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Combined dynamics of mercury and terrigenous organic matter following impoundment of Churchill Falls Hydroelectric Reservoir, Labrador

Roman Teisserenc · Marc Lucotte ·
René Canuel · Matthieu Moingt · Daniel Obrist

Abstract Sediments from two recently (40 years) flooded lakes (Gabbro lake and Sandgirt lake) and an unflooded lake (Atikonak lake) were sampled to investigate the effects of reservoir impoundment on mercury (Hg) and terrigenous organic matter (TOM) loading in the Churchill Falls Hydroelectric complex in Labrador, Canada. Lignin biomarkers in TOM, which exclusively derive from terrestrial vegetation, were used as biomarkers for the presence and source origin of TOM—and for Hg due to their close associations—in sediments. In the two flooded Gabbro and Sandgirt lakes, we observed drastic increases in total mercury concentrations, T-[Hg], in sediments, which temporally coincided with the time of reservoir impoundment as assessed by ^{210}Pb age dating. In the natural Atikonak lake sediments, on the other hand,

T-[Hg] showed no such step-increase but gradually and slowly increased until present. T-[Hg] increases in lake sediments after flooding were also associated with a change in the nature of TOM: biomarker signatures changed to typical signatures of TOM from vegetated terrestrial landscape surrounding the lakes, and indicate a change to TOM that was much less degraded and typical of forest soil organic horizons. We conclude that T-[Hg] increase in the sediments of the two flooded reservoirs was the result of flooding of surrounding forests, whereby mainly surface organic horizons and upper soil horizons were prone to erosion and subsequent re-sedimentation in the reservoirs. The fact that T-[Hg] was still enriched 40 years after reservoir impoundment indicates prolonged response time of lake Hg and sediment loadings after reservoir impoundments.

Keywords Reservoir · Mercury · Lignin biomarkers · Terrestrial organic matter

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Introduction

The creation of man-made reservoirs results in flooding of large areas of terrestrial ecosystems and can induce major environmental effects. Many studies have addressed these effects, which range from drastic landscape changes to large perturbations in elemental biogeochemical cycles (Kelly et al. 1997; St Louis et al. 2000; Hall et al. 2005). One of the most widely documented changes is the alteration of the mercury (Hg) cycle. The creation of artificial water bodies is generally accompanied by increased levels of total (T-[Hg]) and methyl ([MeHg]) mercury in the water column, sediments, and biota (St Louis et al. 2004). High Hg concentrations in fish are of particular concern because they may translate into high Hg exposure for subsistence or sport fishers. Hg is considered one of the greatest drawbacks of reservoir-induced changes.

Hg dynamics in reservoirs have been investigated for more than two decades now (Bodaly et al. 1984), with many investigations ultimately focusing on Hg contamination in fish (French et al. 1999; Verdon et al. 1991). While almost all studies attribute Hg increases in reservoirs to a release of Hg from flooded soils, no study has explicitly tested this hypothesis using biogeochemical tracers. The first specific objective of this study is to confirm this largely used hypothesis using an integrated method that combines conventional analysis of Hg in sediments with age dating (^{210}Pb), and application of biomarker characterization of terrigenous organic matter (TOM).

TOM biomarkers are derived from mild cupric oxide (CuO) oxidation that include lignin derived phenols, tannins, and flavonoid-derived compounds. Formally designated as lignin biomarkers, these compounds are specific markers of TOM because they are directly derived from plants (Hedges and Mann 1979). TOM biomarkers have been successfully used to trace the terrestrial origins of OM in aquatic ecosystems (Goñi and Hedges 1995; Houel et al. 2006), and studies by our group have shown the use of lignin biomarkers in describing TOM source and quality at the watershed scale (Teisserenc et al. 2010). Recent studies have highlighted the potential use of biomarkers in describing TOM associated with Hg dynamics (Caron et al. 2008; Teisserenc et al. 2011). It is known that organic matter plays a critical role in sorption of Hg and in the transfer of Hg from the

terrestrial ecosystem to aquatic environments (Schuster 1991; Kolka et al. 1999). Hg is deposited via dry or wet deposition to vegetation and terrestrial ecosystems where it then strongly sorbs to surface litter and soil horizons (Meili 1991; Grigal 2003; Obrist et al. 2011). These terrestrial stores of Hg may ultimately leach into aquatic systems (Rencz et al. 2003), and this transfer is often directly associated with the transport of organic carbon in either dissolved or particulate form (Kolka et al. 1999; Ravichandran 2004).

Our second objective is to characterize the role of TOM in the transfer of Hg to reservoirs, in particular determine how OM characterization in sediments can be used to track and characterize the origin of Hg in lake sediments. We propose that analysis of TOM in sedimentary deposits in a flooded lake (i.e. incorporated in a reservoir) provide a detailed record of origins of both T-[Hg] and TOM following the impoundment of forest ecosystem. In order to characterize changes in TOM–Hg dynamics in flooded reservoirs, we compared sediment records of two recently flooded lakes, Sandgirt and Gabbro, which are part of the Churchill Falls Hydroelectric complex, with that of Atikonak lake, a natural unflooded lake located upstream (120 km) of these reservoirs. Along the manuscript, flooded lake will refer to these two lakes that have been incorporated in the Churchill Fall Hydroelectric complex. Accumulating zones in reservoir sediments are considered spatially homogeneous, continuously deposited, and unlikely to have been disturbed by wave and currents (Shotbolt et al. 2005). These zones, particularly in flooded lakes, are hence expected to provide detailed temporal records of contaminants and organic matter inputs (Shotbolt et al. 2005). This project is part of the COLlaborative MERcury Research Network (COMERN), which has undertaken an ecosystem study of the mercury cycle in this reservoir in order to minimize Hg exposure of local communities by fish consumption.

Methods

Study sites

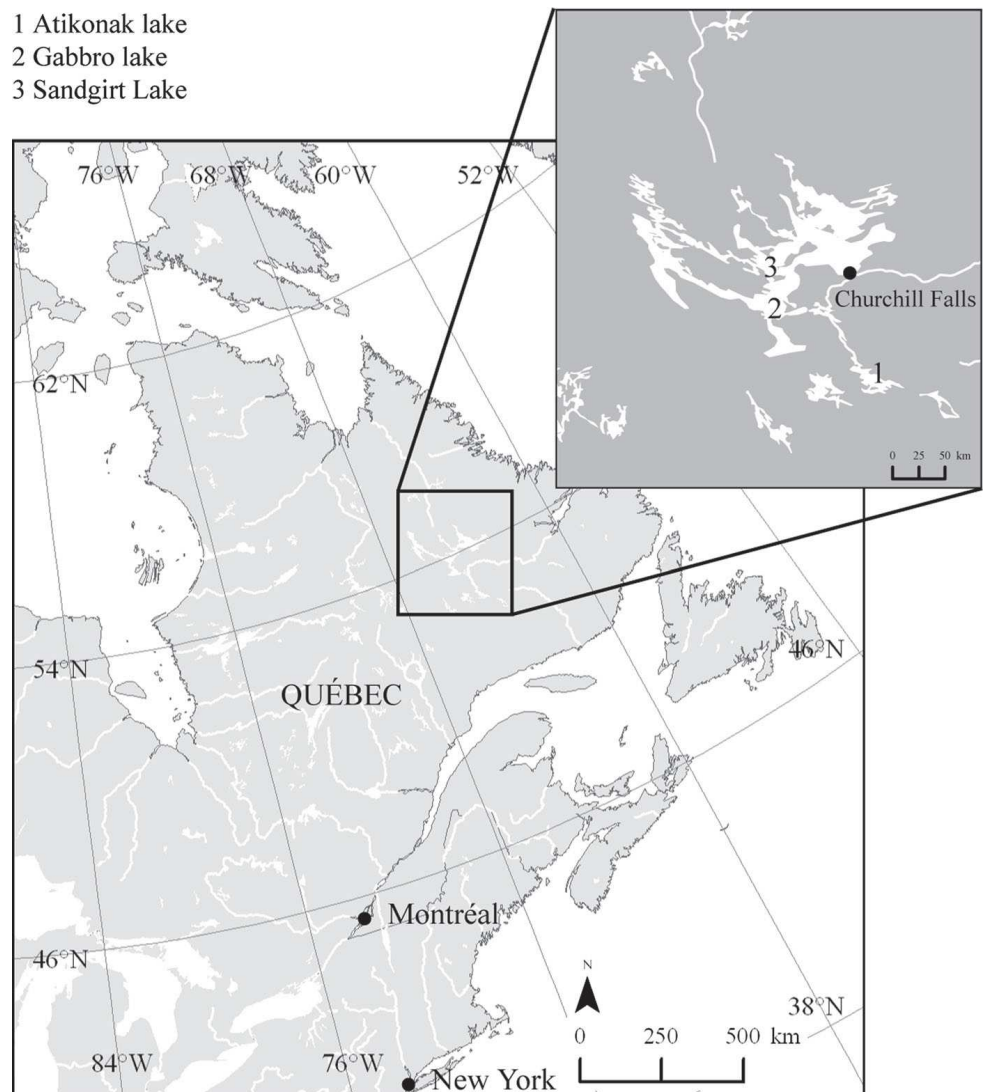
The Churchill Falls Hydroelectric complex is located in central Labrador, Canada (Fig. 1). The bedrock geology in this region is dominated by gneiss and granites that belong to the Precambrian Canadian

Shield. Sandgirt and Gabbro lakes, which are now included in the Churchill Falls Hydroelectric complex, drain water of the Labrador plateau that lies in the Churchill geological province. Glacial retreat in this central part of Labrador occurred around 6,000 years BP. The climate of central Labrador is continental, with long snowy and severe winters. The annual precipitation is from 900 to 1,100 mm and is characterized by heavy snow accumulation (300–400 cm). The annual growing season lasts from 100 to 120 days. The main vegetation is open woodland dominated by black spruce (*Picea mariana*) and lichen (*Cladonia rangiferina*). Soil organic horizons are thin and patchy. Atikonak lake, 150 km to the south of the hydroelectric complex, is located in the eastern part of the Grenville geological province. Its watershed is located at the northern limit of the boreal forest. Black

spruce and lichen still dominate the landscape. However, the tree density is higher and organic horizons of soils are thicker. Peatlands dominate the landscape in both areas along with small and shallow lakes.

Built between 1966 and 1974, the Churchill Falls Hydroelectric complex constitutes the second largest series of reservoirs in the world, with a surface area of 6,650 km². Created by damming the Churchill river and derivation of the Naskapi river, the reservoir is composed of 88 dikes and is divided into three water bodies regulated by three control structures: the Forebay reservoir, the Smallwood reservoir and the Ossokmanuan reservoir. Sandgirt lake is included within the Smallwood reservoir and lake Gabbro within the Ossokmanuan reservoir. 40 and 25 %, respectively of the surface of the Smallwood and Ossokmanuan reservoirs are composed of flooded

Fig. 1 Map of sampled sites



land, which was once forest, peat lands, and barren lands. The drainage area of the complex is now 69,000 km², including diversions.

Sampling

Sediment cores were sampled using a pneumatic Mackereth corer at the focal point of each of the three lakes. The focal point represents the deepest point of the accumulating zone and was located via lakes bathymetry. The technique consists of inserting a 1-m long Plexiglas tube (diameter: 10 cm) into the sediment using compressed air. This corer offers the advantage of producing very few perturbations at the water–sediment interface. Sediment cores were then sub-sampled in 20 mL glass vials (pre-heated at 500 °C for 3 h and capped with Teflon[®] liners) in 1-cm sections using a Teflon[®] spatula. To avoid cross contamination between samples, the sediment contour in contact with the corer was removed. The samples were then freeze-dried and homogenized manually with an agate mortar grinder prior to analysis. Core lengths were 25, 45, and 50 cm in Sandgirt, Atikonak, and Gabbro lakes, respectively.

Chemical analysis

Sediment accumulation rates were determined for the two flooded lakes by alpha spectrometric measurements of ²¹⁰Pb via its daughter product ²¹⁰Po activities following the method initially developed by Flynn (1968). Po isotopes were deposited on a spinning Ag disc (Hamilton and Smith 1986) and activity measured by α -spectrometry using ORTEC silicon surface barrier detectors. Analytical reagent blanks were run throughout the analytical procedure. For each core, ²¹⁰Pb activity was estimated from the average of values where the asymptotic trend does not show difference in the values within the analytical error. Water contents of each sample were determined in order to correct sediment accumulation rates due to possible compaction of the core during sampling.

Analyses of T-[Hg] were performed by cold vapour atomic fluorescence spectrometry (CVA-FS) following the protocol developed by Bloom and Fitzgerald (1988) and adapted by Pichet et al. (1999). Briefly, a mixture of nitric and hydrochloric acid (16 and 6 N, 10:1 mL) was added to approximately 250 mg of

freeze dried, ground sediment sample and heated at 120 °C for 6 h. The solution was then diluted to 30 mL volume using NANOpure[®] water and analyzed by atomic fluorescence. Analyses were carried out in duplicates with a reproducibility of ± 5 %.

Total carbon and nitrogen analyses used a Carlo Erba (NA-1500) elemental analyzer. Analyses were carried out in duplicates with a reproducibility of ± 5 %. Molecular TOM biomarker analyses were performed according to the copper oxidation (CuO) method initially developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). One sample on five was carried in duplicate. Average standard deviation of replicate analysis is below 15 % for the major CuO oxidation products. A “standard” lake sediment sample SAG05 was also regularly analyzed for comparison with previous study (Louchouart et al. 1997; Goñi and Montgomery 2000; Houel et al. 2006). In this SAG05 standard, the average variability for all parameters was better than 10 %. Briefly, a sediment sample including a minimum of 3–5 mg of organic carbon were oxidized with CuO in a 2 mol L⁻¹ NaOH solution under exclusion of O₂ in an oven at 150 °C for 180 min in 3.2 mL stainless steel mini-bombs (Prime Focus[®] Inc, Seattle). Once vials were opened, ethyl vanillin (50 μ L) was added to the solutions as an internal standard. The aqueous solutions were acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. After evaporation in a centrivap coldtrap, reaction products were dissolved in pyridine and derivatized with bis(trimethylsilyl)-trifluoroacetamide–trimethylchlorosilane (BSTFA–TMCS) to form trimethylsilyl derivatives. Extraction products were then analyzed on a Gas Chromatograph–Mass Spectrometer system (Model 3800-Saturn 2000, Varian) fitted with a fused capillary column (Varian FactorFour VF-1 ms 60 m, 0.32 mm).

We analyzed and quantified 12 TOM biomarker compounds, which are classified in 5 groups: (1) vanillyls (V), including vanillin (VI), acetovanillon (Vn), and vanillic acid (Vd); (2) syringyls (S), including syringin (SI), acetosyringone (Sn), and syringic acid (Sd); (3) cinnamyls (C), including coumaric acid, (p-Cd) and ferulic acid (Fd); (4) para-hydroxyphenols (P), including p-hydroxybenzaldehyde (PI), p-hydroxyacetophenone (Pn), and p-hydroxybenzoic acid (Pd); and (5) 3,5-dihydroxybenzoic acid (3,5Bd).

Results

Radiometric measurements in core sediments

In surface sediments, we measured ^{210}Pb activities of 63, 36 and 47 dpm g^{-1} for Atikonak, Gabbro, and Sandgirt lakes, respectively (Fig. 2a–c). Chronology was established using unsupported ^{210}Pb data of the core ($^{210}\text{Pb}_{\text{ex}}$; $T_{1/2} = 22.3$ y), and mass depth was used rather than true depth to take compaction effects into account (Abril 2003). Sediment accumulation rates were estimated using the slope of the relationship between mass depth (g cm^{-2}), the natural logarithm of $^{210}\text{Pb}_{\text{ex}}$ and the ^{210}Pb decay constant. In Gabbro lake, because of bioturbation in the first centimetres of the core, the first two sections were not been taken into account for the estimation of the sediment accumulation rate. Moreover, because of an apparent change in the sedimentation rate of this lake, non-linear profiles have been divided into linear profiles assuming constant sedimentation for each of these segments (Appleby and Oldfield 1990; Houel et al. 2006). Because of high correlation coefficients within each segment ($R^2 = 0.90\text{--}0.99$; Fig. 2e) a minimal mixing and a constancy of accumulation rate can be assumed during the period of each segment. Estimated sediments accumulation rates are $0.02 \text{ g cm}^{-2} \text{ year}^{-1}$ in Atikonak lake, $0.06 \text{ g cm}^{-2} \text{ year}^{-1}$ in Sandgirt lake; 0.03 and $0.07 \text{ g cm}^{-2} \text{ year}^{-1}$ in Gabbro lake before and after impoundment, respectively. Based on these results and using the specific porosity of each layer, we estimated the age of sediments for each core (Fig. 2g–i). Those chronologies situate the impoundment (~ 40 years; 1966–1974) around a depth of ~ 5 and ~ 6 cm for Sandgirt and Gabbro lakes, respectively (Fig. 2h, i).

Mercury

Sedimentary profiles for T-[Hg] show a gradual increase with depth in the unflooded Atikonak lake (Fig. 3). T-[Hg] baseline of this sediment core ranges between 80 to 100 ng g^{-1} , and gradually increases to 220 ng g^{-1} in recent sediments. An inflexion of T-[Hg] occurs at a depth of about 20 cm. Depth distribution patterns of the two flooded lakes show distinctly different patterns to that of Atikonak lake, both showing sharp and sudden increases in T-[Hg] in

recent sediments (i.e. upper 6–7 cm). Sandgirt and Gabbro lakes show T-[Hg] baselines around 20 and 90 ng g^{-1} , respectively, with recent T-[Hg] values increased by a factor of 7.4 and 1.6, respectively. We also observed a noticeable increase in T-[Hg] at about 18 cm depth in Gabbro lake, a peak that then gradually returned to the baseline concentration in overlying depths.

Terrestrial organic matter levels

Terrestrial organic matter biomarkers in sediments are quantified as $\lambda 8$, which signifies the carbon-normalized total yield [in mg per 100 mg organic carbon (mg 100 mg OC^{-1})] of the eight lignin-derived phenols (vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, p-coumaric, and ferulic acids). A second TOM measure are $\Sigma 8$, which expresses the same biomarkers as total yield normalized to total dry mass of samples (in $\text{mg 10 g dry wt}^{-1}$). These two variables hence estimate the relative amount of lignin-products—all of which are directly derived from plants—in sedimentary organic matter thereby indicating the importance of TOM in samples (Houel et al. 2006). In Atikonak lake, $\lambda 8$ and $\Sigma 8$ are stable along the core, indicating no major change in the types of TOM inputs to sediments over time (Fig. 4). $\lambda 8$ ranged between 0.5 and 1.0 mg 100 mg OC^{-1} , which is similar to values observed in previous studies in lake sediments at similar latitudes (Hu et al. 1999; Pempkowiak et al. 2006; Houel et al. 2006). $\Sigma 8$ values stayed closed to values of 5 $\text{mg 10 g dry wt}^{-1}$, which is lower than values observed by Pempkowiak et al. (2006), but in similar range to data reported by Houel et al. (2006).

$\lambda 8$ and $\Sigma 8$ values at the two flooded sites showed a sharp increase in recently deposited sediments at a depth of about 7 cm (Fig. 4). The increase of these lignin biomarkers is most drastic in sediments of Sandgirt lake where baseline values for $\lambda 8$ and $\Sigma 8$ of 0.1 mg 100 mg OC^{-1} and 0.02 $\text{mg 10 g dry wt}^{-1}$, respectively, increase up to 2 mg 100 mg OC^{-1} and 30 $\text{mg 10 g dry wt}^{-1}$. In Gabbro lake, $\lambda 8$ values increased from 0.5 to 2.5 mg 100 mg OC^{-1} , and $\Sigma 8$ values increased from 2 to 20 $\text{mg 10 g dry wt}^{-1}$. In Gabbro lake, we also observed an increase of $\lambda 8$ and $\Sigma 8$ at about centimeter 18.

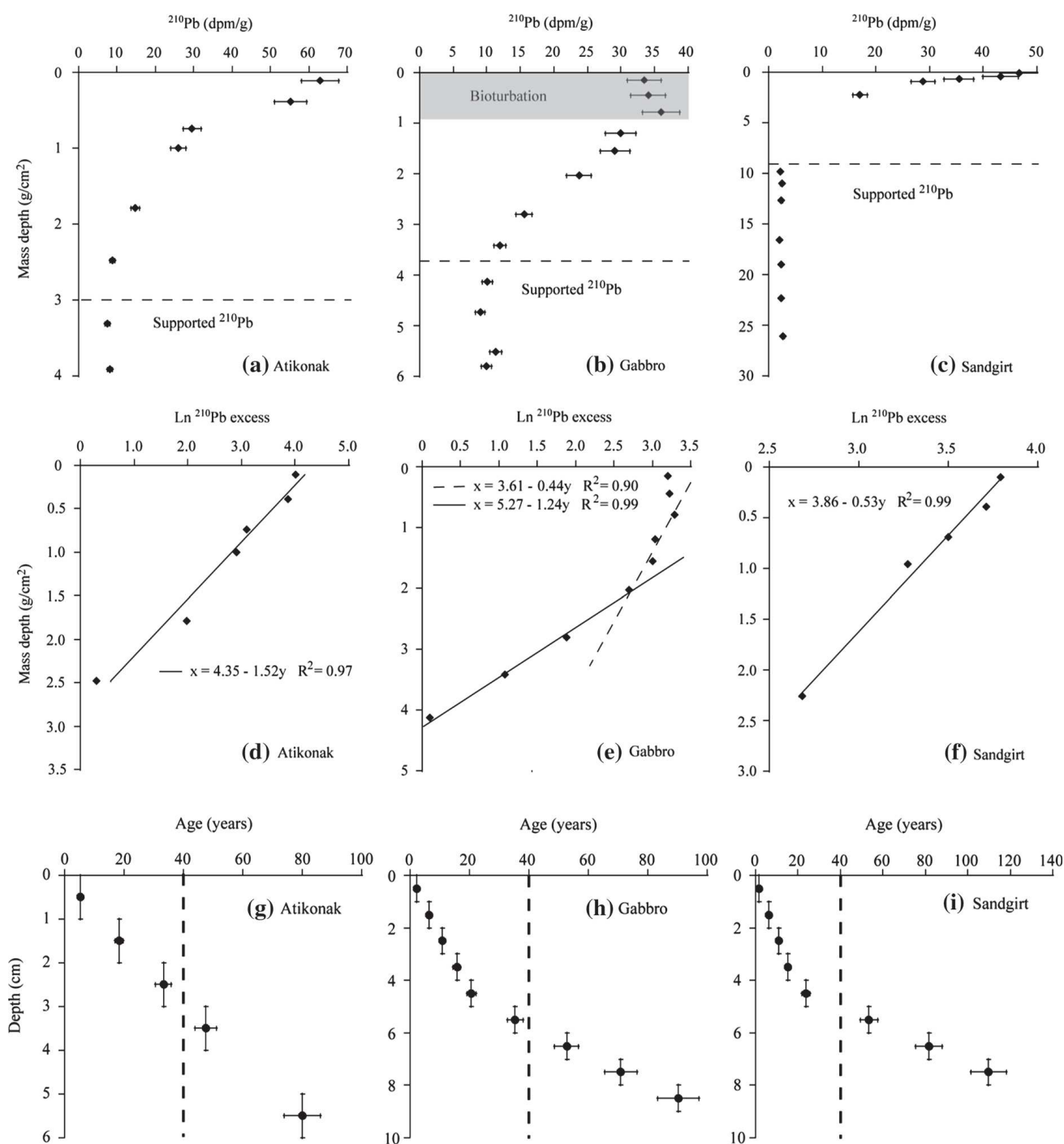


Fig. 2 Total ²¹⁰Pb activity (dpm g⁻¹) (a–c) and natural logarithm of the excess of ²¹⁰Pb versus mass depth (g cm⁻²) (d–f) in Atikonak Lake used as reference lake and in the Gabbro,

and Sandgirt flooded lakes. g–i Age (years) versus depth (cm) of the sediment cores from Atikonak Lake and the Gabbro and Sandgirt flooded lakes

TOM composition

Lignin-derived phenols can be further separated by composition to build ratios of biomarkers to be used to distinguish between origin and sources of TOM. Ratios of S:V, C:V, and P:(V + S) in the sediments

of Atikonak lake remain relatively stable along the core (Figs. 5, 6). S:V ratios are around 0.4, and C:V ratios range between 1.0 and 1.5. P:(V + S) in sediment of Atikonak lake, with an average value around 1.3. In the flooded Gabbro lake, ratios of S:V, C:V, and P:(V + S) are much more variable, and all

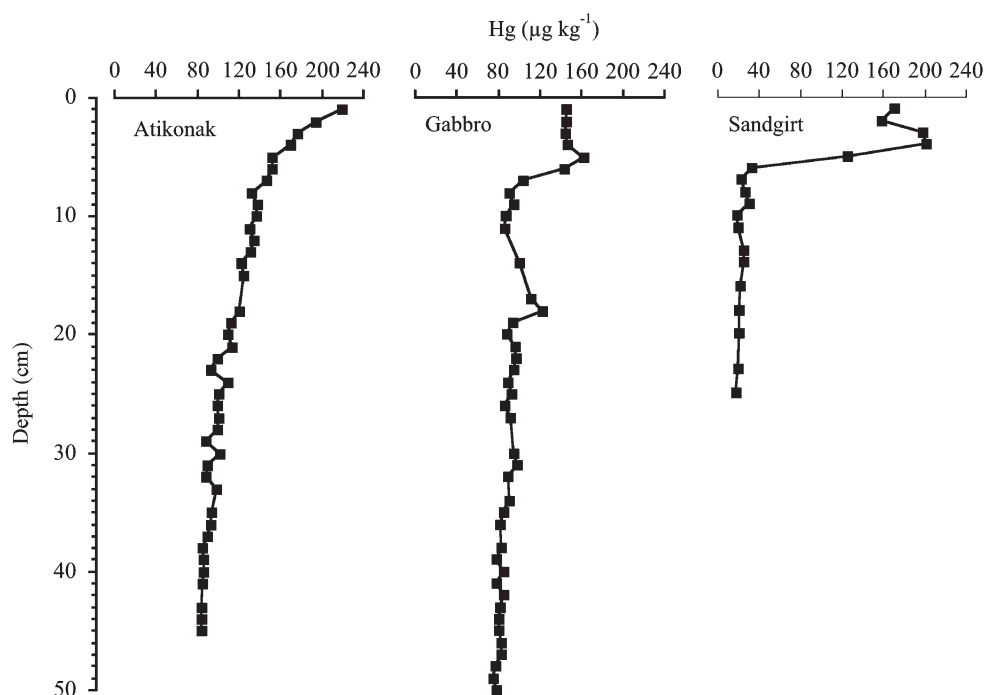
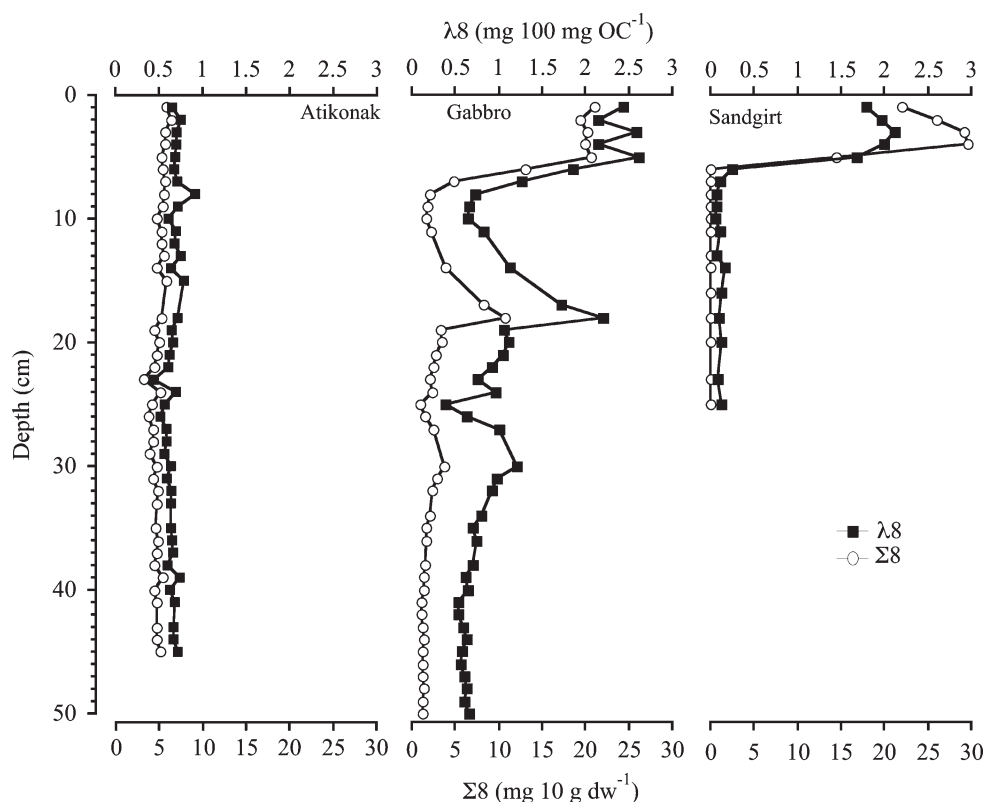


Fig. 3 Sedimentary profiles of mercury (Hg) ($\mu\text{g kg}^{-1}$) of Atikonak (unflooded), Gabbro and Sandgirt (flooded) lakes

Fig. 4 Sedimentary profiles of carbon- and mass-normalized yields of the sum of lignin-derived cinnamyl, vanillyl and syringyl oxidation byproducts: $\lambda 8$ ($\text{mg } 100 \text{ mg OC}^{-1}$) and $\Sigma 8$ ($\text{mg } 10 \text{ g dry wt}^{-1}$), respectively of Atikonak (unflooded), Gabbro and Sandgirt (flooded) lakes



show strong declines in ratios to lowest values at the top of the core (Figs. 5, 6). These variations in ratios are mainly due to changes in the concentration of vanillyl phenols (ΣV), which sharply increases—

similar to $\lambda 8$ and $\Sigma 8$ —in recent sediments. We also observed an important increase of syringyl phenols (ΣS), although the increase was not as pronounced as that of ΣV . No change was observed in cinnamyl

phenols (ΣC) (Fig. 7). For Sandgirt lake, C:V ratios decreased in the upper sediments, although here the decrease is related to a proportionally higher increase of vanillyl phenols than cinnamyl phenols (Figs. 5, 7). In contrast to Gabbro lake, S:V ratios increase in recent sediment, which is mainly due to the fact that syringyl phenols (ΣS) were below detection limits at the bottom of the core (i.e., S:V ratio of null) but showed detectable levels in upper sediments (Figs. 5, 7).

Ratios of 3,5Bd:V ratios at Atikonak lake are generally near a value of 1.0, although between depths 28 and 31 cm the values increase to about 1.50 (Fig. 6). In the two flooded lakes, we observed a common pattern for 3,5Bd:V ratios: ratios are rather variable at the bottom of the cores, but constant and low above centimeter 10 and 5, respectively (Fig. 6). For these variations, it is mainly vanillyl phenol contents of samples that drive these variations, although 3,5Bd also show significant increases in the top of cores.

Sedimentary profiles of atomic carbon to nitrogen (C:N) ratio and of acid to aldehyde ratio for vanillyl (Ad:Al)V and syringyl (Ad:Al)S phenols are presented as supplementary material.

Discussion

Identification of the flooding event in sediment record

Sedimentary records of flooded lakes hold information on both pre- and post-flooding events. Usually, flooding events modify organic matter dynamics in sediments resulting in sharp increases of TOM in recent sediments (Louchouart et al. 1993). In this study, the sum of lignin-derived phenols ($\lambda 8$ and $\Sigma 8$) show drastic changes in organic matter dynamics at sediment core depths of 7 cm and 6 cm in Gabbro and Sandgirt lakes, respectively. To confirm that these changes in patterns in the sediment cores corresponded to the timing of flooding, we performed ^{210}Pb dating of the sediment cores. The results of age dating confirmed that the time of flooding 40 years ago corresponds to sediment core depths of about 5 cm and 6 cm depth for Sandgirt and Gabbro lakes, respectively. These data are hence consistent with the depth where we observed strong increases in T-[Hg] (Fig. 3), strong increases in TOM loadings (Fig. 4), and substantial changes in ratios of individual lignin-derived phenol groups (Figs. 5, 6, 7).

Fig. 5 Sedimentary profiles of lignin source ratios of Atikonak (unflooded), Gabbro and Sandgirt (flooded) lakes. S:V, ratio syringyl to vanillyl phenols; C:V, ratio of cinnamyl to vanillyl phenols

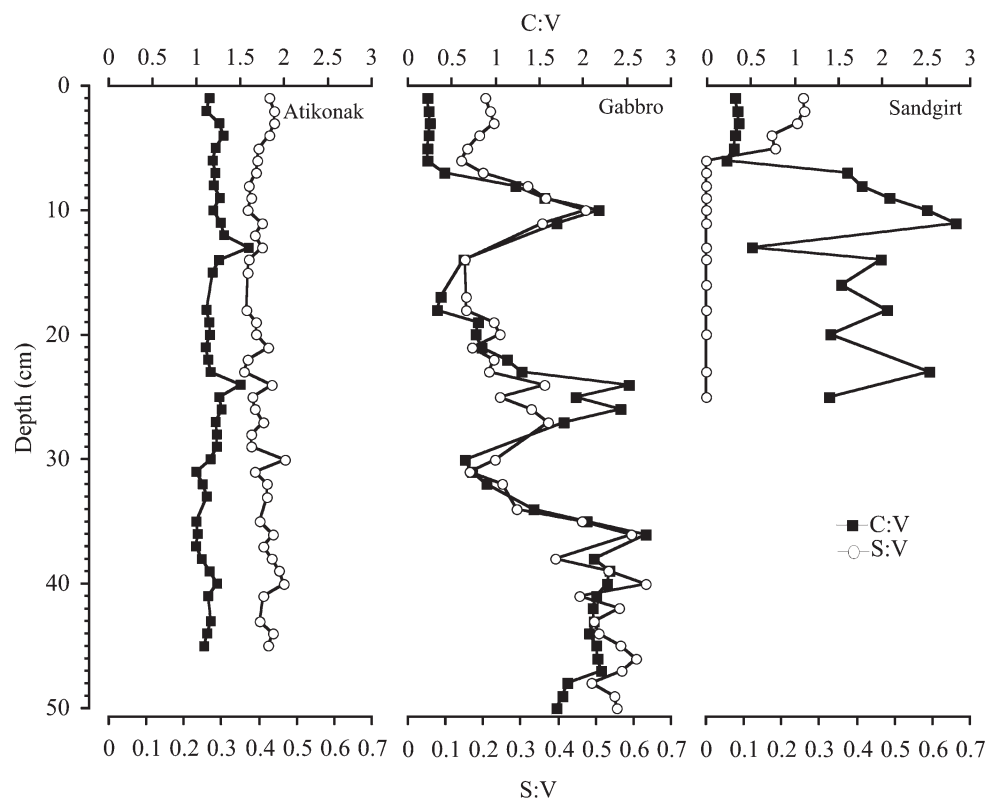


Fig. 6 Sedimentary profiles of lignin and organic matter degradation state indicators of Atikonak (unflooded), Gabbro and Sandgirt (flooded) lakes. P:(V + S), ratio p-hydroxyl phenols to the sum of vanillyl and syringyl phenols. 3,5Bd:V, ratio of 3,5-dihydroxybenzoic acid over vanillyl phenols

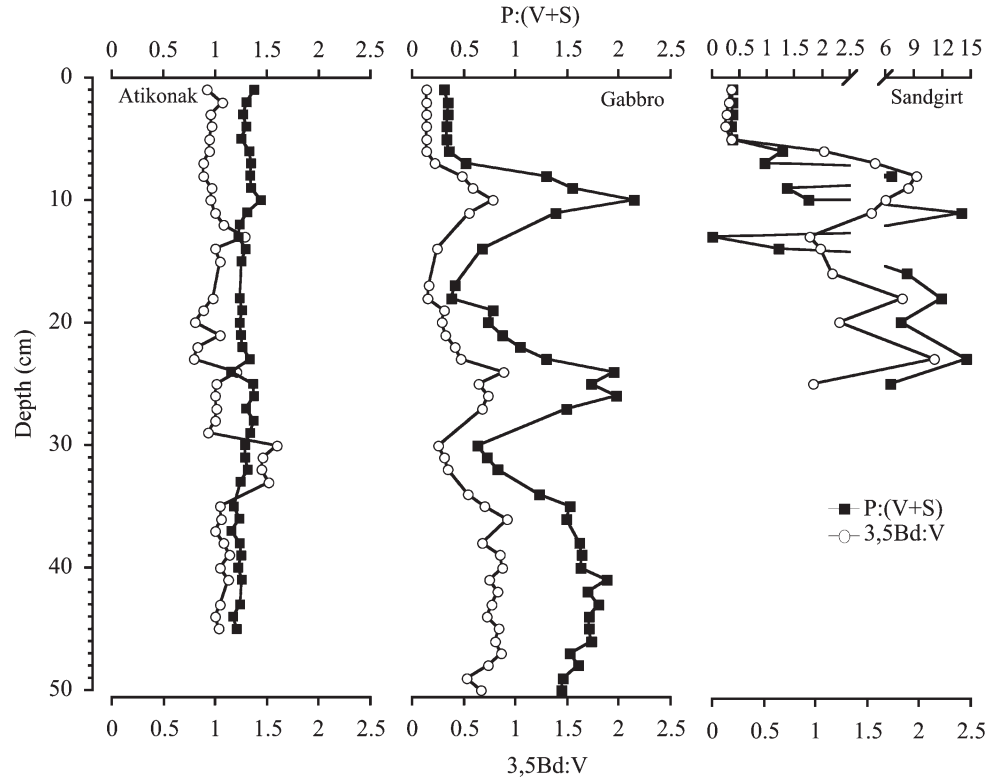
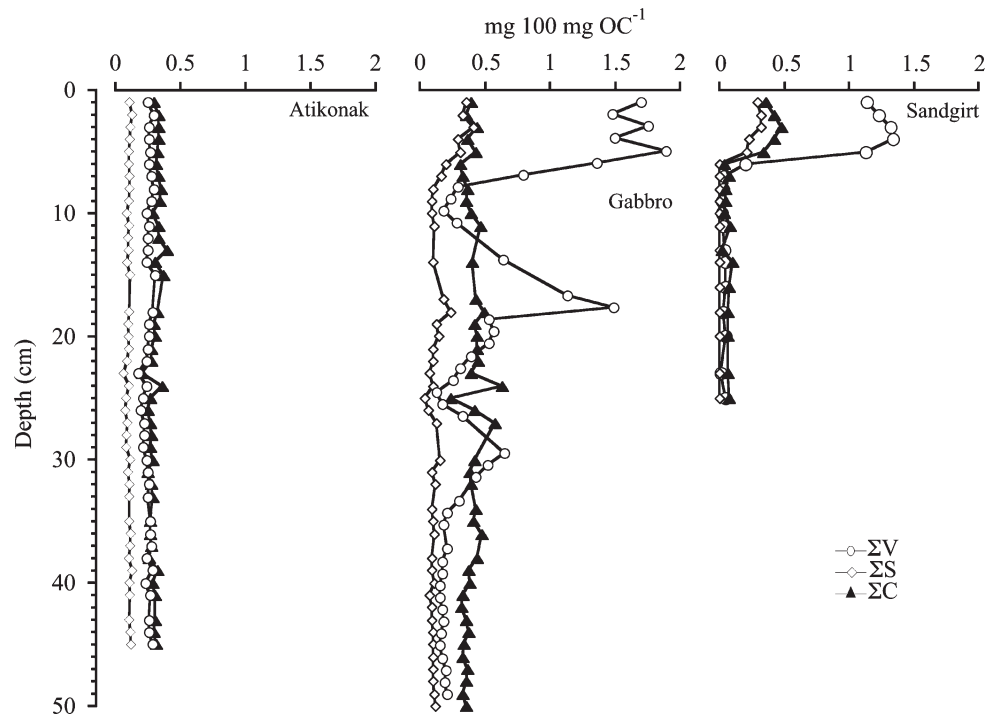


Fig. 7 Sedimentary profiles of sum of vanillyl (ΣV), syringyl (ΣS), and cinnamyl (ΣC) phenols ($\text{mg } 100 \text{ mg OC}^{-1}$) of Atikonak (unflooded), Gabbro and Sandgirt (flooded) lakes



Link between levels of lignin derived phenols and mercury

T-[Hg] in recent sediments of all three lakes under study are much higher than baseline levels observed in

deep sediments. Increases of T-[Hg] in boreal lake sediments may be explained by three principal factors: (i) mercury remobilisation from bottom sediments has been proposed as a potential reason by Rasmussen (1994), but Fitzgerald et al. (1998) demonstrated that

this phenomenon is limited and cannot explain Hg enrichments generally observed in recent lake sediments of the northern hemisphere; (ii) watershed perturbations such as forest fires, landslides, and forest logging, play a key role in the Hg cycle in boreal catchments (Munthe and Hultberg 2004; Garcia and Carignan 2005), and such disturbances are usually recorded in sedimentary profiles (Caldwell et al. 2000), although mostly at local or regional scales; (iii) for unperturbed watersheds, a broad scientific consensus attributes recent sedimentary Hg enrichments to long-range atmospheric transport and deposition of anthropogenic Hg emissions to even remote watersheds where it is ultimately transferred to lakes (Fitzgerald et al. 1998). The sediment profile of T-[Hg] in Atikonak lake, which has not been affected by damming and flooding, shows the classical profile of anthropogenic Hg enrichment observed since the beginning of the industrial era (Lucotte et al. 1995). Increases in T-[Hg] started at centimeter 20, and the enrichment factor between recent sediments and pre-industrial baseline level is 1.5, which is within the range of values observed in lake sediments from the James Bay (Québec, Canada; Lucotte et al. 1995). Results from lignin biomarker profiles in Atikonak lake confirm that increases of T-[Hg] cannot be attributed to particular watershed perturbations as TOM levels and biomarker patterns remained very constant in time. The relative amount of terrigenous material in sediments is also comparable to those reported for similar undisturbed lakes (Hu et al. 1999; Houel et al. 2006).

In the two flooded Gabbro and Sandgirt lakes, T-[Hg] increased abruptly in recent sediments from a baseline in older, deeper depths, and these increases occurred at depths of 8 and 6 cm, respectively. ²¹⁰Pb analysis support that these T-[Hg] increases are associated with the timing of flooding. In addition, corresponding increases in TOM loads, $\lambda 8$ and $\Sigma 8$, support this notion. Flooding hence caused important inputs of new terrigenous organic matter into lake sediments which show the signature of the surrounding terrestrial ecosystems. Our results also indicate that TOM plays a key role controlling Hg inputs to the lakes, a notion that has been shown in many previous studies (Kolka et al. 1999; Teisserenc et al. 2011). Clearly, increased loads of TOM and T-[Hg] still occurred after almost 40 years of flooding (1970 to present), indicating prolonged effects of flooding on

sediment TOM and Hg loadings. Baseline values of TOM ($\lambda 8$ and $\Sigma 8$) also provide insight about the states of the lakes before flooding: Gabbro lake showed levels of $\lambda 8$ and $\Sigma 8$ similar to those of Atikonak lake, likely because both lakes belong to the same Atikonak River drainage basin. Sandgirt lake is mainly drained by the Ashuanipi River, and showed much lower TOM inputs before flooding, and several lignin-derived phenols were below detection. This pattern was accompanied by correspondingly low T-[Hg], further evidence of a close association between TOM and T-[Hg] loading. We attribute the low TOM and T-[Hg] levels in Sandgirt to the fact that this lake was surrounded by a series of small, interconnected lakes and barrens, with little developed forests. Sandgirt lake was also a particularly shallow lake before flooding with a maximum depth of only 6 m (Duthie and Ostrofsky 1974), and baseline sediments of that core were primarily composed of silt and grey clay.

The increase in TOM was much more important in Sandgirt lake than in Gabbro lake upon flooding, which is likely linked to the extent of the flooded area. Gabbro lake is now included within the Ossokmanuan reservoir with a large area of 950 km² at maximum water level, whereas Sandgirt lake is part of the smaller Smallwood Reservoir of 56,000 km². In addition, the terrestrial compartment that was flooded differs between the two lakes: only 25 % of the flooded area of the Ossokmanuan Reservoir was composed of upland forests and muskeg, compared with 40 % in the Smallwood Reservoir (Duthie and Ostrofsky 1974). The profiles of $\lambda 8$ and $\Sigma 8$ for Gabbro lake also indicated a major perturbation of the watershed several years before flooding, an event that modified ecosystem dynamics for some time before TOM inputs returned to baseline levels. The same perturbation caused a temporary enhancement of T-[Hg]. Such simultaneous increases of TOM and Hg in sediment have been related to severe forest fires (e.g., Nelson et al. 2007), which induce increased soil leaching and release of organic matter and associated contaminants (Caldwell et al. 2000), although we have no historic records of wildfire history of this area.

Using TOM as biomarkers in lake sediments

TOM origin can be determined according to ratios of various biomarker groups. (i) Ratios of syringyl to vanillyl phenols (S:V) have been used to distinguish

between angiosperm and gymnosperm plants because only angiosperm plants produce syringyl phenols (syringe aldehyde, aceto syringone, syringic acid) (Hedges and Mann 1979). (ii) Ratios of cinnamyl to vanillyl phenols (C:V) are commonly used as indicator of source tissues because non-woody plants and leaves produce much more cinnamyl phenols (ferulic acid and p-coumaric acid) than woody parts of plants. Meanwhile, vanillyl phenols are ubiquitous in all terrestrial plants. (iii) Ratios of P:(V + S) are used as indicators of the state of degradation of terrigenous organic matter. Pedogenetic demethylation leads to selective loss of methoxylated phenol groups of vanillyl and syringyl phenols, while p-hydroxy phenols are not affected by demethylation. P:(V + S) ratios hence increase with higher states of TOM degradation (Dittmar and Lara 2001). (iv) Finally, 3,5Bd is a common CuO oxidation product found in samples from sediment and soils, but not from fresh vascular plant tissues (Ugolini et al. 1981). It has been suggested that this compound is a product of pedogenesis and is directly linked to lignin degradation (Houel et al. 2006; Teisserenc et al. 2010). As a result, in terrestrial and freshwater ecosystems presence of 3,5Bd biomarkers have been proposed as an indicator of soil organic matter origin (Prahl et al. 1994). The likely precursors of this phenolic product are tannins and other flavonoids (Goñi and Hedges 1995), and because tannin-like materials tend to accumulate within decaying cells a relative increase of 3,5Bd in mineral horizons of soils may reflect extent of degradation and humification of fresh vascular plant tissues (Houel et al. 2006; Teisserenc et al. 2010).

TOM biomarker patterns remained relatively constant in the sediments of Atikonak lake: for example, S:V and C:V showed no clear trends along the core, and we hence conclude that this lake received TOM inputs from a relatively unaltered plant composition with no major changes that occurred in its watershed. S:V ratios were relatively high for a northern conifer-dominated ecosystem dominated by conifers given that only angiosperm plants should produce syringyl monomers (Hedges and Mann 1979). However, we previously found that spruce forests also may produce significant amounts of syringyl monomers (Teisserenc 2009), and leaching and sorption processes in soils may influence S:V and C:V ratios (Hernes et al. 2007). C:V ratios measured in the sediments were much higher than those found in boreal forest soils

(Teisserenc 2009), although Hu et al. (1999) found similar ratios in lake sediments, which they linked to pollen produced by *P. mariana*, the dominant tree species in the region. High P:(V + S) and 3,5Bd:V ratios in Atikonak lake sediments indicate that TOM is highly degraded and has undergone major humification processes in soils before entering the lake sediments as signatures were similar to inorganic horizons in spruce soils. Such high values are usually associated with low mean slope of watersheds causing slow erosion rates and high residence times of TOM (Teisserenc et al. 2010).

In Gabbro lake, S:V and C:V ratios in the sediment profile were highly driven by changes in vanillyl phenols content. Following the impoundment, total yield of vanillyl phenols increased proportionally more than that of the cinnamyl and syringyl phenol families, decreasing both S:V and C:V ratios. The stronger increase of vanillyl phenols compared to cinnamyl and syringyl phenols may be explained by the flooding of vast areas of forest and soil, as cinnamyl and syringyl phenols are specific to certain classes of plants while vanillyl is ubiquitous in terrestrial plants (Hedges and Mann 1979). While C:V patterns at Sandgirt lake showed similar behavior as in Gabbro, this lake showed an absence (i.e., below detection) of syringyl phenols before flooding (a ratio of 0). Increases in syringyl phenols after flooding then caused S:V ratios to be detectable, but they remained low, which is a common characteristic of coniferous boreal forest soils (Teisserenc 2009). Large variability in C:V ratios prior to flooding in both lakes is due to certain compounds being below detection limits at certain core depths, thereby distorting the ratios.

Although P:(V + S) and 3,5Bd:V ratios were also variable due to variability in vanillyl phenols, they showed simultaneous decreases in both lakes after flooding, suggesting that TOM inputs were less degraded following flooding. This is also supported by the (Ad:Al)V and (Ad:Al)S ratios presented as supplementary material. We propose that substantial mobilization of organic carbon, particularly from surface soil layers, explain the drop in these ratios. We tested this hypothesis using a mixing model proposed by Houel et al. (2006). This mixing model is based on mass-normalized yields of the different CuO oxidation parameters in two distinct end-members, namely that originating from surface organic spruce stand soil horizons and from deep mineral soil

horizons from James Bay (Teisserenc 2009). We tested such a model using 3,5Bd:V ratios versus carbon-normalized lignin yields (λ_6) according to the mixing equation:

$$\left(\frac{A}{B}\right)_{sed} = \frac{(A_o \times F_o) + [A_i \times (1 - F_o)]}{(B_o \times F_o) + [B_i \times (1 - F_o)]}$$

where A represents the mass-normalized yields for the parameter in the numerator of the ratio (3,5Bd, P, and λ_6); B represents the mass-normalized yields for the parameter in the denominator (V, [V + S], and OC, respectively); F_o is the fraction of organic matter derived from surface soil litter in the sedimentary mixture; and the subscripts represent the mass-normalized yields observed for the different parameters within sediment intervals (sed), deep soil mineral horizons (i), and surface organic-rich soil litter (o). All mass-normalized yields of the different CuO-derived parameters used in this model are presented in Table 1. Mixing model and observational data fit best when recent sediment in Gabbro and Sandgirt lakes receive input from 3,5Bd:V signatures typical of soil surface horizons (Fig. 8). Highest T-[Hg] are generally observed in organic surface horizons and in top soils of forest soils (Grigal 2003; Friedli et al. 2007; Obrist et al. 2011) due to strong sorption of atmospheric Hg depositions to these upper, carbon-rich surface pools (Harris et al. 2007; Graydon et al. 2009; Pokharel and Obrist 2011). The results of our biomarker study suggest that it is these Hg-enriched surface pools that contribute most strongly to loadings and enrichment of T-[Hg] in reservoir sediments after flooding.

Finally, profiles showing continued high TOM and T-[Hg] loadings since flooding (1968–1974) and continued alterations of all biomarker signatures into most recent sediments in Gabbro and Sandgirt lakes suggest that flooded soils continued to be major sources of mercury and organic matter to sediments of these lakes more than 40 years after impoundment.

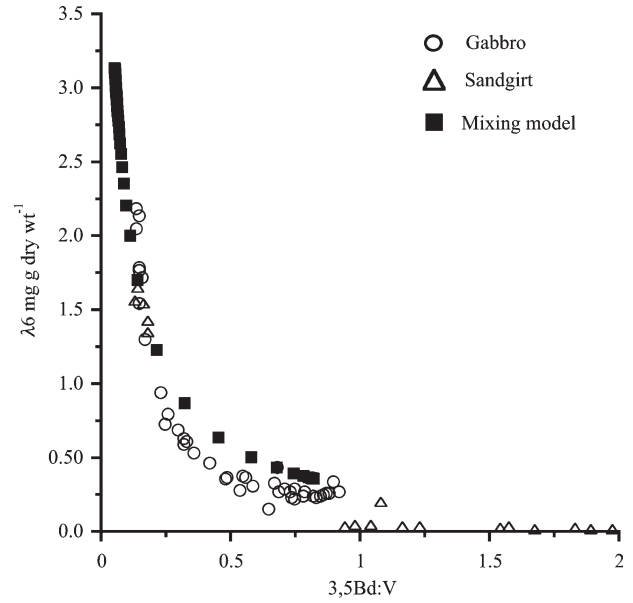


Fig. 8 Measured biomarkers signatures in Gabbro and Sandgirt sediments and comparison to theoretical values based on a mixing model between surface litter and deep mineral SOM end-members. *Box* represent post-flooding sediments of the two flooded lakes (i.e. 7 and 6 cm for Gabbro and Sandgirt, respectively)

Previous studies have shown that remobilization of flooded soil organic matter and mercury were limited to the first years after perturbation (Louchouart et al. 1993; Grondin et al. 1995; Houel et al. 2006), mainly because remobilization was limited to drawdown zones and area of shallow waters (wave influence). The Churchill Falls Hydroelectric complex is characterized by low mean slopes and shallow reservoir depths (about 4 m drawdown in the Smallwood Reservoir and 3.5 m in the Ossokmanuan Reservoir; Duthie and Ostrofsky 1974). These characteristics may be the reasons that large areas of soils are potentially remobilized regularly and continue to be a major source of Hg and TOM to reservoirs.

In summary, combination of ^{210}Pb age dating, use of TOM biomarkers, and measurements of T-[Hg] in lake sediments demonstrate that large increases in

Table 1 Mass normalized concentration of biomarkers used as end-member in the mixing-model (mg g dry wt^{-1})

	λ_6	ΣV	3,5Bd
Surface organic horizon ($n = 18$)	12.9 ± 3.6	6.5 ± 2.1	1.1 ± 0.4
Deep mineral horizon ($n = 28$)	0.12 ± 0.05	0.11 ± 0.09	0.08 ± 0.05

Carbon-normalized yields of the sum of lignin-derived vanillyl and syringyl oxidation byproducts: λ_6 (mg 100 mg OC^{-1}), the sum of vanillyl ΣV (mg 100 mg OC^{-1}), and 3,5-dihydroxybenzoic acid (mg 100 mg OC^{-1})

[Hg] in sediments were a result of flooding of large-scale terrestrial areas included in the reservoir. Based in detailed TOM biomarker characterization, the origin of TOM was tracked to originate from surface litter and soil, and we conclude that this was also the major source for Hg because surface organic horizons and upper soils enriched in Hg were prone to erosion and subsequent re-sedimentation in the reservoirs. Enrichments in TOM and Hg levels are still observed forty years after flooding, suggesting a long-term disruption of TOM and Hg loadings after reservoir impoundment. Differences in TOM and Hg loads between the two flooded Sandgirt and Gabbro lakes demonstrate the importance of the flooded area, surrounding vegetation, and watershed slope for Hg and TOM dynamics.

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