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The influence of anthropogenic disturbances and watershed morphological characteristics on Hg dynamics in Northern Quebec large boreal lakes

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Abstract. Mercury (Hg) dynamics in the boreal environment have been a subject of concern in recent decades, due to the exposure of local populations to the contaminant. Land use, because of its impact on mercury inputs, has been highlighted as a key player in the sources and eventual concentrations of the heavy metal. In order to evaluate the impact of watershed disturbances on Hg dynamics in frequently fished, large boreal lakes, we studied sediment cores retrieved at the focal point of eight large lakes of Québec (Canada), six with watersheds affected by land uses such as logging and/or mining, and two with pristine watersheds, considered as reference lakes. Using a Geographical Information System (GIS), we correlated the recent evolution of land uses (e.g., logging and mining activities) and morphological characteristics of the watershed (e.g., mean slope of the drainage area, vegetation cover) to total Hg concentrations (THg) in sedimentary records. In each core, THg gradually increased over recent years with maximum values between 70 and 370 ng/g, the lowest mercury concentrations corresponding to the pristine lake cores. The Hg Anthropogenic Sedimentary Enrichment Factor (ASEF) values range from 2 to 15. Surprisingly, we noticed that the presence of intense land uses in the watershed does not necessarily correspond to noticeable increases of THg in lake sediments, beyond the normal increment that can be attributed to Hg atmospheric deposition since the beginning of the industrial era. Rather, the terrestrial Hg inputs of boreal lakes appear to be influenced by watershed characteristics such as mean slopes and vegetation cover.

Keywords: Hg; boreal forest; lake sediments; organic matter; GIS approach

1. Introduction

Mercury (Hg) dynamics in boreal lakes are an ongoing topic of serious concern, as human populations are exposed to the contaminant through fish consumption. Natural sources, including re-emissions from top soil and vegetation as well as volatilization from water surfaces and volcanoes, represent more than half of total Hg emissions in the global atmospheric mercury

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budget (Barja *et al*. 2001). However, over the last century, increased anthropogenic emissions of Hg to the atmosphere had led to significant increases of Hg inputs to boreal lake ecosystems (Pacyna *et al*. 2006). Wind currents then transport Hg over long distances from point source emissions (Fitzgerald *et al*. 1998, Pacyna *et al*. 2006) so that even remote areas can be contaminated by dry and wet depositions of atmospheric, anthropogenic Hg. Increases in Hg deposits over time have thus often been reported in sediments of pristine boreal lakes (Lucotte *et al*. 1995, Rognerud and Fjeld 2001). In lakes with large watersheds relative to the size of their water surfaces, processes underlying the transfer of Hg from the terrestrial to the aquatic systems also influence the presence of the heavy metal in the aquatic system (Schelker *et al*. 2011, Teisserenc *et al*. 2011). The presence of wetlands in lake watersheds is recognized to reduce THg in outflow water, though enhancing Hg methylation and thus Hg levels in fish (Greenfield *et al*. 2001, Galloway and Branfireun 2004, Zelenkova and Vinokurova 2008, Riva-Murray *et al*. 2011). Transfers of terrestrial Hg to aquatic systems are also linked to hydrology, land cover, soil type and both the character and availability of binding ligands (Hurley *et al*. 1995, Babiarz *et al*. 1998, Branfireum and Roulet 2002, Selvediran *et al*. 2008, Zelenkora and Vinokurova 2008). Significant Hg inputs from the watersheds are due to high runoff periods, responsible for enhancing the mobility of Hg, linked to both particulate and dissolved organic matter (POM and DOM respectively) (Shanley *et al*. 2002, Mast *et al*. 2005). In Northern Quebec, lake watersheds are also frequently affected by land uses such as logging, mining, road construction and urbanization. These types of activities induce changes in the Hg dynamics of the watershed and can be responsible for additional amounts of Hg reaching the lakes (Porvari *et al*. 2003, Domagalski *et al*. 2004, Garcia and Carignan 2005, Bishop *et al*. 2009, Sampaio da Silva *et al*. 2009, Bergström *et al*. 2011, Petit *et al*. 2011). However all mentioned studies have focused on small lake (0.4 to 1.3 km^2) ecosystems while large lake ecosystems have been ignored despite the fact that they represent the vast majority of systems exploited at a socio-economico-environmental level (fisheries, mining and logging activities). Moreover, small lakes only allow the study of one process one at a time whereas large lake ecosystems integrate a sum of various processes and the inertia of the system. Sediments retrieved in the focal region of the lake constitute a powerful tool to reconstruct the past events that occurred both in the watershed and in the lake itself and to evaluate the corresponding historical Hg inputs.

In order to identify the impact of watershed disturbances on the lakes mercury inputs, we retrieved sediment cores at the deepest section of six large boreal lakes (15 to 210 km^2) with watersheds affected by specific factors including logging, mining and the combination thereof. In addition, two large lakes (22 and 36 km^2) with undisturbed watersheds were sampled as reference lakes. To complete the characterization of the lake environment, we used Geographic Information Systems (GIS) to describe morphological characteristics of the watersheds and to integrate such factors into the analysis. GIS is a powerful tool for analyzing the influence of parameters such as slope, land use, and vegetation cover of watersheds (Longley *et al*. 2005, Beaulne *et al*. 2012) which are recognized to play a role on Hg dynamics in the environment (Börjesson and Torstensson 2000). In this paper, we combined the study of sediment data (C/N atomic ratios and THg) with watershed characteristics to identify the impact of anthropogenic watershed disturbances on Hg dynamics. By their integrative character, sediment cores may be used to reconstruct historical Hg inputs to large boreal lakes over time and to provide a long-term perspective of human-induced changes in Hg dynamics. The combined use of geochemistry and GIS is a novel approach, which allows a comprehensive study of large boreal ecosystems and of the global interactions of a given aquatic ecosystem with its watershed.

2. Material and methods

2.1 Study sites

Large lakes Matagami, Ouescapis, Rodayer, Waswanipi, Dickson and Chibougamau are located in the administrative region of Northern Quebec (Fig. 1). Matagami Lake (210 km^2) lies in a swampy region and represents the confluence point of the Allard, Bell, Gouault and Waswanipi rivers. Disturbances in its watershed include road constructions, logging, mining and golf activities. Mining activities started at the beginning of the fifties and are currently ongoing. The principal mineral deposits exploited are zinc, copper, silver and gold. Currently, the mining facility of the Matagami mine can treat approximately 2950 tons of mineral/day. Ouescapis (36 km^2) and Rodayer (22 km^2) lakes are located approximately 70 and 120 km north of Matagami Lake

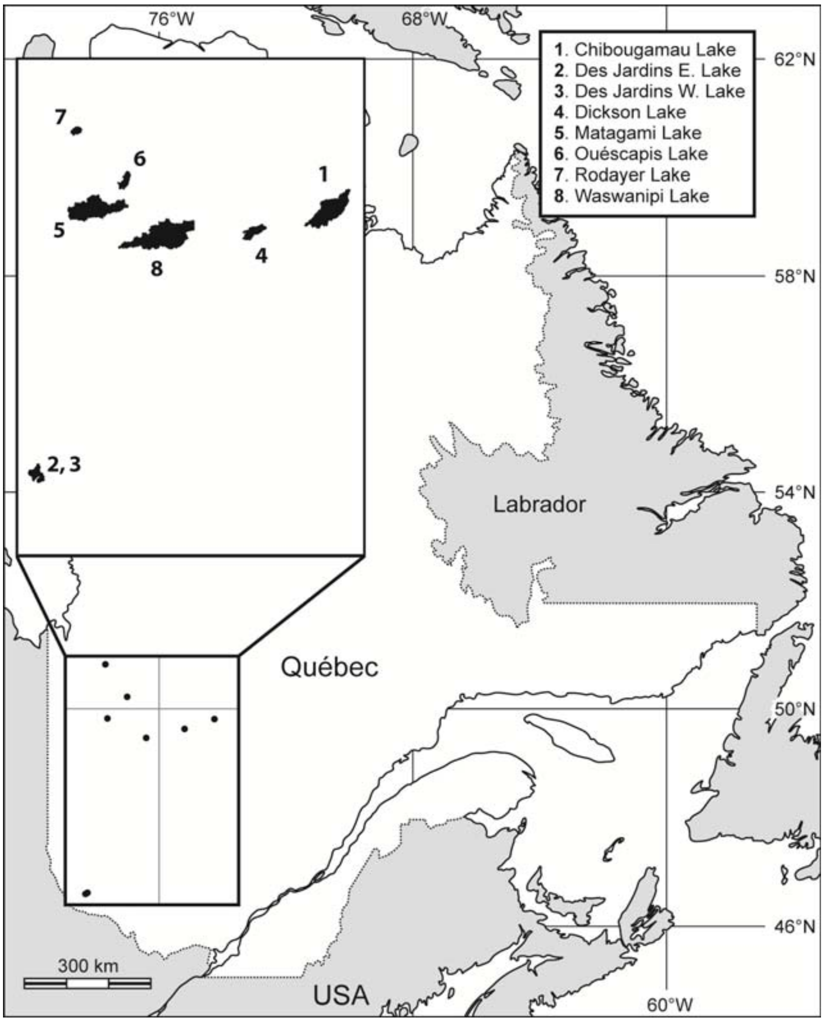

Fig. 1 Localization of the studied lakes in the province of Quebec (Canada)

respectively. Neither lake has been affected by a substantial disturbance in its watershed. Waswanipi Lake (201 km^2) is situated about 100 km south-east from Matagami Lake and linked to Matagami Lake. The watershed of this lake has undergone intense logging activity over the past decades. Chibougamau Lake (201 km^2) is located approximately 10 km south of the town of the same name. This lake is the source of the Chibougamau River and is interspersed with many Matagami Lake by the Waswanipi River. Waswanipi Lake presents a watershed affected by the presence of logging activities, few mining activities (mineral deposits exploited similar to those of Matagami Lake) and gravel roads. Dickson Lake (10 km^2) is located about 180 km south-east from islands, as well as deep and large bays. Intense mining activities have occurred in the watershed of Chibougamau Lake since the fifties and mining companies operated both waste treatment plants and tailing facilities (several large mine tailings lie near its shores containing more than 6.3 megatons of residues). The main mineral deposits exploited were pyrite, pyrrhotite, chalcopyrite, sphalerite and galena (Petit *et al*. 2011). Des Jardins East (10 km^2) and West (5 km^2) lakes are located in the Témiscamingue region (Fig. 1).

These lakes are linked to each other by a small arm (approximately two meters wide and a depth comprised between 20 cm and 80 cm according to the season). Desjardins East Lake flows into Des Jardins West Lake. Des Jardins lakes watershed is covered by mature mixed wood forest. The watershed of Des Jardins East Lake is highly logged as opposed to that of Des Jardins West Lake. Disturbances in the watershed include gravel roads and logging activities. The basic characteristics of each lake studied are presented in Table 1. Due to the pristine character of the watersheds of Lakes Ouescapis and Rodayer, these have been chosen as “reference lakes” whereas the other six lakes of the study are herein identified as “disturbed lakes”.

2.2 Landscape and historical analyses

Landscape characterization was performed with raster satellite images from Landsat 7 satellite imagery with a resolution of 28 m (Natural Resources Canada; http://geogratis.cgdi.gc.ca/ and http://edcsns17.cr.usgs.gov/NewEarthExplorer/). These images were processed using GIS Geographic Resources Analysis Support System (GRASS 6.4; http://grass.fbk.eu/) software to decipher both the morphology and the nature of the vegetation cover of watersheds. We also used the Canadian digital elevation data (scale: 1/50,000), extracted from the hypsographic and hydrographic elements of the National Topographic Data Base (NTDB 2011). For the purposes of our study, the watershed is defined as the land area draining either directly into a lake or into the first lake upstream corresponding to an order 3 watershed level which has been described as the level influencing the most the associated aquatic ecosystem (Magnuson *et al*. 2006, Beaulne *et al*. 2012).

A buffer watershed zone was also delineated as the first kilometer of land around the lake. In order to determine the mean watershed slope and to identify different slope classes (intervals of 2% from 0 to 20%, e.g., 0-2%) within each watershed, the slope of each pixel was calculated. Afterwards, land cover was estimated by applying the Maximum Likelihood Classification (MLC) algorithm modified by Neteler and Mitasova (2008) to the entire set of visible spectral bands. First, each image was subdivided into seven classes based on the spectral reflectance signature. Then the seven classes were reclassified into four classes (water, coniferous forest, mixed forest, > 50% deciduous and unforested) based on on-site validation and eco-forestry maps (scale: 1/20,000; Quebec Forestry Ministry). Historical reconstructions were based on observations coming from satellite images over a 30 year period (1979-2011).

Table 1 Morphological characteristic of the studied lakes. %TWA = percentage of the total watershed area

Lake	Localization lat./long.	Altitude (m)	Lake area (km^2)	Drainage area (km^2)	DA/LA	Mean slope (%)	Year	Water (%TWA)	Coniferous (%TWA)	Mixed forest, deciduous > 50% (%TWA)	Unforested (%TWA)	Number of Mines in the watershed	Major disturbances
Des Jardins	46°39'N 78°15'W	320	15.02	207.39	13.81	5.85	2001	9.62	49.54	32.66	3.57	X	Gr, L
							2004	10.04	66.66	18.46	0.37		
							2010	9.56	40.21	43.36	2.27		
Ouescapis	50°15'N 76°60'W	278	36.41	107.94	2.96	4.84	1979	0.00	87.94	7.01	2.35	X	Gr
							1990	0.00	93.51	1.80	1.80		
							2010	0.02	77.98	5.12	13.98		
Rodayer	50°51'N 77°41'W	249	22.31	57.70	2.59	1.34	1979	1.93	69.59	13.94	3.65	X	Gr
							1990	2.12	80.74	5.33	0.95		
							2010	2.43	81.00	3.27	2.44		
Waswanipi	49°33'N 76°27'W	267	200.69	1483.66	7.39	2.02	1979	1.41	73.51	12.05	7.35	3	Gr, L
							1990	0.65	67.85	5.47	20.38		
							2010	1.36	70.22	7.16	15.62		
Chibougamau	49°50'N 74°13'W	378	201.06	769.87	3.83	4.45	1999	8.68	52.44	18.66	16.31	14	Gr, L, U
							2002	8.76	60.39	21.13	5.82		
							2009	8.61	58.14	19.17	10.18		
Dickson	49°38'N 75°11'W	342	10.00	227.59	22.76	3.23	1979	0.85	64.06	11.63	5.65	1	Gr, L
							1990	1.58	65.36	2.63	12.65		
							2010	1.30	62.77	10.37	7.78		
Matagami	49°50'N 77°37'W	248	209.86	951.36	4.53	2.84	1979	2.15	69.20	12.94	8.72	7	Gr, L, U, Go
							1990	0.24	57.01	8.46	27.27		
							2010	1.14	71.41	12.15	8.28		

* Gr = gravel roads, L = logging activities, U = urbanization, G = golf

2.3 Sampling

Core sampling was done at the deepest region of the lake, determined by echo-sounding, in order to account for spatial variations of overall lake/watershed organic matter and Hg dynamics (Hakanson and Jansson 1983, Teisserenc *et al*. 2010). Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth 1958). This type of corer presents the advantage of reducing both disturbances at the water-sediment interface and compaction phenomena. The technique consists of inserting a 1.5-meter long Plexiglas tube (diameter 10 cm) into the sediment using compressed air. Sediment cores were then sub-sampled in 20 ml glass vials every centimetre using a Teflon® spatula. Vials were pre-combusted at 500°C for 3 hours to avoid carbon contamination of the vessel and capped with Teflon® liners. In order to avoid cross contamination between samples, only the center of each slice was kept. The samples were then freeze-dried prior to analysis.

2.4 Chemical analyses

A total of 275 sediment samples were analyzed from the following sites: Matagami Lake (51), Dickson Lake (31), Des Jardins East (31), Des Jardins West (31), Waswanipi Lake (25), Rodayer Lake (31), Ouéscapis Lake (25) and Chibougamau Lake (50). The number of samples analyzed per core was a function of the length of each sediment core. Sediment samples were homogenized using a mechanic firing pin before performing total carbon and nitrogen analyses. Replicate measurements on samples, treated and untreated by vapor acidification, were performed to verify that the inorganic carbon fraction was negligible. Acidified sample measurements systematically fell within the range of the non-acidified sample, thus demonstrating that total carbon content can be considered as organic carbon (OC) content. Atomic C/N ratios for sedimentary organic matter were calculated by dividing the weight percentage of organic carbon by the weight percentage of total nitrogen, measured using a CE-Instruments model NC2500™ elemental analyzer with a relative precision of ± 5% (1σ), corrected for atomic weight.

Replicate THg analyses were performed on sediment samples by cold vapour atomic fluorescence spectrometry (CVA-FS) following the protocol developed by Bloom and Fitzgerald (1988) and adapted by Pichet *et al*. (1999). In brief, a combination of HNO_3 (16N) : HCl (6N) (10 mL:1 mL) was added to approximately 250 mg of freeze dried, grounded sediment and then heated to 120°C for 6 hours. The remaining solution was brought back to a volume of 30 ml with NANOpure® water and analysed by atomic fluorescence. Calibration was done by injecting known quantities of Hg (II) (400-1000 pg of Hg). The detection limit for a 250 mg sample was 0.1 ng/g. The accuracy of the method was verified using the Mess-3 certified standard. With an average value of 87 ± 3 ng/g for seven aliquots, our results fell within the certified value (92 ± 9 ng/g).

2.5 Statistical analyses

Statistical tests were applied to the regression observed between the enrichment in THg from the deeper sections of the cores to the surface ones. Such tests were also applied to the morphological characteristics of the watersheds. In all cases, normal distribution of residuals was tested by performing a Shapiro-Wilk goodness of fit test, using a statistical analysis program (JMP 7) and accepted W values > 0.05. The F-ratio was then computed in order to evaluate the effectiveness of the model and the student parametric test (t-test) was processed to evaluate the pertinence of regression parameters ($p < 0.05$).

2.6 Modelling of the sources of sedimentary organic matter

We used two simple models to determine the relative contributions of autochthonous and allochthonous OM found in sediment cores. To do so, we considered that typical C/N atomic ratios measured in humus sampled in the pristine areas (i.e., C/N = 35.5) of the lake watersheds of the present study were representative of terrestrial plant material. We chose to use the average humus value since it represents an integrative signal of the vegetation cover in a given watershed (Teissernc 2009). Indeed, although we also measured C/N ratios for pure vegetation sources in the region of our study as indicated by several biomarkers studies, the use of pure sources rather than humus should be less effective due to pedological processes during the transfer of terrestrial OM to the lake (Hernes *et al*. 2007, Teisserenc 2009). The average C/N atomic ratio of 6 for autochthonous aquatic organic matter was found in the literature (Goldman *et al*. 1987, Lee and Fuhrman 1987)

$$(\mathrm{C/N})_{\mathrm{sediment}} = (\alpha_N)_{\mathrm{autochthonous}} * (\mathrm{C/N})_{\mathrm{autochthonous}} + (1-\alpha_N)_{\mathrm{allochthonous}} * (\mathrm{C/N})_{\mathrm{allochthonous}}$$

and

$$1/(\mathrm{C/N})_{\mathrm{sediment}} = (\alpha_C)_{\mathrm{autochthonous}} * \left[1/(\mathrm{C/N})_{\mathrm{autochthonous}}\right] + (1-\alpha_C)_{\mathrm{allochthonous}} * \left[1/(\mathrm{C/N})_{\mathrm{allochthonous}}\right]$$

Based on the general formula: $(\mathrm{X/Y}) = \sum_{i=1}^{n} i(\mathrm{X/Y})i$

Then by assuming that OM mostly corresponds to carbon and nitrogen contents, we were able to make the following calculations

$$\alpha_{N\ \mathrm{autochthonous}} * N + \alpha_{C\ \mathrm{autochthonous}} * C = \%\text{of OM}_{\mathrm{autochthonous}}$$

and

$$\alpha_{N\ \mathrm{allochthonous}} * N + \alpha_{C\ \mathrm{allochthonous}} * C = \%\text{of OM}_{\mathrm{allochthonous}}$$

2.7 Determination of the THg Anthropogenic Sedimentary Enrichment Factor (ASEF) and the surficial sediment Hg anthropogenic enrichment concentration (EHg)

The ASEF is defined as the ratio of THg at the surface of the core to the levels observed in the deeper baseline level (Lucotte *et al*. 1995). In the present study, we define THg at the surface as the highest levels measured within the first three centimeters of the core, whereas the deeper baseline level corresponds to the average THg measured at the bottom of the core, before any THg peak is observed. The mercury anthropogenic enrichment concentration corresponds to the differences between THg at the surface of the sediment core and the levels measured in the deeper baseline level of the same core (Lucotte *et al*. 1995).

3. Results

3.1 Spatial and historical characteristics of lakes and their watersheds

The spatial characteristics of the lakes and their respective watersheds are presented in Table 1. Mean slopes of the watersheds were between 1 and 6% with no specific trends according to the location of the lakes.

The Drainage Area to Lake Area ratio (DA/LA) varied from 2.59 to 22.77. Two of the eight lakes have large DA/LA ratios of 13.81 and 22.77 (Lakes Des Jardins and Dickson, respectively). Lake Waswanipi also has a relatively high DA/LA ratio of 7.39, whereas the remaining lakes have relatively low DA/LA ratios, with values ranging from 2.59 to 4.53.

The watersheds of the lakes studied were dominated by coniferous stands with a vegetation cover varying from 40.21 to 93.51% over a 30 year period (Table 1). The class “unforested” was used to detect the presence of logging activities in the watershed. According to this classification, the peak of logging activity took place during the nineties for most of the lakes. However, further observations of satellite images showed that the adopted logging technique (patch vs. cutting with protection of regeneration and soils; CPRS) can induce an underestimation of the unforested class. In addition, four of the eight lakes had mines in their watershed (i.e., Lakes Waswanipi, Chibougamau, Dickson and Matagami; Table 1).

3.2 Organic carbon contents and C/N atomic ratios in sediments

Reference lakes (i.e., Lakes Ouescapis and Rodayer) had organic carbon contents ranging from

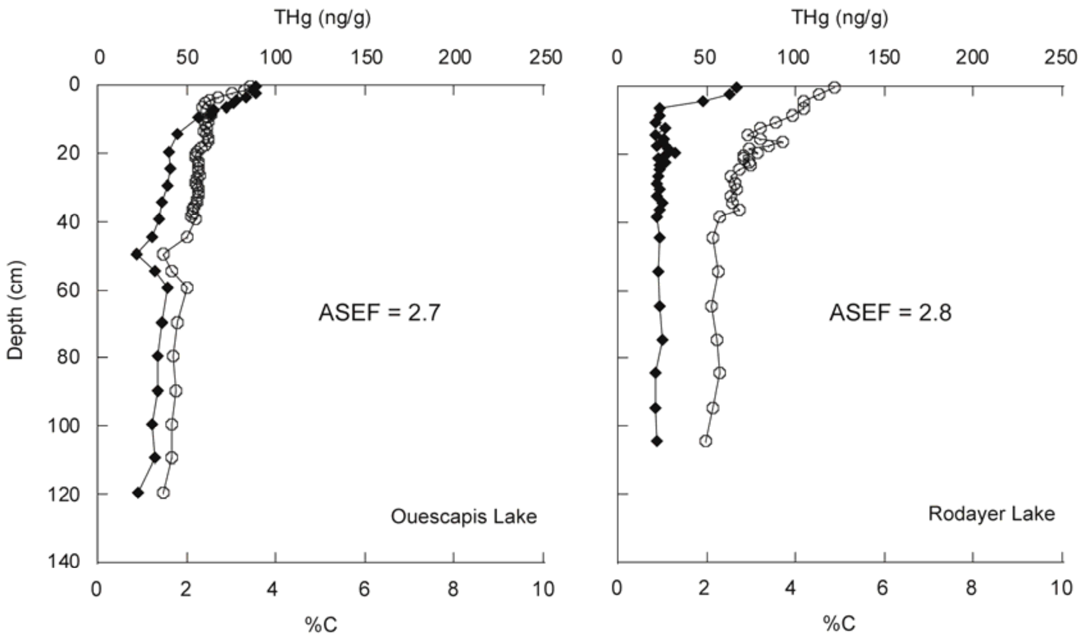

Fig. 2 Organic carbon (white circles) and THg (black rhombs) contents profiles in sediment cores from Lakes Ouescapis and Rodayer

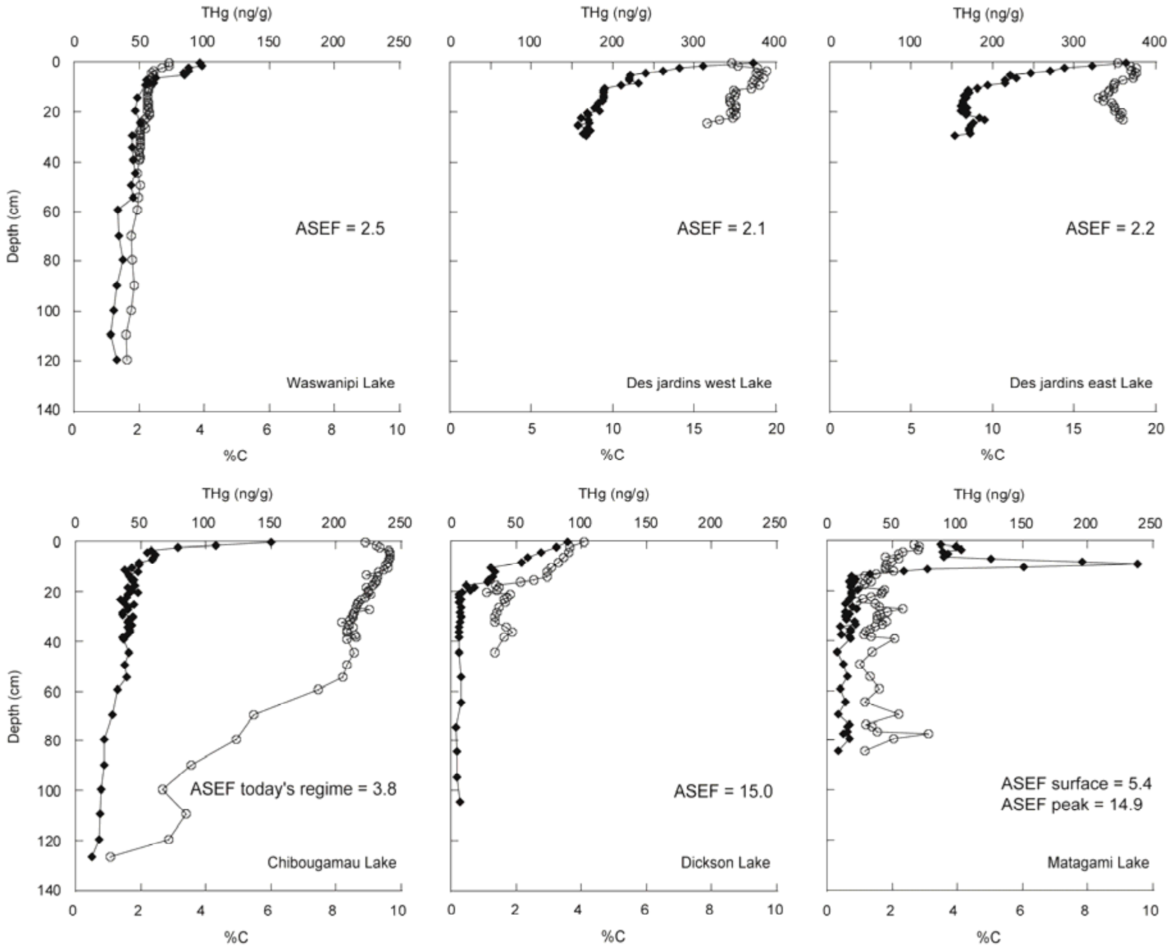

Fig. 3 Organic carbon (white circles) and THg (black rhombs) contents profiles in sediment cores from Lakes Waswanipi, Des Jardins East, Des Jardins West, Chibougamau, Dickson and Matagami

1.47% to 3.42% and from 0.91% to 4.86% respectively (Fig. 2). Organic carbon content in the two Organic carbon contents in disturbed-lake sediment cores are presented in Fig. 3. Lakes Des Jardins East and West have significantly higher OC content than other lakes, with concentrations of between 15 and 20% (Fig. 3). All other lakes displayed values ranging from 1 to 10%.

Applying the model described in section 2.6, no relation could be observed between THg and the relative proportion of allochthonous/autochthonous OM in surface sediments in the eight lakes studied.

3.3 Total mercury content in sediments

Mercury sedimentary profiles of lakes are presented in Figs. 2 and 3. Ouescapis and Rodayer lakes displayed similar THg core profiles (Fig. 2). In these cores, baseline THg varied from 20 to

25 ng/g and then progressively increased near the surface of the core to reach maximum values of 89 and 67 ng/g in the respective lakes.

Disturbed lakes presented THg varying from 4 to 373 ng/g with values increasing from the bottom to the top of the core (Fig. 3). With the exception of Lake Matagami, all disturbed lakes presented THg profiles similar to those of reference lakes, with low and stable THg in the deeper part of the cores followed by an increase in concentrations near the surface. The highest THg were observed in Des Jardins and Matagami sediment cores (373 ng/g and 238 ng/g respectively; Fig. 3).

3.4 Organic carbon contents vs. THg profiles in boreal lake sediment cores

Organic carbon contents and THg by depth in the sediment cores of the two reference lakes (i.e., Ouescapis and Rodayer lakes) are reported in Fig. 2. In these core profiles, THg followed OC contents variations ($r = 0.83$, $p = 0.0001$ and $r = 0.71$, $p = 0.0001$ for Ouescapis and Rodayer lakes respectively).

Organic carbon contents and THg by depth in the sediment cores of disturbed lakes are shown in Fig. 3. In Lakes Waswanipi and Dickson OC contents and THg profiles show the same pattern as the two reference lakes ($r = 0.89$, $p = 0.0001$ and $r = 0.93$, $p = 0.0001$ respectively). Lake Chibougamau samples did not result in a correlation between OC contents and THg in the first 40 cm of the cores ($p = 0.0718$). However, this could be explained by the fact that close to the surface, we could observe a weak increase of OC contents with depth while at the same time THg decreased (Fig. 3). When the first three centimeters of this core were excluded, we observed a significant correlation between OC contents and THg in Lake Chibougamau ($r = 0.71$, $p = 0.0001$). Similarity between OC contents and THg profiles along the sediment cores were weaker in Lake

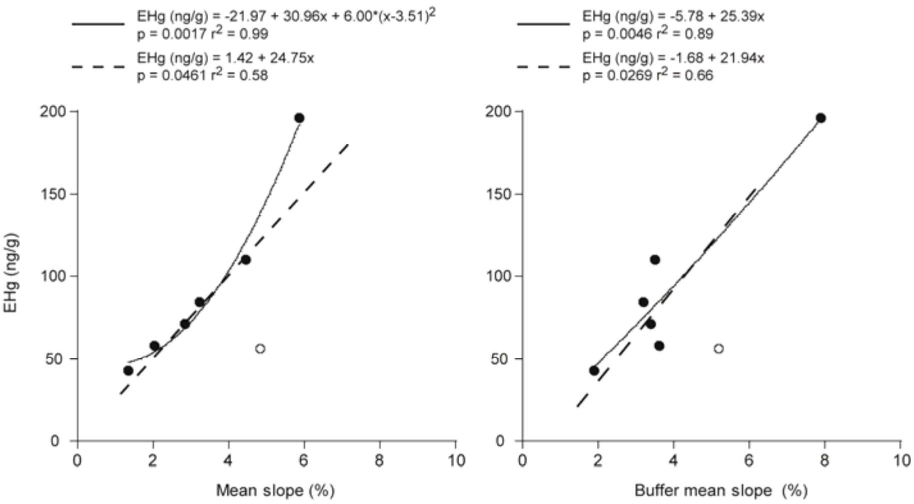

Fig. 4 EHg (ng/g) *vs.* mean slope (%) of both the drainage area and the buffer zone for the lakes of the study. The term EHg refers to the surficial sediment Hg anthropogenic enrichment concentration. Solid black line corresponds to the polynomial regression calculated among the lakes excluding Lake Ouescapis (white rhombs). Dotted black line corresponds to the linear regression calculated among the lakes including Lake Ouescapis

Matagami (r = 0.52, p = 0.0006; Fig. 3) and Lake Des Jardins East (r = 0.60, p = 0.0017). Finally, no correlation was observed in Lake Des Jardins West (p = 0.0740).

3.5 Mercury anthropogenic enrichment concentration vs. morphological characteristics

Fig. 4 presents the positive relationship between EHg and the mean slope of the drainage area of the lakes studied (Fig. 4; r^2 = 0.99, p = 0.0017). This relationship suggests that a higher mean slope induces higher EHg values in the sediment core. The association was stronger when considering the entire drainage area rather than just the buffer zone (r^2 = 0.99 and r^2 = 0.89 respectively). Moreover, the exclusion of Lake Ouescapis improved the regression model presented on Fig. 4.

In order to evaluate the impact of slope gradient on Hg inputs reaching the lake from the drainage area, we also separated the slopes into different classes (i.e., low: 0-2%, intermediate: 2-6% and high: 6-20$^+$%). This partitioning showed that both the proportion of low and high slope areas in the watersheds appeared to have an impact on Hg enrichment in sediment cores, while intermediate slopes did not present any correlation (Fig. 5).

In the present study, strong regression coefficients were observed between EHg and both coniferous and deciduous land cover (Fig. 6; r^2 = 0.95 and r^2 = 0.95 respectively).

4. Discussion

4.1 Allochthonous vs. autochthonous OM in boreal lake sediment cores

C/N atomic ratios are commonly used in biogeochemical studies dealing with terrestrial, riverine, lacustrine, estuarine, and marine environments to elucidate the sources and the fate of organic matter (Hedges and Parker 1976, Lobbes *et al*. 2000, Goni *et al*. 2003, Countway *et al*. 2007). C/N atomic ratios encompass a large range of values (12 to 500) that generally decrease with diagenetic processes (Thornton and McManus 1994, Moingt 2008). Organic matter that originates in bacteria or algae presents C/N atomic ratios under 8 (Goldman *et al*. 1987, Lee and

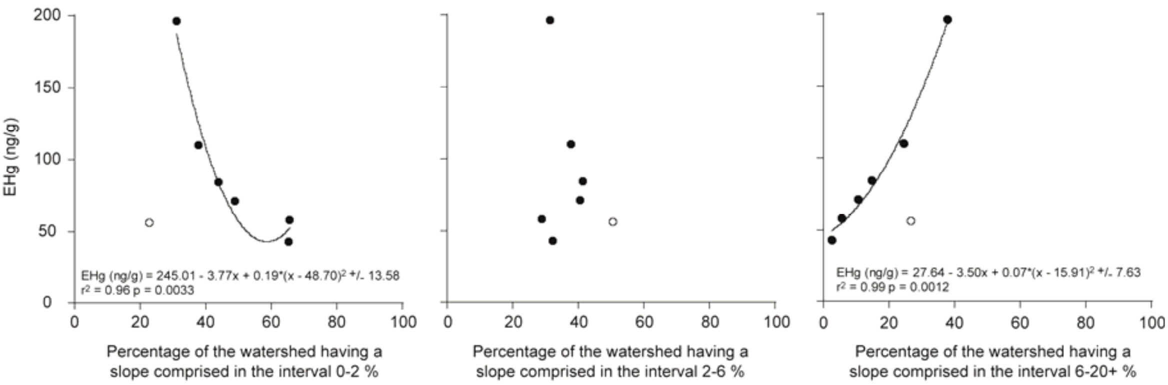

Fig. 5 EHg (ng/g) vs. slope intervals (%) of the watersheds for the studied lakes. The term EHg refers to the surficial sediment Hg anthropogenic enrichment concentration. The X-axis represents the percentage of the watershed having the corresponding slope interval

Fuhrman 1987). For all lakes studied, OM inputs to sediments are predominantly of terrestrial origin, as shown by C/N atomic ratio values ranging from 12.97 ± 0.49 to 21.54 ± 3.54.

4.2 Total Hg concentrations profiles

4.2.1 Anthropogenic sedimentary enrichment factor

In both reference lakes (i.e., Lakes Ouescapis and Rodayer), the ASEF value is approximately 3. This ratio is typical of ASEF values for undisturbed boreal lakes (Lucotte *et al*. 1995, Lindberg *et al*. 2007, Bishop *et al*. 2009) and has been interpreted to be representative of the anthropogenic impact of Hg release in the atmosphere since the onset of the industrial era.

Disturbed lakes show the same pattern as reference lakes: an increase in THg from the bottom of the core to the surface. However, ASEF values are not homogeneous, varying from 2 to 15 (Fig. 3). Indeed, only three out of the six disturbed lakes present ASEF values greater than to 3 (Lakes Chibougamau, Matagami and Dickson). Thus, intense land use in a watershed does not seem to necessarily translate into a noticeable increase of THg in the sediment core. This is surprising given that both mining and logging activities have been reported to increase Hg loading (Wong *et al*. 1999, Porvari and Verta 2003, Bishop *et al*. 2009). However, our finding is in agreement with a study of Petit *et al*. (2011) in which two sediment cores were sampled near the shores of Lake Chibougamau, one close to a mine tailing and one far from the tailing. THg in both cores had drastically different ASEF values of 9.7 and 2.4 (respectively), whereas our sediment core has an intermediate ASEF value of 3.8. This observation suggests that in large lakes, local disturbances such as mining activities have an effect on THg in sediments, but limited to areas nearest to the disturbances. This observation about undetectable mining impact in the middle of large lakes seems to be corroborated by the data from Lake Waswanipi, which results in an ASEF value of 2.5, typical of pristine boreal environment, despite the presence of mining activities in its watershed. Since several disturbed lakes present both ASEF and THg profiles similar to the ones measured in reference lakes, THg found in sediments seems to originate primarily in the transfer of atmospherically deposited Hg from the watershed into the aquatic system. This conclusion is agreement with sedimentation rates previously reported in the literature for boreal lakes (0.22 ± 0.06 $cm.year^{-1}$) (Lucotte *et al*. 1995, Teisserenc *et al*. 2010, Teisserenc *et al*. 2011), which indicate that in sediment core, the THg increases coincide with the onset of the industrial era.

The link between total OC contents and THg in lake sediments remains unclear. Indeed, some studies found a relationship between these two parameters (Kolka *et al*. 1999, Ethier *et al*. 2010) whereas others studies did not show any correlation (He *et al*. 2007, Teisserenc *et al*. 2011). Because of these conflicting observations, THg and OC contents association is unlikely due to the nature of the OM involved (autochthonous vs. allochthonous) and/or the quality of this OM.

4.2.2 Mercury anthropogenic enrichment concentration vs. morphological characteristics

As shown on Fig. 4, the regression analysis from Lake Ouescapis does not produce a strong coefficient. A combined effect of two parameters could explain this observation. First, Ouescapis Lake presents a watershed with specific morphological characteristics in comparison to the other lakes: a different distribution of slope classes and a small DA/LA ratio (Drainage Area/Lake Area; Table 1). Moreover, the regression observed for the buffer is not significant when Lakes Des Jardin East and West are excluded (p = 0.08346) suggesting that the impact of the buffer on sedimentary THg is negligible in large lakes with large watersheds, and that the entire watershed governs sedimentary Hg inputs.

The relation between slope gradient and Hg enrichment in lake sediments (Figs. 4 and 5) could be at least partially explained by terrestrial OM fluxes coming from the drainage area. Indeed, it is recognized that Hg has affinity for terrestrial OM (Kolka *et al*. 1999, Kainz *et al*. 2003). Organic matter acting as a ligand, speciation factor or vector for Hg can influence both Hg bioavailability and mobility (Goñi and Montgomery 2000, Porvari and Verta 2003, Chadwick *et al*. 2006). Moreover, in a recent study, Ouellet *et al*. (2009) have shown a positive relationship between terrestrial OC contents and THg measured in the water column. The importance of terrestrial OM as a vector for Hg from the watershed to the lake can be explained by the fact that atmospheric Hg deposition is closely associated with ground vegetation and soils (Abdullah *et al*. 1995, Hintelmann *et al*. 2002, Ouellet *et al*. 2009, Teisserenc *et al*. 2011) which are in turn the major contributors of OM to lakes. In addition, a study by Teisserenc *et al*. (2010) showed a positive correlation between terrestrial OM fluxes and the mean slope of the watershed, highlighting the fact that watershed mean slope is a key factor in controlling the amount of terrestrial OM reaching lake sediments. In the boreal forest, the hydrological cycle depends upon the watershed slopes, the steepness influencing both water infiltration and percolation in soils (Chang 2006, Teisserenc *et al*. 2010). In watersheds with steep slopes, weathering mostly occurs on the soil surface and contributes to higher erosion processes for OM and Hg rich horizons (Klaminder *et al*. 2008, Teisserenc *et al*. 2010). On the other hand, in watersheds with weak slopes, percolation is more efficient, therefore water reaching deeper soil horizons becomes impoverished in both OM and Hg (Houel *et al*. 2006, Klaminder *et al*. 2008). Since Hg is lost in mineral soil when OM is transported downwards in percolating soil-water (Bishop *et al*. 1995, Schlüter and Gäth 1997), a more efficient water percolation should induce lower Hg inputs reaching the lake in comparison to areas with steeper slopes. Moreover, low slope areas are often associated with wetland areas, which are recognized as sinks for Hg since they reduce THg in outflow water and are important sites of methyl mercury production in near pristine boreal ecosystems (Galloway and Branfireun 2004, Selvendiran *et al*. 2008, Zelenkova and Vinokurova 2008, Chen *et al*. 2013).

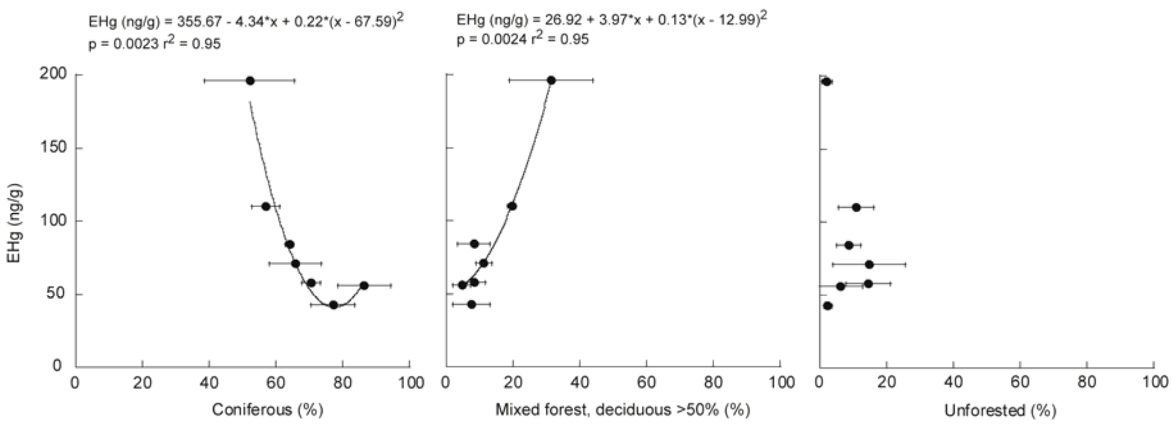

Fig. 6 EHg (ng/g) *vs.* land cover of the watersheds for the studied lakes. The term EHg refers to the surficial sediment Hg anthropogenic enrichment concentration. Each black circle represents the vegetation cover obtained from satellites images and averaged over the years specified in Table 1

As shown in Fig. 6, the presence of conifers in the watershed seems to lower the amount of Hg coming from the drainage area to the lake, whereas deciduous vegetation seems to increase the transfer of Hg to the lake. These observations can be explained by two facts. First, litter dynamics are different in coniferous and deciduous forest stands. Second, in forest floor leachates, coniferous stands display lower Hg inputs than deciduous ones (Demers *et al*. 2007, Teisserenc *et al*. 2011). Atmospheric Hg is the principal source of mercury in forest foliage, with a tendency to accumulate over time (Ericksen *et al*. 2003, Frescholtz *et al*. 2003). Besides, in angiosperm forests, 80% of the fraction of THg not found in soils is accumulated in leaves (Ericksen *et al*. 2003). Coniferous species thus appear lesser contributors to Hg inputs reaching boreal lakes than angiosperm species (Ouellet *et al*. 2009). Because slope is a principal factor determining vegetation types in a watershed, it can in part explain why EHg is superior in lakes with steeper mean slopes in their watersheds than the ones with low mean slopes in their watersheds (Fig. 4). Contrary to what has been reported in scientific literature (Porvari *et al*. 2003, Garcia and Carignan 2005), clear-cut areas resulting from recent logging activity do not seem to have a noticeable influence on Hg inputs reaching lake sediments (Fig. 6). However, based on satellite image analyses, deciduous species represent most of the second growth vegetation after logging operations. Consequently, logging activities increase the relative proportion of deciduous vegetation cover in the drainage area, which in turn could potentially increase the amount of Hg reaching boreal lakes. Another point to highlight is that in the present study, the fraction of logged land in the watershed is always less than to 25%. Thus, the deforestation of up to a quarter of the surface of a watershed (though a significant anthropogenic disturbance) seems to be indiscernible in sediment cores whose analysis considers the entire watershed.

5. Conclusions

This study highlights several points with major implications for a better knowledge of Hg cycles and dynamics. The combination of GIS analyses with THg measurements in sediment cores, thus including variations in time and space, is a powerful strategy to evaluate the impact of both morphological characteristics and localized disturbances in large boreal lake ecosystems at the watershed scale. Such an approach allows drawing integrated pictures of watershed-lake interactions, bypassing the inherent local and short term fluctuations of the systems. These analyses allowed us to emphasize the importance of three factors controlling terrestrial Hg inputs to lakes, i.e., mean watershed slope inclination, the distribution of slopes in classes and vegetation cover in the drainage area. Our results suggest that in large boreal lake ecosystems, slope and vegetation cover of lake watersheds often override the influence of land use in sedimentary THg profiles. In the present study the sedimentary enrichment in Hg was higher for lakes whose watersheds have steeper mean slopes and/or higher percentages of deciduous vegetation. On the other hand, deforestation (up to 25% of the drainage basin area) or mining activities (up to 14 mining sites) in the watershed had undetectable effects on sedimentary THg. Moreover, in large boreal lake ecosystems, sedimentary Hg profiles retrieved around the focal point seem to be governed by inputs coming from the entire watershed rather than by a given proximate area. This study provides evidence that reductions in Hg atmospheric deposition and careful watershed management are necessary in order to limit terrestrial Hg transfer into lakes.

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