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Temporal and spatial distribution and production of dissolved gaseous mercury in the Bay St. François wetland, in the St. Lawrence River, Quebec, Canada

Edenise Garcia [a], Jerôme Laroulandie [b], Xavier R. Saint-Simon [b], Marc Amyot [a,*]

[a] *Groupe de Recherche Inter-universitaire en Limnologie (GRIL) Département des sciences biologiques, Université de Montréal, C.P. 6128, Succursale Centre-Ville, Pavillon Marie-Victorin, Montréal, Que., Canada H3C 3J7*

[b] *Institut national de la recherche scientifique (INRS), Eau, Terre et Environnement, Université du Québec, 490, rue de la Couronne, Que., Canada G1K 9A9*

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Abstract

Wetlands are valued for their high biodiversity and for their ecosystem services. However, we still do have a poor understanding of their role in the redox transformation of contaminants such as mercury, particularly in fluvial settings. Seasonal and spatial variations in dissolved gaseous mercury (DGM) distribution and production were studied in the Bay St. François, a wetland in the St. Pierre Lake, a fluvial lake of the St. Lawrence River, in Quebec, Canada. A high spatial resolution for DGM, with samples taken every 10-cm depth, was used in field measurements. Through a series of parallel field and incubation experiments, we assessed the main factors determining Hg(0) transformations as a function of depth, seasons, and presence/absence of macrophyte beds. Besides light penetration in the water column and water temperature, iron and dissolved organic carbon likely stimulated Hg(II) reduction. Inversely, chloride favored Hg(0) oxidation. Macrophytes and associated epiphytes appeared to be important sites of adsorption/absorption of Hg(II) and likely of DGM. It seems however that the effects of macrophytes were restricted to immediately adjacent waters. Near the bottom, under anoxic conditions, the reduction of Hg(II) was highly promoted. In addition, sediments and decomposing macrophytes seemed to release DGM and/or reducible Hg to bottom waters. Overall, differences in DGM between surface and bottom waters tended to be more accentuated than observed differences in DGM between macrophyte beds and sites devoid of plant.

1. Introduction

One of the major features of wetlands is the presence of vegetation adapted to water-saturated soils, likely controlling major aspects of nutrient and contaminants biogeochemistry. Macrophytes, in combination with permanent or temporal flooding, provide favorable conditions for settling of particulate matter: low current velocity, shallow water and the physical filtering action of plant stems and leaves (Petticrew and Kalff, 1992). Live macrophytes, associated epiphytes and dead plant material also constitute substrates for a large number of chemical and microbiological processes in the water column and in the sediments (Lalonde and Downing, 1991). Moreover, during periods of flooding, an oxygen-depleted layer tends to be formed in the sediment–water interface. This anoxic condition favors methanogenesis, denitrification, as well as Fe(III) and sulfate reduction, and influences nutrient cycling and the redox chemistry of metals.

Redox chemistry of mercury may be affected by biotic and abiotic factors. It has been shown that the reduction of Hg(II) to Hg(0), the main species of dissolved gaseous mercury (DGM) in aquatic systems, is mainly induced by sunlight (Amyot et al., 1994). The production of DGM may be also biologically mediated (Mason et al., 1995; Siciliano et al., 2002; Poulain et al., 2004) and influenced by water chemistry (Allard and Arsenie, 1991; Zhang and Lindberg, 2001). Because Hg(0) tends to be lost to the

* Corresponding author. Fax: +1 514 343 6216.
E-mail address: m.amyot@umontreal.ca (M. Amyot).

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atmosphere, DGM formation may be an important step in the mercury cycle. In wetlands, macrophytes may potentially affect the photoreduction of Hg(II). Emergent and submerged plants interfere with light penetration in the water column. Macrophytes can also limit water exposure to wind and waves, and thus reduce the evasion of Hg(0) to the atmosphere. Besides interfering with environmental conditions, aquatic plants can play an active role in the biogeochemistry of Hg. Root uptake of Hg and its subsequent translocation to above-ground tissues may be an important path for remobilization of Hg buried in sediments (Coquery and Welbourn, 1994). In addition, transpiration of DGM from emergent macrophytes has been reported (Lindberg et al., 2002). Also, macrophytes can influence Hg cycle by providing nutrients that enhance microbial activity, particularly in the sediments, by releasing reducing/oxidizing compounds, or by adsorption and/or absorption of Hg. Rooted submerged aquatic plants, for instance, can release oxygen from root surfaces (Armstrong and Armstrong, 1990), potentially favoring oxidation of reduced metallic ions. Floating macrophytes, in turn, can reduce ionic Hg to Hg(0) (Siegel et al., 1987).

High concentrations of dissolved organic carbon (DOC) in wetlands can also have an effect on the redox chemistry of Hg. DOC tends to complex Hg(II) and to affect its availability (Allard and Arsenie, 1991). DOC also interferes with light penetration. The absorption of light by chomophoric DOC (CDOC), particularly in the UV range, may lead to the formation of photoreactive intermediates that can alter the redox state of Hg (Bertilsson and Tranvik, 2000; Alberts et al., 1974).

Wetlands have been shown to be sites of formation of methyl mercury (St. Louis et al., 1994), but processes leading to the production of highly volatile DGM are less understood. In this context, the overall objective of this study was to evaluate the distribution and net production of DGM in the Bay St. François (BSF), a wetland of the St. Lawrence River, in Quebec, Canada. We also aimed to investigate the mechanisms leading to the reduction of Hg(II). Evaluating the redox chemistry of Hg in wetlands is not a simple task however. Wetlands form a mosaic of interconnected macrophyte-free pools, channels and macrophyte beds, with diverse structural and functional characteristics. Impacts of macrophytes on water quality vary therefore both spatially and seasonally. To take into account such a spatial and temporal variability in the biogeochemistry of Hg, we conducted a series of in situ and laboratory experiments. More specifically, our objectives were: (1) to determine DGM distribution and production at different periods of the day in water from submerged, emergent, and floating macrophyte beds, as well as in water from macrophyte-free areas within or around the BSF; (2) to investigate, at a fine spatial scale, seasonal variations in DGM depth profiles and their relationships with total Hg concentration and with several physico-chemical variables measured concurrently in a submerged macrophyte bed and in a macrophyte-free area; and (3) to examine the direct role of an abundant macrophyte (*Ceratophyllum demersum*), its associated epiphytes, and of sediments on the redox chemistry of mercury. To our knowledge, this is the most detailed study of the redox chemistry of Hg conducted in a temperate wetland.

2. Materials and methods

2.1. Study site

The Bay St. François is a 16-km^2 wetland located in the Lake St. Pierre, an enlargement of the St. Lawrence River (Fig. 1), ~60 km downstream from Montreal (46°06′N, 74°17′W). Two important tributaries, the Yamaska and the St. François rivers, drain into BSF western and eastern ends, respectively. Agricultural pollutants in the BSF originate from these rivers, whereas industrial contaminants

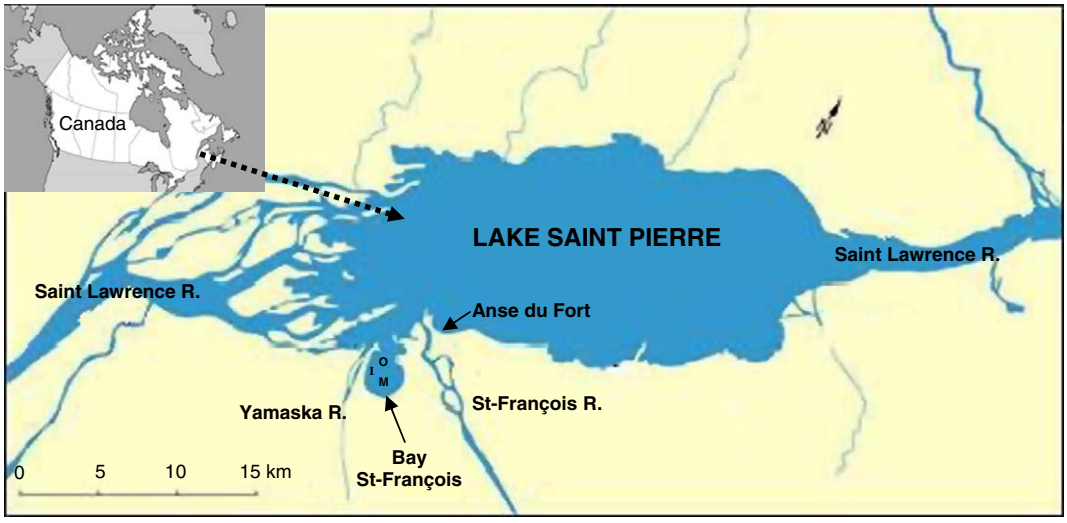

Fig. 1. Map showing the study sites: macrophyte beds (M) and macrophyte-free areas within (O) or at the border (I) of the Bay St. François wetland, the Yamaska and in the St. François rivers, and the Anse du Fort.

Table 1
Physical and chemical characteristics of water from a *Ceratophyllum demersum* bed and from a macrophyte-free site in the Bay St. François wetland at different seasons in 2002–2003

	C. demersum bed				Macrophyte-free site			
	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer
pH	6.6–8.7	na	7.4–7.7	6.8–7.2	6.8–6.9	6.8–6.9	7.6–7.7	6.8–6.9
Temperature (°C)	16.3–23.2	0.3–4.0	7.4–12.3	24.1–29.0	16.7–23.3	1.1–2.9	5.8–12.2	12.5–17.8
Water depth (cm)	80	80	180	80	130	130	200	150
Depth 1% light (cm)	25	na	180	80	80	na	180	140
% light subsurface	36.7	na	79.5	98	30	na	95	95
Dissolved oxygen (mg L^{-1})	0.1–16.2	0–8.4	7.0–12.0	7.6–10.8	0.05–6.6	0–6.6	9.8–11.3	na
DOC (mg L^{-1})	14.8–18.3	9.7–12.0	11.1–11.7	9.6–12.0	15.0–21.5	10.6–14.8	12.3–13.8	16.0–18.0
Cl^- (μg L^{-1})	38.9–39.6	46.7–53.6	18.6–26.3	26.5–27.4	38.9–39.6	51.4–55.7	30.2–32.4	27.1–28.4
Fe^{3+} (μg L^{-1})	0.63–11.9	0.05–12.9	0.6–0.8	1.1–2.7	0.5–1.4	0.3–0.8	1.0–1.1	2.0–2.5
Total Hg (ng L^{-1})	3.0–3.2	0.9–6.6	4.3–12.4	1.0–1.8	2.4–2.9	0.6–0.9	15.1–26.1	1.6–2.8
DHg (ng L^{-1})	1.9–3.1	0.5–3.1	2.1–4.0	na	1.9–2.5	0.3–0.7	9.7–21.0	0.9–1.5

Data correspond to minima and maxima values; na indicates data not available. DHg, dissolved total Hg.

reaching the BSF come mostly from the St. Lawrence River, either from farther upstream or from an adjacent industrial area in the cities of Sorel and Tracy. Environmental characteristics of the BSF wetland at different seasons are shown in Table 1.

2.2. Experiments

Clean procedures were adopted during sample collection and analysis: powder-free latex gloves were worn at all times; the glassware was soaked in 20% HNO_3 and rinsed with Milli-Q water, and the sampling bottles were rinsed three times with natural water prior to use.

All experiments were conducted in 2002 and 2003. Quartz bottles (∅ 8 cm × 40 cm) were used in incubations to assure complete sunlight penetration and to prevent losses through the bottle wall. Subsurface samples were collected by hand filling quartz bottles, whereas water for depth profiles was sampled using a Teflon tube connected to a peristaltic pump. No headspace was present within the bottles to avoid loss of Hg(0) by volatilization to the headspace. For incubation experiments, samples were collected between midnight and 4:00 a.m. in order to avoid the presence of photoreactive radicals before the beginning of exposure to sunlight. The quartz bottles were kept sideway during all incubation periods.

DGM distribution in the BSF and nearby areas was determined during the day and at night. Water samples were collected in July 2002 in five macrophytes beds consisting of: *Scirpus* spp. and *Pontederia cordata*, emergent rooted plants; *Elodea canadensis* and *C. demersum*, submerged macrophytes; and *Nuphar variegatum*, a floating species. Water samples were also taken from macrophyte-free areas located within (open water site) or at the border of the wetland (interface site), as well as in the Yamaska and in the St. François rivers, and in the Anse du Fort, a bay located in the south shore of St. Pierre Lake (Fig. 1). Day samples were collected around midday on sunny days and night samples between midnight and 4:00 a.m.

To determine diurnal variations in net DGM production, during summer 2002 subsurface water samples from macrophyte beds (*N. variegatum*, *Scirpus* sp., and *P. cordata*) were incubated in situ, at ~10 cm depth. For sites devoid of macrophytes (interface site, Anse du Fort, and Yamaska and St. François rivers), samples were incubated in a 10-cm depth water bath filled with water from the respective sampling site. Incubations took place from sunrise to 6:00 p.m. DGM concentrations were measured each hour or half hour. The rate of DGM production was then estimated for three periods of the day: morning (6:00 a.m. to 10:00 a.m.), around noon (10:00 a.m. to 2:00 p.m.) and afternoon (2:00 p.m. to 6:00 p.m.), as well as for the first hour of exposure following sunrise. Three quartz bottles were kept in the dark, as controls, during the incubation period. The photoproduction rate of DGM (PRD) was estimated using the following equation:

$$\mathrm{PRD} = ([\mathrm{DGM}]_t - [\mathrm{DGM}]_0)/T, \quad (1)$$

where $[\mathrm{DGM}]_t$ and $[\mathrm{DGM}]_0$ are DGM concentrations at time t and at the onset of the incubations, respectively, and T corresponds to incubation period (in hours). It has been shown that in freshwater oxidation and reduction of mercury occur simultaneously, with DGM formation prevailing over Hg(0) oxidation under sunlight (Garcia et al., 2005a,b). Hence, in this study, we assumed that the formed DGM corresponded to the net product of the two opposite processes.

To assess the seasonal variations in DGM distribution throughout the water column, samples were collected in September and November 2002 and in April and June 2003 from *C. demersum* bed and from the open water site. Throughout the year, water level varied from 80 to 180 cm and from 130 to 200 cm in *C. demersum* bed and in the open water site, respectively. Water was collected each 10–20 cm from the subsurface to close to the bottom. Depth profiles of dissolved oxygen, temperature, incident light penetration, total Hg, total dissolved Hg, DOC, and major ions were also performed.

To examine the role of microbial activity in the redox of Hg, water and sediment from the anoxic bottom of the BSF were collected through diving in September 2003. Water was kept in 1-L Teflon bottles and was bubbled with Hg-free argon; hence water at the beginning of the incubations was DGM-free. The treatments consisted of: (1) water alone; (2) water + chloroform at a final concentration of 1.6% (v/v); (3) water + ~100 g of wet sediment; and (4) water + ~100 g of wet sediment + chloroform 1.6% (v/v). Chloroform was expected to inhibit microbial reducing activity (Wolf et al., 1989). All treatments were done in triplicate, and bottles were kept in the dark, in a cooler, for 12 h. DGM was measured at the end of the incubation period.

To investigate the direct participation of macrophytes and associated epiphytes in redox reactions affecting the oxidation state of Hg, a series of short-term incubation experiments (3–4 h) were conducted during summer 2003. DGM-free subsurface water from *C. demersum* bed filtered at 0.45 μm was used in all treatments, which consisted of: (1) *C. demersum* and associated epiphytes at concentrations of 10 or 20 g wet mass L^{-1}; (2) *C. demersum* without epiphytes at concentrations of 10 g wet mass L^{-1}; (3) epiphytes isolated from ~40 g *of C. demersum*; and (4) water. Samples were incubated in the dark or under natural sunlight. DGM production in light exposed samples was estimated and normalized for cumulative PAR. Total Hg in water was measured at the onset and at the end of the incubations, except for the treatment containing epiphytes only. Epiphytes were separated from macrophytes after vigorously hand shaking for nine minutes ~40 g *of C. demersum* disposed in a 1-L Teflon bottle containing filtered DGM-free subsurface water from the BSF.

2.3. Analytical methods

DGM analyses were performed within minutes of water collection or of the end of the incubation periods. For DGM determinations, approximately 250 or 500 mL of water were slowly decanted into 1-L glass bubblers and purged for 15 min with Hg-free air with a Tekran 1100 zero air generator. The volatile Hg compounds were trapped on a gold-coated sand column which was then placed in an argon gas stream. The trap was dried for 3 min and Hg was subsequently desorbed by pyrolysis at a flow rate of 60 mL min^{-1}, using the double amalgamation technique. Hg was quantified by gas-phase atomic fluorescence spectrometry with Tekran Hg analyzer model 2500. Five or six system blank checks were performed before the beginning of analyses. Analytical blanks for the different experiments averaged 6.7–9.4 pg L^{-1}, and mean detection limit (3 × SD of blanks) for a ~500-mL sample was 7.4 ± 1.1 pg L^{-1}.

Total Hg in water was determined using atomic fluorescence spectrometry, following BrCl oxidation/$SnCl_2$ reduction, according to EPA method 1631. Analytical blank averaged 0.092 ng L^{-1} and the detection limit for a 60-mL sample was 0.099 ng L^{-1}. Reactive Hg (HgR), an operationally defined labile inorganic fraction of Hg(II), was measured by gas-phase atomic fluorescence spectrometry. Analyses were carried on in 100-mL water samples, following acidification to pH < 1 with 6 N HCl and reduction using $SnCl_2$.

Photochemical transformations of DOC were followed with DOC fluorescence (DOCF) measurements done in parallel with DGM determinations. DOCF was measured with a Perkin–Elmer 204 spectrofluorometer equipped with a 10 mm × 10 mm quartz cuvette, at 355 nm excitation and 455 nm emission wavelengths. The average coefficient of variation for samples analyzed in triplicate during summer 2002 corresponded to 0.8%. A 0.05 M H_2SO_4 solution was used as a blank. Values were calibrated against the fluorescence of quinine sulfate using standard solutions, with one quinine sulfate unit (QSU) = 1 ppb quinine sulfate in 0.05 M H_2SO_4.

Dissolved oxygen and water temperature were measured using an YSI, model 50B oxygen meter (Yellow Springs, USA). Water pH was determined with a pH meter model HI9024/HI9025 (Hanna Instrument, Woonsocket, USA). Anions were analyzed by ion chromatography using a DIONEX ICS 2000. Cation analyses were performed using an inductively coupled plasma atomic emission spectrometer (ICP-AES Vista AX). DOC was determined with a Shimadzu TOC-5000 analyzer.

Surface irradiance was measured at the UV and PAR ranges with a spectroradiometer ASD FieldSpec Pro, and was recorded at 10-min intervals and integrated for all incubation periods. PAR extinction coefficient (ε_{PAR}) was measured using a Li-Cor LI-192SA sensor.

2.4. Statistical analyses

DGM differences among sites and among seasons were tested using ANOVA. Whenever variations were significant ($p < 0.05$), Fisher's least significant difference (LSD) test was performed to determine where differences laid. Variations in DGM depth profile between *C. demersum* bed and the open water site were assessed using *t* test. Pearson correlation coefficients (*r*) were calculated between DGM and chemical and physical variables, and Bonferroni test was used to correct for Type I error. Stepwise multiple linear regressions were used to define empirical relationships between DGM and environmental variables. When necessary, data were log transformed to achieve normality and homoscedasticity. All analyses were performed using Statigraphics Plus 5.1 for Windows.

3. Results and discussion

3.1. DGM and total Hg distribution in macrophyte beds and open areas

DGM concentrations observed around noon, during the summer, varied from 52 to 75 pg L^{-1} in water from

macrophyte beds and from macrophyte-free areas in the BSF (Fig. 2). Mean DGM in macrophyte beds (67 ± 10 pg L^{-1}) did not differ significantly (t test, $p > 0.05$) from sites devoid of plants (61 ± 10 pg L^{-1}). In general, DGM levels in the BSF tended to be higher than the ones observed in different sites in the Florida Everglades, as summarized in Zhang and Lindberg (2000), as well as in other temperate and arctic wetlands (Table 2). DGM concentrations within the BSF were also greater than in the St. Lawrence River upstream from Lake St. Pierre (31 pg L^{-1}, Amyot et al., 2000) and than concentrations measured at the Yamaska and St. François rivers nearby the BSF (44 and 49 pg L^{-1}, respectively). These differences in DGM concentration can be related to several factors, including differences in sources of reducible Hg, in light penetration in the water column or in DOC concentrations, which directly affect DGM production. Alternatively, they can reflect variations in wind-driven Hg(0) volatilization related to among site differences in fetch and turbulence.

At night, DGM levels observed in areas devoid of plants and in all macrophyte beds, except in *Scirpus* spp., were lower than 24 pg L^{-1} (Fig. 2). These concentrations were comparable to the ones measured at night at the Yamaska and St. François rivers (29 and 23 pg L^{-1}, respectively). Variations in DGM among sampling periods (noon vs. night) were more noticeable than those observed among sites. Subsurface DGM concentrations observed at night in all study sites excluding *Scirpus* spp. were around 2–5 times lower than those measured around noon. In *Scirpus* spp. bed, DGM concentration at night was the highest (44 pg L^{-1}) among all study sites, but was still significantly lower than noon values (ANOVA-LSD, $p < 0.05$). These results are consistent with a photo-induced DGM production. Depletion in DGM concentrations at night in the BSF have been previously observed by Amyot et al. (2001) and would be triggered by oxidation of Hg(0) (Garcia et al., 2005b) rather than by higher evasion flux at this period. In fact, Poissant et al. (2004) observed in the BSF wetland peaks in DGM flux during daytime, with nighttime fluxes approaching zero. Similarly, Leonard et al. (1998) have reported Hg(0) emissions by plants in the dark one order of magnitude lower than under light.

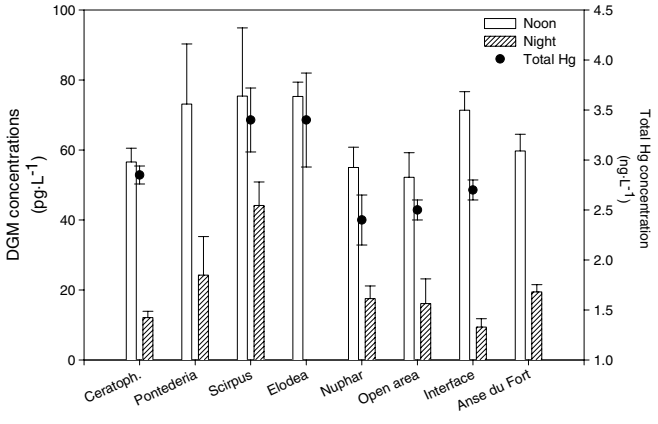

Fig. 2. Average DGM concentrations measured in July 2002, around noon (white bars) or during the night (hatched bars) in water from the different study sites. The x-axis indicates macrophyte-free sites and macrophyte beds in the Bay St. François, as well as in the Lake St. Pierre (Anse du Fort). Dark circles indicate average total Hg concentrations at noon. Error bars correspond to SD of three replicates.

Total Hg levels in the BSF ranged from 2.4 to 3.4 ng L^{-1} (Fig. 2). Differences in mean total Hg between macrophyte beds and macrophyte-free areas within the BSF were not significant (t test, $p > 0.05$). Total Hg concentrations in the BSF tended to be higher than those observed in areas adjacent to the wetland located in the St. Lawrence, Yamaska and St. François rivers (0.5, 1.3, and 1.1 ng L^{-1}, respectively). However, total Hg levels in the BSF were lower than concentrations measured by Thompson-Roberts and Pick (2000) ~300 km upstream the BSF, in water from inland and riverine wetlands of the St. Lawrence River (range from 3 to 34 ng L^{-1}, mean 12.9 ± 8.1 ng L^{-1}). Total Hg in the BSF was also in the lower end of the range observed in Florida Everglades wetlands (0.3–15.5 ng L^{-1}, Strober et al., 1995) or in various boreal forest wetlands (range 3.4–13.5 ng L^{-1}, St. Louis et al., 1996). DGM represented at most 3.3% of total Hg in the BSF around noon, during the summer. This value was lower than the fraction of total Hg as DGM (between 10 and 16%) estimated for the Upper St. Lawrence River (Amyot et al., 2000). No significant correlation was observed between DGM and total Hg concentrations in the study sites, which suggests that formation of DGM in the BSF was not directly related to total Hg concentrations in water. It has been proposed that available dissolved reactive Hg(II) regulates DGM formation in aquatic systems (Zhang and Lindberg, 2000). To test this hypothesis, in June 2003, DGM and reactive Hg were concurrently measured in the subsurface water of one of our sites, *N. variegatum* bed, at one to three-hour intervals, over a period of 96 hours. A weak

Table 2
DGM concentrations in wetlands and in the St. Lawrence River reported in the literature

Location	DGM (pg L^{-1})	Period	Type of wetland	Reference
High Arctic	~48	July 95	Lake	Amyot et al. (1997)
Florida Everglades	<43	Summers 96–98	Everglades	Krabbenhoft et al. (1998) Zhang and Lindberg (2000)
Tahquamenon river watershed	54	Summer 98	River	Zhang and Lindberg (2002)
Experimental Lakes area	~20	Summer 2001	Lake	Poulain et al. (2004)
Upper St. Lawrence River	31	July 98	—	Amyot et al. (2000)

but significant correlation between both species of Hg was observed ($r = +0.23$, $p < 0.05$), and reactive Hg was also correlated with conductivity ($r = +0.79$, $p < 0.0001$). The observed relationship does not clarify, however, if reactive Hg acted mainly as a precursor of DGM or was rather a product of Hg(0) oxidation.

3.2. Diurnal variations in DGM production in water from macrophyte beds and from open areas

DGM production rates in water from *Scirpus* spp., *N. variegatum* and *P. cordata* beds estimated for different periods of the day except sunrise varied from 3.9 to 8.2 pg L^{-1} h^{-1} (Fig. 3). These rates were comparable to the ones observed in the Yamaska and St. François rivers (5.2–9.7 pg L^{-1} h^{-1}, Fig. 3). However, DGM production rates in the three macrophyte beds tended to be lower than in the interface site (8.4–15.7 pg L^{-1} h^{-1}) as well as than in St. Pierre Lake (Anse du Fort, 4.0–18.0 pg L^{-1} h^{-1}). No clear diurnal pattern in DGM production could be noticed in macrophyte beds and in macrophyte-free sites (Fig. 3).

A positive relationship between DGM concentrations measured throughout the day and cumulative PAR was observed in all sites (Table 3). Although some of these relationships did not remain significant after the Bonferroni correction (Table 3), overall they suggest that photoreduction is an important mechanism in the control of DGM production even in environments where light penetration is limited.

In all sites in the BSF wetland, as well as in the St. François River, DGM concentrations were also significantly correlated with DOCF at $p = 0.05$ level (Table 3). Losses in DOCF under sunlight have been suggested as a proxy to the formation of photoreactive intermediates that participate in the reduction of Hg(II) (Garcia et al., 2005a).

In three sites, a peak in DGM production was observed in the first hour following sunrise (Fig. 3). DGM production rates at sunrise ranged from 4.8 to 110 pg L^{-1} h^{-1} (Fig. 3) and were in general higher than rates observed during daytime in the different sites (range between 3.9 and 16.4 pg L^{-1} h^{-1}). In *N. variegatum* bed, and in the Yamaska and St. François rivers, the peak was particularly high relative to other periods of the day. Likewise, Amyot et al. (2001) observed very high DGM levels at sunrise in waters of the BSF wetland. These findings are in agreement with those of Poissant et al. (2004), who reported a daytime bimodality in the emission flux of Hg(0) over the BSF, with a peak in early morning and again around midday. A similar pattern was observed by Lindberg et al. (2002) over emergent macrophytes in a Florida wetland.

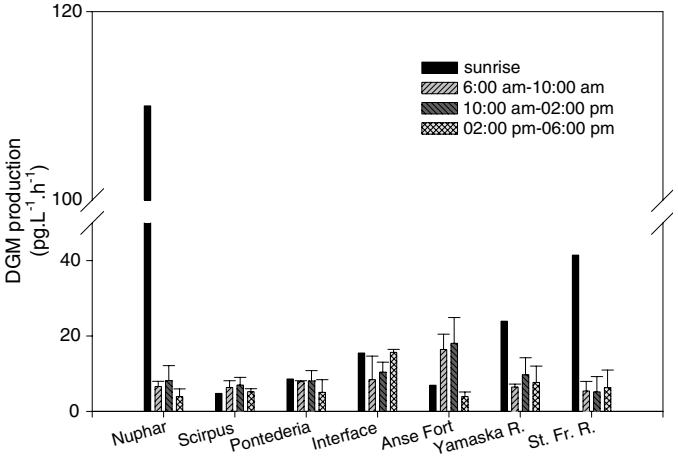

Fig. 3. Average net DGM production rates at different periods of the day estimated from in situ incubation of water from macrophyte beds and from macrophyte-free sites in the Bay St. François, as well as from adjacent areas during summer 2002. Error bars correspond to SD of three to six samples.

Table 3
Pearson's coefficient of correlation (r) between diurnal variations in DGM concentration and DOCF or cumulative PAR, observed during the summer 2002 in water from macrophyte beds (*Scirpus* spp, *P. cordata*, *N. variegatum*) and from macrophyte-free areas in the Bay St. François (interface site); in the Yamaska and in the St. François River, and in the Lake St. Pierre (Anse du Fort)

	DGM versus DOCF		DGM versus cumulative PAR	
	r	p	r	p
Scirpus spp.	0.64	0.0106	0.72	0.0008*
Pontederia cordata	0.59	0.0418	0.84	0.0007*
Nuphar variegatum	0.54	0.0308	0.63	0.0166
Interface site	0.92	0.0000*	0.84	0.0001*
Anse du Fort	0.24	0.391	0.08	0.771
Yamaska River	0.79	0.0013*	0.85	0.0003*
St. François River	0.38	0.16	0.51	0.0501

* Significant correlations at $p = 0.0036$ level, obtained after the Bonferroni correction for multiple analyses.

To further investigate the sunrise peak in DGM production, water from the open area of the BSF was incubated for a period of 4 h, starting 30 min before sunrise. DGM concentration and production rate were then measured and estimated approximately each 15–20 min (Fig. 4). Immediately after sunrise, an important peak in DGM production was observed (187 pg L^{-1} h^{-1}), followed by a sharp decrease. Around 1 h after the onset of sunlight exposure, a plateau in DGM production rates was reached (7–12 pg L^{-1} h^{-1}). These results suggest an accumulation of substrate available for photoreduction during the night, which can be rapidly depleted after sunrise through photoreduction. This substrate (or the intermediates involved in the photoreduction) seems to be photoreactive even under low sunlight radiation (<15 kJ m^{-2}). Amyot et al. (1997) have also indicated that the pool of photoreducible substrate could be replenished during the night. Indeed, low DGM concentrations during the night or in dark conditions observed in this study and in the Florida Everglades (Krabbenhoft et al., 1998) suggest that DGM net production in wetlands ceases in the absence of sunlight. Alternatively, it could be hypothesized that, in the early morning, photoproduced oxidants have not yet built up to their steady-state levels, which contributes to the abnormal higher levels of DGM at this period of the day.

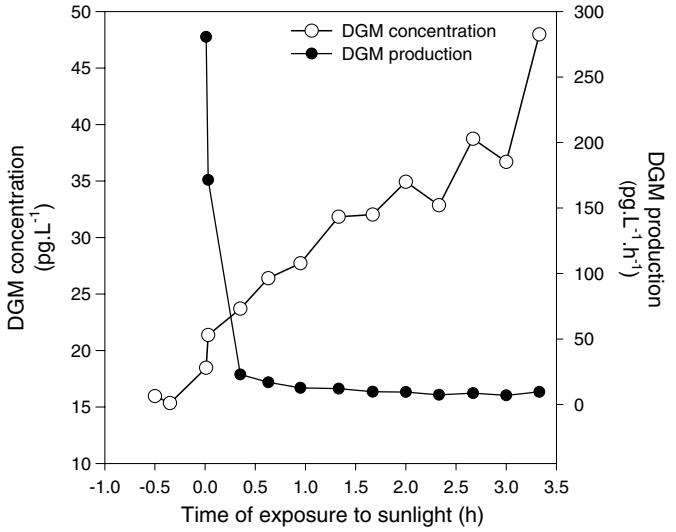

Fig. 4. DGM concentrations and net production rates in water from a macrophyte-free site within the Bay St. François incubated for a period of 4 h, from 30 min before sunrise during the summer 2002.

3.3. Seasonal variations in DGM depth profiles

To investigate the effects of the presence of macrophytes on the DGM distribution throughout the water column, seasonal variations in DGM in *C. demersum* bed were compared with those observed in the open water site (Fig. 5). *C. demersum* was chosen among the most abundant species in the BSF because, being a submerged macrophyte, it was expected to interact more actively within the water column than emerged or floating plants. Additionally, water levels in *C. demersum* bed tended to be higher than in other macrophyte beds, where water levels as low as 20 cm were observed. It should be noted, however, that the *C. demersum* bed height was quite variable from one season to another, corresponding to 10, 50, 95, and 60% of the water column height in spring, summer, fall and winter, respectively. Given this unstable environment, a high spatial resolution in depth profiles was required in order to verify the impacts of macrophytes on Hg redox chemistry. Such a resolution was achieved by measuring DGM and other physico-chemical variables each 10–20 cm (Figs. 5 and 6).

Among-season variations in DGM depth profiles were observed in the open water site and in *C. demersum* bed (Fig. 5). Seasonal variations in total Hg and in total dissolved Hg (Fig. 5), as well as in DOC (Fig. 6) concentrations were less noticeable. DGM concentrations during the spring (Fig. 5A) were intermediate in both sites. The highest DGM concentrations throughout the water column in the open area were observed in summer (Fig. 5B), whereas in the macrophyte bed DGM was the highest in fall (Fig. 5C, ANOVA-LSD, $p < 0.0001$). As expected, in both sites the lowest DGM levels along the water column occurred in November (Fig. 5D), under a 15-cm ice cover. In all seasons except in summer, average DGM values in the water column did not differ significantly between *C. demersum* bed and the open water (ANOVA, $p > 0.05$). Indeed, a similar DGM depth profile was observed in both sites, as indicated by the significant correlations between DGM in open area and in *C. demersum* bed at similar depths in spring, fall and winter ($r = 0.78$, 0.91, and 0.92, respectively, $p < 0.05$).

In spring, DGM distribution along the water column tended to be uniform in the macrophyte bed and in the open water sites (Fig. 5A). Macrophytes were observed only in the bottom and both sites were quite homogeneous in terms of incident light intensity and water chemistry (Fig. 6A). Snowmelt contributed to a significant increase in water levels, which were between 30 and 125% higher relative to other seasons.

In summer (Fig. 5B), average DGM concentration in the water column tended to be significantly higher in the open area than in the macrophyte bed (t test, $p < 0.05$). Light penetration in the whole water column likely favored DGM photoproduction in the macrophyte-free site (Fig. 5B). In *C. demersum* bed, the presence of macrophytes, even if they occupied only half of the water column height, restrained light penetration and may have interfered with DGM production. It should be noted that, in summer, contrary to the other sampling periods, water from the two sites was not collected the same day. Although intensity of incident light at the surface was comparable in the two sampling days, wind speed in the open water area (1.9–4.7 m s^{-1}) was much lower than in *C. demersum* bed (7.2–8.3 m s^{-1}). Thus, higher evasion rates in the macrophyte bed could also explain the lower DGM levels observed in this site compared to the macrophyte-free area.

In fall, a stratification of the water column was noted and the two sites were in general comparable in terms of water physical and chemical characteristics (Fig. 6C), except for light penetration. In *C. demersum* bed, light penetration was much lower than in the macrophyte-free area (Fig. 5C), likely due to the presence of *C. demersum* over the entire water column. DGM and total Hg concentrations in the macrophyte-free site did not differ significantly from levels observed in the macrophyte bed (t test, $p > 0.05$; Fig. 5C). The observed DGM concentrations in *C. demersum* bed in fall were the highest among all seasons. It was also observed that DGM concentrations tended to increase towards the anoxic bottom. It seems that at this period DGM production was controlled by two different processes: at the upper portion of the water column, DGM formation was predominantly photo-mediated, whereas from the middle to the bottom portion reducing conditions stimulated the production of Hg(0).

The lowest DGM concentrations in the water column observed in November (Fig. 5D) are likely the result of a combination of low water temperature (Fig. 6D) and light penetration due to the presence of ice and snow. In both sites, a peak in DGM was observed near the bottom, indicating the presence of reducing conditions, as corroborated by the dissolved oxygen depth profiles (Fig. 6D). Additionally, DGM concentration in the *C. demersum* bed was

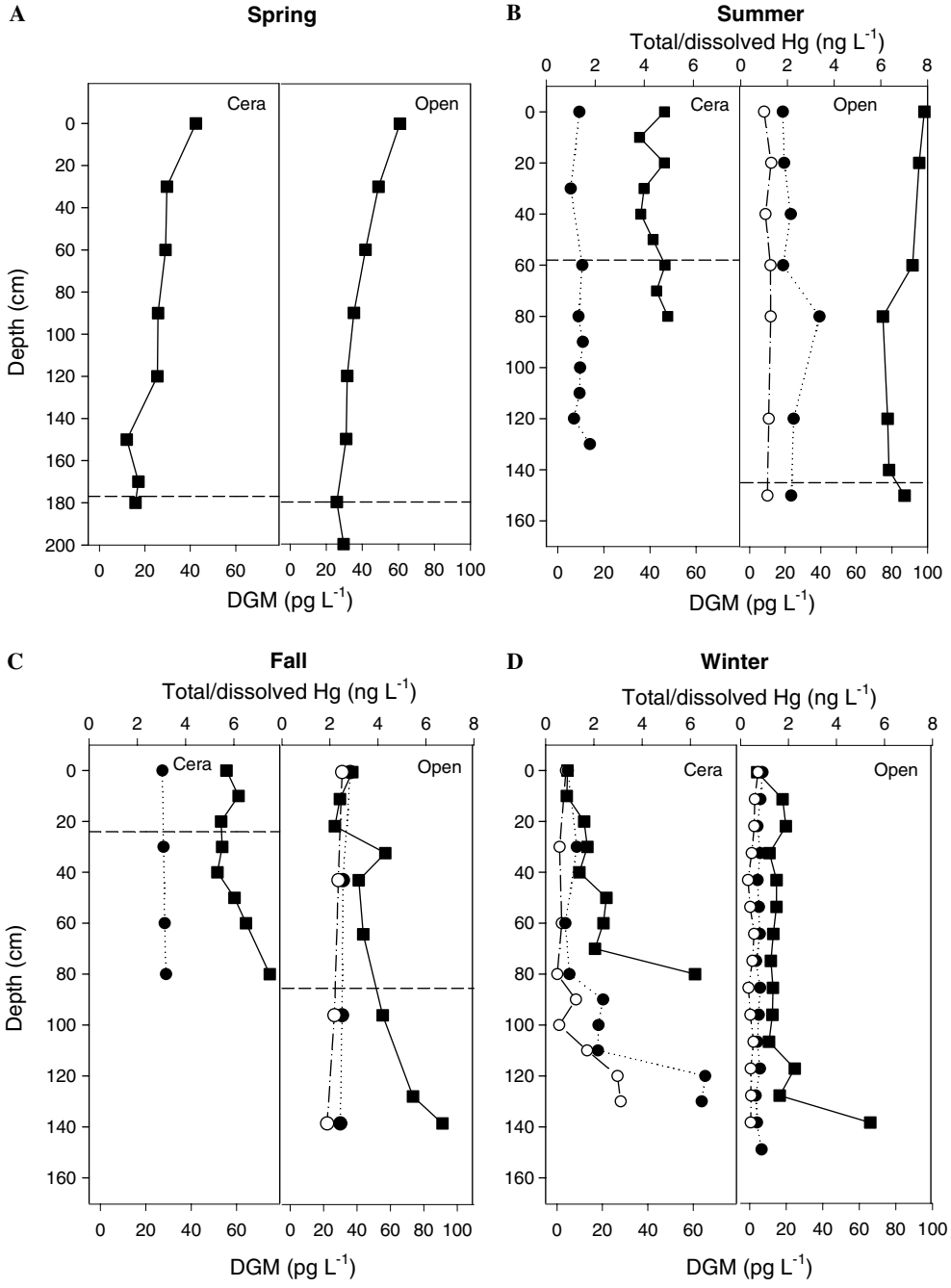

Fig. 5. Seasonal variations in DGM (black square and solid line), total Hg (black circle and dotted line) and dissolved Hg (white circle and dash-dotted line) depth profiles in *Ceratophyllum demersum* bed (Cera) and in a macrophyte-free site (open), in the Bay St. François wetland. Dashed horizontal lines correspond to the depth of 1% of incident light.

significantly correlated with total and dissolved Hg ($r = 0.70$, $p < 0.05$). In this macrophyte bed, concentrations of total Hg and DGM tended to increase from the middle to the bottom of the water column (Fig. 5D), which corresponded to the portion occupied by decomposing *C. demersum*. It seems therefore that, besides anoxic sediment, macrophytes in decomposition could also release reducible Hg in the adjacent waters.

In this study, DGM concentrations in each site, all seasons confounded, were significantly correlated with water temperature, as well as with iron and chloride concentrations (Table 4). Seasonal variations in light intensity and in water temperature are known to influence DGM photoproduction and saturation (Amyot et al., 1994; Vette et al., 2002). Water temperature may also stimulate biological reduction of Hg(II) (Mason et al., 1995; Poulain et al., 2004). In surface waters of a temperate estuary, for example, Rolfhus and Fitzgerald (2001) observed higher DGM concentrations and saturation during the warmer months.

It has been shown that iron species may induce photochemical reduction of Hg(II) (Zhang and Lindberg, 2001), which can explain the positive correlation between

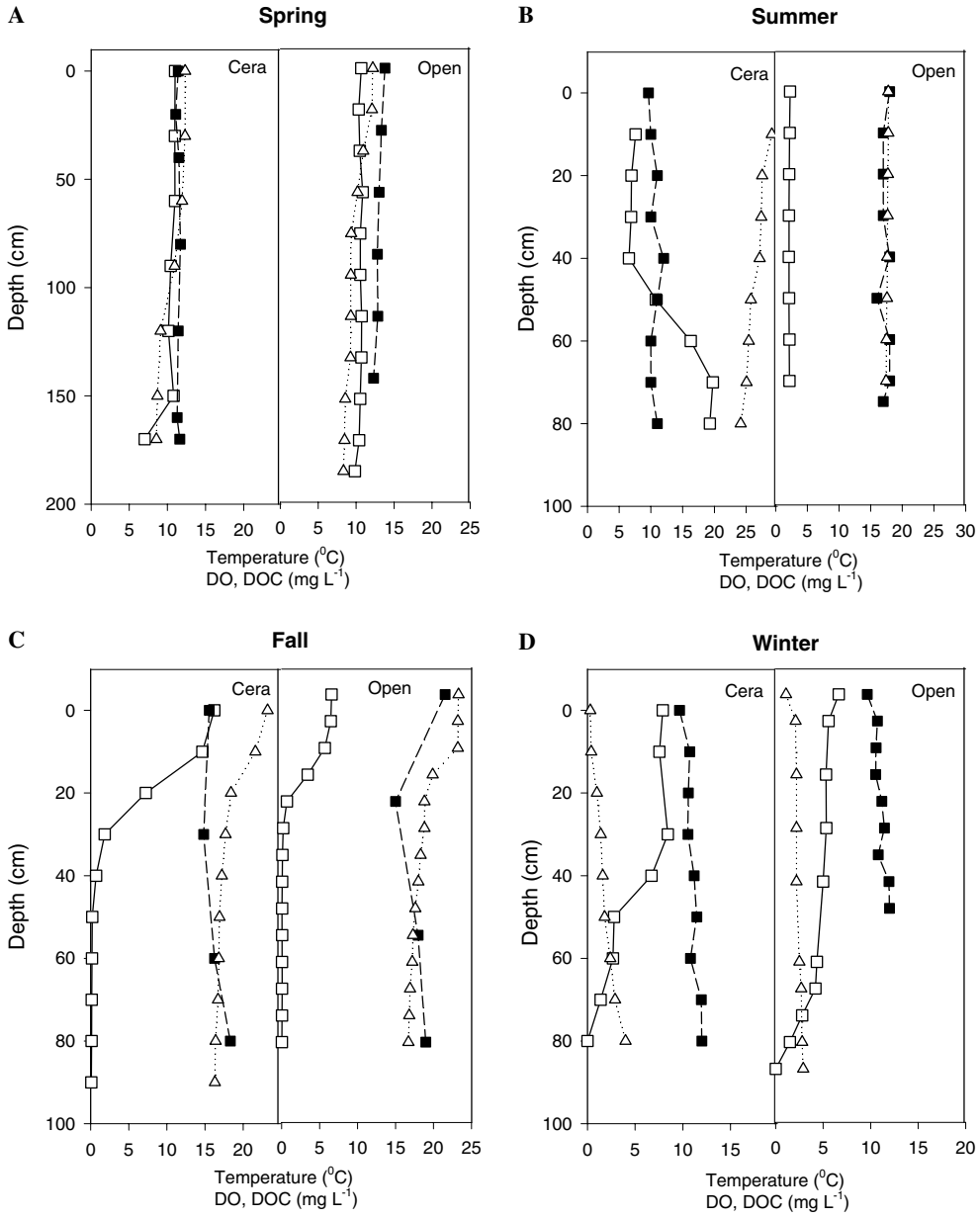

Fig. 6. Seasonal variations in depth profiles of temperature (white triangle and dotted line), dissolved oxygen (DO, white square and solid line), and dissolved organic carbon (DOC, black square and dashed line) in waters of *Ceratophyllum demersum* bed (Cera) and of a macrophyte-free site (open).

DGM and iron observed here. The negative correlation between DGM and Cl^- is in agreement with results indicating that chloride can favor oxidation of Hg(0) (Lalonde et al., 2001). DGM in the open water and in *C. demersum* bed also showed a significant positive correlation, at a significance level of 0.05, with DOC and percent of light penetration in the water column, and was negatively correlated with dissolved oxygen (Table 4). However, following the use of Bonferroni correction these correlations only remained significant in the macrophyte-free site.

Temperature and iron concentrations were the variables retained in the stepwise multiple regression models developed for *C. demersum* bed and the open water site (Table 5), which explained 68 and 75%, respectively, of the variance in DGM.

3.4. DGM production in the water–sediment boundary

In the *C. demersum* bed and the open water site, vertical distribution of DGM was not homogenous throughout the water column (Fig. 5). In general, DGM concentrations tended to increase near the bottom. Such an increase was particularly accentuated in fall and in winter, and was not related to photochemical process, given that no light reached the bottom. In both sites, average DGM concentration near the bottom under anoxic conditions (67.1 ± 13.4 pg L^{-1}) was significantly higher than under oxic conditions (27.7 ± 4.5 pg L^{-1}), or than mean DGM observed in the surface (37.4 ± 8.4 pg L^{-1}). Similarly, a high DGM concentration has been reported at the sediment–water interface in the anoxic hypolimnion of a boreal

Table 4
Pearson's coefficient of correlation (r) between DGM concentration and physical and chemical variables along the water column from *Ceratophyllum demersum* bed and from a macrophyte-free area in the Bay St. François sampled in fall and winter 2002, and in spring and summer 2003

	C. demersum bed		Macrophyte-free site	
	r	p	r	p
Water temperature	0.61	0.0000*	0.70	0.0000*
% of incident light	0.29	0.0149	0.55	0.0006*
Dissolved oxygen	−0.24	0.0277	−0.53	0.0003*
DOC	0.27	0.0182	0.73	0.0000*
Cl	−0.49	0.0026*	−0.72	0.0000*
Fe	0.58	0.0014*	0.81	0.0000*

* Significant correlations at $p = 0.0042$ level, obtained after the Bonferroni correction for multiple analyses.

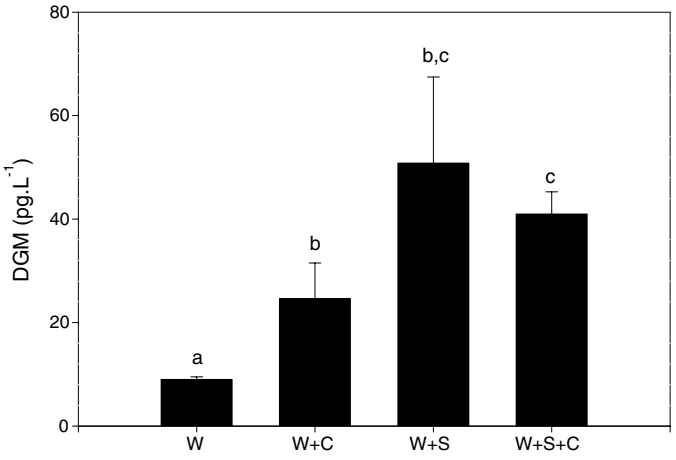

Fig. 7. DGM concentrations in anoxic water from the Bay St. François wetland measured following a 12-h incubation period in the dark. Treatments consisted of water (W), water plus chloroform at a final concentration of 1.6% (W + C), water containing 100 g of anoxic sediment from the Bay St. François (W + S), and water plus 100 g of anoxic sediment plus chloroform at a final concentration of 1.6% (W + S + C). Error bars correspond to SD of three replicates, except for the treatment W + S + C, where one of the replicates was discarded due to analytical problems. Letters on top of the bars indicate between-treatment differences: bars with different letters are significantly different (ANOVA-LSD, $p < 0.05$).

lake (Poulain et al., 2004). At the end of fall, bacterial decomposition of the organic matter leads to oxygen depletion near the bottom that can persist over the winter. Reducible Hg could then be released from sediments or, in the macophyte beds, from plant decomposition. Subsequently, microbial activity in the sediments or adjacent waters could be responsible for the observed peak in DGM (Baldi, 1997). Alternatively, the presence of humic acids could promote DGM production under anoxic conditions (Alberts et al., 1974; Allard and Arsenie, 1991), or both processes could occur simultaneously.

To further investigate the role of biotic and abiotic production of DGM at the sediment–water interface, an incubation experiment was carried on in the dark using anoxic water alone, and anoxic water plus sediment. Both treatments were incubated with and without the addition of chloroform, an inhibitor of bacterial activity (Fig. 7). At the end of the incubation period, DGM concentration in the treatment with water plus sediment (50.8 ± 16.7 pg L^{-1}) was 5.5 times higher than DGM in the treatment containing water alone (9.0 ± 0.5 pg L^{-1}). The higher DGM concentrations observed in the presence of sediment could result from diffusion to water of DGM found in the sediment prior the beginning of the incubation. Alternatively, biotic or abiotic Hg(II) reduction could have been stimulated in the presence of anoxic sediment. The addition of chloroform to the water provoked an increase in DGM to 24.6 ± 6.9 pg L^{-1} (Fig. 7). This variation in DGM can be attributed either to a contamination with DGM in the chloroform solution or with Hg(II) that was subsequently reduced. However, in the treatment containing water and sediment, addition of chloroform did not result in an increase in DGM levels (Fig. 7). Overall, this experiment suggested that sediments can be an important source of DGM and/or reducible Hg to adjacent waters. It was not clear, however, if biotic or abiotic reduction of Hg(II) rather than DGM diffusion was responsible for the observed increase in DGM in the water containing sediment. In a study conducted in anoxic tropical environments, Peretyazhko (2002) observed that the formation of Hg(0) was mainly biologically driven, but abiotic reduction of Hg by Fe(II) adsorbed to the particulate matter was also reported.

3.5. The role of Ceratophyllum demersum on DGM production

In order to investigate the role of submerged macrophytes in the production of DGM, *C. demersum* was incubated in filtered water from the BSF. Because submerged portions of macrophytes provide extensive substrata for epiphytic algae, which can also influence Hg redox, the

Table 5
Multiple regression models for DGM concentrations in water from *Ceratophyllum demersum* bed and from macrophyte-free sites

C. demersum bed	$\text{Log(DGM)} = 2.66(\pm0.14) + 0.042(\pm0.009)$ temperature$^{***} + 0.29\ (\pm0.08)$ log(Fe)** $F = 24.6$, $R^2 = 0.68$, $\text{SE}_{\text{est}} = 0.44$, $p = 0.0000$, $N = 27$
Macrophyte-free site	$\text{Log(DGM)} = 3.09(\pm0.22) + 0.051(\pm0.018)$ temperature$^{*} + 0.73\ (\pm0.21)$ log(Fe)** $F = 33.4$, $R^2 = 0.75$, $\text{SE}_{\text{est}} = 0.45$, $p = 0.0000$, $N = 26$

* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

experiments were conducted using *C. demersum* with and without associated epiphytes, as well as isolated epiphytes (Fig. 8A). Under sunlight, the presence of macrophytes and/or epiphytes interfered with the formation of DGM. Average DGM production rate normalized for PAR in water incubated with *C. demersum* or epiphytes was approximately half of the production observed in water alone (Fig. 8A). Doubling the amount of macrophytes or removing epiphytes associated to *C. demersum* did not result in significant variations in the rates of DGM formation (ANOVA, $p > 0.05$). Epiphytes alone yielded a DGM production rate similar to the ones observed in the presence of macrophytes. In all treatments, DGM variations observed in dark controls during the incubation period were not significant. Overall the results of the incubation experiments were in agreement with observations in the field, indicating decreased DGM concentrations in a macrophyte populated wetland relative to open water in the summer.

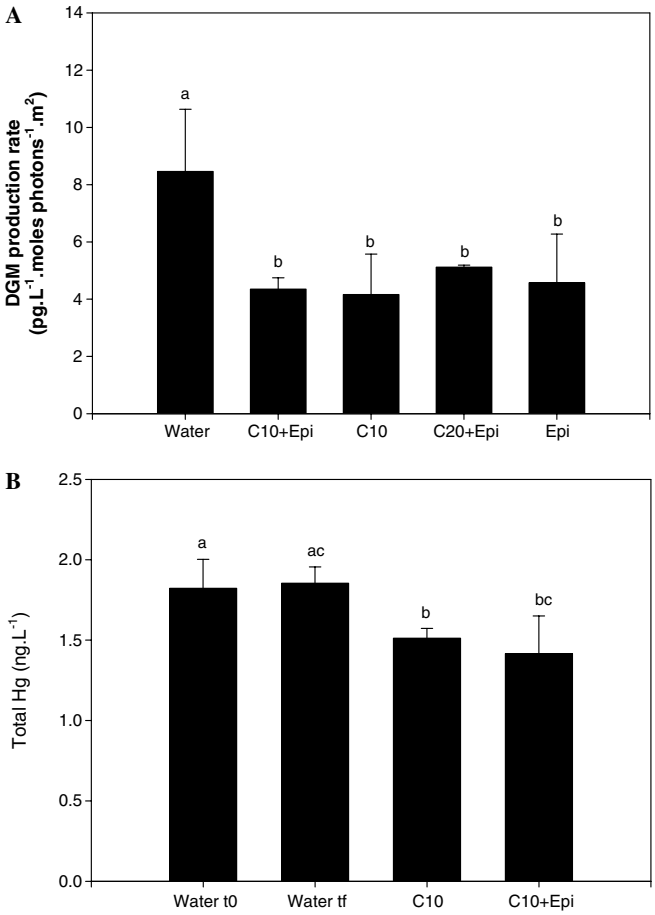

Fig. 8. (A) DGM net production rates normalized for PAR radiation in water from the Bay St. François wetland estimated following 3- or 4-h incubation periods under natural sunlight. Treatments consisted of: water alone, water plus *Ceratophyllum demersum* at concentrations of 10 and 20 g L^{-1} and associated epiphytes (C10 + Epi and C20 + Epi, respectively), water plus *C. demersum* at a concentration of 10 g L^{-1} (C10), and water plus epiphytes (epi). Error bars correspond to SD of three to eight replicates. Letters on top of the bars indicate between-treatment differences: bars with different letters are significantly different (ANOVA-LSD, $p < 0.05$). (B) Variations in total Hg concentrations in water from the Bay St. François wetland incubated under natural sunlight for 3–4 h. Water t_0 and t_f indicates total Hg levels in water prior and after the incubation. Error bars correspond to SD of three to five replicates. Letters on top of the bars indicate between-treatment differences: bars with different letters are significantly different (ANOVA-LSD, $p < 0.05$).

Several hypotheses can explain the role of macrophytes and epiphytes on DGM production. First, they could affect DGM photoproduction by limiting light penetration. Second, submerged macrophytes would be able to adsorb and/or absorb Hg(II) and consequently could limit Hg availability for photoreduction. It has been shown that, in contrast to floating plants, submerged species tend to act as accumulators rather than sources of trace metals, including Hg (St-Cyr and Campbell, 1994; Thompson-Roberts et al., 1999). Third, macrophytes could absorb newly produced Hg(0). Indeed, being neutral, Hg(0) could cross cellular membranes passively. Finally, macrophytes and epiphytes could participate in the oxidation of Hg(0) to Hg(II) through the liberation of oxidizing agents.

To investigate if macrophytes were able to adsorb and/or absorb Hg(II) and to limit Hg(II) reduction, total Hg concentrations in the water were measured at the onset and at the end of incubation experiments (Fig. 8B). Total Hg levels in the water alone remained approximately constant throughout the incubation (~1.8 ng L^{-1}), indicating that Hg was not adsorbed to the quartz bottles wall. In the presence of *C. demersum* with or without associated epiphytes, average total Hg concentration at the end of the incubation period had decreased by ~20% (Fig. 8B). This finding suggests that the hypothesis of adsorption and/or absorption of Hg(II) by *C. demersum* is plausible. It does not exclude, however, the participation of *C. demersum* and associated epiphytes in the oxidation of Hg(0).

4. Summary and conclusions

The results reported here suggest that processes involved in the production and distribution of DGM in wetland waters largely vary both in time and space. In this context, the merit of this study consisted in the integration of both kinds of variability at different scales, contrary to most studies focusing on Hg(II) reduction. Potential physical and chemical factors affecting the production and distribution of DGM in the Bay St. François wetland at different seasons are summarized in Fig. 9. In this diagram, the thickness of arrows indicates the qualitative importance of different processes affecting the redox chemistry of mercury according to our knowledge.

During the spring, when water levels are the highest and macrophytes are almost absent (Fig. 9A), sunlight driven processes in surface waters control the redox chemistry of Hg. This photoproduction of DGM is associated to water temperature and tends to be more important under the presence of iron, DOC and their intermediates. In the oxic waters near the bottom, where light penetration is limited, sediment or biotic reduction of Hg(II) could be the main sources of DGM.

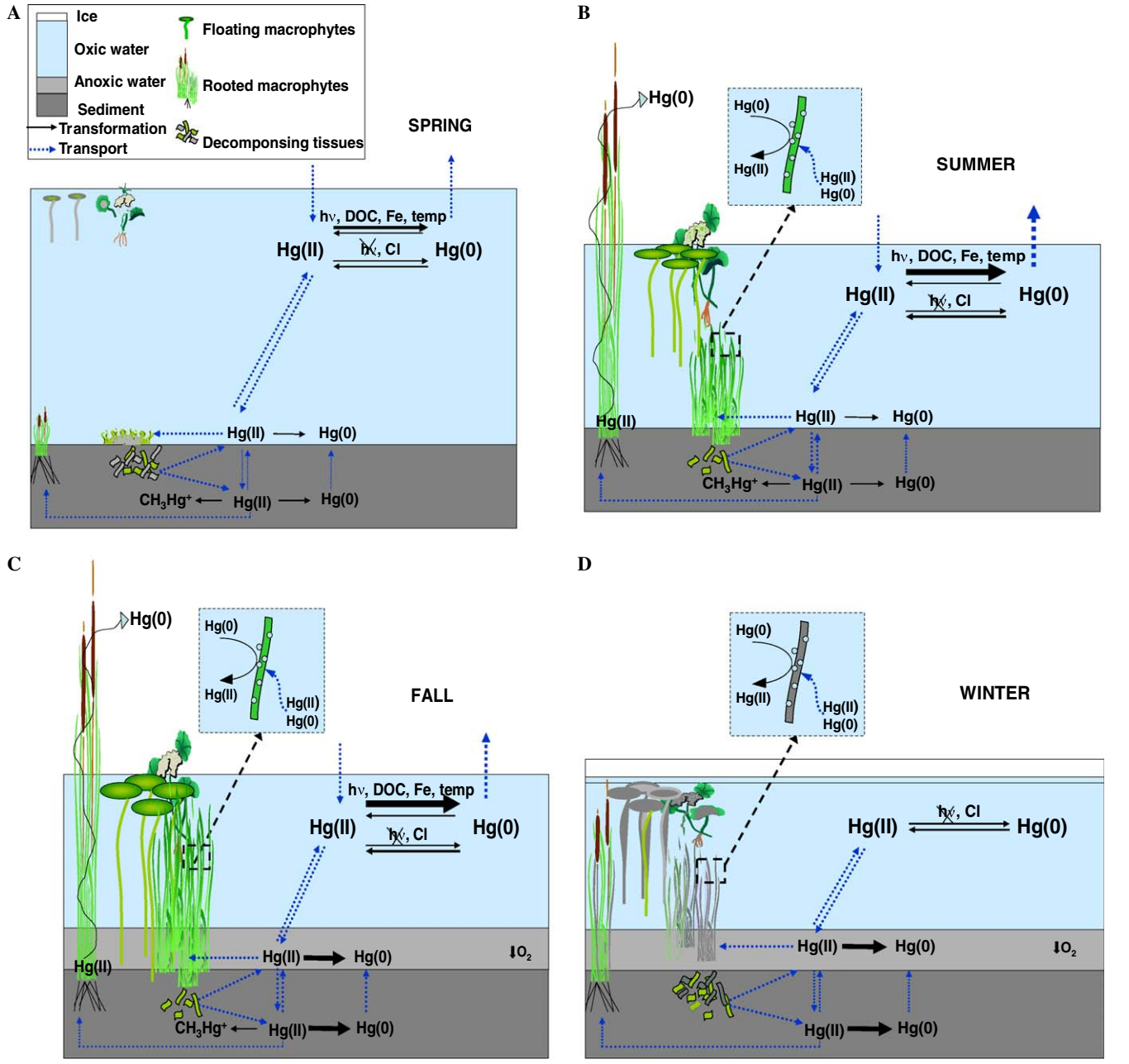

Fig. 9. Diagrammatic representation of potential physical and chemical factors affecting DGM distribution and production in the Bay St. François wetland at different seasons. Variations in arrows thickness indicate differences in the relative importance of Hg transport or transformation. Inset shows processes involving macrophyte and associated epiphytes.

During the summer (Fig. 9B), under higher solar radiation and water temperature, the production of DGM in the relatively shallow waters of the BSF is at its maximum, and Hg(0) evasion is also the highest (Poissant et al., 2004). At this season, approximately 90% of the BSF wetland surface is occupied by macrophytes and associated epiphytes, which appear to be important sites of adsorption/absorption of Hg(II) and likely of DGM. As a consequence, transpiration of DGM from emergent macrophytes, as reported by Lindberg et al. (2002), may be an important path leading to the depletion of Hg from the water. In contrast, the role of macrophytes in the oxidation of Hg(0), albeit not demonstrated, cannot be ruled out (Figs. 9B–D, inset). Furthermore, in summer, as well as in fall, the presence of dense macrophyte beds can affect DGM production and evasion by sheltering from light, wind and water current (Figs. 9B and C).

Factors controlling the redox chemistry of mercury in surface waters during the autumn (Fig. 9C) are essentially the same as the ones observed during the summer. Near the bottom, however, in the anoxic layer generated by the decomposition of macrophytes, the reduction of Hg(II) is

highly promoted. In addition, sediments and decomposing macrophytes seem to release DGM and/or reducible Hg to bottom waters.

In winter, low light penetration due to the presence of an ice layer and snow, together with low water temperature seemingly result in decreased levels of DGM in the upper part of the water column (Fig. 9D). In the beginning of the winter, even if macrophytes still occupy 60% of the water column (Fig. 9D), their shelter effect is annulled by the ice and snow cover. In the bottom, as observed in the autumn, production of DGM is mainly determined by anoxic conditions.

In any season, oxidation and reduction of mercury occur simultaneously, with DGM formation prevailing over Hg(0) oxidation under sunlight. During the night or under the presence of chloride, Hg(0) oxidation overcomes Hg(II) reduction, reducing the pool of DGM. Methylation processes, which are known to occur in low oxygen zones at warm periods, may also potentially decrease the pool of DGM in wetlands by affecting the availability of inorganic Hg to reduction processes.

In general, our results indicate that the effects of macrophytes are limited to immediately adjacent surface waters. In fact, in all seasons but summer, DGM levels in surface waters from macrophyte beds are comparable to DGM levels in macrophyte-free sites. Actually, differences in DGM between macrophyte beds and sites devoid of plants tend to be less important than observed differences in DGM from surface and bottom waters.

A previous study has shown that the BSF wetland constitutes a source of Hg(0) to the atmosphere (Poissant et al., 2004). These findings are in agreement with the higher DGM levels observed in the BSF waters compared to other wetlands (Table 2) during the summer, with possible implications in the availability of Hg(II) to methylation process. Extrapolations to other periods of the year, however, should be perceived with caution. As indicated here, several complementary and sometimes opposite mechanisms can take part in the DGM production and distribution, and the relative importance of these mechanisms vary seasonally.

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