Trends in historical mercury deposition inferred from lake sediment cores across a climate gradient in the Canadian High Arctic

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Abstract

Recent climate change may be enhancing mercury fluxes to Arctic lake sediments, confounding the use of sediment cores to reconstruct histories of atmospheric deposition. Assessing the independent effects of climate warming on mercury sequestration is challenging due to temporal overlap between warming temperatures and increased long-range transport of atmospheric mercury following the Industrial Revolution. We address this challenge by examining mercury trends in short cores (the last several hundred years) from eight lakes centered on Cape Herschel (Canadian High Arctic) that span a gradient in microclimates, including two lakes that have not yet been significantly altered by climate warming due to continued ice cover. Previous research on subfossil diatoms and inferred primary production indicated the timing of limnological responses to climate warming, which, due to prevailing ice cover conditions, varied from ~1850 to ~1990 for lakes that have undergone changes. We show that climate warming may have enhanced mercury deposition to lake sediments in one lake (Moraine Pond), while another (West Lake) showed a strong signal of post-industrial mercury enrichment without any corresponding limnological changes associated with warming. Our results provide insights into the role of climate warming and organic carbon cycling as drivers of mercury deposition to Arctic lake sediments.

KEYWORDS: Cape Herschel, paleolimnology, algal scavenging, climate warming, ice cover

Capsule –Climate warming has the potential to enhance mercury sequestration to Arctic lake sediments, but is not a necessary precondition for substantial post-industrial mercury enrichment.

INTRODUCTION

Lake sediment cores are commonly used to reconstruct the history of atmospheric mercury deposition in the Arctic (reviewed in MacDonald et al. 2000; Chételat et al. 2015a, 2015b). However, it has been noted that discrepancies exist between mercury fluxes measured from lake sediments and modelled and measured atmospheric deposition since 1990, as sedimentary mercury concentrations continued to increase despite stable or decreasing anthropogenic emissions (Goodsite et al. 2013). Several suggestions have been put forward to explain this apparent contradiction: 1. Difficulties in establishing ^{210}Pb chronologies for Arctic lake sediment cores (Wolfe et al. 2004; Cooke et al. 2010) make it challenging to accurately quantify lake sedimentation rates, influencing calculations of sediment mercury flux rates; 2. Limited measurements of atmospheric mercury in Arctic environments results in considerable uncertainty in deposition estimates over the past several decades (Chetelat et al. 2015a); 3. Recent anthropogenic climate change may be enhancing mercury fluxes to Arctic lakes (MacDonald et al. 2000; Chetelat et al. 2015a, 2015b).

Climate warming has the potential to modify mercury fluxes to high latitude lake sediments through a variety of mechanisms. Permafrost thaw and associated hydrological changes from active layer deepening may accelerate the release of mercury from the catchment to surface waters, especially in organic-rich peatlands (e.g. Klaminder et al. 2008). Changes in the cryosphere can also influence mercury accumulation in lake sediments, especially if changes modify the timing and volume of the spring freshet, often a primary source of mercury to High Arctic lakes (Semkin et al. 2005). In addition, increases in primary production have been observed in lakes across the circumpolar Arctic in response to recent warming (Michelutti et al. 2005; Michelutti and Smol 2016). Since mercury has a high affinity for algal-derived organic matter, increased primary production may be enhancing the sequestration of mercury to lake sediments (Sanei and Goodarzi 2006; Sanei et al. 2012). The role of the "algal scavenging hypothesis" for influencing mercury accumulation in Arctic lake sediments is inconclusive: while Outridge et al. (2007) documented strong relationships between estimates of past algal production and sedimentary mercury, Kirk et al. (2011) and Cooke et al. (2012) found little evidence to support algal scavenging, and instead highlighted the importance of atmospheric transport and run-off from the catchment for delivering mercury to Arctic lake ecosystems. Furthermore, in Lake DV09 on Devon Island (Canadian High Arctic), algal carbon was observed to be an important driver of sedimentary mercury concentrations in recent sediments, but not over the entire Holocene (Outridge et al. 2017).

Assessing the effects of climate warming on mercury sequestration in Arctic lake sediments is confounded by the temporal overlap between warming temperatures and increased long-range transport of atmospheric mercury following the Industrial Revolution. However, local, site-specific factors, such as elevation and shading, create microclimatic gradients that can be used to help disentangle climate warming effects on mercury sequestration from anthropogenic emissions. Such gradients exist on Ellesmere Island (Nunavut) in the Canadian High Arctic. Lakes and ponds at Ellesmere Island have been categorized *a priori* into four different climate groups based on observational data on seasonal ice-cover patterns collected over thirty years, which was then supplemented with diatom-based (siliceous algae) paleolimnological reconstructions of changes in lake ice-cover regime and primary production (Griffiths et al. 2017). "Warm" ponds are among the first to lose ice cover in the summer, and exhibited early (~1850) limnological responses to anthropogenic climate warming. Lakes and ponds in Arctic "oasis" sites also lose ice cover early in the season, but have had historically elongated seasonal ice-free periods prior to the onset of anthropogenic climate warming (Griffiths et al. 2017). Ponds at “Cool” sites have a shorter ice-free period relative to “Warm” sites, and exhibited a later response to anthropogenic climate warming (~1950). “Cold” lakes and ponds are located at high elevation on nearby Pim Island, are rarely ice-free, and have exhibited little biotic response to anthropogenic climate warming thus far (Griffiths et al. 2017).

Griffiths et al. (2017) used the local microclimatic gradients described above to demonstrate that the length of the ice-free season is a primary driver of lake ecological responses to climate warming, mainly via increases in primary production inferred from VIRS-inferred chlorophyll *a* concentrations (Michelutti and Smol 2016), and the establishment of new aquatic habitats arising from enhanced growth of aquatic vegetation (inferred from fossil diatom assemblages). In doing so, they generated a multi-proxy paleoecological record of the timing of limnological shifts, linked to local microclimates, occurring in response to climate warming at and around Cape Hershel, Ellesmere Island (Canada). These multi-proxy paleolimnological records provide us with a unique opportunity to investigate the influence of limnological changes resulting from climate warming on historical trends in sediment mercury accumulation, in particular changes in lake ice-cover regime and organic carbon cycling. If warming-induced changes in algal production and organic carbon in High Arctic lakes are important drivers of sediment mercury accumulation, we would expect that:

1. “Warm” lakes, simultaneously experiencing a coupled history of increased atmospheric mercury deposition and enhanced primary production due to climate change, will exhibit a greater magnitude of mercury enrichment in recent sediments compared to “Cold” sites that have been minimally altered by recent climate change.

2. “Cool” sites will exhibit a two-stage pattern of mercury enrichment: (1) An increase in sediment mercury concentrations following the Industrial Revolution (~1850), and (2) a later intensification of mercury enrichment consistent with diatom-inferred limnological responses to climate warming.

STUDY SITE DESCRIPTIONS

We selected eight lakes and ponds on Ellesmere Island, with two lakes/ponds in each of the four microclimate categories described above (Figure 1, Table 1). Ellesmere Island is the northernmost island in the Canadian High Arctic archipelago. The general climate of central Ellesmere Island has a mean annual air temperature of -19 ºC (maximum daytime temperatures 5-9 ºC in the summer months), and mean annual precipitation of 79 mm, most of which falls as snow (Environment Canada 2016).

“Warm” sites (Col Pond, Elison Lake) are located at Cape Herschel (78º37'N, 74 º 42'W). Bedrock at Cape Herschel is Archean granites with outcrops of calcareous glacial tills (Frisch 1984). Elison Lake is a low elevation pond (23 m a.s.l.) located on a valley floor, and has a maximum depth of 1.5 m. Col Pond (unofficial name) has a depth of 0.5 m, and is located within a topographic col. Both ponds have been visited regularly by our research group (approximately every three years) for the last 30 years, and are thought to have the longest ice-free seasons on Cape Herschel. Both ponds are oligotrophic, and contained submerged aquatic mosses at the time of sampling. In general, shoreline vegetation is sparse.

“Cool” sites (Moraine Pond, Paradise Pond) are among the last at Cape Herschel to lose their ice cover in the summer. Moraine Pond is shaded by cliffs, and receives hydrological inputs from a large catchment through a stream. Submerged aquatic mosses were observed at the time

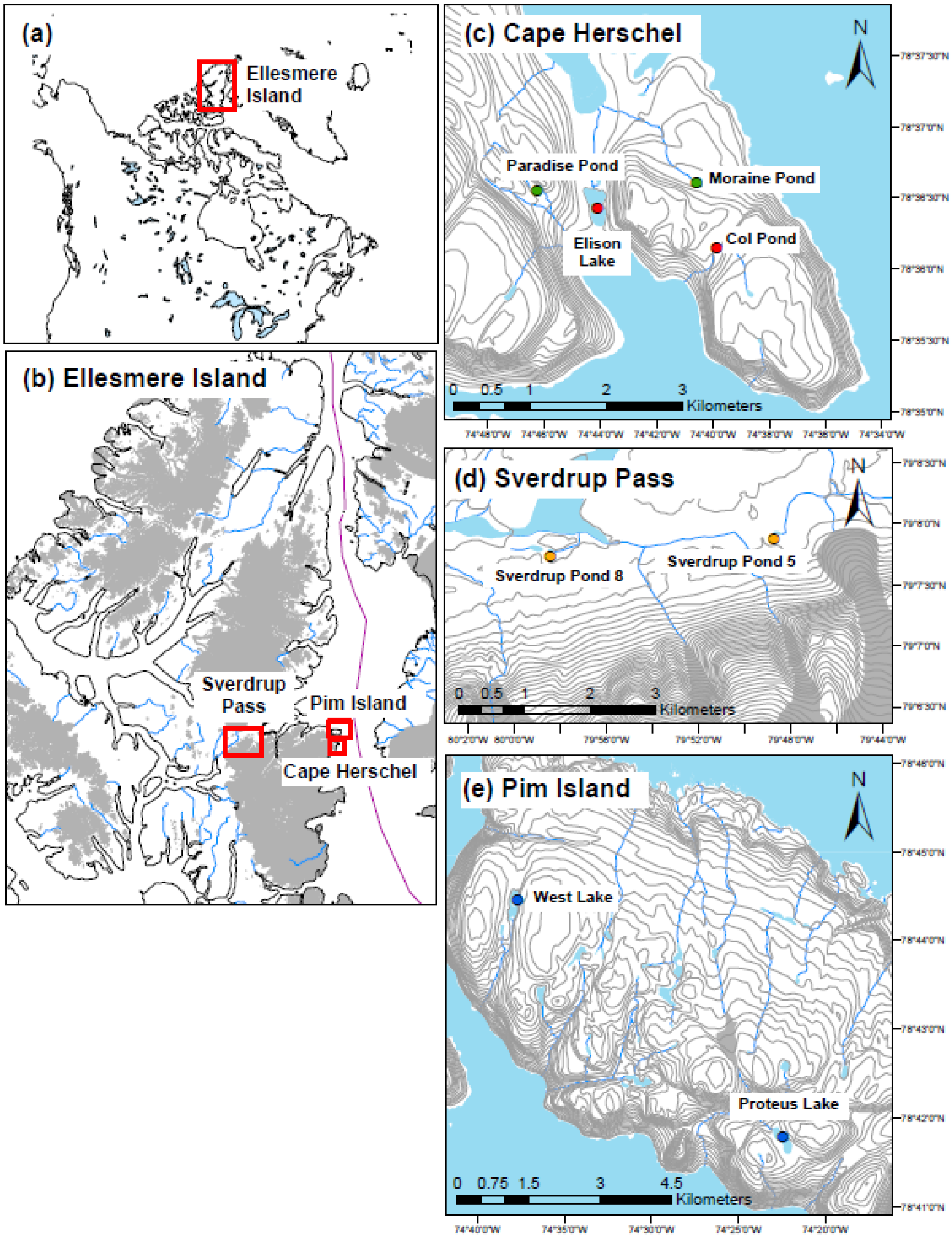


Figure 1 – A map of the study site locations on or near Ellesmere Island, Nunavut, Canada. a) location of Ellesmere Island in the Canadian High Arctic; b) Inset showing the three main regions of study, including Sverdrup Pass ("Oasis"), Cape Herschel ("Warm" and "Cool"), and Pim Island ("Cold"); c-e) Insets showing the location of the individual 8 study lakes and ponds. Coloured dots indicate lake category: "Warm" lakes/ponds are in red, "Cool" lakes/ponds in green, "Oasis" ponds in yellow, and "Cold" lakes in blue.

Table 1 – Lake physical characteristics and water chemistry measurements from July 2011 for the 8 study lakes near Cape Herschel, Nunavut, Canada. TP= total dissolved phosphorus; DOC = dissolved organic carbon.

Lake Name	Category	Latitude (N)	Longitude (W)	Elevation (m a.s.l.)	Max. Depth (m)	pH	TP µg/L	Specific Conductance µS/cm	DOC mg/L
Col Pond	Warm	78° 36.154’	74° 39.758’	137	0.5	8.2	6.4	143	1.9
Elison Lake	Warm	78° 36.487’	74° 44.414’	23	1.5	8.4	6.0	357	4.0
Moraine Pond	Cool	78° 36.685’	74° 40.977’	89	0.5	8.8	13.6	208	2.3
Paradise Pond	Cool	78° 36.530’	74° 46.117’	134	1.8	8.4	4.4	35	0.8
SV5	Oasis	79° 7.951’	79° 48.582’	299	0.5	8.6	15.8	365	14.6
SV8	Oasis	79° 7.680’	79° 58.498’	296	0.3	8.7	13.9	571	20.1
Proteus Lake	Cold	78° 41.876’	74° 23.022’	376	6.9	8.7	4.2	73	1.0
West Lake	Cold	78° 44.491’	74° 37.751’	323	12.1	8.0	5.8	48	0.6

of sampling. Paradise Pond is at relatively high elevation (134 m a.s.l.) and exposed. No aquatic mosses were observed in July, 2011. Both ponds maintained persistent snowbanks in the summer.

“Oasis” sites (SV5, SV8; unofficial names) are located at Sverdrup Pass (79º8'N, 79º50'W) on central Ellesmere Island (Figure 1). Sverdrup Pass is a low-lying valley bordered by high cliffs which shelter the pass from winds, resulting in warmer temperatures, a longer growing season (late May to early September; Elster et al. 1999), and higher productivity and biodiversity relative to the rest of Ellesmere Island (Lévesque 1996). SV5 and SV8 are mesotrophic ponds (depth ~0.5 m) with 100% vegetated shoreline (lichen, bryophytes, cotton grass) and abundant submerged macrophyte growth.

“Cold” sites are located on Pim Island (78º43’N; 74º27’W), located ~10 km northeast of Cape Herschel (Figure 1). Lakes and ponds on the island are located in exposed, relatively high elevation (300-500 m a.s.l.) sites. Vegetation is sparse. Ponds on Pim Island have no appreciable sediment accumulation, and consequently only deeper lakes were sampled (Griffiths et al., 2017). West Lake (unofficial name; depth 12.1 m) typically maintains 90-100% ice cover throughout the summer, with the exception of July 2011 when it was ice-free. Proteus Lake has a depth of 6.9 m, and maintains partial ice coverage throughout the summer. No aquatic vegetation was observed at either site during the sampling period in July, 2011.

MATERIALS AND METHODS

Field methods

To facilitate direct comparisons between the previously published paleoecological records and our new sediment mercury reconstructions, we conducted our analyses on the same sediment cores analyzed in Griffiths et al. (2017). Sediment cores were taken from each of the 8 lakes and ponds in July, 2011, using a Glew (1989) gravity corer in sites >1 m deep, and a push corer (Glew and Smol 2016) for ponds <1 m deep. Cores were extruded in the field using a Glew (1988) vertical extruder at 0.25-0.5 cm resolution. Sediments were kept frozen until analysis.

Sediment core chronologies

We used the same sediment cores analyzed in Griffiths et al. (2017), and a detailed description of the methods and results for sediment core dating can be found therein. Briefly, sediments were freeze-dried and dated using ^{210}Pb gamma spectrometry at the Paleoecological Assessment and Research Laboratory, Queen's University (Kingston, Ontario, Canada) using standard methodologies (Appleby 2001; Schelske et al. 1994), and a chronology was established using the Constant Rate of Supply (CRS) model (Appleby 1978). Dates were corroborated using ^{137}Cs as an independent marker (Jaakkola et al. 1983). Col Pond and Elison Lake were originally cored in 1978 and dated using radiocarbon and ^{210}Pb geochronology (Douglas et al. 1994). The new cores collected in 2011 were matched to the ^{210}Pb chronology from the 1978 core using marked shifts in diatom assemblages.

Low ^{210}Pb activities in SV5 meant that no chronology could be established for this pond, and instead basal core dates were established using ^{14}C dating of terrestrially-derived woody material (Griffiths et al. 2017).

The low ^{210}Pb activities in our cores resulted in a high degree of uncertainty for reconstructing accurate sedimentation rates (Table 2). As such, we were unable to calculate mercury flux rates for our study lakes, a common challenge for High Arctic paleolimnology studies (Wolfe et al. 2004). Instead, we focused on investigating relationships between mercury accumulation and organic carbon/algal production for this study.

Inferring the timing of historical changes in ice-cover regime

We used the record of diatom species assemblage shifts reported in Griffiths et al. (2017) to determine the timing of lake changes linked to decreased ice cover occurring in response to climate warming. The timing of shifts in diatom assemblages was determined by identifying stratigraphic zones using constrained incremental sum-of-squares (CONISS) cluster analyses (Grimm 1987), with significance of identified breaks assessed using the broken stick model (Bennett 1996), using the vegan package v. 2.0 ±10 (Oksanen et al. 2013) for the R software environment. Diatom assemblage changes were reported as a shift from low diatom species diversity dominated by epipelic and epilithic taxa, to increased diversity and a greater proportion of epiphytic taxa occurring in response to a lengthening of the ice-free season. The "Warm" sites (Col Pond, Elison Lake) exhibited this transition *circa* 1850, while, as hypothesized, the "Cool" sites exhibited this transition later (~1960 for Moraine Pond, ~1990 for Paradise Pond). The

Table 2 – ^{210}Pb-inferred sedimentation rates (Sed. Rate) and standard deviation (SD), based on the constant rate of supply model. Due to low ^{210}Pb activities, no sedimentation rates could be inferred for SV5, Col Pond, and Elison Lake.

Moraine Pond			**Paradise Pond**		
Depth (cm)	Sed. Rate (g cm^{-2} yr^{-1})	SD (g cm^{-2} yr^{-1})	Depth (cm)	Sed. Rate (g cm^{-2} yr^{-1})	SD (g cm^{-2} yr^{-1})
0	0.038	0.012	0	0.056	0.019
1	0.011	0.005	1	0.077	0.03
2	0.014	0.008	2	0.032	0.021
3	0.039	0.021	3	0.01	0.03
4	0.068	0.041			
5	0.035	0.035			
6	0.064	0.074			
7	0.034	0.069			
West Lake			**Proteus Lake**		
Depth (cm)	Sed. Rate (g cm^{-2} yr^{-1})	SD (g cm^{-2} yr^{-1})	Depth (cm)	Sed. Rate (g cm^{-2} yr^{-1})	SD (g cm^{-2} yr^{-1})
0	0.009	0.006	0	0.009	0.011
1	0.006	0.005	0.5	0.005	0.009
2	0.006	0.005	1	0.013	0.023
3	0.004	0.005	1.5	0.009	0.022
4	0.008	0.008	2	0.002	0.018
5	0.01	0.012			
6	0.006	0.008			
7	0.019	0.026			
8	0.005	0.011			
9	0.015	0.037			
10	0.005	0.015			
SV8					
Depth (cm)	Sed. Rate (g cm^{-2} yr^{-1})	SD (g cm^{-2} yr^{-1})			
0	0.016	0.003			
0.25	0.025	0.015			
1.25	0.014	0.004			
2.25	0.01	0.003			
3.25	0.006	0.002			
4.25	0.004	0.002			

"Cold" sites exhibited this transition only in the uppermost sediment interval (Proteus Lake), or not at all (West Lake), as hypothesized based on known ice cover patterns. The "Oasis" sites had high diatom diversity and abundant epiphytic taxa throughout the sediment record, even prior to 1850, though subtle diatom assemblage changes were reported consistent with additional warming in SV5 (Griffiths et al. 2017).

Laboratory analyses

For organic carbon analysis, freeze-dried sediments were acid-digested in concentrated HCl for 48 hours in an acid desiccator to remove inorganic carbon (Harris et al. 2001). Sediment samples were then rinsed with deionized water three times and freeze-dried again. Between 45-90 mg of sample was weighed into tin capsules containing 20 mg tungsten trioxide, and analyzed using an Elementar Micro Cube Elemental Analyzer (Elementar, Germany) at the G.G. Hatch Stable Isotope Laboratory (Ottawa, Ontario, Canada). The sample was flash combusted with oxygen at ~180 °C using ultra-pure helium as a carrier. N_2, CO_2, H_2O and SO_2 were separated using gas chromatography and trapped with a single "trap and purge" adsorption column, released separately and measured using a thermal conductivity detector. Select intervals from each sediment core were run in triplicate for quality assurance. Sulfanilic acid was used as a blind standard. Analysis precision for the instrument is ±0.1% (Pella, 1990).

For total mercury analysis, 30 mg of freeze dried sediment was weighed into ceramic boats and analyzed via dual step gold amalgamation and detection via cold-vapor atomic absorption on a Nippon Sp-3D mercury analyzer (UOP Method 938-00, detection limit 0.01 ng Hg; Fox et al. 2005). For quality assurance, Marine Sediment Certified Reference Materials from the National Research Council of Canada (MESS-3) was used, and select intervals from each sediment core were run in triplicate.

In order to reconstruct algal production and test the algal scavenging hypothesis, the visual reflectance spectroscopy (VRS) method was used to infer trends in sediment chlorophyll *a* (Michelutti et al. 2010; Michelutti and Smol 2016), consistent with Cooke et al. (2012). Briefly, sediment was freeze-dried, homogenized, and sieved through a 125 mm screen, and placed into cuvettes for analysis of reflectance spectra between 350-2500 nm on a FieldSpec1 Pro Spectroradiometer. VRS-chl *a* provides a good approximation of overall temporal trends in primary production, and measures both chlorophyll *a* and its main products of degradation (Michelutti et al. 2005). Previous investigations into algal scavenging of mercury (e.g. Outridge et al. 2007; Outridge et al. 2017; Jiang et al. 2011; Kirk et al. 2011) used Rock-Eval pyrolysis techniques, which provide more targeted information on sources of organic carbon than VRS-chl *a*, but may be more susceptible to diagenetic effects. For example, Kirk et al. (2011) documented strong correlations between sedimentary mercury and S2 (algal-derived) carbon in five High Arctic lake sediment cores, but evidence of S2 diagenesis was apparent in each.

Data Analysis

Mercury enrichment factors (EF) in lake sediment cores were calculated using the following formula:

$$EF = \text{recent (post-1990) [THg] / pre-industrial [THg]}$$

To examine general relationships between mercury and algal production, Spearman correlations were run for total mercury (per gram dry weight) and VRS-inferred chlorophyll *a* using the basic package in the R software environment.

Results

Analytical results for the MESS-3 SRM ranged from 111.7-116.4 ng g^{-1}, slightly higher than the certified value of 91 ±9 ng g^{-1}. Percent relative standard deviation (RSD) was 1.2%. Subsequent Canadian Association for Laboratory Accreditation proficiency testing of the instrument showed that the discrepancy was due to the MESS-3 material itself, which was several years old. Further testing with new MESS-3 material produced results within the expected 91 ±9 ng g^{-1} range. At least one sample from each lake sediment core was run in triplicate. Percent relative standard deviation of triplicate samples ranged from 0-8.9% (average 4.8%). The highest RSD value was obtained for SV5, which had among the lowest Hg concentrations (7.8-8.7 ng g^{-1}).

Some degree of post-industrial enrichment in mercury is evident in all lake sediment cores, calculated as enrichment factors (Table 3) ranging from 1.1 to 5.6, with the exception of SV5, for which no EF was calculated due to difficulties with the ^{210}Pb dating profile. There is no apparent relationship between enrichment factors and climate categories.

Table 3 - Mercury enrichment factors, calculated as recent (post-1990)/pre-industrial (pre-1850) total mercury concentrations per gram dry weight.

Lake Name	**Category**	**Enrichment Factor**
Col Pond	Warm	5.4
Elison Lake	Warm	1.5
Moraine Pond	Cool	5.6
Paradise Pond	Cool	1.1
SV5	Oasis	-
SV8	Oasis	2.4
Proteus Lake	Cold	1.3
West Lake	Cold	4.4

Down-core mercury trends: "Warm" sites

In Col Pond, a clear increase in total mercury concentrations (THg) occurs above a core depth of 1 cm (EF = 5.4; Table 3), corresponding to ~1850, consistent with both the timing of increasing long-range transport of mercury following the industrial revolution, and diatom-inferred changes in lake ice-cover regime in response to a warming climate (Figure 2a). THg concentrations are relatively stable in the pre-industrial period (5-7 ng g^{-1} dry weight), increasing to 34 ng g^{-1} dry weight in the surface interval. The post-industrial enrichment trend is no longer apparent in Col Pond when mercury concentrations are corrected for sediment organic carbon content (Figure 2a).

Elison Lake exhibits a small magnitude of post-industrial enrichment (from ~7-9 to 12 ng g^{-1} dry weight; EF = 1.5; Table 3) above a core depth of ~2cm, consistent with ~1850 and the timing of diatom-inferred lake response to climate warming, similar to Col Pond (Figure 2b). This trend is still apparent when corrected for sediment organic carbon content, but a pre-industrial peak in %OC-corrected THg is also observed (Figure 2b). There is a positive correlation between total mercury concentrations and VRS-inferred chlorophyll *a* in Elison Lake (Figure 3).

In the post-industrial period, Col Pond also shows a generally positive correlation trend between total mercury concentrations and VRS-inferred chlorophyll *a*, but this is not statistically significant over the entire sediment core (Figure 3).

Down-core mercury trends: "cool" sites

In Moraine Pond, an increase in THg is observed above a core depth of 10 cm (~1850), from ~7 to ~12 ng g^{-1} dry weight, and an additional increase is observed between a core depth of

Figure 2 – Down-core sediment profiles of total mercury, expressed in both ng g^{-1} dry weight (white triangles) and ng g^{-1} organic carbon (black circles) for lakes in each of the four climate categories: a) warm lakes; b) cool lakes; c) oasis lakes; d) cold lakes. Dashed lines represent the timing of the change in diatom communities from "zone 1" to "zone 2", indicating a shift in lake ice cover regime occurring in response to climate warming (Griffiths et al. 2017). Where different from the diatom-inferred lake ice cover regime, the onset of the post-industrial period, ~1850, is denoted with a solid black line. For SV5, no 210Pb dating profile could be generated, and so the timing of ~1850 and the diatom assemblage change, is unknown.

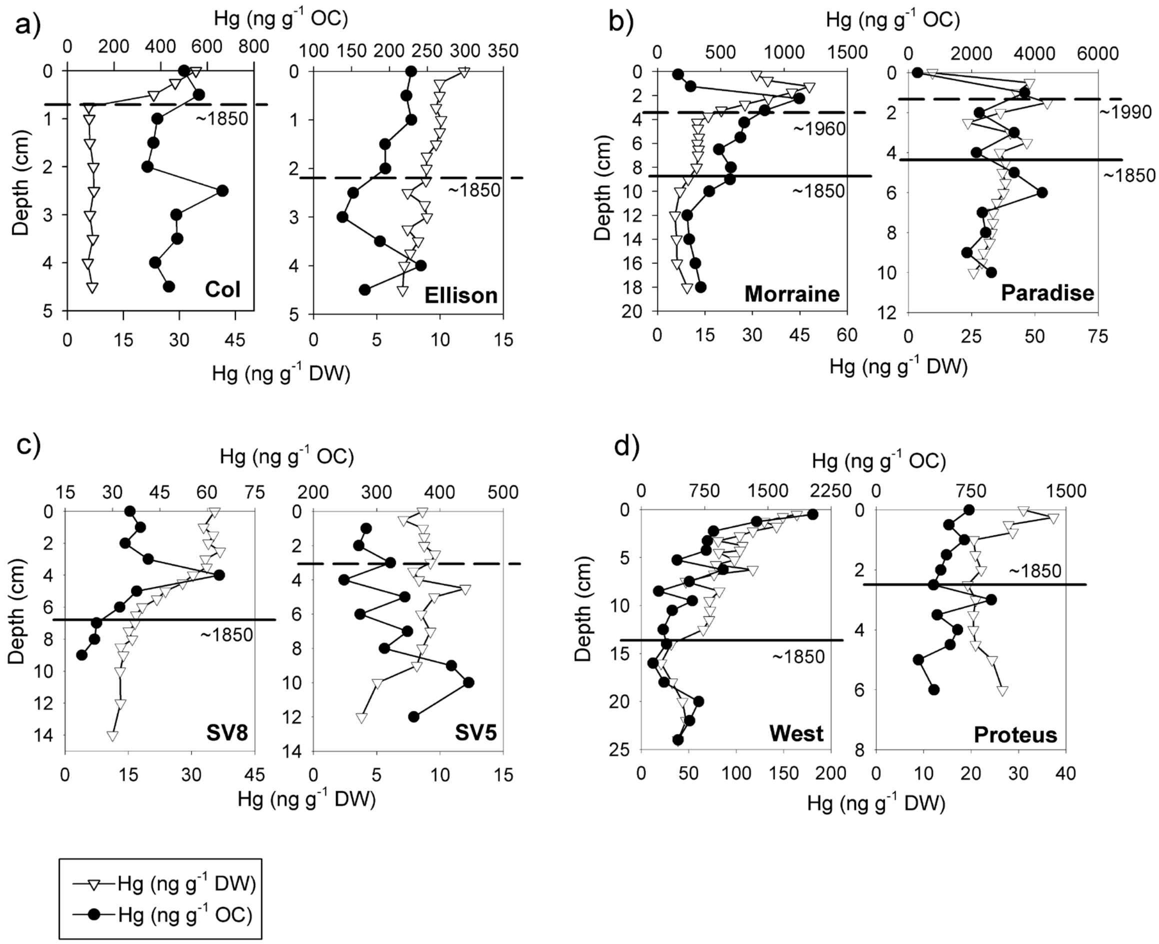
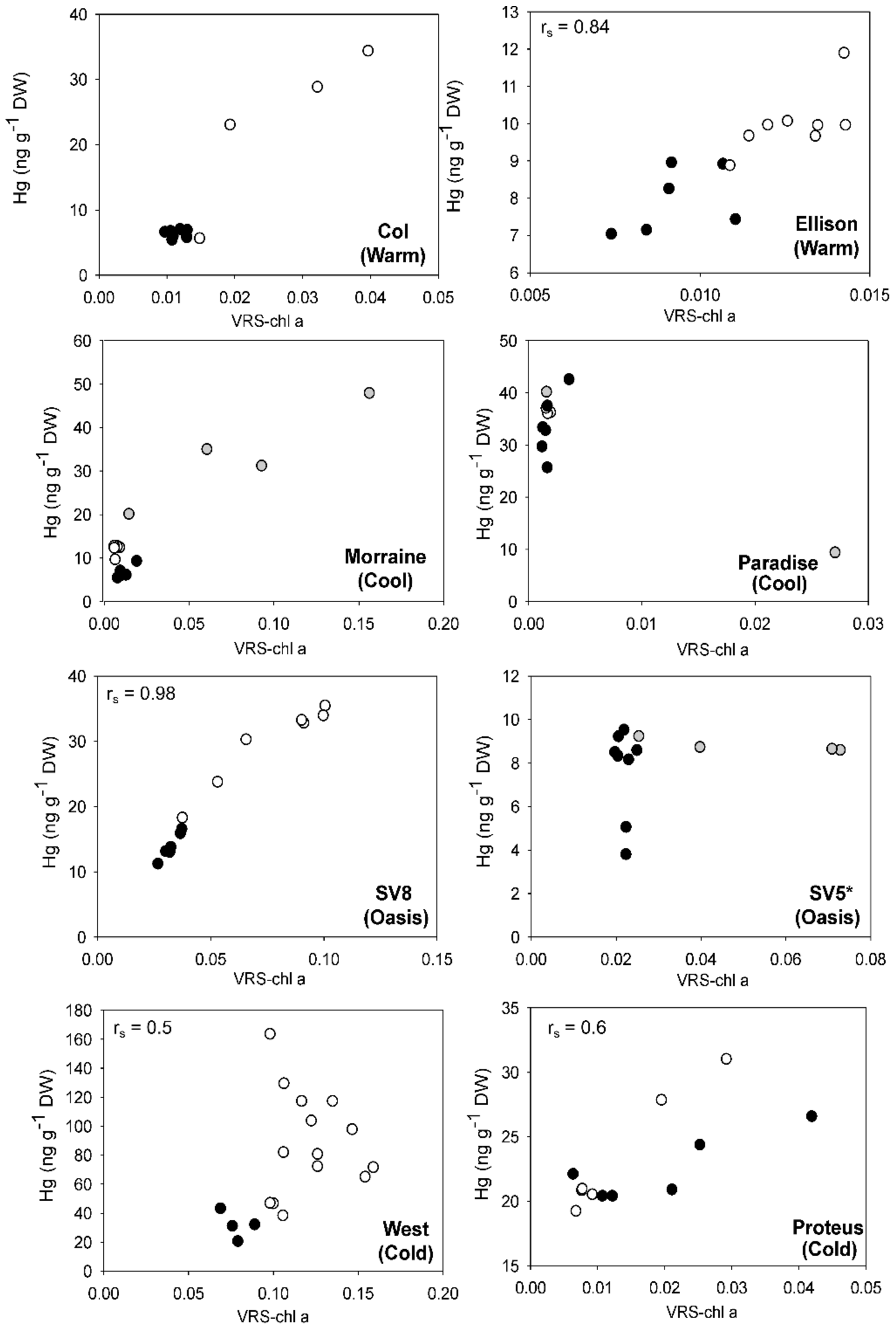


Figure 3 – Regression plots showing the relationship between sediment total mercury (ng g-1 dry weight) and visual reflectance spectrally (VRS) inferred chlorophyll *a* for each of our study lakes. Where significant ($p<0.05$), the Spearman correlation results (rs) are shown. Black circles represent sediment intervals deposited in the pre-industrial period. White circles represent sediment intervals deposited in the post-industrial period. Grey circles represent sediment intervals deposited after diatom-inferred shifts in lake ice cover regime (Griffiths et al. 2017), for lakes where diatom changes are offset from the onset of the post-industrial period. For SV5, grey circles represent the sediment intervals corresponding to diatom assemblage changes linked to recent climate warming, as no ^{210}Pb sediment core chronology is available to denote 1850.



~4-1 cm, from 12 to 48 ng g^{-1} dry weight, consistent with the timing of diatom assemblage shifts (Figure 2b). A decline in THg to 31 ng g^{-1} dry weight is observed for the uppermost two sediment intervals. Even accounting for the THg decline in the surface sediments, the enrichment factor is 5.6 (Table 3). The overall trend is still apparent when THg is corrected for %OC (Figure 2b). Total mercury is positively correlated with VRS-inferred chlorophyll *a* after ~1960, but this is not statistically significant over the entire sediment core (Figure 3). Similar to mercury concentrations, inferred chlorophyll *a* increases between a core depth of 3 cm to 1 cm, and decreases from 1 cm to the surface of the sediment core (Griffiths et al. 2017).

Paradise Pond exhibits a general increase in THg from the bottom of the core at 10 cm depth to 0.5 cm (increasing from ~26 to 47.8 ng g^{-1} dry weight), well before ~1850, which corresponds to a core depth of ~4 cm. A decrease in THg to 9.4 ng g^{-1} dry weight occurs in the surface interval, resulting in a final enrichment factor of 1.1 (Table 3). The overall trend remains consistent when corrected for sediment %OC (Figure 2b). There is no correlation between mercury and VRS-inferred chlorophyll *a* in Paradise Pond (Figure 3), and, in fact, chlorophyll *a* increased in the surface interval while mercury concentrations decreased (Griffiths et al. 2017).

Down-core mercury trends: "Oasis" sites

In SV8, an increase in mercury begins *circa* 1850, above a core depth of 7 cm (from ~16.5 to ~34 ng g^{-1} dry weight), and stabilizes at a core depth of 3 cm (~1960) (Figure 2c), for a final enrichment factor of 2.4 (Table 3). When corrected for OC, the increase begins at 8 cm, peaking at a core depth of 4 cm, and declining from 4 cm to the surface of the sediment core (Figure 2c). For SV5, the lake that could not be ^{210}Pb-dated, mercury concentrations are variable, and opposite trends were observed between sediment THg concentrations per dry weight and

THg corrected for %OC (Figure 2c). There is a significant, positive correlation between sediment mercury and VRS-inferred chlorophyll *a* in SV8, with both increasing after ~1870 (Figure 3). No relationship was observed in SV5 (Figure 3), as mercury remained relatively stable (Figure 2c) while inferred chlorophyll *a* showed recent increases (Griffiths et al. 2017).

Down-core mercury trends: "Cold" sites

In West Lake, a steady increase in mercury concentrations is observed, increasing from 31 ng g^{-1} dry weight at a core depth of 15 cm (~1850) to 164 ng g^{-1} dry weight at the surface of the sediment core (Figure 2d), an enrichment factor of 4.4 (Table 3). There are minimal changes in %OC in the sediment core, and correspondingly, correcting mercury concentrations for organic carbon does not change the down core trends (Figure 2d). VRS-inferred chlorophyll *a* was variable, with no directional increase observed (Griffiths et al. 2017), although there is still a statistically significant correlation between VRS-chlorophyll *a* and total mercury (Figure 3). In Proteus Lake, a slight post-industrial enrichment of total mercury concentrations is observed (Figure 2d; enrichment factor 1.3, Table 3), but an increasing trend above core depth 1 cm is more readily apparent when corrected for organic carbon, corresponding to ~1990, and consistent with both subtle changes in diatom assemblages inferred as a recent response to climate warming, and recent increases in VRS-inferred chlorophyll *a* (Figure 2d). Mercury concentrations in Proteus Lake are significantly, positively correlated to VRS-inferred chlorophyll *a* (Figure 3).

Discussion

Due to significant temporal overlap, it is challenging to disentangle the influence of climate change processes on mercury deposition to Arctic lake sediments from the signal arising from long-range transport of anthropogenic mercury emissions. Previous studies (Cooke et al. 2012, Outridge et al. 2017) have addressed this challenge by examining sedimentary mercury trends in lake sediment cores spanning the entire Holocene, in order to document trends in sediment mercury deposition during previous warm periods (for example, the Holocene Thermal Maximum) that occurred prior to anthropogenic mercury emissions. Our approach is to examine the recent (last several hundred years) sediment history in a series of Arctic lakes that span a gradient in microclimates, centered on Cape Herschel in the Canadian High Arctic. We tested two *a priori* hypotheses, based on the assumption that climate warming-induced changes in algal production and organic carbon cycling in High Arctic lakes can enhance mercury deposition to lake sediments:

1. *"Warm" lakes, simultaneously experiencing a coupled history of increased atmospheric mercury deposition and enhanced primary production due to climate change will exhibit a greater magnitude of mercury enrichment in recent sediments compared to "Cold" sites that have been affected minimally by recent climate change.* (Not Supported)

At least one lake in each of our four climate categories archived a clear record of a post-industrial, long-term increase in sediment mercury concentrations (Warm: Col Pond; Cool: Moraine Pond; Oasis: SV8; Cold: West Lake) consistent with previous observations from high latitude lake sediments (Muir et al. 2009). Enrichment factors were comparable among all 4 categories, inconsistent with our hypothesis that lakes dually experiencing anthropogenic mercury loading and increased primary production would show a greater magnitude of post-industrial mercury enrichment. When normalized to sediment organic carbon, to account for the export of mercury from the catchment associated with organic matter, the enrichment trend was no longer evident in Col Pond (Warm), and a recent, declining trend was observed for SV8 (Oasis). We also document strong, significant correlations between sediment mercury concentrations (uncorrected for organic carbon) and VRS-chl *a* in SV8 (Oasis), and Elison Lake (Warm), and for Col Pond when only the post-industrial period is considered. This suggests that mercury deposition in these lakes is strongly influenced by organic carbon dynamics related to the export of organic carbon from the catchment and/or internal primary production. In contrast, normalizing for organic carbon in Moraine Pond and West Lake did not alter down-core mercury trends.

West Lake (Cold) typically maintains 90-100% ice cover, even at the height of summer, with summer melt limited to a narrow moat along the shoreline, and has not experienced increases in primary production or any substantial changes in diatom assemblages, consistent with its ice cover conditions (Griffiths et al. 2017). According to the algal scavenging hypothesis, substantial post-industrial enrichment of mercury in the sediments should be limited to regions where lakes have also experienced simultaneous increases in primary production (Outridge et al. 2007), and yet the West Lake sediment core shows a clear post-industrial increase in mercury, with an enrichment factor of 4.4. Although we are unable to calculate mercury flux rates, the exponential decay of ^{210}Pb in the West Lake core indicates a relatively continuous (if low) sedimentation rate. There is a significant, but weak correlation between total mercury and VRS-chl *a* (Fig. 3), but while there is a sustained increase in mercury towards the surface of the sediment core (Fig. 2), there is no corresponding directional increase in VRS-chl *a* (Griffiths et al. 2017). West Lake provides a useful control site, and demonstrates that substantial post-industrial mercury enrichment can occur in the absence of increased organic carbon sources as a confounding factor. This is consistent with a Holocene sediment mercury record collected from Lake CF3 on Baffin Island, where increases in mercury concentration and flux in the post-industrial period also occurred in the absence of any increase in inferred primary production (Cooke et al. 2012).

2. *"Cool" sites will exhibit a two-stage pattern of mercury enrichment: (1) An increase in sediment mercury concentrations following the industrial revolution (~1850), and (2) a later intensification of mercury enrichment consistent with diatom-inferred limnological responses to climate warming.* (Partially Supported).

Consistent with our original hypothesis, Moraine Pond, a "Cool" site, exhibited a two-stage pattern of mercury enrichment, with post-industrial enrichment followed by a later intensification of mercury enrichment at the time of diatom-inferred limnological response to climate warming. This pattern, however, was not observed in our second "cool" site, Paradise Pond, which showed recent declines in sedimentary mercury. In Moraine Pond, there is a positive association between mercury and VRS-chl *a* only for the post-1960 period corresponding to diatom assemblage changes indicative of a longer ice-free period, consistent with the algal scavenging hypothesis (Outridge et al. 2007; Stern et al. 2009). We also document strong, significant correlations between mercury and VRS-chl *a* in SV8 (Oasis), and Elison Lake (Warm), and for Col Pond when only the post-industrial period is considered. However, increases in inferred primary production in Col Pond began at the same time as the onset of anthropogenic mercury emissions, creating challenges for disentangling their relative effects. Moraine Pond, in contrast, responded later to climate warming, reducing temporal overlap between climate effects and anthropogenic mercury emissions, and clearly shows an intensification of mercury enrichment when diatom assemblages indicate limnological responses to climate warming.

The Moraine Pond sediment core supports a potential effect of algal scavenging on sedimentary mercury, though our study also supports the findings of Kirk et al. (2011), that an algal scavenging effect is less widespread than has been previously suggested (Outridge et al. 2007), and the correlation may be spurious. Increases in VRS-inferred algal production were also observed in SV5 (Griffiths et al. 2017), with no corresponding mercury increases. In Paradise Pond, there was an increase in VRS-chl *a* in the surface sediment interval (Griffiths et al. 2017), which corresponds to a decrease in mercury concentrations expressed as both dry weight and normalized for organic carbon (Fig. 2). The identification and down-core sedimentary mercury analysis of additional lakes that responded later (~1950) to climate warming, similar to Moraine Pond and Paradise Pond, would be an interesting avenue for further research to determine whether Moraine Pond is indicative of a wider trend, or an isolated case.

Conclusions

Our results suggest that climate warming has the potential to enhance mercury sequestration to lake sediments in certain cases (as observed in Moraine Pond), but is not a necessary precondition for substantial post-industrial mercury enrichment (as observed in West Lake). Arctic lake sediment cores are not passive recorders of atmospheric mercury deposition, but instead reflect the interacting effects of mercury delivery to lakes, and the influence of limnological processes such as primary production and ice cover dynamics on mercury biogeochemical cycling. Studies such as ours, which provide insights into the role of climate history on temporal mercury and organic carbon sedimentary profiles, will help improve our interpretations of historic atmospheric mercury deposition in the Arctic based on lake sediment core trends.

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