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Mercury–organic matter relationships in pre-pollution sediments of thermokarst lakes from the Mackenzie River Delta, Canada: the role of depositional environment

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Abstract This study investigates the influence of organic matter (OM) on the historical variations of Hg in sediments from two closely-situated Canadian Arctic lakes, prior to the advent of Hg pollution inputs. Because of variable landscape evolution in the Mackenzie River Delta over the past 1–3 millennia, the lakes provide distinctly different histories of OM sources, types, and degree of aquatic productivity (i.e., depositional environments). They also differ significantly in their pre-1900 Hg concentration profiles. When labile, kerogen-like carbon ("S2") from aquatic sources (diatoms and other unicellular algae) increased between 750 and 1900 A.D. in the more productive lake (Nesbitt), Hg concentrations also increased by ca. 50%. In contrast, S2 carbon concentrations in the nearby organic-poor lake (Big Lake) were several-times lower than in Nesbitt and decreased over the past millennium, while Hg concentrations showed no trend probably reflecting the stable input of clastic material from tundra soils. The contrast between lakes suggests that OM derived from unicellular algae is more effective at scavenging Hg than OM from terrestrial plants or aquatic macrophytes, possibly because of a higher content of labile, sulphur-rich compounds, high particle surface area and its dispersion throughout the water column. The results indicate that, in the absence of anthropogenic Hg inputs, increasing phytoplankton productivity and Hg scavenging alone can lead to significant increases in the Hg content of lake sediments. This finding is consistent with the hypothesis that increasing lake productivity because of climate warming during the twentieth century has confounded the interpretation of recently increasing Hg levels in northern lake sediments as being unequivocally due to anthropogenic Hg deposition. This study also suggests that sedimentary TOC by itself is a poor and sometimes misleading indicator of possible changes in the source and quality of OM in aquatic systems, which can have a major impact on Hg concentrations in sediments.

Keywords Arctic · Mercury · Recent sediments · Rock-Eval · Thermokarst lakes · Algae

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Introduction

In the Arctic, lake sediments and other natural archives provide almost all of the historical trend data available on mercury (Hg) deposition from the atmosphere, given the near-total absence of long-term instrument-based monitoring in this region (AMAP 2005). There is a large body of evidence that Hg dynamics and fate in aquatic ecosystems generally may be strongly influenced by variations in the composition (source and type) and quantity of organic matter (OM) produced in or entering the water body (e.g., Jackson 1986; Kainz et al. 2003; Sanei and Goodarzi 2006). Although this evidence applies mainly to spatial patterns within and across freshwater systems, it is also relevant to temporal patterns. Thus, studies on Hg in sediments, especially those using these archives as recorders of atmospheric Hg deposition, should consider the possible impact that temporal changes in the sources, quality and quantity of OM in the system may have on the sedimentary Hg record independently of atmospheric inputs.

Recently, a growing number of studies on Arctic and sub-Arctic lake sediments has reported significant associations between the concentrations and fluxes of Hg and of certain operationally-defined classes of organic carbon compounds derived mainly from autochthonous (algal) primary productivity (Outridge et al. 2007; Carrie et al. 2009; Stern et al. 2009). These associations support the hypothesis (Outridge et al. 2005) that recent climate-related increases in algal productivity and in the rate of scavenging of available Hg from the water column may have accelerated the delivery of Hg to northern lake sediments, and may explain at least part of the three- to fourfold increases reported in sedimentary Hg fluxes during the twentieth century. If this hypothesis is true, then the inputs of airborne anthropogenic Hg to the Arctic calculated from sediment records (e.g., see Lockhart et al. 1998; Muir et al. 2009) have been significantly overestimated. Preliminary calculations suggest that no more than 20–30% of the twentieth century increase in sediment Hg concentrations may be due to Hg pollution while the balance is due to the scavenging effect (Outridge et al. 2007; Stern et al. 2009), although this remains to be confirmed by further investigation. The hypothesis is therefore potentially important, and could also explain why Arctic lake sediment Hg fluxes have rapidly increased over recent decades (see Muir et al. 2009; Fig. 3) while the trends of gaseous and particulate Hg in the Arctic atmosphere have been stable or significantly decreasing (Temme et al. 2007; Faïn et al. 2009; Li et al. 2009).

A key question concerning this hypothesis is whether changes in autochthonous productivity by themselves could significantly alter Hg concentrations in Arctic lake sediments. There are a number of approaches by which this question can be investigated. The approach chosen here is to study Hg–OM relationships in a pair of adjacent northern lakes which have undergone dramatic but contrasting natural changes in OM type and quantity prior to the twentieth century. Anthropogenic Hg was not detectable in Canadian Arctic and sub-Arctic lakes prior to 1900 (Muir et al. 2009). The advantage to investigating this question in the absence of anthropogenic Hg is that any alterations in sedimentary Hg profiles can be attributed to natural processes alone. Here, we characterize the pre-1900 profiles of sedimentary OM, diatom community abundance and taxonomy, and Hg concentrations in two Arctic thermokarst (“thaw lake”) and tundra lakes which have undergone contrasting geomorphological changes because of landscape evolution over the last one to three millennia. We explore the relationships between Hg concentrations and changing depositional environments, particularly OM sources and quality (aquatic versus terrestrial; changing aquatic productivity during lacustrine phases) during distinct periods of lake development in the pre-twentieth century period.

Study area

We studied two thermokarst channel and tundra lakes located on Richards Island, in the Mackenzie River Delta, Northwest Territories, Canada (Fig. 1). The lakes were part of a larger number of lakes in this area whose sediment stratigraphy and development had been studied by Dallimore et al. (2000). The study lakes were chosen because they are among the largest in the region, and were large enough so that their maximum depths exceeded the average winter ice thickness, meaning that some part of their water

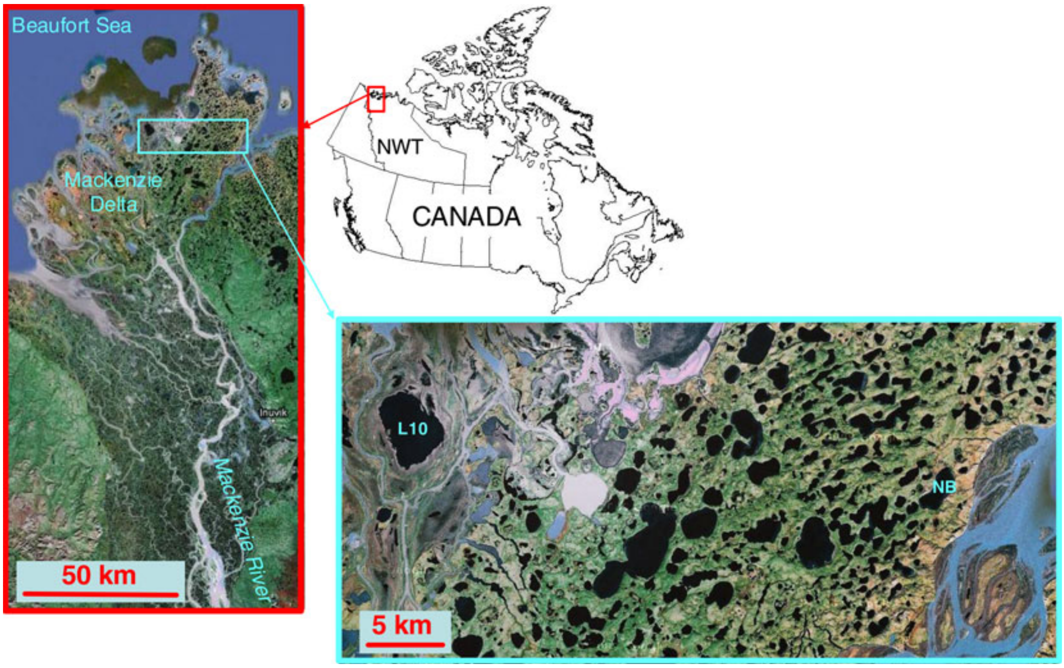


Fig. 1 Map of the study area showing locations of Nesbitt Lake (NB) and Big Lake (L10) within the Mackenzie Delta, Northwest Territories (NWT), Canada

columns always remained unfrozen. The channel lake, Big Lake (also known as "L10"; 69°26.51′N, 134°56.01′W; Fig. 1), has been located within a seasonally-active river channel since about 1000 years B.P. Prior to this, it was a peat bog and prior to about 2700 years B.P. subaerially-exposed tundra (Dallimore et al. 2000). Climate warming around 1000 years B.P. is probably responsible for deepening the active surface layer and creating the depression that became the lake. Presently, the lake has a maximum depth of 3.3 m, and is frozen over for about 9 months each year with a maximum ice thickness of ~1.5 m. It has a non-stratified, oxygenated water column in summer; in winter, when stratification occurs, higher temperatures and oxygen levels in bottom waters are probably indicative of active gas flux into the lake (Dallimore et al. 2000). Big Lake exchanges water with the Mackenzie River during ice-free periods.

Nesbitt Lake (69°22.60′N; 134°4.40′W; Fig. 1), near the East Channel estuary of the Mackenzie River, has been a wetland or shallow tundra lake for at least 3000 years based on dating of nearby lake sediments (Dallimore et al. 2000). It occupies what was once a glacial drainage channel that moved meltwaters north to the Beaufort Sea. Presently it is ~3.0 m maximum depth, with a similar winter ice cover depth and seasonal extent as Big Lake. However, Nesbitt is relatively isolated from the river and estuary, and thus receives Hg and OM inputs solely from its catchment and the atmosphere except during rare flood events (see below). The water column is oxygenated, and non-stratified year-round.

Methodology

Sediment coring

Single sediment cores were obtained from each lake using a Livingstone corer in April 2004, by coring through the ice platform. The study lakes contain single basins and have small surface areas relative to others studied by our group. Previous studies have shown that multiple cores from larger lakes in the Canadian Arctic provide very similar results (see Outridge et al. 2005, 2007; Stern et al. 2009). Therefore, a single sediment core provides sufficient representation of the lakes' depositional basins. Total core lengths were 114 cm for Big Lake, and 211 cm for Nesbitt Lake. They were kept at ambient cool temperatures, and returned to Geological Survey of Canada laboratories where they were stored at 4°C. The cores were split vertically, and separate subsamples for Hg and organic analyses described in this paper were taken at 1 cm intervals from the sediment surface. Because of increasing amounts of peat moss and sparse sediments in the lower parts of the cores, only the upper 120 cm of the Nesbitt core, and the upper 110 cm of Big Lake, were sampled for this study. Discrete intervals in each core containing only peat moss and no aquatic sediments were not sampled, as these were clearly not representative of an aquatic environment. Subsamples were removed from the centre of one core half after scraping away the exposed face with a stainless steel knife, and placed in 50 ml screw-capped polyethylene tubes where they were frozen. They were later freeze-dried, and homogenized with an acid-cleaned mortar and pestle. Plant macro-fossils for radiocarbon dating were removed from the other core half at measured depths from the sediment surface.

Radiocarbon dating

Radiocarbon (^{14}C) dating of plant macro-fossils was carried out by accelerator mass spectrometry at the University of California (Irvine). The plant samples included twigs, wood pieces, grass stalks, charcoal, pine cone pieces or bulk peat. Calibrated ^{14}C dates were calculated against the radiocarbon calibration curve of Reimer et al. (2002), using the on-line program CALIB (version 5.0.1; www.calib.qub.ac.uk/calib) and are expressed as median ages within 2δ probability intervals, relative to 1950 A.D. (Table 1). Where a consistent sequence of declining age with increasing depth was found (in Nesbitt Lake), ages of intervening slices between dated samples were calculated assuming a linear accumulation rate.

Organic geochemistry (Rock-Eval analysis)

Rock-Eval® 6 (Vinci Technologies, France) analysis, a widely-accepted analytical technique in organic carbon geochemistry, was used to characterize the organic geochemistry of OM matter in the sediment samples. Rock-Eval characterizes the quality and quantity of OM in samples based on the degree of thermal degradation for various organic carbon compounds. For this purpose, a bulk sediment sample (30 mg) is the subject of the programmed temperature heating (at the heating rate of 25°C), first in the pyrolysis oven (under inert conditions), and then in the oxidation oven.

Table 1 Radiocarbon dates on plant macrofossils from cores in Nesbitt and Big lakes, Mackenzie Delta

Depth interval (cm)	UCIAMS sample ID	δ^{14}C (‰)	^{14}C age (yr B.P.)	Calibrated date (yr A.D. or B.C.)
Nesbitt Lake (NB)				
19–20	24805	−128.3	1115 ± 15	930 A.D. (892–976 A.D.)
42–43	24806	−133.7	1165 ± 15	850 A.D. (803–897 A.D.)
75–76	24807	−201.1	1815 ± 15	190 A.D. (135–239 A.D.)
102–103	24808	−307.1	2990 ± 50	1280 B.C. (1387–1109 B.C.)
113–114	24809	−306	2970 ± 40	1180 B.C. (1316–1052 B.C.)
Big Lake (L10)				
35–36	13532	−61.4	540 ± 35	1410 A.D. (1387–1439 A.D.)
43–44	25291	−112.1	970 ± 15	1070 A.D. (1020–1124 A.D.)
52–53	24810	−103.3	890 ± 20	1130 A.D. (1046–1214 A.D.)
55–56	25290	−146.6	1290 ± 20	720 A.D. (668–772 A.D.)
56–57	13533	−84	720 ± 15	1280 A.D. (1267–1289 A.D.)
73–74	13534	−108	930 ± 15	1100 A.D. (1039–1155 A.D.)
78–79	10368	−114.4	995 ± 20	1020 A.D. (992–1045 A.D.)

Calibrated dates given as median (rounded to three significant figures) of 2δ probability ranges shown in brackets

UCIAMS refers to University of California (Irvine) accelerator mass spectrometer laboratory

Pyrolysis step

In the first heating episode, the bulk sample is transferred to the pyrolysis oven and heated from 100 to 650°C under nitrogen. The on-line FID detector measures two specific populations of H–C pyrolysates released from the organic content of the sample. The most volatile and thermally unstable portion of OM is “S1”, which decomposes between 100 and 300°C. S1 is geochemically identified as volatile, free hydrocarbons in the sample. In recent sediments, S1 is attributed to the volatile portion of the diagenetically produced substances of algal origin and in general aquatic geolipids with short carbon chain and easily degradable pigments (Sanei et al. 2006). In the temperature range of 300–650°C, the second peak “S2” is evolved, also under nitrogen. S2 corresponds to the H–C bonds released mainly due to thermal cracking of hydrogen-rich aliphatic biomacromolecules forming the cell walls of algal matter (Sanei et al. 2006). During the pyrolysis step, two online infrared (IR) detectors also measure the quantity of CO and CO_2 released due to thermal cracking of oxygen-bearing organic compounds (“S3”; mg CO–CO_2/g of sample). The analyses take appropriate measures to avoid interference by releases of inorganic CO and CO_2 at temperatures higher than 570 and 400°C, respectively (Lafargue et al. 1998).

Hydrogen index (HI) is calculated by normalizing the quantity of S2 to total organic carbon (S2/TOC × 100) and is proportional to the kerogen elemental H/C ratio (Espitalié et al. 1977). Similarly the quantity of CO–CO_2 released during pyrolysis is normalized to TOC to produce the oxygen index (OI) (S3/TOC × 100), which is proportional to the elemental O/C ratio of the kerogen (Espitalié et al. 1977). The type of kerogen (or humic substances in recent sediments) in samples is characterized by plotting HI and OI on a Van Krevelen diagram (Van Krevelen 1961) and on a S2 versus TOC plot (Langford and Blanc-Valleron 1990). The kerogens showing the highest HI (or S2/TOC) are classified as Type I and the lowest as Type III (Tissot et al. 1974). Kerogens of algal origin are known to have high HI relative to OI or S2 relative to TOC, because of the aliphatic hydrocarbon pyrolysate released during high temperature cracking of algal-derived kerogen. These hydrocarbons are dominantly originating from scission of lipid-derived elements in the kerogen macromolecules (Larter and Horsfield 1993). In contrast, terrestrial plant kerogen is characterized by higher OI than HI.

Oxidation step

After the completion of pyrolysis, the sample is automatically transferred to an oxidation oven and re-heated from 400 to 850°C in the presence of oxygen. The quantity of CO and CO_2 (mg CO–CO_2/g of sample) released due to combustion of sample below 650°C corresponds to the portion of residual organic carbon (RC). In general, the RC content represents the quantity of highly refractory OM. The total organic carbon (TOC; wt%) in the sediment sample is quantified as the sum of the total quantity of OC emitted during pyrolysis (Pyrolysable carbon; 100–650°C) and oxidation (Residual carbon; 400–850°C).

Hg analysis

Total Hg in sediment samples was analysed by laboratories of Fisheries and Oceans Canada using cold vapour AAS (see Lockhart et al. 1998). Analyses of standard reference material sediments (MESS-2 and PACS-2, National Research Council of Canada) showed accuracy and precision to be better than 3% and 5% RSD, respectively.

Organic petrology

Freeze-dried sediment samples were placed in isolated 1 cm diameter Teflon molds and then impregnated with a cold-setting EPOTECH® epoxy–resin mixture. Sample pellets were kept covered until the epoxy–resin mixture was cured, and then were ground using carborundum grit. The pellets were subsequently polished on Pelon® and then on a silk-covered lap using alumina-water slurries of 0.3 and 0.05 µm, respectively, in final preparation for microscopy. Organic petrography was carried out using an incident light Zeiss Axioplan II microscope system equipped with white and fluorescent light sources, a J & M® photometer, and a spectrometer (300–1100 nm). Oil-immersion objectives attaining magnifications of 100–2500× were used for the microscopic study. Fluorescence microscopy of OM represents the ultraviolet G 365 nm excitation with a 420 nm barrier filter. Digital images were captured using Zeiss Axiocam® and Axiovision® software.

Diatom distribution

For diatom analyses ca. 0.05 g of dry sediment from selected core sections were digested with hot 50:50 nitric:sulfuric acid for 20–30 min. After digestion, the acid was removed through a series of five deionized water washes. The remaining solution was set to 45 ml of slurry solution. Subsamples ranging from 8 to 15 ml from each treated sample were distributed into 51 mm diameter plastic settling trays, each containing two 18 × 18 mm No. 1 coverslips and allowed to dry. Once dried, the coverslips were mounted on microscope slides using the heat curing Naphrax® mountant with a refractive index of 1.65. Diatom numerations were conducted at 1000× magnification using a Leica DMR microscope with Brightfield and DIC optics (100×: Plan Apo HCX 100/1.35 objective). Randomly selected transects with a width of 240 μm were examined for each sample. The examined area on each coverslip varied from 1.5 to 15% depending on diatom densities. Nesbitt Lake valve counts ranged from 146 to 876; on average 564 valves were counted per sample. In contrast, Big Lake had fewer diatoms in each sample with counts ranging from 1 to 175 valves; on average 56 valves were counted per sample. To verify the reliability of low valve counts in Big Lake, valve fragments were also enumerated. Valve fragments were also rare, ranging from 1 to 153 fragments per sample. There was a good correlation between valve counts and valve fragments ($r^2 = 0.812$). Total valves estimated (per g dry weight) were subsequently determined. All the samples including the enumerated diatom sample slides, along with metadata for verifying the counts, are deposited at the Canadian Museum of Nature (CANA 83535–83668).

Results and discussion

Dating of cores—exclusion of twentieth century sediments

For the purposes of this paper, we wish to consider only sediment Hg–OM relationships prevailing before the advent of anthropogenic Hg in the Arctic in the twentieth century (see Muir et al. 2009). Radiocarbon dating of terrestrial plant macro-fossils showed that the twentieth century, in the study lakes, was represented by only the upper few centimeters, which will be ignored subsequently in this paper. Nesbitt Lake exhibited a reasonably consistent sequence of increasing dates with depth (Table 1), with calibrated radiocarbon dates ranging from 930 A.D. at 20 cm depth to 1180 B.C. at 114 cm (for convenience, depths cited in the text are the lower edges of the slices). The year 1900 in Nesbitt Lake is estimated to have occurred in the 4–5 cm core slice, extrapolated from the total sediment accumulation (94 cm, i.e., 20–114 cm) over 2100 years. This is a conservative (maximum) estimate because the most recent date available (930 A.D. at 20 cm) suggests 1900 may have occurred at ~2 cm assuming a constant sedimentation rate since then. The radiocarbon dating—depth sequence was inconsistent for Big Lake (Table 1), because of intrusion of younger or older plant material into the sequence, or reworking of sediments by infaunal or physical disturbance. The estimated depth of 1900 A.D. in Big Lake ranged from ~4 to 8 cm, depending on which age-depth data were chosen; conservatively, the upper 10 cm is excluded. No macro-fossils occurred above 20 cm in Nesbitt and above 36 cm in Big Lake, and so these estimates could not be constrained by more recent dates.

Depositional environment—Nesbitt Lake (NB)

OM in the recent sediments from Nesbitt Lake is uniformly classified as Type II kerogen, based on the Van Krevelen diagram (HI:OI; Fig. 2a) and S2:TOC kerogen diagram (Fig. 2b), which suggests a predominantly aquatic origin. There is an overall decrease of ~50% in TOC down-core with large fluctuations of up to 30% throughout the profile (Fig. 3a). There is a similar downward decreasing pattern of concentrations of labile (S1) and more resistant aliphatic kerogen (S2) carbon compounds (Fig. 4a). However, the more readily degradable S1 fraction, which comprises lipids, sugars and pigments (Sanei et al. 2006), shows faster degradation and loss (as indicated by the steeper regression slope versus depth) than the S2 fraction. Superimposed over this overall down-core decrease in organic carbon content, periodic oscillations and marked shifts in composition may reflect changing environmental conditions and lake morphology (see below). Four distinct periods in Nesbitt Lake's evolution are

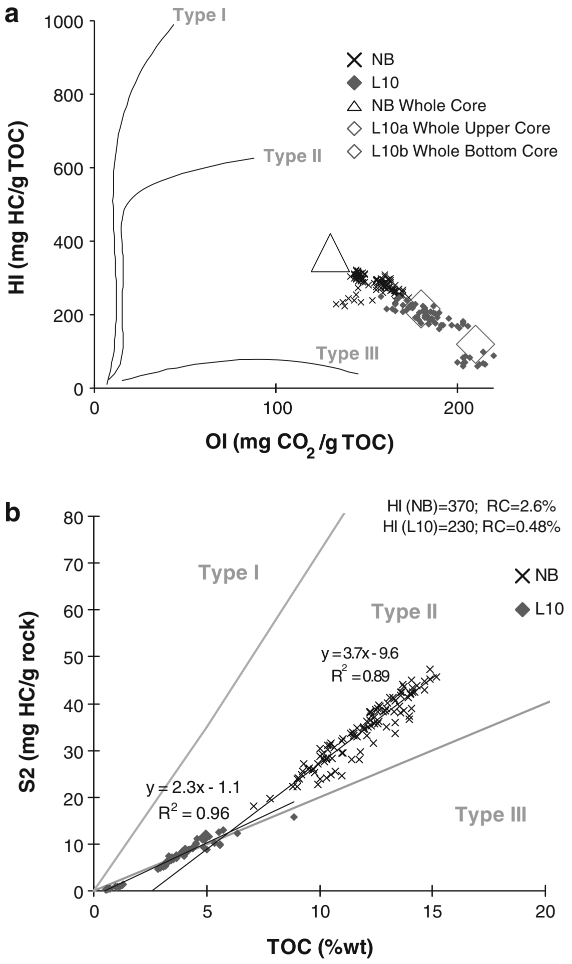


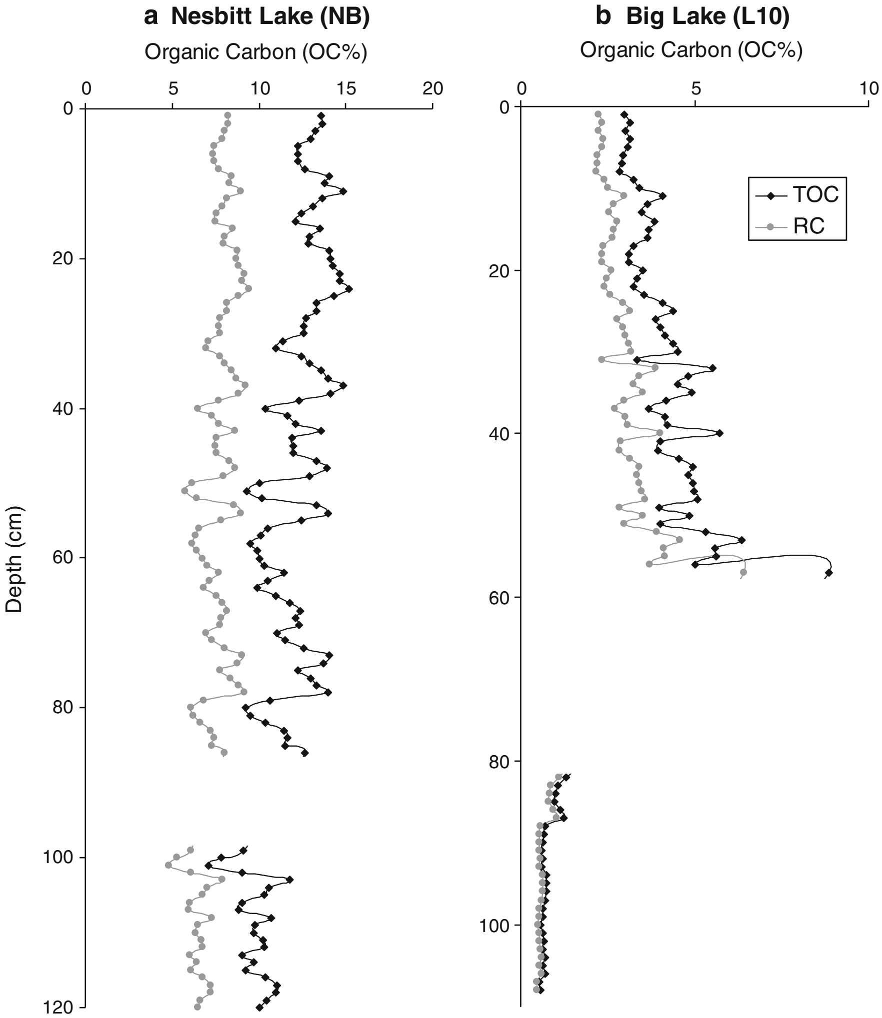
Fig. 2 Kerogen types for sediments OM in Nesbitt (NB) and Big (L10) lakes as determined by Van Krevelen diagram (HI:OI) (**a**) and S2:TOC (**b**) (in **a**, the kerogen types for each sediment interval and the whole core values estimated using regression lines of S2:TOC (for HI) and S3:TOC (for OI). In **b**, HI and residual carbon (RC%) values for the whole core estimated using the cores' regression lines in S2:TOC (slope of the line = HI; interception of the line with TOC axis = RC))

recognized based on organic petrology, geochemistry and diatom abundance (see Fig. 4a).

In general, Nesbitt Lake shows higher TOC than Big Lake (Fig. 3a, b), and higher S1 and S2 (Fig. 4a, b), which is consistent with a long-established lacustrine depositional environment allowing for higher algal production of OM. This is also evident from the total diatom counts which show on average 138 times greater abundance throughout the Nesbitt Lake core (3.9 × 10^7 valves/g DW) than in Big Lake (2.8 × 10^5 valves/g DW). However, within this broadly lacustrine pattern, there is evidence of significant shifts in the quantity, source and type of OM which may reflect periodic interactions with the Mackenzie River and changes in the lake's limnological conditions and depositional environment. Temporal variations of HI and OI can be informative in this regard. The upper ~5–45 cm of the core (extrapolated to represent approximately 750–1900 A.D.) showed relatively high HI and low OI values (section 4 in Fig. 4a) compared with the lower core, which are consistent with its recent history as an isolated lake and with a dominance of algal OM. The higher S2 and HI values in Nesbitt were substantially greater than at any time in Big Lake (Fig. 4b). Petrographic analyses of the upper section of the Nesbitt core show mainly organic-rich clay sediments with an increase towards the top of the core in the dominance of diatoms and other algal OM. Total diatom counts follow a similar increasing temporal variation to that of the hydrogen-rich (HI) and algal-derived organic parameters (S2).

Prior to this recent period, from ~45 to 87 cm (ca. 0–750 A.D.; section 3 in Fig. 4a), HI declined and OI increased but the kerogen remained classified as Type II (aquatic). This section is petrographically distinct and characterized by organic clay with substantial amounts of vascular aquatic plants, humified peat, and some land-derived moss fragments throughout (Fig. 5). Diatoms were also present with about the same abundance as in section 4 (i.e., on the order of 10^7 valves/g DW). Anoxic conditions may have prevailed in this section and underlying sections as evidenced by large bacterially-derived framboidal pyrites (Fig. 5). These features suggest a depositional environment which was either a marshy wetland, or a shallow pond covered by extensive aquatic macrophytes. An exception occurred during an interval (~58–70 cm, extrapolated to be ca. 300–500 A.D.) which is associated with a sharp decline of all organic parameters, notably HI and OI indices, and S1, S2 and TOC contents (section 3′, Fig. 4a). Associated compaction of the sediments at this point suggests that an input of inorganic clastic or fluvial sedimentary material significantly diluted the OM. Such a sudden increase in inorganic flux in thermokarst lakes could be caused by slumping due to rapid warming of permafrost and/or by a significant inflow of Mackenzie River water, i.e., a flood event (e.g., Sanei et al. 2000, 2001).

Fig. 3 Sediment profiles of total organic carbon (TOC %) and refractory residual carbon (RC %) for **a** Nesbitt Lake (NB) and **b** Big Lake (L10) (gaps in the profiles for both lakes are explained by the presence of bulk peat layers at those depths in the cores. As peat clearly indicates a non-lacustrine period, these intervals were excluded from study. The pre-1900 period was taken as below 5 cm in Nesbitt Lake and below 10 cm in Big Lake)



From 87 to 100 cm (section 2, Fig. 4a; approximately 800 B.C. to 0 A.D.), a layer of black peat moss without sediment was present, which was not analysed for this study, but which clearly indicates a temporary transition to peat bog conditions. Below 100 cm, the trend to higher OI and lower HI values continued, again suggesting a wetland or macrophyte-covered pond (section 1, Fig. 4a). Organic petrology shows marshy wetland/pond sediments with a significant amount of aquatic vascular plant remains and peat fragments, with increasing amounts towards the transition to the overlying peat (Figs. 4a, 5). Anoxic conditions persisted as evidenced by large bacterially-derived framboidal pyrites (Fig. 5).

Diatoms valves in the sediments of Nesbitt Lake were dominated by *Staurosira venter* (sensu lato) and *Staurosirella pinnata* sensu lato. Across the Canadian Arctic Archipelago, these taxa are typically found in oligotrophic cold water environments with circumneutral pH (optima, 7.5; range, 6.8–8.1) and moderately low levels of DOC (optima, 1.3; range, 0.76–2.12) (Antoniades et al. 2008). In our study lakes these two taxa groups represented 53–64% of the intact diatom valves observed and this proportion was consistent throughout the core. The diatom *Pseudostaurosira pseudoconstruens* showed the most evident change in numbers from rare (<1.5% of total counts) in the upper sediments to 5.5% between 40 and 60 cm, with ca. 1.5% in the lower sections of the core. Total diatom abundance shows a point-to-point similarity to the S2 parameter through most of the NB core down to a depth of 60 cm (Fig. 4a). This

Fig. 4 Depositional environment and limnological changes in **a** Nesbitt Lake (NB) and **b** Big Lake (L10) as reconstructed using sedimentary records of OM (Rock-Eval parameters: mainly algal-derived OM (S1 and S2), hydrogen and oxygen indices (HI and OI)), total diatom counts, and Hg concentration as well as their relationships throughout the sediment profiles

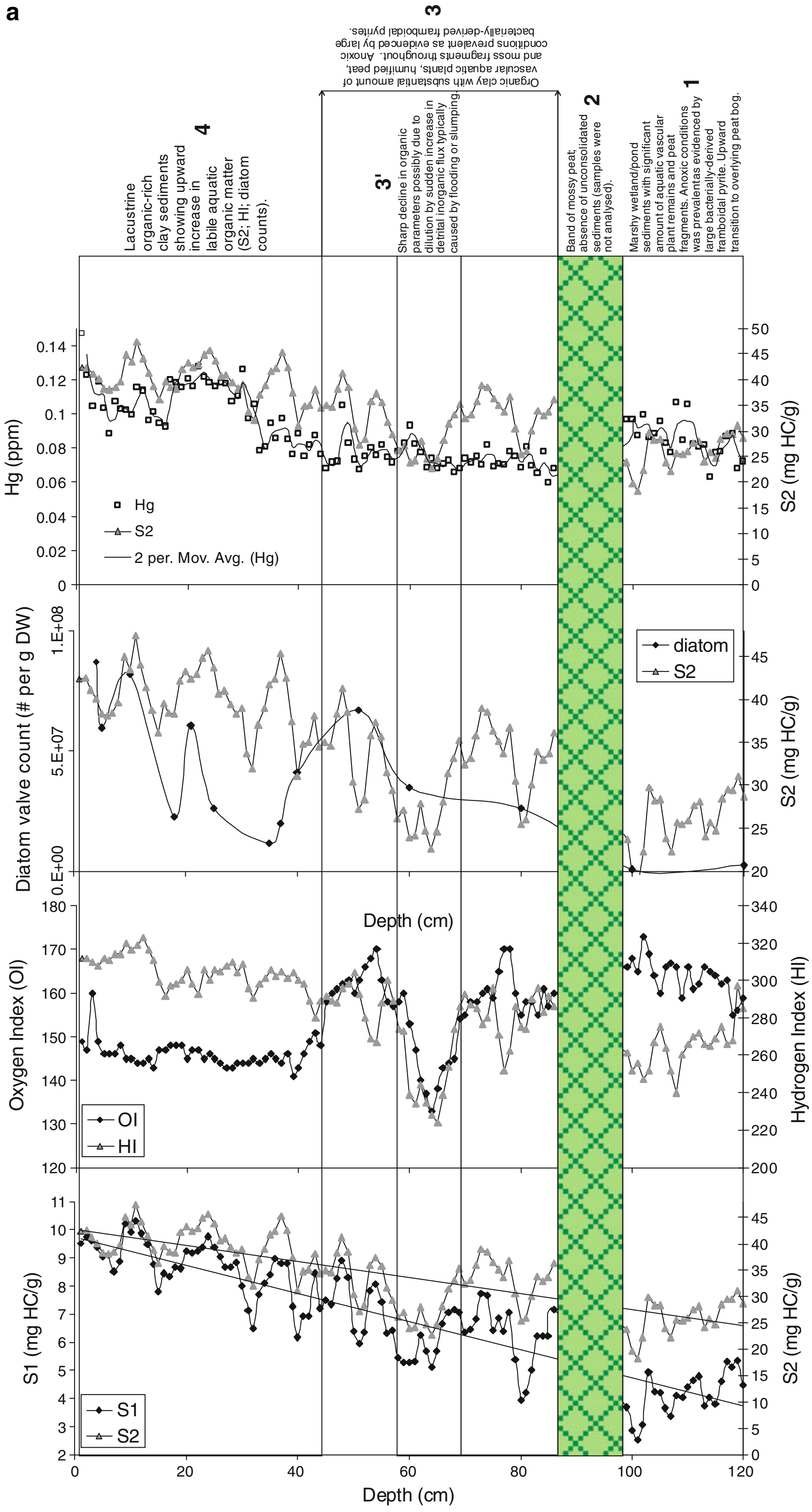
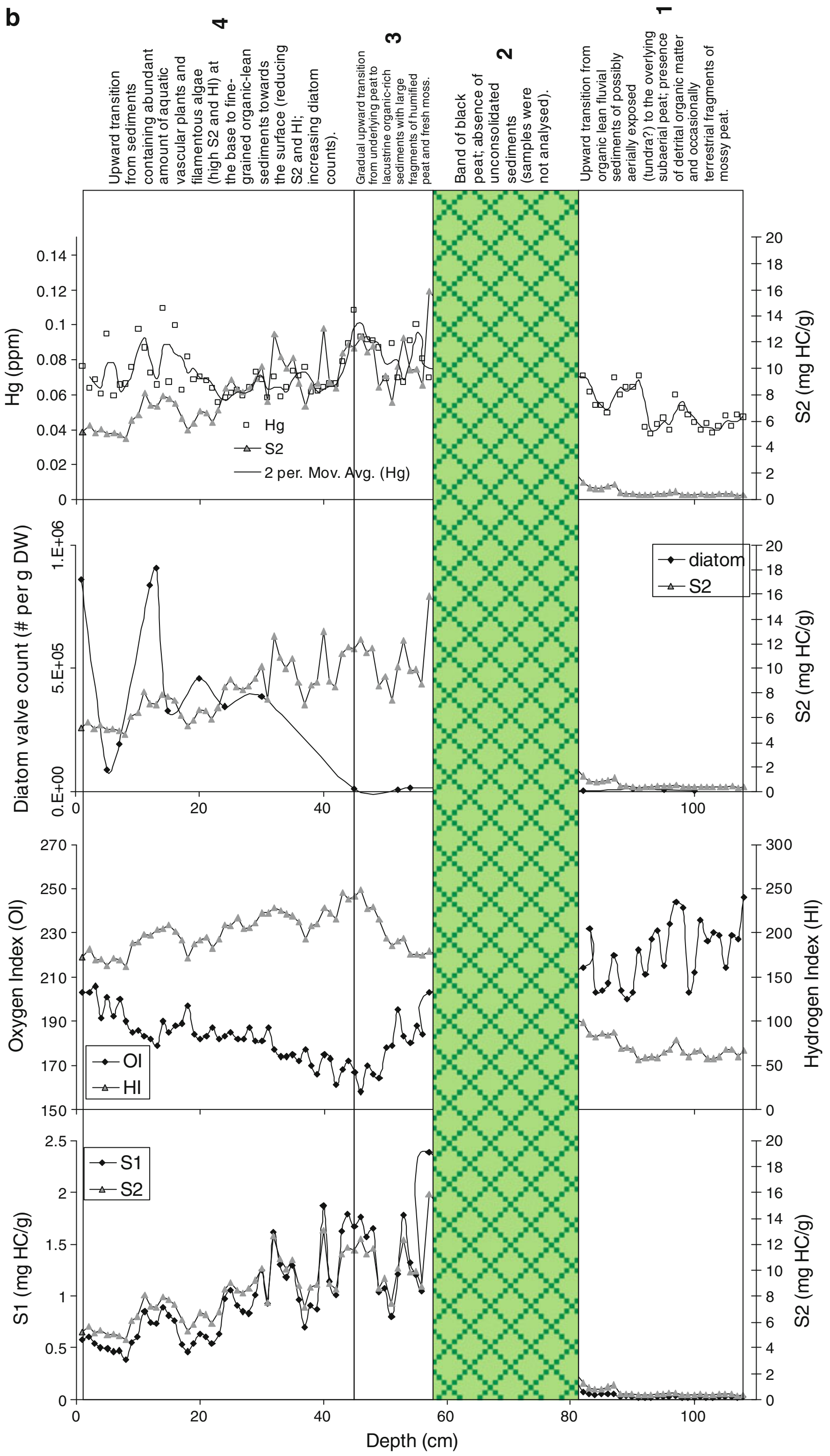


Fig. 4 continued



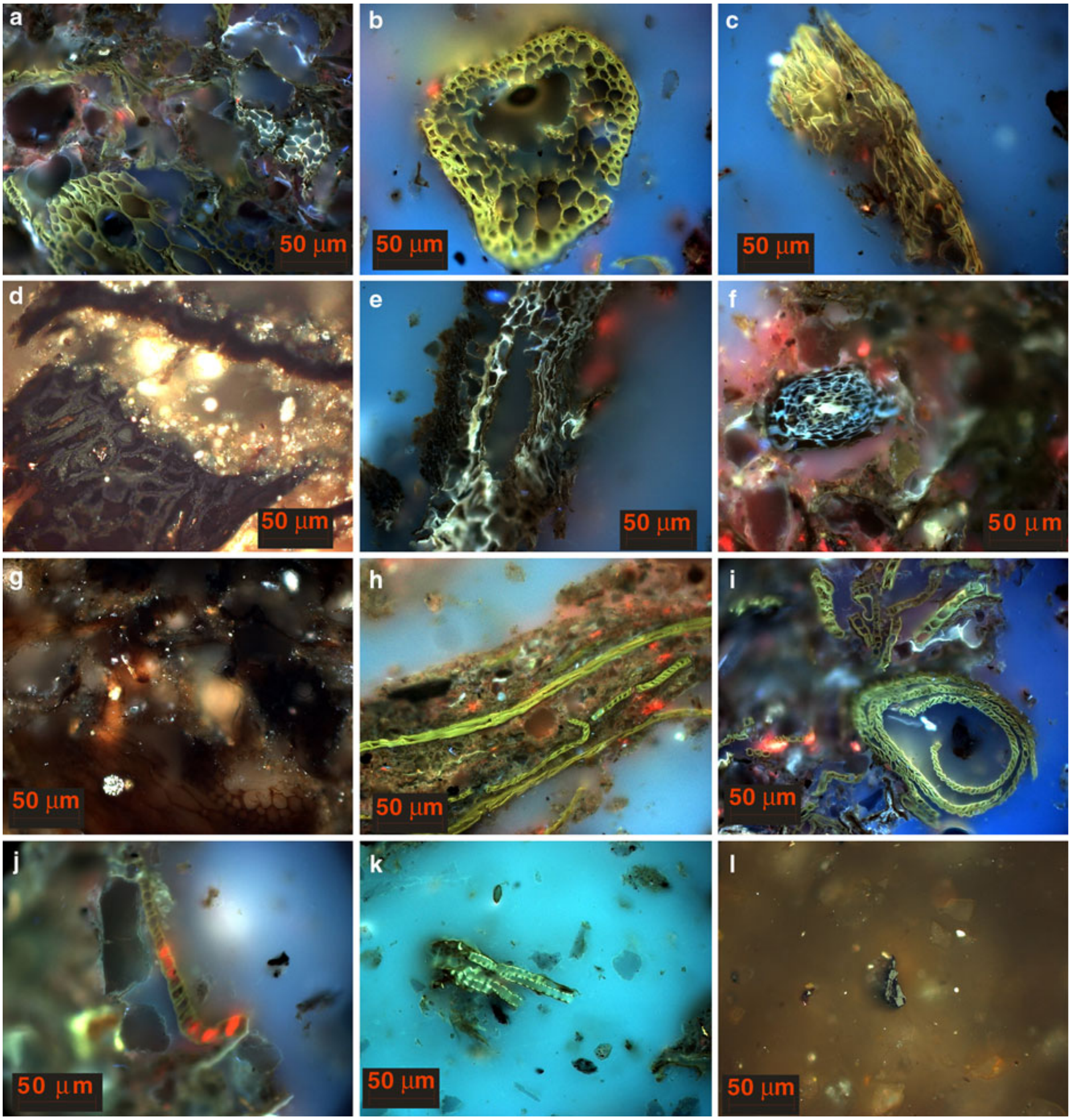


Fig. 5 Photomicrographs of various OM within the sediment profiles of Nesbitt Lake and Big Lake under incident-light fluorescent (**a**, **b**, **c**, **e**, **f**, **h**, **i**, **j**, **k**) and white light (**d**, **g**, and **l**) microscopy: **a**–**c** cellulosic cell structure of moss fragments, **d** partly humified peat fragment within the transitional lacustrine sediment intervals, **e** lignin-based land-derived OM impregnated by tannin/resin, **f** well-preserved cork cell structure impregnated by tannins, **g** bacterially-formed framboidal pyrite showing bright crystals growth in a shape of spherical conglomerate, **h**–**j** filamentous algae with entrapped brightly fluorescent red pigments within its cell structures, **k** siliceous diatom valves, **l** brightly reflecting reworked, refractory organic carbon

confirms the overall change in algal productivity as interpreted by RockEval parameters (especially S2 and HI) throughout the sediment profile, and especially the important role that phytoplankton and tychoplankton had in this lake's depositional environment. Below depth 60 cm, diatom counts gradually decrease to almost zero, corresponding to an overall decrease in the S2 fraction downcore, and with changes in the depositional environment as explained above.

Depositional environment—Big Lake (L10)

The OM composition history of Big Lake shows some broad similarities to Nesbitt Lake, with four distinctly different depositional environments being present. However, overall the OM is distinctly more mixed terrestrial/aquatic in origin than in Nesbitt, with the relative balance between these two sources changing over time. The type of aquatic plant OM in the sediment also changed significantly over time. The Van Krevelen (HI:OI) and S2:TOC kerogen diagrams depict two distinct groupings of OM kerogens in Big Lake, but both of these are closer to Type III (terrestrial) than are Nesbitt sediments (Fig. 2a, b). The lower grouping of Big Lake kerogens (see Fig. 2b) is distinctly Type III and these all occur below 82 cm depth in section 1 (Fig. 4b; no dates will be assigned because of the inconsistent radiocarbon age-depth sequence in this sediment profile). These deep sediments are organic-lean with a very low average TOC of 0.76% (Fig. 3b). The very low S1 and S2 content, relatively high OI and low HI indices and the petrology findings suggest a tundra soil originally derived from fluvial sediments with predominantly terrestrial OM input. Organic petrology shows the presence of detrital OM and occasionally fragments of terrestrial peat in this section (Fig. 5).

The transition between the two kerogen types and depositional environments occurs at a depth interval of 57–81 cm, with a sharp contact at 81 cm depth to a homogeneous layer of black peat (section 2, Fig. 4b). As mentioned above, this transition to peat has been dated to about 700 B.C. (Dallimore et al. 2000), consistent with the transition to peat in Nesbitt at ~800 B.C. (extrapolated from Table 1). Above 57 cm, an upward transition from peat to lacustrine organic-rich sediments is evident, showing a sharp decrease in OI and increase in HI to its maximum level at approximately 45 cm (section 3, Fig. 4b). This transitional section is documented by petrographical observations showing organic-rich sediments mixed with large fragments of humified peat and fresh moss (Fig. 5).

In section 4, and especially above 45 cm (Fig. 4b), kerogens are mainly Type II (aquatic; Fig. 2b) with relatively high HI (values of 160–250) and low OI (170–200), which represents the founding of the lacustrine system that exists today. However, since then the S2:TOC ratios and HI and OI values have gradually shifted in recent sediment layers to OM that contains more Type III-like kerogen, especially in the upper 10–30 cm (Fig. 2b). This shift indicates an increasing amount of terrestrial OM input mixing with aquatic OM produced in the lake. Organic petrology of the section above 45 cm reveals an upward transition from sediments containing abundant amounts of aquatic vascular plants and filamentous algae (the latter also have a high S2 and HI) at the base to fine-grained sediments containing relatively low levels of diatoms and other aquatic species mixed with terrestrial OM towards the surface (thereby reducing S2 and HI; section 4, Fig. 4b). Although diatoms were present at higher amounts in the upper part of section 4 than lower in the core, their abundance (~10^5 valves/g DW) was more than two orders of magnitude lower than in Nesbitt Lake, and their influence on S2 and HI values was insignificant compared to the decline in aquatic macrophytes (especially filamentous algae) during this interval. Diatoms in Big Lake showed the same dominant pattern of fragilarioid taxa (including *S. construens*, *P. pseudoconstruens* and *Fragilaria* spp. sensu lato) as seen in Nesbitt Lake. No clear changes in the relative abundance of taxa were observed. Other less prominent taxa observed in both lakes included *Achnanthidium* spp., *Cavinula* spp., *Amphora* spp., *Gyrosigma obtusatum*, *Reimeria sinuata*, *Planothidium calcar*, *Diploneis marginestriata* and *Hygropetra balfouriana*. All of these less prominent taxa are associated with oligotrophic cold waters (alpine or polar) with low to moderate levels of electrolytes. Taxa like *H. balfouriana* are indicative of shallow water moss environments, while *Cavinula* spp. are commonly observed in low numbers across the circumpolar Arctic region.

The source of terrestrial OM in the most recent core section of Big Lake could be runoff from the surrounding tundra, but another possible source is terrigenous plant detritus washed into the lake from the Mackenzie River via the deltaic channels. Carrie et al. (2008) reported that particulate OM in the fine (<63 µm) surface sediment fraction of the Mackenzie

River main channel was dominated by refractory terrestrial OM which clearly classified as Type III kerogen; inflows of similar material into Big Lake with suspended sediments could account for the shift of kerogen values towards Type III. A notable feature of this sediment profile is the apparent absence of significant diagenesis of S1 or S2 carbon as suggested by the similar profiles of S1 and S2 to those of RC and TOC, which also increase down-core during the recent lacustrine phase (Figs. 3b, 4b).

The depositional environments revealed in the study lakes are considerably more complex than those seen in previous studies by our research group (Outridge et al. 2005, 2007; Stern et al. 2009) which concerned shorter cores and more recent time periods, as well as simpler limnological histories and depositional environments. In the High Arctic lakes, phytoplankton and other algal productivity dominated the depositional environments, without any petrological or organic geochemical evidence of significant inputs of OM from terrestrial or aquatic macrophyte (vascular plants and filamentous algae) sources. The patterns of OM composition in these study lakes provide contrasting examples of how long-term geomorphological changes can influence the depositional environment of a lake, as reflected in the type and geochemical characteristics of the OM found in its sediments.

Hg–OM relationships as a function of depositional environment

Nesbitt was more productive than Big Lake during its lacustrine phase, as shown by higher diatom, TOC, S1 and S2 concentrations, and higher HI values (280–320 vs. 160–250, respectively). Hg profiles in the study lakes were also distinctly different from each other. In Nesbitt Lake, Hg concentrations were intermediate to low in the lowest and middle sections of the core when the lake was a wetland or macrophyte-rich pond, and consistently increased by about 50% from ~0.07 to 0.11 μg/g DW in the upper core after Nesbitt's lacustrine phase was established (Fig. 4a). Excluding the twentieth century samples (upper 5 cm), there is a significant positive correlation ($r^2 = 0.17$, $P < 0.001$) between Hg and S2 carbon concentrations overall in Nesbitt Lake, but especially above 50 cm where the lacustrine system clearly began ($r^2 = 0.32$, $P < 0.001$). By contrast, in Big Lake during the lacustrine period (10–57 cm), fluctuations of Hg and S2 were not significantly correlated ($r^2 = 0.02$, $P > 0.10$; Fig. 4b). It is important to note that Hg concentrations in Nesbitt and Big were of similar magnitude (~0.06–0.08 μg/g DW) before the increase of Hg and S2 occurred in Nesbitt over recent centuries.

The significant Hg–S2 correlation co-efficient in Nesbitt is lower than we reported from other northern lakes (in the range of 0.7–0.8; Outridge et al. 2007; Stern et al. 2009) possibly because overall Nesbitt Lake contains higher organic content of mixed and more complex sources (of both aquatic and terrestrial OM) which may combine in varying degrees to produce the sediment S2 concentrations. Even though S2 concentrations and HI values are much higher in phytoplankton and algal OM relative to lignin-based terrestrial plant and dominantly cellulosic aquatic vascular plant OM, these other sources can contribute to S2 levels if they are present in significant amounts. The value of combining petrology and diatom enumeration with organic geochemistry for complex systems like these is that the alternative sources of S2 carbon can be clearly identified. In Nesbitt Lake's recent lacustrine phase, the changes in S2 concentration were largely coincident with changes in diatom numbers which, together with the relatively high total diatom abundance, suggests that pelagic phytoplankton and tychoplankton were the most important single source of S2 carbon in this lake over recent centuries, and were most important in scavenging Hg from the water column.

An alternative explanation to the Hg scavenging hypothesis is that the Hg–S2 correlation reflects coincidental but unrelated patterns brought about by (1) increasing Hg inputs from an external source, and (2) significant and continual degradation and loss (diagenesis) of S2 carbon compounds down-core. There was evidence of degradation of labile S1 carbon in Nesbitt Lake. But unlike S1 compounds which include lipids, pigments and simple carbohydrates (Sanei et al. 2006), the complex and chemically-resistant macro-molecules in plant cell walls which comprise S2 kerogens are unlikely to be degraded to a significant degree during the short time period and anaerobic conditions represented by these recent sediments. Although the S2 compounds may be affected to some degree by oxic degradation in the water column before burial in sediment, S2 kerogen, especially under anaerobic sediment conditions, is resistant to biochemical degradation over geological time periods (Tissot et al. 1974; Tyson 1995, 2001). This resistance accounts for its high temperature (300–650°C) of yield during Rock-Eval pyrolysis. Significant losses of S2 in geological sedimentary rocks are expected only at the stage known as "thermal maturity", in which kerogen is thermally cracked and expelled from the rock during diagenesis and catagenesis processes. Over short periods of centuries or millennia in recent sediments, therefore, losses of S2 compounds should be at most minor, and temporal variations of S2 throughout the sediment profile are likely to be largely controlled by variations of primary productivity and OM flux. In Big Lake, the down-core pattern of S2 concentrations to 60 cm depth was similar to residual carbon and TOC, which argues against a significant alteration of S2. In Nesbitt Lake, down-core fluctuations in S2 were also matched by residual carbon and TOC to ~60 cm depth (where a flood event interrupted the lacustrine record), and confirmed by diatom enumeration. Similarly, an absence of diagenetic reductions of S2 carbon was reported in a High Arctic lake sediment over >1000 years, as revealed by significant correlations between S2 carbon and diatom concentrations (Outridge et al. 2007).

Regarding alternative explanations for the increasing Hg levels in Nesbitt Lake between ~750 and 1900 A.D., significant amounts of anthropogenic Hg were absent from Arctic lake sediments prior to the twentieth century (see Muir et al. 2009). Thus, the increase of Hg concentrations in Nesbitt Lake cannot be due to increases in atmospheric Hg deposition from anthropogenic sources. Given the proximity of the study lakes to each other, it is unlikely that variations in atmospheric deposition of natural airborne Hg could account for the differences between the lakes' Hg profiles. Inputs of Hg from riverine sources can also be excluded as a possible explanation, because Nesbitt appears to have been mostly isolated from major flood events during its lacustrine phase. When a significant inflow of riverine sediment did occur in Nesbitt (core depths 58–70 cm), no major changes in Hg concentration resulted. Sediment Hg concentrations in the Mackenzie River (0.017 ± 0.009 μg/g DW; Leitch et al. 2007, Table 1) are well below those found in Nesbitt or Big lakes (ranges 0.06–0.12 and 0.04–0.10 μg/g DW, respectively). Hg inputs from terrestrial sources including melting permafrost (see Rydberg et al. 2010) may be a possibility. Major inputs of tundra plant detritus and associated trace metals can affect northern lake sediment metal profiles (Wolfe and Härtling 1997), although this has not been demonstrated specifically for Hg. However, the OM characterization carried out here using well-established geochemical methods suggests that aquatic (phytoplankton and other algal) OM dominated Nesbitt Lake during its lacustrine phase. Terrestrial OM, although present, did not increase up-core along with Hg concentrations. The largest increase in Hg content in Nesbitt occurred at a depth of 19–33 cm, which coincided with a spike in algal-derived OM (S1, S2; Fig. 4a), and which petrological examination showed did not contain unusually high amounts of terrestrial OM (grasses, peat, other mosses, shrubs, etc.).

Therefore, these results are consistent with the hypothesis that the concentration of Hg in lake sediments can be significantly altered by the degree of algal productivity, regardless of whether the productivity changes occur as a result of climatic, geomorphological or other factors. An example of climate influencing aquatic productivity and Hg concentrations in pre-twentieth century sediments was reported from a shallow High Arctic lake, DV-09 (Outridge et al. 2007). During several centuries corresponding to the end of the Medieval Warm Period, S2 concentrations, diatom abundance and Hg concentrations in this lake increased coincidentally.

In Big Lake, which has been more seriously affected by landscape change over recent millennia than Nesbitt, and especially by inorganic and organic material inflows from the Mackenzie River, the Hg–OM relationships are more complex. Hg contents below 81 cm depth (before the lake as such existed) probably reflect mainly tundra soil Hg concentrations, with minimal modification by the very low amounts of OM present. During its lacustrine phase, S1, S2, and TOC concentrations decreased towards the top of the core whereas Hg remained relatively stable with no overall increasing or decreasing trend. The Hg profile in the lacustrine phase of Big Lake is likely to reflect a mixture of inputs from surrounding soils, tundra plants and riverine detrital sources, unmodified (i.e., not increased) by a within-lake aquatic productivity process.

Therefore, this study's results support the hypothesis advanced by Outridge et al. (2005, 2007) that increasing algal productivity can significantly alter sedimentary Hg concentrations, and can explain part of the Hg increase in Arctic lake sediments during the twentieth century. While anthropogenic Hg is clearly present in the Arctic atmosphere and in deposition, its rate of accumulation in lake sediments can be significantly accelerated by with-lake processes. The last century has seen an unprecedented rate of increase in aquatic primary productivity in northern lakes because of climate warming (Michelutti et al. 2005; Smol et al. 2005). A second mechanism by which climate warming may impact Hg fluxes into northern lake sediments is through the release of natural and anthropogenic Hg from nearby thawing permafrost and peatlands (Rydberg et al. 2010). Either process, if not recognized and corrected for, may result in over-estimation of the anthropogenic Hg component in recent sediments.

Results of the present study also suggests that OM produced by diatoms and other unicellular algae (as in Nesbitt Lake) plays a more important role in the sedimentary accumulation of Hg than OM from terrigenous and aquatic macrophyte (vascular plant and filamentous algae) sources. The initially high amount of aquatic macrophyte OM present in Big Lake's lacustrine phase, which increased sediment S2 concentrations, did not correspond to high sediment Hg concentrations. Similarly, the declining macrophyte OM inputs and increasing proportion of terrestrial OM in the upper core of Big Lake were not associated with altered Hg concentrations. An explanation for this difference between plant sources in their effect on Hg levels may be lower concentrations of labile, chemically reactive organic compounds and thiol (SH^-) groups in lignin-rich, refractory terrestrial OM. Thiols are believed to be the key binding group for Hg^{2+} attachment to freshwater OM (Gasper et al. 2007) as well as soil OM (Skyllberg 2010). Aquatic macrophytes, although containing higher S2 concentrations than terrestrial plants, do not offer the same abundant surface area for Hg binding as phytoplankton and tychoplankton which are also dispersed throughout the water column and emergent plant beds. This suggestion may help to explain the lack of strong Hg:TOC relationships sometimes observed in Arctic and sub-Arctic lakes (e.g., Muir et al. 2009). Sanei and Goodarzi (2006) showed that TOC is a crude measure of total OM, which does not convey any information about possible qualitative changes in the Hg-binding capacity of OM over time. These changes may be brought about by a varying balance of aquatic/terrestrial plant OM inputs due to, for example, catchment vegetation disturbances, climate change, permafrost melt and runoff, hydrological variations, or nutrient inputs. In contrast, detailed organic geochemical, diatom and petrographical analyses of OM sources and type can help to tease out underlying patterns which TOC data can not reveal.

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