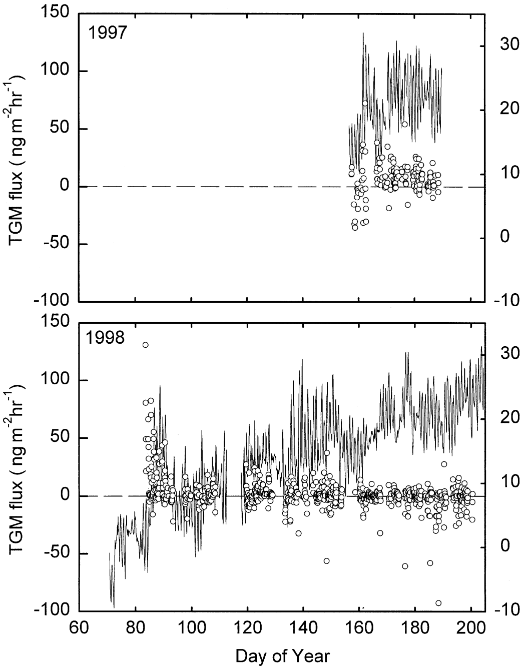

Fig. 4. TGM flux (circle) plotted with air temperature (line) for 1997 and 1998.

Positive correlation of TGM flux with temperature is expected if the flux is caused by vaporization of Hg or if microbial activities are involved (Gustin et al., 1997). The TGM flux before the complete leaf-out (Day 95 – 129) was positively correlated with the 1-cm sediment temperature, T_s (Table 1 and Fig. 5), and did not show a discernible influence of inudation. (The influence of inudation was not discernible over other periods either.) The data in Fig. 5 can be represented by the regression equation

$$F_c = -3.2 + \exp(-0.81 + 0.15T_s), \tag{3}$$

which captures 27% of the observed variance. Eq. (3) shows that over this particular time period the flux increased by a factor of 4.5 over an increase of 10°C in the sediment temperature ($Q_{10} = 4.5$) and that the marsh was a small sink of TGM at low temperatures. Depositional flux was also seen at a forest floor site and over a lake in the cold season (Xiao et al., 1991). Model calculations suggest that cold condensation and fractionation at low temperatures could drive Hg from the atmosphere into the water and sediment (MacKay et al., 1995).

Table 1

Means and standard deviations of TGM flux over the experimental period in 1997 and four periods in 1998, with n being number of observations. Also given are r_{T} and r_{S}, coefficients of linear correlation with sediment temperature and solar radiation, respectively, fraction of negative TGM flux, and confidence level (***, $p < 0.001$; *, $p < 0.10$)

Year	1997	1998	1998	1998	1998
Day of year	157–188[a]	83–94[b]	95–129[c]	130–179[a]	180–200[d]
Mean (ng m^{-2} h^{-1})	6.5	13.2	1.8	– 0.4	– 3.3
STD (ng m^{-2} h^{-1})	14.0	23.3	7.2	9.0	12.0
n	152	101	169	284	159
r_T	0.02	– 0.10	0.47***	0.11*	0.05
r_S	0.36***	0.69***	0.32***	0.04	– 0.13*
Negative fraction	0.24	0.29	0.38	0.48	0.55

[a] Early growth.

[b] Episodic event.

[c] Period before complete leaf-out.

[d] Full foliage.

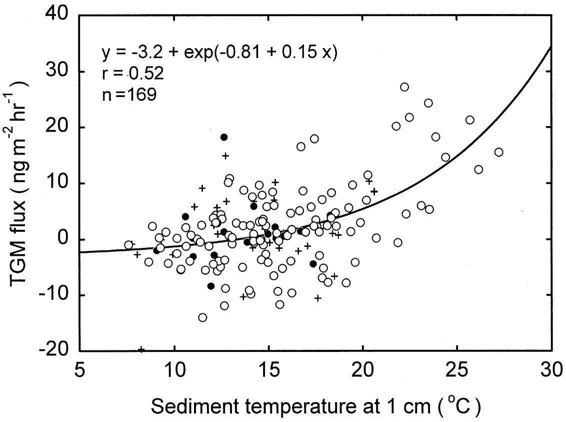

Fig. 5. TGM flux plotted against 1-cm sediment temperature before leaf-out (Day 95–129) in 1998: circle, no inudation; bullet, full inudation; cross, tidal water present over a portion of the 90-min period.

Table 1 and Fig. 4 show that the TGM flux was bi-directional at our site, consistent with previous observations (Kim et al., 1995; Lindberg et al., 1998; Xiao et al., 1991). Upward flux dominated the observations prior to the complete leaf-out (Day 83–129) while downward flux occurred over more than half of the observations during the fully leafed period (Day 180–200). The downward flux of the latter period appears to be related to photosynthesis or some unknown photochemical processes because the negative flux was observed mainly in the daylight hours. Of 15 d having more than 3 daytime samples, the averaged daytime (9:00–18:00 EDT) flux was negative on 13 d. Furthermore, the negative linear correlation with solar radiation was significant at the 10% confidence level. The correlation improved slightly if we used the following Michaelis–Menten model, a model that has been frequently used to describe the light control on canopy carbon uptake (correlation coefficient 0.18, confidence level 5%),

$$F = 3.2 - \frac{8.1S}{65 + S}, \tag{4}$$

where S is global radiation flux in W m^{-2}.

Two biological processes are proposed to play a role in TGM exchange with the salt marsh. The first one is diffusion through stomatal openings in daylight (Taylor et al., 1988; Lindberg et al., 1992). Chamber observations by Hanson et al. (1995) showed evidence for a compensation point in the 10–25 ng m^{-3} range beyond which the foliage served as a TGM sink. The depositional flux of this study is not attributed to a compensation-point phenomenon because flux data with $C > 4$ ng m^{-3} were excluded from this analysis to minimize the influence of local anthropogenic sources. In order to gain some understanding of stomatal control on Hg exchange with the marsh plants, we analyzed the energy balance and evapotranspiration data collected in 1997. Our data support previous observations that these plants were in a state of biological drought due to salinity stress. Despite ample water supply, the latent heat flux, λE, was only slightly greater than the sensible heat flux, H, as shown in Fig. 6, where R_n is net radiation, and the sum of the heat flux into the ground (G) and heat transport by tidal water (T) is computed as a residual of the energy balance as $G + T = R_n - H - \lambda E$. In comparison to the standard value of 1.26, the Priestley-Taylor constant was 0.81 over the period 7 June–5 July, 1997, indicating that the evapotranspiration rate was lower than the potential rate by 36% (Priestley and Taylor, 1972). Furthermore, the mid-day canopy resistance under low saturation vapor

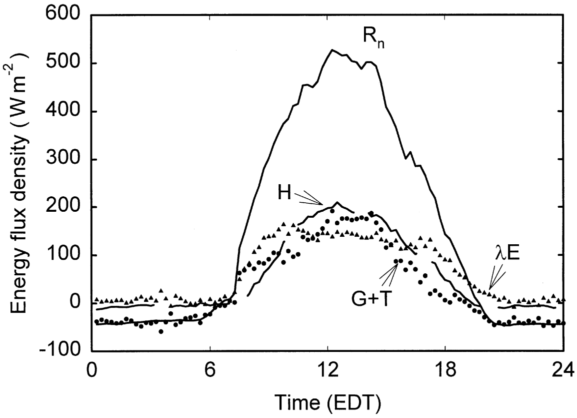

Fig. 6. Energy flux densities of net radiation (R_n, solid line), sensible heat (H, dashed line), latent heat (λE, triangles) and the sum of heat conduction into the soil and heat transport by tidal water ($G + T$, filled circles) averaged over the 1997 experimental period. The mean values were 153, 57, 64, 4 and 28 W m^{-2} for R_n, H, λE, G and T, respectively. (The mean G value was estimated using the change of sediment temperature over the period of observation).

density conditions, estimated with the Penman–Monteith big leaf model, was on average 220 s m^{-1}, similar to arctic lichen/moss tundra which also suffers from physiological drought (Kelliher et al., 1995). Given a typical mid-day aerodynamic resistance of 40 s m^{-1}, C of 1.8 ng m^{-3}, and foliage resistance (canopy resistance plus mesophyll resistance) of 1320 s m^{-1} (6 times the canopy resistance for water vapor, Lindberg et al., 1992), we estimate the deposition flux to be -4.8 ng m^{-2} h^{-1}, comparable to the observed flux over the fully leafed period (Table 1).

The second biological process is transport of oxygen to the sediment by *Spartina* plants via their roots. This process peaks during spring and early summer (early growth) when the plant growth rate is at its highest (Pellenbarg, 1984; Williams et al., 1994; Luther et al., 1991). Under aerobic conditions sulfide is oxidized to sulfate, resulting in an increased solubility of Hg^{2+} (Fagerstrom and Jernelov, 1971; Robinson and Tuovinen, 1984), which can be reduced to the elemental form either within the plants or outside the thin oxidizing layers surrounding individual roots. Under this scenario, oxygen respiration of *Spartina* roots could enhance evasive flux of Hg, consistent with our data during early growth in 1997 and 1998. We may argue that the net flux could result from three competing mechanisms: Hg vaporization and microbial activities (controlled by sediment temperature), root zone redox potential (dependent upon the vigor of plant growth) and diffusion into plants via stomata (highest at full foliage). This may explain why only weak correlations existed with sediment temperature during the early growth and fully leafed periods (Table 1).

3.3. Annual budget

In order to evaluate the role of the gaseous Hg pathway in local Hg cycling, it is necessary to extrapolate the short-term flux to the full year. If we exclude the episodic event and consider the averaged flux observed in 1998 to be representative of the full year, we arrive at an estimate of the annual flux of -5.0 μg m^{-2} yr^{-1}. An alternative method is to divide the full year into three periods, dormancy (Day 310–129), spring to early summer transition (130–179) and full foliage (180–310), and use the observed fluxes of 1.8, -0.4, and -3.3 ng m^{-2} h^{-1} for these periods, respectively (Table 1). This gives an estimate of -3 μg m^{-2} yr^{-1}. We therefore conclude cautiously that the marsh appears to be a weak TGM sink, but we also recognize the large uncertainty inherent in any such attempt at extrapolation due to the small temporal scale of measurements. The estimate would be more negative if we consider the slight depositional flux at low temperatures in the winter months (Fig. 5) or if we account for the inlet bias (Section 2.3). (The inlet bias amounts to -3 to -5 μg m^{-2} yr^{-1}.) On the other hand, the episodic event, which is not included in the annual estimate, released about 4 μg m^{-2} to the atmosphere. It is difficult to tell, however, whether this type of episodic event will occur every year. Another uncertainty is the interannual variability as seen over the early growth periods (Table 1). The annual flux would be $+5$ μg m^{-2} yr^{-1} if the 1997 value were used for the spring to early summer transition. In view of these uncertainties, we consider -4 ± 7 μg m^{-2} yr^{-1} to be our best estimate of the annual TGM flux at the marsh site.

Table 2
Annual fluxes at the Farm River salt marsh. Estimates of particulate and wet (rain) deposition are based on observations near Long Island Sound by Fitzgerald et al. (1991) and sediment Hg accumulation rate is the average over the period 1975–1996 (Varekamp, 1998)

	Flux (μg Hg m^{-2} yr^{-1})	Reference
Sediment accumulation	187 ± 95	Varekamp (1998)
Wet deposition	− 11 ± 5	Fitzgerald et al. (1991)
Particulate deposition	− 10 ± 8	Fitzgerald et al. (1991)
Gaseous exchange	− 4 ± 7	This study

Table 2 compares the gaseous flux with fluxes via other pathways. The gaseous exchange was similar in magnitude to wet and particulate depositions. The total surface-exchange accounted for only 13% of the Hg accumulation rate in the sediment (Varekamp, 1998). This suggests that nonlocal processes, such as transport by tidal water from Long Island Sound and by freshwater from the watershed, are the dominant components of the Hg budget.

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