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Climate Change and Mercury Accumulation in Canadian High and Subarctic Lakes

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Mercury (Hg) profiles were compared to profiles of climate indicators including microfossil remains and algal-derived or S2 carbon (C) in dated sediment cores from 14 lakes spanning latitudinal and longitudinal gradients across the Canadian high and subarctic. Hg fluxes increased postindustrialization (post-~1850) in 11 of these lakes (postindustrialization Hg fluxes (ΔHgF_F) = 2−24 μg m^{-2} y^{-1}). Correction of HgF_F for catchment contributions demonstrated that Hg deposition originating from catchment-independent factors, such as atmospheric deposition, increased since industrialization in all 14 lakes. Several of these lakes also showed postindustrial shifts in algal assemblages consistent with climate-induced changes. Eleven lakes showed post-1850s increases in $S2F_F$, suggesting that lake primary productivity has recently increased in the majority of our sites ($\Delta S2F_F$ = 0.1−4 g m^{-2} y^{-1}). Other studies have interpreted significant relationships between Hg:S2 concentrations in Arctic sediment as support for the algal scavenging hypothesis, which postulates that Hg fluxes to Arctic sediments are largely driven by S2. However, in six of our lakes we observed no Hg:S2 relationship, and in one lake a significant negative Hg:S2 relationship was observed due to increased Hg and decreased S2 C deposition during the postindustrialization period. In six of the seven lakes where a significant positive Hg:S2 relationship was observed, algal assemblages either did not change through time or the timing of the shifts did not correspond to changes in Hg deposition. Our results demonstrate that, although Arctic lakes are experiencing a myriad of changes, including increased Hg and S2 deposition or changing algal assemblages, increased lake primary productivity does not appear to be driving changes in Hg fluxes to sediments.

Introduction

Mercury (Hg) is a global pollutant with potential human health impacts, and because of its long atmospheric residence time (~1.5 y), it can be transported far from point sources to remote regions (*1*). In fact, analysis of Hg in dated sediment cores obtained from ~100 lakes spanning the circumpolar Arctic have shown that Hg fluxes to Arctic sediments have increased since the industrial revolution (~1850), with the magnitude of increase varying between ~1.5- and 12-fold among lakes (*2*−*11*). The reason for these increases is, however, debated. In several studies (*4, 5, 8*), postindustrialization increases in Hg fluxes have been attributed mainly to increased anthropogenic atmospheric Hg deposition. In fact, patterns of atmospheric circulation, mainly the Pacific North America and Northern Atlantic oscillations, result in the transport of Hg emissions from Asia, Europe, and North America to the Arctic (*12*−*15*), with east Asia being the primary source area according to global modeling (*16*).

In other studies (*7, 9, 10*), a large portion (~70−78%) of increased postindustrialization Hg deposition in Arctic lakes has been attributed to increased algal scavenging brought about by climate-induced changes. This "scavenging hypothesis" is based upon the use of Rock-Eval analysis (*17, 18*) to examine the S2, or algal-derived, fraction of organic carbon (OC) in lake sediments, as well as upon the numerous paleolimnological studies that have demonstrated widespread, climate-induced changes in Arctic lakes. For example, increased algal production and sedimentation of the resulting detritus have been observed in numerous Baffin Island (Nunavut) lakes (*19*) and changes in algal and invertebrate species composition beginning in ~1850 have been observed in a wide spectrum of lakes spanning the circumpolar Arctic (*20*). Most commonly, post-1850 shifts in species composition of Arctic lakes include decreased relative abundance of small, benthic diatom taxa associated with cold conditions and extended ice cover and increased abundance of diatom taxa characteristic of more ecologically complex littoral habitats and mossy substrates, decreased ice cover, or enhanced thermal stratification (*20*−*23*). These changes in algal community assemblage thus likely reflect increased lake primary productivity as warming and decreased ice cover generally stimulate algal production. To date, sediment cores from only four Canadian high and subarctic lakes have been analyzed for Hg and S2 and all show significant positive relationships between Hg and S2 (*7, 9, 10*). However, observations of correlation between Hg and lake productivity are not evidence of causation. Furthermore, owing to the limited geographical coverage of current data sets and complex combination of environmental changes that are occurring in freshwater Arctic ecosystems, further study is clearly warranted to determine factors driving Hg deposition to Arctic sediments.

To examine the scavenging hypothesis, we compared Hg concentrations and flux profiles to profiles of climate indicators, including microfossil remains and algal-derived

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FIGURE 1. Location of 14 Canadian high and subarctic lakes where sediment cores were collected then analyzed for Hg and climate-change indicators including microfossils and algal-derived, or S2, carbon.

or S2 C, in dated sediment cores from 14 lakes spanning latitudinal and longitudinal gradients across the Canadian Arctic. To date, this study represents the most geographically extensive data set of Hg-climate dynamics in the Arctic and includes more comprehensive microfossil data than previous studies of its kind as species-level diatom analysis was obtained in a subset of study lakes.

Methods

Site Selection, Sample Collection, Hg Analysis, and Dating. Sediment cores were collected from 14 Canadian Arctic lakes spanning a latitudinal (from northern Manitoba and Labrador to Ellesmere Island, Nunavut) and a longitudinal gradient (from the Mackenzie River valley in the Northwest Territories to Ellesmere Island) from 2000 to 2005 (Figure 1). The 14 cores presented here were selected from a larger collection used to examine spatial trends and historical deposition of Hg in eastern and northern Canada; thus, details on the lakes selected, core collection and ^{210}Pb dating, Hg, and aluminum analysis are described in ref *8* as well as in the Supporting Information and Table S1.

Microfossil Analysis. In eight of the study lakes, counts of diatoms, chrysophyte cysts, blue-green algae, and green algae were determined as in refs *24* and *25*. Briefly, subsamples of freeze-dried sediment were rehydrated in distilled water and sonicated, and different algal groups were then enumerated. In three lakes (BK-AH, West, and Hazen), species-level diatom analysis was carried out using standard methods. Diatom slides were prepared, enumerated, and identified using procedures outlined in ref *26*.

Total OC and Rock-Eval Analysis. Total OC and C speciations were determined on all sediment samples by Baseline Resolution Inc. (Shenandoah, TX, U.S.) by the LECO and Rock-Eval 6 methods, respectively. Rock-Eval 6 analysis separates OC based on the thermal devolatilization of C compounds (*17, 27*). The S1 fraction includes volatile hydrocarbons, such as short-chain hydrocarbons, pigments, and diagenetically produced humic substances. S2 is of most interest here as it represents high molecular weight, kerogen-derived aliphatic hydrocarbons which correspond to the biomacromolecular structure of algal cell walls (*17, 18*). S2 has therefore been referred to as algal-derived OC (*7, 9, 10*). S3 represents the CO_2 produced during pyrolysis, while the residual C (RC) fraction represents allochthonous inputs of organic matter including reworked C or remains of terrestrial plants. RC was calculated by

$$\mathrm{RC(mg\ g^{-1})} = \mathrm{TOC} - (\mathrm{S1} + \mathrm{S2} + \mathrm{S3}) \quad (1)$$

Rock Eval 6 analysis also provides measures of hydrogen and oxygen index (HI and OI, respectively), expressed in mg HC g^{-1} TOC and mg CO_2 g^{-1} TOC, which are indicative of kerogen type (*17, 27*).

Flux Calculations and Statistical Analysis. Recent and preindustrial horizons in each core were defined by the median ages assigned to each core section using the constant rate of supply model. Hg and S2 fluxes (HgF and S2F), anthropogenic fluxes (ΔHgF) or, in the case of S2, changes in fluxes since industrialization (ΔS2F), and flux ratios (FR) were calculated as in ref *8* (see also the Supporting Information).

Relationships between Hg, S2, and algal abundance were examined using general linear models (GLM) (Systat Software Inc., San Jose, CA). Prior to running the GLM, Hg concentrations were log transformed whereas % algal abundances were normalized using the following equation:

$$x_i = (x_i - x_{\min}) / (x_{\max} - x_{\min}) \quad (2)$$

In lakes where species-level diatom analysis was carried out, normalized first axis principal component analysis (PCA)

scores were used as a measure of diatom community change to input into the GLM.

Results and Discussion

Sedimentation Rates, Hg Concentrations, and Fluxes. Because sedimentation rates, Hg concentrations, and fluxes have been reported previously for the cores presented here (*8*), a detailed discussion of these results is provided in the Supporting Information. Briefly, average sedimentation rates were 50−704 g m^{-2} y^{-1} (Table S1), and all cores exhibited near-logarithmic declines in excess ^{210}Pb with depth, indicating relatively constant sediment accumulation rates (Figure S1). Sedimentation rates were higher post-1990 compared to preindustrial times in half of the lakes examined (Figure S3). Increased sedimentation rates may reflect climate-induced changes to precipitation, permafrost degradation, and catchment erosion as most lakes which experienced increased sedimentation rates are located in regions where mean annual snowfall has increased in recent decades (*8, 28, 29*).

Mean sediment Hg concentrations were 14−131 ng g^{-1} dry weight (dw) and were comparable to those reported by others for the Canadian Arctic (*8*−*11*). Average fluxes, corrected for sediment particle focusing (FF), were 1−72 μg m^{-2} y^{-1} (Table S1). Hg fluxes increased dramatically after industrialization in 11 of 14 of the lakes, changed very little in 1, and decreased in 2 ($\Delta HgF_F = -5-24\ \mu g\ m^{-2}\ y^{-1}$) (Figure 2). To tease apart Hg inputs from catchment erosion and other sources (which include anthropogenic atmospheric sources), HgF_F values were adjusted for postindustrialization changes in sedimentation rate to obtain $HgF_{F,adj}$ following the methods of ref *8*. Average $HgF_{F,adj}$ values were 57−110% lower than F_F values for each lake, demonstrating that a large portion of Hg inputs to Arctic lakes originates from catchment contributions. In fact, although HgF_F increased in 11 of the 14 lakes, $HgF_{F,adj}$ increased in all lakes since industrialization ($\Delta HgF_{F,adj} = 0.3-16\ \mu g\ m^{-2}\ y^{-1}$) (Table 1; Figure S4). These results suggest that while climate-induced catchment erosion is impacted to some extent by localized factors, increases in anthropogenic atmospheric Hg deposition are widespread across the Canadian Arctic.

Algal Microfossils. Paleolimnological analysis of algal fossil remains, including diatoms, chrysophytes, blue-green and green algae, was conducted on cores from eight lakes, whereas species-level diatom analysis was conducted on three (Figure 2). Microfossil analysis was not conducted on BI-02, DVE, and Romulus lakes due to insufficient sample quantities. Algal assemblages shifted at some point after ~1850 in 8 of the 11 lakes examined but do not appear to have changed through time in Shipiskan, SHI-L4, and MB-AC. Four of the eight lakes (Fisherman, BK-AH, West, and Hazen) that experienced shifts in algal assemblages underwent changes that are typical of climate-induced reductions in summer ice cover and lengthening of the growing season. These lakes thus likely also experienced increases in primary productivity. In Fisherman, for example, until ~1969, diatoms were the dominant algal group (relative abundance 94−100%) but have subsequently been replaced by chrysophytes over the last four−five decades (relative abundance increased from 0 to 78% between ~1969 and the present). This switch is characteristic of the climate-induced regime shifts in algal assemblages recently documented in numerous Arctic lakes, where planktonic taxa or more complex benthic algal assemblages tend to be more competitive with a reduction in ice cover, longer growing seasons, and other climate-related limnological changes (*20, 21, 23*).

In BK-AH, West, and Hazen, where species-level diatom analysis was carried out, replacement of small, benthic *Fragilaria* spp., typical of undisturbed ice-dominated oligotrophic, high Arctic lakes by small, planktonic *Cyclotella* spp., epiphytes, or other benthic species characteristic of longer ice-free seasons was generally observed. These changes were accompanied by increased species diversity (as measured by Hill's N2 index (*30*)), which is also associated with climate-induced changes (*20, 26*). In the last four lakes (Mista, Cli, Char, and Amituk) that experienced postindustrialization shifts in algal assemblages, several regime shifts were generally observed between ~1850 and the present. Although diatoms were typically the dominant taxonomic group in these lakes (relative abundance 53 ± 15%), there were periods where chrysophytes, green, and blue-green algae predominated (Figure 2). These shifts may be indicative of regional climate changes or of more localized factors, such as large runoff events which released nutrients and stimulated lake primary productivity.

Algal-Derived or S2 C. Average sediment S2, or algal-derived OC concentration, was 1−94 mg g^{-1} but was low (<5 mg g^{-1}) in 8 of 14 of the study lakes. S2 concentrations were highest in a subarctic lake in northern Manitoba (mean ± standard deviation: 94 ± 12 mg g^{-1}) and were lowest in high latitude lakes, West and Hazen (1 ± 0.3 and 1 ± 0.2 mg g^{-1}, respectively) (Figure S5). However, as the factors controlling primary productivity are complex, the relationship between average S2 concentrations and latitude was not significant ($r^2 = 0.21$, $p = 0.10$). The S2 concentrations reported here were similar to those observed in other Arctic sediment cores (0.3−15 mg g^{-1} *7, 9, 10*). S2 comprised 23 ± 12% of the sediment TOC in all the lakes, whereas RC comprised roughly half (51 ± 18%), indicating that much of the OC in Arctic lake sediments is char, coal, or reworked oxidized organic matter (*10, 27*). This is not surprising since primary productivity and terrigenous OC inputs are low and OC recycling is often intensive in Arctic lakes. In six lakes (Cli, BK-AH, West, DVE, Romulus, and Hazen), the ratio of S2 to RC was consistent throughout the core, indicating that S2 was well preserved (Figure S6). In six lakes, S2:RC fluctuated slightly throughout the core, suggesting that S2 and RC inputs were independent in these lakes (i.e., catchment vs in-lake sources). However, it is also possible that the fluctuations in S2:RC reflect postdepositional degradation of S2, since C losses of up to 23% within 27 years of deposition have been observed in other systems (*31*). In Shipiskan and Fisherman lakes, S2:RC decreased consistently (from 0.66 to 0.55 and from 0.39 to 0.18, respectively) from the top to the bottom of the cores indicating postdepositional degradation of S2 to RC (Figures S6A and C). In a previous study (*7*), both S2 and diatom flux were used as proxies for primary productivity; however, we found no significant relationship between S2 concentration and total algal or diatom counts (no. g^{-1} dry sediment) in seven of the eight cores where microfossil analysis was carried out. We therefore analyzed microfossil data in terms of % relative abundance, which is the most common and generally accepted measure of algal assemblage (*20*−*23, 26, 28*).

The hydrogen index (HI) was generally low in all lake sediments (202 ± 78 mg HC g^{-1} TOC), whereas the oxygen index (OI) was high (223 ± 99 mg CO_2 g^{-1} TOC), characteristic of type III and type II/type III kerogen mixtures as determined by plotting HI and OI values on a van Krevelen diagram (*27*) (Figure S7). These values are similar to those observed in surface sediments of the Mackenzie River basin, NWT (HI and OI = 107 ± 44 mg HC g^{-1} TOC and 210 ± 109 mg CO_2 g^{-1} TOC, respectively (*10*)) and suggest that, despite the limited vegetation cover in terrestrial Arctic ecosystems, the catchment may be an important source of OC to Arctic lakes as type III originates from terrestrial plants whereas type II kerogen is derived from a mixture of algal, invertebrate, and bacterial debris (*27*).

Average S2 fluxes, corrected for lake focusing ($S2F_F$), were 0.1−33 g m^{-2} y^{-1}. $S2F_F$ increased dramatically since industrialization in 11 lakes (6−374% increases, $\Delta S2F_F = 0.1-4$ g

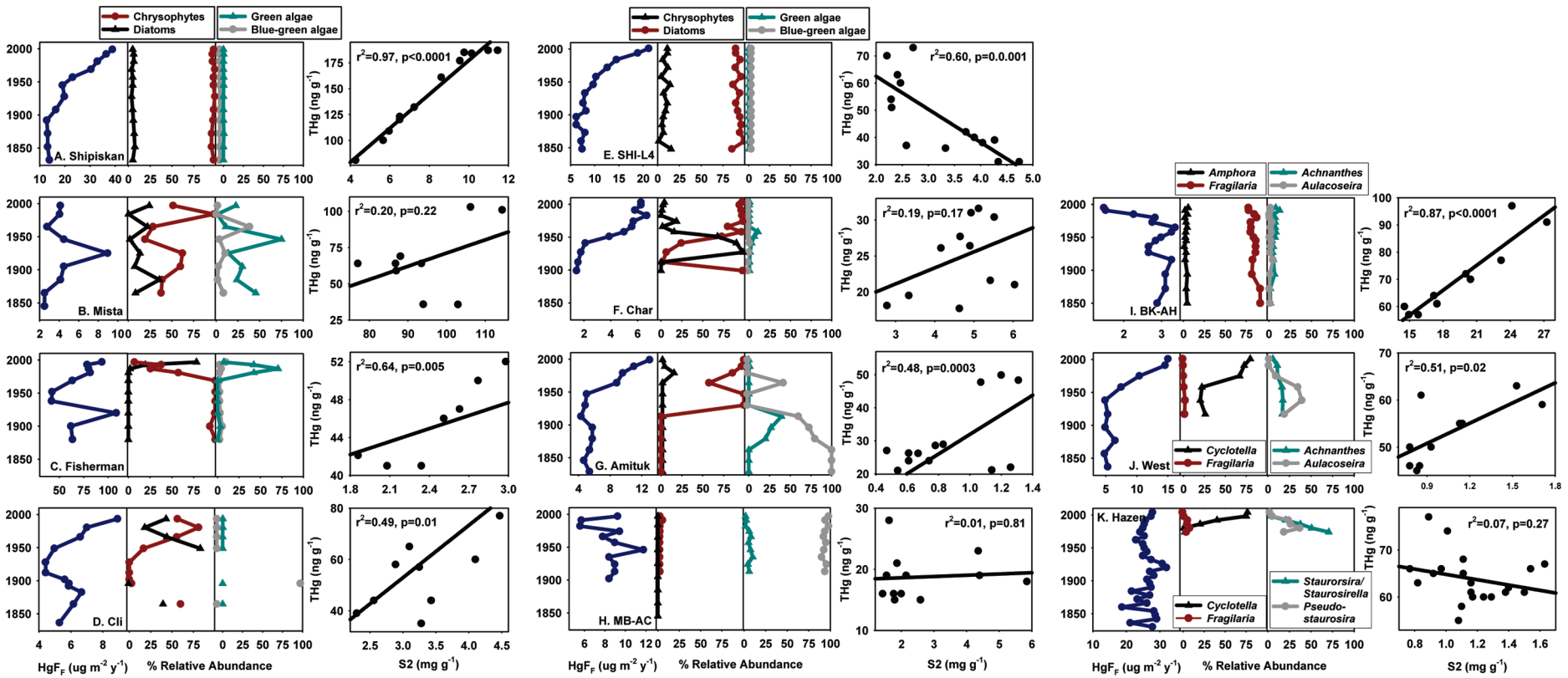

FIGURE 2. Focusing adjusted Hg fluxes (HgF_F), relative abundance (%) of microfossils including either diatoms, chrysophytes, green algae, and blue-green algae (A–J), or predominant diatom species (I–K), and the relationship between Hg and S2 C concentration (ng g^{-1}) in dated sediment cores from 11 Canadian Arctic lakes.

TABLE 1. Sediment Particle Focusing Factors (FF), Postindustrialization Hg and S2 Fluxes Corrected for FF (ΔHgF_F and $\Delta S2F_F$), and Postindustrialization Hg Fluxes Adjusted for FF and Changes in Sedimentation Rate ($\Delta HgF_{F,adj}$)

lake	FF	ΔHgF_F $\mu g\ m^{-2}\ year^{-1}$	$\Delta S2F_F$ $g\ m^{-2}\ y^{-1}$	$\Delta HgF_{F,adj}$ $\mu g\ m^{-2}\ y^{-1}$
Shipiskan	3.1	8	0.7	7
Mista	0.2	9	−16	14
Cli	2.2	4	0.02	4
Fisherman	0.2	24	4	16
SHI-L4	1.8	7	0.1	6
BI-02	0.9	3	0.5	4
BKAH	1.3	−1	−0.2	0.8
Char	3.1	2	0.2	0.6
West	1.7	9	0.3	3
Amituk	3.7	2	0.2	2
DVE	0.5	2	0.1	0.8
MB-AC	0.7	−5	−0.7	0.9
Romulus	5.1	3	0.1	2
Hazen	1.2	0.3	0.3	0.3

$m^{-2}\ y^{-1}$) and decreased in three (19−50% decreases, $\Delta S2F_F$ = −0.2 to −16 g $m^{-2}\ y^{-1}$) (Figure S8). In seven lakes, $S2F_F$ fluxes were 3−149% higher in the most recent sediment horizons than in ∼1970−1980, suggesting that S2 deposition continued to increase to the present in some systems.

Significant correlations between Hg and S2 in Arctic sediment cores have been interpreted as evidence for the algal scavenging hypothesis, which postulates that Hg fluxes to sediments are largely driven by S2 (*7, 9, 10*). Therefore, we examined relationships between Hg and S2 in our sediment cores. Surprisingly, significant positive relationships between S2 and Hg concentrations were observed in only roughly half the lakes (Figure 2). The S2:Hg relationship was strong in five lakes ($r^2 = 0.51-0.97$, $p < 0.02$ in Shipiskan, Fisherman, BK-AH, West, and DVE) but was weaker, albeit still significant, in three lakes ($r^2 = 0.30-0.49$, $p < 0.05$ in Cli, Amituk, and Romulus) (Figure 2). There was no Hg:S2 relationship in five lakes (Mista, BI-02, Char, MB-AC, and Hazen), and in one lake, SHI-L4, there was a strongly significant negative relationship ($r^2 = 0.60$, $p = 0.001$). These results prompted us to critically examine trends in Hg, algal assemblages, and S2 through time in each lake to elucidate the processes responsible for the changes occurring in these systems.

Lakes where Hg:S2 was significant were first examined to determine if increases in Hg and S2 in these lakes coincided with changes in algal assemblages generally associated with climate change. The strongest relationship between Hg and S2 of all lakes was observed in a subarctic Labrador lake, Shipiskan ($r^2 = 0.97$, $p < 0.0001$). However, the S2 profile and near perfect S2:Hg relationship are likely artifacts of post-depositional degradation of S2 as the ratio of S2:RC decreased fairly consistently from the top to the bottom of the core (Figure S6A). In fact, although Hg concentrations and fluxes (Table 1) have increased consistently from ∼1830 to present in this lake, the algal assemblage, which has consistently been dominated by diatoms (relative abundance ∼95−99%), has changed very little during this period. These results are consistent with other findings which show that Labrador and northern Quebec lakes did not experience temperature warming, decreased summer ice cover, or associated shifts in algal assemblage generally associated with climate-induced changes in other Arctic regions (*20*), at least until the 1990s.

Cli and Fisherman are also subarctic lakes, located only ∼185 km from each other. Cli and Fisherman lakes have similar sedimentation rates, Hg concentrations, and thus Hg flux profiles. Both lakes show an increase in sedimentation rate and HF_F beginning in the ∼1950s and continuing to the present (Figure 2). $HgF_{F,adj}$ increased steadily from the bottom to the top of the cores ($\Delta HgF_{F,adj}$ = 4 and 16 $\mu g\ m^{-2}\ y^{-1}$, respectively) suggesting that catchment-independent Hg inputs have increased through time in these lakes. These results indicate that Cli and Fisherman lakes coincidentally experienced catchment disturbances which altered sedimentation rates and catchment Hg inputs, as well as increased anthropogenic atmospheric Hg inputs. Interestingly, the algal records of Cli and Fisherman lakes differ greatly. In Cli, numerous shifts in the algal community have occurred since the ∼1880s (Figure 2). In Fisherman, algal communities were stable and dominated by diatoms until the 1970s, when the abundance of chrysophytes and green algae increased, which is consistent with a climate-induced switch to more planktonic algal communities in recent years (Figure 2). Finally, in Fisherman, although there was a significant Hg:S2 relationship, there was a consistent decrease in S2:RC from the top to the bottom of the core suggesting that the significant S2:Hg relationship is an artifact of S2 diagenesis (Figure S6C). Overall, the similar Hg and sedimentation rate profiles but differing algal histories suggest that regional-scale factors control Hg flux to sediments but that in-lake variables control algal dynamics in these two lakes.

Moving to the high Arctic, in Amituk Lake, algal assemblages have gone through several shifts beginning in the late 1800s and continuing to the present. Diatoms predominated from ∼1930 to the present (relative abundance ∼58−100%), whereas blue-green and green algae were in greatest abundance prior to ∼1930 (combined relative abundance ∼100%) (Figure 2). The timing of the algal assemblage shifts do not correspond to the steady increases in Hg and S2 fluxes observed in this lake from ∼1947 to the present (HgF_F and $S2F_F$ increased from 1−4 $\mu g\ m^{-2}\ y^{-1}$ and 0.05−0.2 g $m^{-2}\ y^{-1}$, respectively), suggesting that Hg deposition in Amituk is not directly related to the observed changes in algal communities. Amituk sediments have been analyzed for Hg and S2 previously by Outridge et al. (*7*). Although the Hg:S2 relationship reported here ($r^2 = 0.48$, $p = 0.0003$, $N = 14$) is comparable to the one reported in ref *7* ($r^2 = 0.82$, $p < 0.001$, $N = 45$), Outridge et al. presented only diatom flux and not relative abundance of different algal groups and thus did not observe the timing of the shifts in algal assemblage. It should also be noted that, although the shapes of the HgF and S2F profiles were comparable between this study and ref *7*, our fluxes were lower, mostly due to lower sedimentation rates reported here (maximum sedimentation rates, HgF, and S2F were ∼800 vs 290 g $m^{-2}\ y^{-1}$, ∼37 vs 13 $\mu g\ m^{-2}\ y^{-1}$, and ∼1.1 vs 0.6 g $m^{-2}\ y^{-1}$ in Outridge et al. (*7*) and this study, respectively). The variation likely reflects differences in sampling locations. Our sedimentation rates and HgF_F profiles for Amituk Lake are comparable to those reported in refs *32* and *33*.

A significant Hg:S2 relationship was also observed in BK-AH and West lakes, which are lakes where detailed species-level diatom analysis was carried out. In BK-AH, sedimentation rate, HgF_F, and $S2F_F$ decreased since the ∼1970s. However, $HgF_{F,adj}$ and $S2F_{F,adj}$ both increased steadily from 0−0.6 $\mu g\ m^{-2}\ y^{-1}$ and from 0−396 g $m^{-2}\ y^{-1}$, respectively, between ∼1916 and 1980, suggesting that catchment-independent Hg inputs and primary productivity increased since industrialization. Changes in Hg and S2 fluxes coincided with subtle shifts in the diatom assemblage of this lake. After ∼1916, the relative abundance of the benthic *Fragilaria* complex dropped from 90% to 82%, with a compensatory increase in epiphytic and other benthic taxa, such as *Achnanthes*, *Amphora*, *Cocconeis*, and *Cymbella* spp. (*26*). However, changes in diatom assemblage continue in the most recent sediments, while $HgF_{F,adj}$ and HgF_F decreased from ∼1980 to 1995 suggesting that, while subtle climate-induced

shifts in diatom assemblage continue in BK-AH, Hg inputs may be decreasing.

In West Lake, sedimentation rates, HgF_F, $S2F_F$, and $HgF_{F,adj}$ increased dramatically from ~1950 to present, and on average, Hg_F values were ~8 times higher than $HgF_{F,adj}$ values, suggesting that a large portion of the increased Hg flux originated from the catchment. This is not surprising since the West Lake catchment has experienced severe permafrost degradation in recent years and receives large amounts of suspended sediment from the major inflow each year (63−447 Mg 2004−2007) (*34*)). Post-1950s increase in Hg and S2 fluxes directly coincided with a replacement of *Achnanthes*, *Achnanthidium*, *Aulacoseira*, and *Fragilaria* spp. with *Cyclotella* spp. The appearance of *Cyclotella* spp. in post-19th century sediments of Arctic lakes has been associated with increased duration of the ice-free season or enhanced thermal stratification due to climatic warming (*20*). These results imply that West Lake and its catchment are undergoing major climate-related changes that are resulting in increased delivery of sediment and Hg from the catchment, altered diatom assemblages likely due to changes in ice cover and increased nutrient loading from the catchment, as well as increased Hg deposition from catchment-independent sources. Overall, a critical examination of sediment profiles in the above lakes suggests that significant positive Hg:S2 relationships in Arctic sediments are not indicative of increased algal scavenging of Hg from lake water columns in recent years.

There were five lakes where Hg, S2, and algal assemblage analyses were carried out that did not exhibit a significant Hg:S2 relationship. First, in Mista Lake, sedimentation rates fluctuated several times from ~1845 to the present, and, although Hg concentrations increased consistently throughout this time period, S2 concentrations fluctuated, suggesting that while catchment-independent Hg sources increased, sedimentary S2 was diluted and concentrated as sedimentation rates changed. Fluctuations in the relative abundance of different algal groups, algal counts g^{-1}, and fluxes of algal cells also coincided with fluctuations in sedimentation rates, suggesting that algal communities have responded to changing catchment inputs of sediment and possibly nutrients to this lake (Figure 2b).

Results from SHI-L4, located on Southampton Island, most clearly demonstrate the independence of Hg and S2 sediment fluxes. In this lake, although sedimentation rates fluctuated by up to 60% throughout the core, Hg concentrations, HgF_F, and $HgF_{F,adj}$ all steadily increased from ~1946 to the present, demonstrating that Hg deposition originating from catchment-independent sources increased substantially during this period (ΔHgF_F and $\Delta HgF_{F,adj}$ = 3.7 and 5.8 $\mu g\ m^{-2}\ y^{-1}$, respectively). S2 concentrations and fluxes fluctuated slightly throughout the core and decreased from ~1885 to 1958, resulting in a significant negative relationship between Hg and S2 concentrations ($r^2 = 0.6$, $p < 0.001$). Interestingly, the fossil algal community of SHI-L4 was dominated by diatoms (~85−99%) throughout the core. These results demonstrate that Hg deposition is independent of algal-derived C in SHI-L4 and suggests that delivery of Hg to lakes is a key factor determining Hg deposition to sediments.

Moving northward to Char Lake, sedimentation rates, HgF_F, and $HgF_{F,adj}$ steadily increased from ~1899 to the present while S2 concentrations and fluxes fluctuated. Algal assemblages remained quite constant during this time, with the exception of the period ~1927−1958 when chrysophytes replaced diatoms as the dominant fossil algal group. Although reasons for the algal community shift are not apparent, it is clear that changes in Hg deposition are not related to S2 or algal assemblage in Char Lake. Unlike the other study lakes, MB-AC has not experienced postindustrialization increases in sedimentation rates or primary productivity. MB-AC sedimentation rates decreased from ~1958 to the present, while $HgF_{F,adj}$ fluctuated about a trend toward increasing values (Figures 2 and S4L). S2 concentrations and fluxes also fluctuated throughout the core and were actually lowest in most recent sediment horizons. Microfossil analysis indicates that MB-AC has been consistently dominated by blue-green algae (relative abundance 90−99%); however, we are reluctant to overinterpret the lack of change given that some samples of this core had evidence of diatom dissolution. Overall, results from this core suggest that unlike numerous other Arctic lakes which are experiencing widespread changes driven by regional-scale climate forcing, changes in MB-AC are driven by local factors.

Finally, results from Lake Hazen, our highest latitude and largest study lake (538 km^2), suggest that this lake is experiencing climate-induced changes; however, these changes are not altering Hg deposition to sediments. HgF_F values fluctuated slightly over time (range = 22−32 $\mu g\ m^{-2}\ y^{-1}$) but have not increased since industrialization, as ΔHgF_F was only 0.3 $\mu g\ m^{-2}\ y^{-1}$. This is consistent with atmospheric Hg monitoring at Alert (Nunavut) from 1995 to 2005, which indicates that gaseous elemental Hg concentrations have not increased in this region during this period (*35*). S2 fluxes increased since ~1974 ($\Delta S2F_F$ = 0.3 mg $m^{-2}\ y^{-1}$) and the diatom community shifted from dominance by *Fragilaria*, *Pseudostaurosira*, and *Staurosirella* spp. to dominance of planktonic *Cyclotella* spp. beginning in ~1962 (Figure 2I). These results suggest that a decrease in summer ice-cover extent in Hazen has altered the diatom community and intensified primary production. Nevertheless, it is clear that these changes have not driven up the flux of Hg to the sediments, thus highlighting the importance of Hg loading to a lake, whether from the catchment or atmosphere, in determining the flux of Hg to lake sediments.

To examine Hg-climate-indicator dynamics across all lakes, we determined the relationship between Hg, S2, and algal abundance in the 11 lakes where these parameters were available using a GLM. We obtained an excellent fit (r^2 = 0.93, $p < 0.001$) for the following model:

$$\log Hg_{conc} = lake + S2_{conc} + DIATOM_{\%\ abundance,\ norm} + lake{*}S2_{conc} \quad (3)$$

85% of the variation in Hg concentration, however, was accounted for by the parameter "lake", which incorporates the effect of lake-specific variables, such as sedimentation rate, catchment Hg contribution, and atmospheric Hg inputs. Adding S2 concentration, diatom abundance, and the lake*$S2_{conc}$ interaction term improved the fit of the model only slightly (r^2 = 0.93 vs 0.85). Most importantly, the $S2_{conc}$ term was not significant (p = 0.51) while the interaction lake*$S2_{conc}$ term was ($p < 0.001$), demonstrating that the relationship between Hg and S2 is quite different among lakes, not only in magnitude but also in direction. These results demonstrate that S2 and diatom abundance do not play an important role in determining Hg concentrations in Arctic sediments, and we conclude that although many Arctic lakes are simultaneously experiencing climate-induced changes and increased Hg deposition, algal scavenging is not an important process governing Hg fluxes to sediments. Finally, our results suggest that in the absence of "real-time" measurements, dated sediment cores can provide valuable information on regional Hg deposition if catchment contributions of Hg are considered.

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Supporting Information Available

Analytical details, additional results and discussions, and eight figures. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Schroeder, W. H.; Munthe, J. Atmospheric mercury—An overview. *Atmos. Environ.* **1998**, *32*, 809–822.
(2) Landers, D. H.; Gubala, C.; Verta, M.; Lucotte, M.; Johansson, K.; Vlasova, T.; Lockhart, W. L. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. *Atmos. Environ.* **1998**, *32*, 919–928.
(3) Lockhart, W. L.; Wilkinson, P.; Billeck, B. N.; Danell, R. A.; Hunt, R. V.; Brunskill, G. J.; Delaronde, J.; St. Louis, V. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* **1998**, *40*, 163–173.
(4) Bindler, R.; Renberg, I.; Appleby, P. G.; Anderson, N. J.; Rose, N. L. Mercury accumulation rates and spatial patterns in lake sediments from West Greenland: A coast to ice margin transect. *Environ. Sci. Technol.* **2001**, *35*, 1736–1741.
(5) Fitzgerald, W. F.; Engstrom, D. R.; Lamborg, C. H.; Tseng, C.-M.; Balcom, P. H.; Hammerschmidt, C. R. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. *Environ. Sci. Technol.* **2005**, *39*, 557–568.
(6) Lindeberg, C.; Bindler, R.; Renberg, I.; Emteryd, O.; Karlsson, E.; Anderson, N. J. Natural fluctuations of mercury and lead in Greenland lake sediments. *Environ. Sci. Technol.* **2006**, *40*, 90–95.
(7) Outridge, P. M.; Sanei, H.; Stern, G. A.; Hamilton, P. B.; Goodarzi, F. Evidence for control of mercury accumulation rates in Canadian high Arctic lake sediments by variations of aquatic primary productivity. *Environ. Sci. Technol.* **2007**, *41*, 5259–5265.
(8) Muir, D. C. G.; Wang, X.; Yang, F.; Nguyen, N.; Jackson, T.; Evans, M.; Douglas, M.; Köck, G.; Lamoureux, S.; Pienitz, R.; et al. Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. *Environ. Sci. Technol.* **2009**, *43*, 4802–4809.
(9) Stern, G. A.; Sanei, H.; Roach, P.; De La Ronde, J.; Outridge, P. M. Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a subarctic lake in Yukon, Canada: Further evidence toward the algal-mercury scavenging hypothesis. *Environ. Sci. Technol.* **2009**, *43*, 7684–7690.
(10) Carrie, J.; Wang, F.; Sanei, H.; Macdonald, R. W.; Outridge, P. M.; Stern, G. A. Increasing contaminant burdens in an arctic fish, burbot (Lota lota), in a warming climate. *Environ. Sci. Technol.* **2010**, *44*, 316–322.
(11) Cooke, C. A.; Hobbs, W. O.; Neal, M.; Wolfe, A. P. Reliance on ^{210}Pb chronology can compromise the inference of preindustrial Hg flux to lake sediments. *Environ. Sci. Technol.* **2010**, *44*, 1998–2003.
(12) Wallace, J. M.; Gutzler, D. S. Teleconnections in the geopotential height field during the northern hemisphere einter. *Mon. Weather Rev.* **1981**, *109*, 784–812.
(13) Barnston, A. G.; Livezey, R. E. Classification, seasonality and persistence of low-frequency atmospheric circulation patterns. *Mon. Weather Rev.* **1987**, *115*, 1083–1126.
(14) Macdonald, R.; Harner, T.; Fyfe, J. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5–86.
(15) Travnikov, O. Contribution of the intercontinental atmospheric transport to the mercury pollution in the northern hemisphere. *Atmos. Environ.* **2005**, *39*, 7541–7548.
(16) Durnford, D.; Dastoor, A.; Figueras-Nieto, D.; Ryjkov, A. Long range transport of mercury to the Arctic and across Canada. *Atmos. Chem. Phys. Disc.* **2010**, *10*, 4673–4717.
(17) Lafargue, E.; Espitalité, J.; Marquis, F.; Pillot, D. Rock-Eval 6 applications in hydrocarbon exploration, production and soil contamination studies. *Rev. French Petroleum Inst.* **1998**, *53*, 421–437.
(18) Sanei, H.; Stasiuk, L. D.; Goodarzi, F. Petrological changes occurring in organic matter from recent lacustrine sediments during thermal alteration by Rock-Eval pyrolysis. *Org. Geochem.* **2005**, *36*, 1190–1203.
(19) Michelutti, N.; Wolfe, A. P.; Briner, J. P.; Miller, G. H. Climatically controlled chemical and biological development in arctic lakes. *J. Geophys. Res. G: Biogeosciences* **2007**, *112*, G03002.
(20) Smol, J. P.; Wolfe, A. P.; Birks, H. J. B.; Douglas, M. S. V.; Jones, V. J.; Korhola, A.; Pienitz, R.; Rühland, K.; Sorvari, S.; Antoniades, D.; et al. Climate-driven regime shifts in the biological communities of arctic lakes. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4397–4402.
(21) Douglas, M.; Smol, J.; Blake, W. Marked post-18th century environmental change in high arctic ecosystems. *Science* **1994**, *266*, 416–419.
(22) Rühland, K.; Priesnitz, A.; Smol, J. P. Paleolimnological evidence from diatoms for recent environmental changes in 50 lakes across Canadian arctic treeline. *Arctic Antarctic Alpine Res.* **2003**, *35*, 110–123.
(23) Smol, J. P.; Douglas, M. S. V. From controversy to consensus: Making the case for recent climatic change in the Arctic using lake sediments. *Front. Ecol. Environ.* **2007**, *5*, 466–474.
(24) Kling, H. J. A summary of past and recent plankton in Lake Winnipeg, Canada using algal fossil remains. *J. Paleolimn.* **1998**, *19*, 297–307.
(25) Findlay, D. L.; Kling, H. J.; Ronicke, H.; Findlay, W. J. A limnological study of Arendsee (Germany). *J. Paleolimn.* **1998**, *19*, 41–54.
(26) Lim, D. S. S.; Smol, J. P.; Douglas, M. S. V. Recent environmental changes on Banks Island (N.W.T., Canadian Arctic) quantified using fossil diatom assemblages. *J. Paleolimn.* **2008**, *40*, 385–398.
(27) Peters, K. E.; Walters, C. C.; Moldowan, J. M. The biomarker guide. *Biomarkers and isotopes in the environment and human history*, 2nd ed.; Cambridge University Press: Cambridge. U.K., 2005; Vol. 1.
(28) Michelutti, N.; Douglas, M. S. V.; Smol, J. P. Diatom response to recent climatic change in a high arctic lake (Char Lake, Cornwallis Island, Nunavut). *Global Planet Change* **2003**, *38*, 257–271.
(29) ACIA. *Arctic Climate Impact Assessment*; Cambridge University Press: New York, 2005.
(30) Hill, M. O. 1973. Diversity and evenness—Unifying notation and its consequences. *Ecology* **1973**, *54*, 427–432.
(31) Galman, V.; Rydberg, J.; Sjostedt de-Luna, S.; Bindler, R.; Renberg, I. Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. *Limnol. Oceanogr.* **2008**, *53*, 1076–1082.
(32) Lockhart, W. L.; Wilkinson, P.; Billeck, B. N.; Hunt, R. V.; Wagemann, R.; Brunskill, G. J. Current and historical inputs of mercury to high-latitude lakes in Canada and to Hudson Bay. *Water, Air, Soil Pollut.* **1995**, *80*, 603–610.
(33) Semkin, R. G.; Mierleb, G.; Neureuther, R. J. Hydrochemistry and mercury cycling in a high arctic watershed. *Sci. Total Environ.* **2005**, *342*, 199–221.
(34) Dugan, H. A.; Lamoureux, S. F.; Lafrenière, M. J.; Lewis, T. Hydrological and sediment yield response to summer rainfall in a small high arctic watershed. *Hydrol. Process.* **2009**, *23*, 1514–1526.
(35) Steffen, A.; Douglas, T.; Amyot, M.; Ariya, P.; Aspmo, K.; Berg, T.; Bottenheim, J.; Brooks, S.; Cobbett, F.; Dastoor, A.; et al. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos. Chem. Phys.* **2008**, *8*, 1445–1482.

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