BAIE ST-FRANÇOIS WETLAND (QUÉBEC) MERCURY AIR-SURFACE EXCHANGE EXPERIMENTS

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ABSTRACT- In order to evaluate and to understand the mercury exchange processes in riverine wetlands, related researches were initiated in a St. Lawrence River wetland (Baie St-François) (Yamaska, Québec). Mercury fluxes were measured using micrometeorological methods. Those techniques were coupled with an automatic mercury vapor phase analyzer (namely, Tekran®, Model 2537A). Mercury surface-air exchanges as well as meteorological observations were measured during an intensive field campaign from July to September, 1999. Median values for Total Gaseous Mercury concentrations and Hg fluxes during this period were respectively, 1.39 ng/m^3 and 0.83 ng/m^2/h. Hg flux was strongly correlated with soil temperature (R^2 = 0.70) and weakly correlated with solar radiation (R^2 = 0.20). Measured Hg fluxes were representative of drying wetlands due to extreme low water levels in the St. Lawrence River that occur in water year 1999.

INTRODUCTION

Wetlands are very rich in biodiversity and may be subject to mercury contamination. Mercury air-surface exchange may be (or not) an important route of mercury transfer to wetlands. In order to evaluate and to understand the mercury exchange processes in riverine wetlands, related researches were initiated in a St. Lawrence River wetland (Baie St-François) (Yamaska, Québec). Despite their close proximity to mercury point sources, wetlands along the St. Lawrence River contain, on the average, lower Hg concentrations in sediments and in water than inland wetlands (Thompson-Roberts and Pick, 2000). Recent mercury air/surface exchange study in Florida wetlands (Everglades) has pointed out low evasion rates for Hg° (<3 ng/m^2/h) which were smaller, on the average, than those measured at northern sites (mean Hg evasion rates of 3.43 ng/m^2/h at Burt Lake, MI) (Lindberg *et al.*, 1999). This paper presents and discusses the first *in situ* Hg surface/air exchange measurements in riverine marsh along the St. Lawrence River (Baie St-François wetland).

METHODS

Site description

The Baie St-François wetland site is located in the Lake St. Pierre (a fluvial lake of the St. Lawrence River) at 46°06' latitude North and 72°56' longitude West. This wetland covers 1600 ha and is part of the Ramsar Convention (UNESCO). The average concentrations of total Hg and CH_3Hg^+ in soil (beneath the chamber) were respectively, 12 ng/g and 0.58 ng/g (dry weight). Measurements were performed over mixed vegetation (e.g., grass, reed) and soil. A designed floating platform (30'X30') with air conditioned shelter including a floating bridge (200' long) was installed in the bay (Fig. 1). The mercury air/surface exchanges study was conducted in drying wetland due to extreme low water conditions in the St. Lawrence River in water year 1999.

Analytical devices

The Total Gaseous Mercury (TGM) analysis was achieved using an automatic analyzer (Tekran 2537A). Briefly, the analytical train of this instrument is based on amalgamation of mercury onto a pure gold surface followed by a thermodesorption and analysis by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS) providing analysis of TGM in air at sub-ng/m^3 levels (*Bloom and Fitzgerald*, 1988). Dual cartridge designs allow alternate sampling and desorption, resulting in continuous measurement of mercury in the air stream.

Mercury flux measurement techniques

Two methods were used for mercury flux measurements. The first method was a dynamic flux chamber and the second technique was the Modified Bowen Ratio (MBR). The two methods have been previously intercompared during an international study conducted in Reno, Nevada (Gustin *et al.*, 1999; Poissant *et al.*, 1999). Only flux chamber results are presented in this paper.

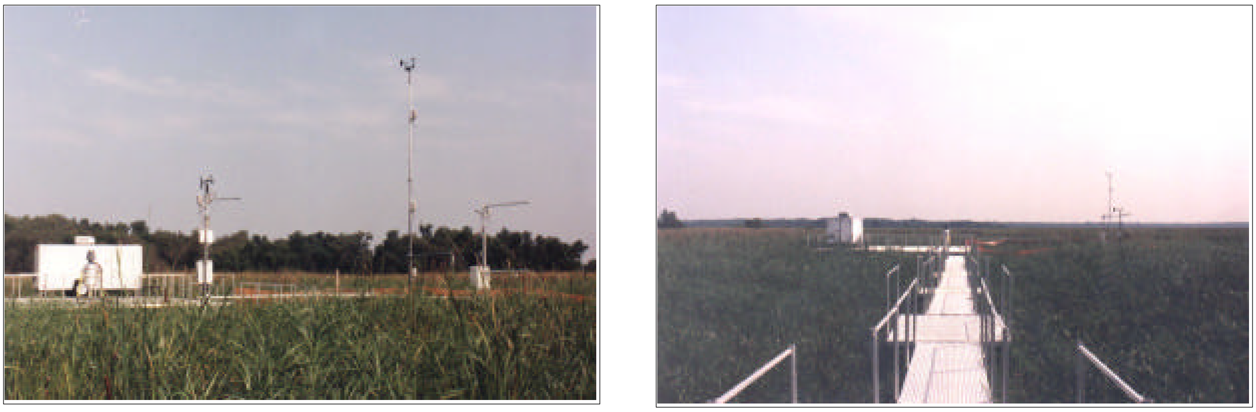

Figure 1. Baie St-François research station is dedicated to surface air gas exchanges in wetlands.

Dynamic flux chamber

The dynamic flux chamber was built in our laboratory. The chamber consists of a hemispheric stainless steel bowl coated with Teflon® (Fig. 2). The open area of the chamber was 0.125 m^2 and its volume was 0.010 m^3 (details in Poissant and Casimir, 1998). The mercury flux ($ng/m^2/h$) from the dynamic flux chamber (FC_{Hg}) was computed using the mass balance equation (Xiao *et al.*, 1991) (Eq. 1)

$$FC_{Hg} = \frac{[Hg]_o - [Hg]_i}{A} * Q \quad \textbf{(1)}$$

where $[Hg]_o$ is the outlet air concentration, $[Hg]_i$ the inlet air concentration in the chamber, A is the open surface of the chamber and Q the flow rate into the chamber (0.09 m^3/h).

Figure 2. Flux chamber (this chamber was intercompared during Reno study).

The measurement of the mercury concentrations in the inlet and outlet air sample ports was achieved through the mercury analyzer ; a peripheral device using a solenoid valve forced the sample to be directed through a specific cartridge of the analyzer. Hence, the analyzer did sequential measurements of the ports. The inlet measurements were made by measuring mercury concentrations in the ambient air at about 0.15 m from the chamber at a height of ~0.10 m. Each measurement was integrated over 5 minutes. Sampling was made at a rate of 1.5 L/min and directed through the analyzer located inside the station shelter via a 15 m heated Teflon tubing line. The time resolution for the flux measurement was 10 minutes. Before installing the chamber, a circular groove of about 1 cm was cut in the soil where the chamber was then placed. Once the chamber was in place, the edge was covered with soil with weights (~ 20 kg) put on it to ensure a tight seal. A complete set of meteorological and micrometeorological parameters was measured in parallel (e.g., K_w, Net Solar Radiation, etc.).

RESULTS AND DISCUSSION

The TGM concentrations were between 0.56 and 5.65 ng/m^3 throughout the experiment and the median was 1.39 ng/m^3 (Fig. 3). This median value is comparable to continental background (Poissant, 2000). But maximum value suggested some local source signatures. The median mercury flux during that period was 0.83 ng/m^2/h with minimum and maximum values between –1.50 ng/m^2/h and 2.40 ng/m^2/h (Fig. 4) (Table 1).

Table 1. Statistical summary of TGM and Hg flux measured at the Baie St-François wetland in 1999.

	min.	**Max.**	**Median**	**n**
TGM ng/m^3	0.56	5.65	1.39	2710
Hg flux ng/m^2/h	-1.50	2.40	0.83	5096

Maximum diurnal Hg fluxes were recorded, on an average, during late mid-afternoons (14 :00 - 16 :00) whereas minimum Hg fluxes were generally measured during nighttime. However, some Hg depositions were observed during daytime and nighttime in the Baie St-François. This pattern was not similar to Hg fluxes measured over pasture site at St. Anicet where strong diel Hg fluxes and no deposition were observed (Poissant and Casimir, 1998). Figure 5 shows the regressions between Hg fluxes with Net Solar Radiation (R^2 = 0.2) and Soil temperature (R^2 = 0.7). These results suggested that Hg fluxes were more related to thermodynamic processes. Hg fluxes in the Baie St-François appeared to be less related to solar radiation. Hg deposition is likely to be important in the Baie St. François, and its role in the Hg uptake in the environment will be further explored in a more holistic study in 2000.

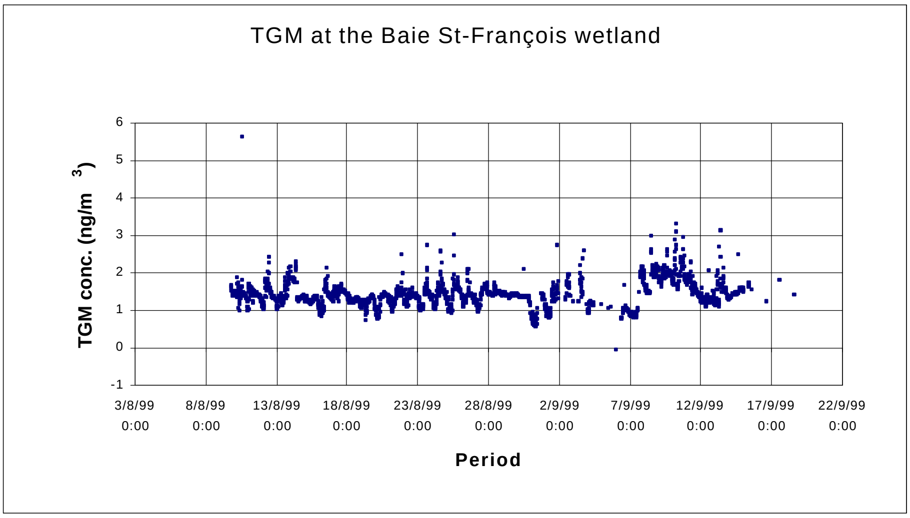

Figure 3. Time series of TGM measured during the experiments.

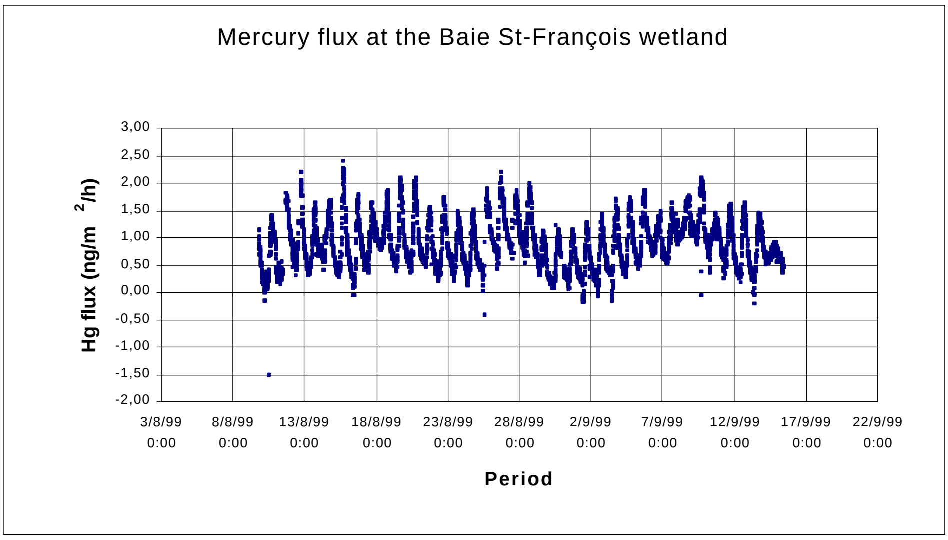

Figure 4. Time series of surface-air Hg gas exchange during the experiments.

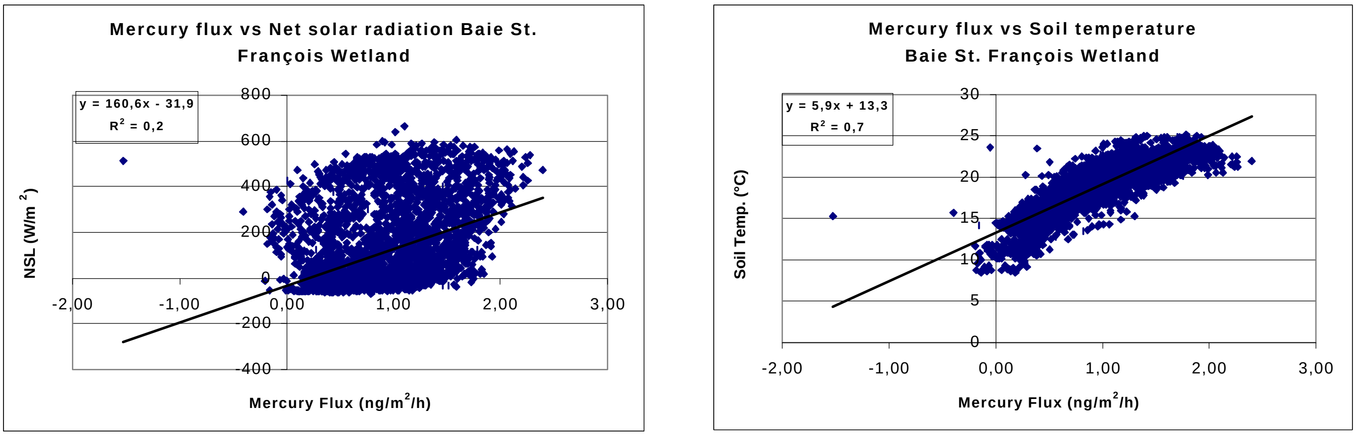

Figure 5. Regressions between Hg flux and NSL (left panel) as well as between Hg flux and Soil temperature (right panel).

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