The ratio of methylmercury to dissolved organic carbon in water explains methylmercury bioaccumulation across a latitudinal gradient from north-temperate to Arctic lakes

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Author contributions

JC, MR, GM and MA designed the study. All authors contributed to data generation. Data were analyzed by JC and MR. JC prepared the manuscript and all authors edited the manuscript.

Notes

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ABSTRACT

We investigated monomethylmercury (MMHg) bioaccumulation in lakes across a 30° latitudinal gradient in eastern Canada to test the hypothesis that climate-related environmental conditions affect the sensitivity of Arctic lakes to atmospheric mercury contamination. Aquatic invertebrates (chironomid larvae, zooplankton) provided indicators of MMHg bioaccumulation near the base of benthic and planktonic food chains. In step with published data showing latitudinal declines in atmospheric mercury deposition in Canada, we observed lower total mercury concentrations in water and sediment of higher latitude lakes. Despite latitudinal declines of inorganic mercury exposure, MMHg bioaccumulation in aquatic invertebrates did not concomitantly decline. Arctic lakes with greater MMHg in aquatic invertebrates either had: (1) higher water MMHg concentrations (reflecting ecosystem MMHg production) or (2) low water concentrations of MMHg, DOC, chlorophyll and total nitrogen (reflecting lake sensitivity). The MMHg:DOC ratio of surface water was a strong predictor of lake sensitivity to mercury contamination. Bioaccumulation factors for biofilms and seston in Arctic lakes showed more efficient uptake of MMHg in low DOC systems. Environmental conditions associated with low biological production in Arctic lakes and their watersheds increased the sensitivity of lakes to MMHg.

INTRODUCTION

Lakes in the Canadian Arctic are exposed to inorganic mercury deposition through long-range atmospheric transport from emission sources in North America, Europe and East Asia.[1] Atmospheric deposition rates of mercury decline with latitude in Canada, in part due to greater distance from emission sources and lower annual precipitation.[2, 3] Paradoxically, levels of mercury accumulating in northern fish species such as Arctic char (*Salvelinus alpinus*) do not concomitantly decline with latitude in the Arctic[4, 5], and elevated mercury (above 0.5 µg/g wet weight) has been observed in fish muscle from remote Arctic regions.[6] Together, these observations suggest that Arctic lakes may be more sensitive to mercury loadings, and there is broad interest from governments and the scientific community to better elucidate the controls on mercury bioaccumulation in fish and wildlife that are traditional foods for northern peoples.[7, 8]

Environmental conditions that are characteristic of northern latitude lakes could increase the sensitivity of those freshwater ecosystems to mercury bioaccumulation. Lake sensitivity, as defined by Munthe et al.[9], is "the ability of an ecosystem to transform inorganic mercury load to methylmercury in biota". On a broad scale, temperature and precipitation decline with latitude in Canada, and those key climate drivers control biological production of lakes and their watersheds[10]. In this study, we hypothesized that Arctic lakes may be more sensitive to mercury bioaccumulation as a result of distinct features of those systems, specifically colder temperatures, lower aquatic primary production, and low terrestrial inputs of organic matter.

Monomethylmercury (MMHg) is the dominant bioaccumulative form of mercury, and climate-related variation in lake ecosystem characteristics could affect how it accumulates in

food chains. Organic matter strongly binds mercury and affects its availability for transfer across bacterial or algal cell membranes, referred to as bioavailability.[11] Low amounts of organic carbon in Arctic lakes may result in greater MMHg bioavailability to food chains through a greater portion of the inorganic mercury pool being bioavailable for microbial methylation[12] or a greater portion of water MMHg being bioavailable for uptake by algae and bacteria.[13-15] Separately, high algal biomass in water and on biofilms of temperate lakes will reduce mercury bioaccumulation in aquatic food chains because the cellular uptake of water MMHg is partitioned among more cells, a process referred to as biodilution.[16-18] Biodilution may not occur in Arctic lakes where little algal biomass is present, resulting in greater MMHg concentration per unit biomass at the base of the food chain. Although these environmental controls on MMHg bioaccumulation have been demonstrated for temperate systems, much less is known about their applicability in Arctic environments.

This paper presents a study of MMHg bioaccumulation in lakes from four study regions spanning 30° latitude in eastern Canada. We collected aquatic invertebrates from planktonic and benthic environments, specifically zooplankton and chironomid larvae (Insecta: Diptera), as indicators of MMHg accumulation near the base of the food chain. These invertebrate prey are effective indicators of MMHg accumulation in fish because fish are exposed to mercury primarily through their diet.[19] Chironomids are a major food source for non-anadromous Arctic char in high-latitude lakes.[20] We also examined bulk organic matter of seston and rock biofilms to estimate the efficiency of MMHg uptake from water. The main objectives of this research were to 1) characterize MMHg bioaccumulation in distinct ecosystem types (north temperate, sub-Arctic taiga, Arctic tundra, polar desert) found within the study's latitudinal gradient; and 2)

to investigate the importance of mercury exposure (water and sediment concentrations) and other potential environmental controls on lake sensitivity to MMHg bioaccumulation.

MATERIALS AND METHODS

Study Sites. Field programs were conducted between 2011 and 2014 in four study areas that span a 30° latitudinal gradient in eastern Canada (Figure 1). Base map imagery for Figure 1 was obtained from ESRI.[21] The north-temperate study area, Gatineau Park (46°N), is located in mixed deciduous and conifer forest, just north of Ottawa, Ontario. A sub-Arctic taiga landscape was investigated at Kuujjuaraapik-Whapmagoustui in northern Quebec (55°N), located approximately 200 km south of the treeline boundary. Arctic tundra and polar desert landscapes were investigated in Nunavut at Iqaluit (64°N) and Resolute Bay (75°N), respectively. These study areas cover a large climate gradient, with declining mean daily air temperature (21° to 5°C in July) and mean annual precipitation (940 mm to 160 mm) from the most southern to northern areas.

Field Sample Collection. A total of 35 lakes were investigated for MMHg bioaccumulation (see Supplementary Table S1 for locations and morphometry of lakes). Within each of the four study areas, 8 to 10 lakes were selected to encompass a range in lake surface area and depth, and thereby account for local physiographic influences on methylmercury exposure. The lakes were relatively small in size (range of surface area = 0.01–7.06 km^2) and shallow (range of lake-mean depth = 0.5–13.7 m). Lake morphometry was measured in a boat using GPS-linked sonar, and watershed areas were computed using available digital elevation models and standard terrain analysis methods. Water chemistry and biological sampling was conducted on one occasion in July at each lake in the three Arctic study areas. For Gatineau Park lakes, water chemistry was measured in spring and late summer over a two year period (3 or 4 sampling dates in 2011-12), while biological sampling was conducted on one occasion in the fall of 2011 or 2012.

At each lake, *in situ* water temperature, specific conductivity, pH, and dissolved oxygen were measured with a YSI multi-parameter sonde (YSI Inc., Yellow Springs, Ohio, USA). Water was sampled in duplicate from each lake for mercury, dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP) (for Arctic lakes only) and chlorophyll *a* (Chl). In the Arctic study areas, lakes were not thermally stratified or only weakly stratified, and water was collected as sub-surface grabs in Nalgene® PETG bottles for mercury analysis and in HDPE bottles for other water chemistry. In thermally stratified lakes at Gatineau Park, both surface water and deep hypolimnetic water (1 m above the sediment) were sampled for water chemistry by peristaltic pump and acid-washed teflon tubing or by acid-washed teflon Kemmerer bottle. Details of water sampling, including clean protocols for trace metals, are provided in the supplemental information.

Zooplankton and chironomid larvae were collected in each lake as representative invertebrates of pelagic and benthic environments, respectively. These freshwater invertebrates are ubiquitous, and within the Arctic, chironomids are the dominant benthic invertebrate in lakes.[22] Two or three zooplankton samples per water body were collected with a large diameter 200 µm mesh net by vertical or horizontal tows, depending on lake depth and ice conditions. Chironomid larvae were collected mainly from deeper, offshore sediments with an Ekman grab, although shoreline areas were occasionally sampled with a kicknet to increase yield. Typically, 3 replicate chironomid samples were collected per lake (range of 1–8). Prior to passing Ekman sediment grabs through a 500 µm sieve, the top 1–2 cm of surface sediment was collected for chemical analysis. On the same day of collection, chironomid larvae were removed from sediment material with tweezers, washed in ultrapure water, and frozen.

Planktonic and benthic sources of basal organic matter were collected in the three Arctic study areas. Rock biofilms were sampled by scraping surface material from shoreline rocks with a nylon bristle brush. Three replicates (each composed of 5–10 rock scrapings) were collected per lake. Duplicate (or sometimes triplicate) seston samples were collected from nearshore water of lakes by passing 0.6–4 L of surface water (< 0.5 m depth) through a pre-weighed ashed GFF glass fibre filter (0.7 µm pore size). Large particles were removed by pre-filtration at 53 µm with an in-line system. Seston filtration was conducted either directly in the field with a peristaltic pump and acid-washed teflon line or in the lab on the same day of water collection using an acid-washed filtration tower.

Laboratory Analyses. Water was analyzed for mercury by cold vapor atomic fluorescence spectrometry (CVAFS) with a Tekran 2600 (total mercury [THg], n = 268) or Tekran 2700 (MMHg, n = 266) (Tekran® Instruments Corporation, Toronto, Canada). Water for MMHg analysis was distilled prior to derivatization by aqueous ethylation. Details of analytical methods for water mercury are in the supplementary information. Water Chl was measured by spectrophotometer after ethanol extraction, with the exception of Gatineau Park lakes where *in situ* Chl was measured with a YSI fluorescence probe, validated with Chl analyses by ethanol extraction of filtered seston for a subset of six lakes (Supplemental Figure S1). Water DOC was measured with a Pt-catalyzed Shimadzu TOC 5000 analyzer. Total nitrogen in water was determined as nitrate after potassium persulfate alkaline digestion, and total phosphorus was determined by spectrophotometer using the molybdenum blue method.

Freeze-dried and homogenized samples of chironomid larvae (n = 84) and biofilm organic matter (n = 70) from Arctic lakes were analyzed for MMHg by pretreatment with an alkaline

then acidic digestion, extraction in dichloromethane, isolation with sodium thiosulfate and detection by capillary gas chromatography coupled with atomic fluorescence spectrometry at the Laboratory for the Analysis of Natural and Commercial Environmental Toxins (LANCET, University of Ottawa, Ottawa, Canada). Concentrations of MMHg in chironomid larvae from Gatineau Park (n = 38) and all seston (n = 48) and zooplankton (n = 55) samples were determined by acid digestion, derivatization by aqueous ethylation, and detection by CVAFS at the Laboratoire de biogéochimie environnementale (Université de Montréal, Montreal, Canada). Method details are provided in the supplementary information.

The THg concentration of freeze-dried and homogenized surface sediment (n = 151) was measured with a Direct Mercury Analyzer (Milestone Inc, Shelton, Connecticut, USA). The nitrogen content of sediment (on a percent mass basis) was measured at the G.G. Hatch Stable Isotope Laboratory with a Vario EL III elemental analyzer. Organic matter content by loss on ignition (LOI) was measured on rock biofilms and a subset of sediment samples by combustion in a muffle oven at 550°C for 4 h. Because some sediment samples from Gatineau Park lakes were lost before LOI determinations could be completed, %N was used as a surrogate measure of organic matter in sediment. For a subset of sediment samples, percent organic matter content by LOI was strongly correlated with sediment %N across study regions (Pearson $r = 0.91$, $p<0.001$, $n=102$).

Quality assurance and quality control information for mercury analyses (ie. recoveries of certified reference materials, duplicate repeatability, method detection limits) are provided in the supplementary information. All chemical concentrations in biological samples and sediment are presented on a dry weight basis. The MMHg concentration in rock biofilm was normalized for

percent organic matter content (ng/g OM) by loss on ignition measurements due to variable amounts inorganic material. Seston MMHg concentration was normalized for the mass of particulate matter on the sample filter (ng MMHg/g of seston). Half the detection limit was used for MMHg results below detection for 16 seston samples (< 0.4 ng/g) and three unfiltered water samples (< 0.01 ng/L).

Data Analysis. Mercury concentrations in water, sediment and biota were compared with annual deposition fluxes of atmospheric mercury obtained from Muir et al.[2]. Those estimates were generated from simulations of the Global/Regional Atmospheric Heavy Metals model (GRAHM) for the year 2001 and corroborated with flux estimates from lake sediment cores collected in 50 lakes along a 40° latitude gradient.[2] We present the modelled mercury deposition flux in relation to latitude (Figure 1), which strongly explained geographic variation among sites within Canada (exponential decay model: $r^2 = 0.93$, $p < 0.001$, $n = 50$). We used the relationship with latitude to estimate atmospheric deposition fluxes to our study lakes, which were consistent with sediment core flux estimates available for two of the study areas (Resolute Bay, Kuujjuaraapik).[2]

Principal component analysis (PCA) was conducted with R statistical package (http://cran.r-project.org) using the vegan library to identify the main environmental gradients in the lake dataset. Fifteen variables were included to characterize: 1) water body morphometry and catchment characteristics (lake area, mean depth, water residence time [WRT], catchment area to lake area ratio [CA:LA], lake volume to catchment area ratio [LV:CA]), 2) water quality (surface water temperature, bottom temperature, DOC, TN, Chl, pH, specific conductivity), and 3) mercury levels in water (unfiltered surface THg and MMHg) and sediment (surface THg). Lake

194 WRT was estimated using lake volume, lake and catchment area, and the mean annual runoff
195 (mm/year) specific to each study region (see supplementary information for details). Filtered
196 water MMHg concentrations were not available for all lakes but filtered and unfiltered MMHg
197 concentrations were highly correlated (*Pearson r* = 0.98, $p < 0.001$) for a subset of 25 lakes.
198 PCA variables were log-transformed, centered and standardized. In the case of missing values
199 for sediment THg (1 lake), water Chl (2 lakes), and zooplankton MMHg (1 lake), the mean value
200 of all lakes in that study area was used for the PCA.

201 A non-parametric approach, Spearman correlation analysis, was used to assess the importance
202 of water quality variables on MMHg bioaccumulation in invertebrates due to non-linearity of
203 some relationships. Partial Spearman correlation coefficients were calculated in R using the
204 PPCOR library to control for the effect of water MMHg concentration.

205 Bioaccumulation factors (BAFs) were calculated to estimate the efficiency of uptake of water
206 MMHg in planktonic and benthic organic matter from Arctic lakes. No data were available for
207 basal organic matter components from the Gatineau Park study area. The BAFs were determined
208 as the logarithm of seston or biofilm MMHg concentration (ng/kg) divided by dissolved MMHg
209 concentration in surface water (ng/kg), following conversion of the water concentration from a
210 volume basis (ng/L) to a weight basis (ng/kg). Correlation analysis was conducted between
211 BAFs in basal organic matter and water DOC, TN, and Chl concentrations to test the hypothesis
212 that water quality conditions affected the efficiency of MMHg uptake at the base of the food
213 chain.

RESULTS AND DISCUSSION

Latitudinal Trends. Model estimates of atmospheric mercury deposition (from Muir et al.[2]) indicate that recent annual fluxes decline approximately five-fold between the most southern study area, Gatineau Park (46°N), and the most northern area, Resolute Bay (75°N) (Figure 1). Lower mercury deposition at higher latitudes is related to less annual precipitation and greater distance from major anthropogenic emission sources.[3] In step with the deposition pattern, we observed significant latitudinal declines of THg concentration in both water (*Spearman rho* = -0.43, $p = 0.011$, $n = 35$) and sediment (*Spearman rho* = -0.86, $p < 0.001$, $n = 34$) (Figure 1). Surface sediment THg was correlated with %N (a surrogate of organic matter content) and lake depth (Supplemental Figure S2). After controlling for those two factors, a latitudinal decline in sediment THg concentration was still evident (Supplemental Figure S3). Water MMHg concentration also declined with latitude (*Spearman rho* = -0.73, $p < 0.001$, n =35; Figure 1), and low levels (< 0.05 ng MMHg/L) were found in tundra and polar desert lakes. For north-temperate lakes in Gatineau Park, water THg and MMHg were affected by thermal stratification, with low concentrations found in the epilimnion (surface water) and, on average, 2-fold and 12-fold higher values of THg and MMHg, respectively, in the hypolimnion (1 m above sediment, depth range of 7–21 m among lakes; Supplemental Figure S4). Thermal stratification and higher water column sedimentation rates may explain the somewhat lower concentrations of water THg in the Gatineau Park study region (Figure 1). When only considering surface waters, MMHg concentrations were highest at sub-Arctic Kuujjuaraapik (Supplemental Table S3).

Despite the latitudinal decline in inorganic mercury exposure in our study lakes, methylmercury bioaccumulation in aquatic invertebrates did not concomitantly decline (Figure

2). The highest concentrations of MMHg in both zooplankton and chironomids were observed in sub-Arctic and polar desert lakes even though the latter study area was estimated to receive the lowest atmospheric mercury deposition and had the lowest THg in water and sediment. Mean MMHg concentrations of chironomids (69 ng/g) and zooplankton (65 ng/g) from polar desert lakes were higher than mean or median MMHg levels (< 50 ng/g) in zooplankton and primary consumer invertebrates reported in the literature for north-temperate lakes.[23, 24] These observations contrast with earlier reports of strong positive correlations between wet atmospheric deposition of inorganic mercury and MMHg bioaccumulation in aquatic invertebrates[25] and fish[26] from a broad-scale sampling of water bodies in the United States. We do not view these results as contradicting the importance of atmospheric deposition, given the well-established experimental relationship between inorganic mercury loading and methylmercury bioaccumulation in lakes.[27, 28] Rather the findings suggest there are unique environmental characteristics in high latitude lakes that enhance MMHg bioaccumulation in spite of low inorganic mercury loads.

Environmental Gradients among the Study Lakes. The study lakes varied in size as indicated in the PCA by the clustering of lake area, mean depth, WRT, and LV:CA (Figure 3). A range of lake sizes were sampled within each study area, although sites from Kuujjuaraapik and Resolute Bay tended to be smaller. There were lower values of water Chl, surface water temperature, water DOC, and sediment THg (and to a lesser extent water TN and bottom temperature) in the tundra and polar desert lakes, and higher values in temperate and sub-Arctic lakes (Figure 3, Table S3). These variables reflect a latitudinal decline in the presence of organic matter (DOC range: 0.8–7.6 mg/L; Chl range: 0.1–3.0 µg/L) and temperature conditions (range

for surface water: 2–22°C) within the dataset. Water TP data were only available for Arctic lakes but concentrations were consistently low (*median* = 4.7 µg/L, *range* = 1.2–9.6 µg/L, *n* = 25 lakes, Table S3) and did not differ significantly among Arctic study regions (one way ANOVA, $p = 0.15$, $n = 24$ lakes). Water pH and specific conductivity (correlated with the CA:LA ratio) also varied among lakes (Figure 3), although the waters had circumneutral or alkaline pH (among-lake *mean* pH = 7.5, *range* = 6.6–8.3).

Water Quality Controls on Invertebrate MMHg. We tested the influence of water quality variables on MMHg concentrations in aquatic invertebrates across the latitudinal gradient. Surface water MMHg concentration best explained MMHg levels in both groups of aquatic invertebrates (Table 1). These correlations reflect the importance of water MMHg exposure for food chain bioaccumulation.[27, 28] After controlling for the effect of surface water MMHg using partial correlation analysis, three water quality variables—DOC, TN, and Chl—showed significant negative correlations with invertebrate MMHg concentrations (Table 1). Thus, greater bioaccumulation was also associated with Arctic lakes that had lower water concentrations of DOC, Chl and TN. Water temperature, specific conductivity and pH were not significant explanatory variables of invertebrate MMHg concentrations (Table 1). We generated multiple regression models using surface water MMHg and each of the three water quality variables (DOC, TN, Chl) to identify the strongest explanatory variables for invertebrate MMHg concentrations (Supplemental Table S3). Surface water MMHg and DOC together best explained MMHg in both chironomids (*model* $r^2_{adj} = 0.55$, $p < 0.001$, $n = 35$) and zooplankton (*model* $r^2_{adj} = 0.45$, $p < 0.001$, $n = 34$). For zooplankton, the models including TN or Chl had similar though slightly lower explanatory power (r^2_{adj} of 0.41 and 0.39, respectively). This analysis indicates

that low DOC and oligotrophic conditions of Arctic lakes enhanced MMHg bioaccumulation near the base of benthic and planktonic food chains.

An important implication of these findings is that MMHg bioaccumulation in northern Canadian lakes reflects a balance between MMHg supply to the water column and lake sensitivity to uptake in the food chain. This balance can be empirically represented by the ratio of MMHg to DOC concentrations in surface waters (Figure 4). Across our latitudinal gradient, lakes with greater levels of MMHg in aquatic invertebrates either had high surface water MMHg concentrations (greater ecosystem production of MMHg) or lower MMHg in water but also very low water DOC (greater lake sensitivity to MMHg exposure). We propose that this water quality variable (the MMHg:DOC ratio) may be useful to identify Arctic lakes that are more sensitive to MMHg bioaccumulation, and further research is warranted to investigate its broader applicability. For example, we tested the MMHg:DOC ratio on a previously published dataset of chironomid larvae from 20 lakes in the Canadian high Arctic[29] and found a strong positive correlation between chironomid MMHg concentration and the MMHg:DOC ratio in surface waters (r^2_{adj} = 0.52, $p < 0.001$, n = 20; Supplemental Figure S5).

Bioaccumulation Factors for MMHg in Benthic and Planktonic Organic Matter. Concentrations of MMHg in basal organic matter varied among our Arctic study lakes from 2–12 ng/gOM in rock biofilms (*mean ± 1 standard deviation* = 5 ± 2 ng/gOM, n = 24 lakes) and <0.4–30 ng/g in seston (*mean ± 1 standard deviation* = 4 ± 7 ng/g, n = 22 lakes). The Arctic biofilm MMHg concentrations were lower than values reported for boreal lakes in eastern Canada (47–50°N), which averaged 11 ng/g (*range* = 3–55 ng/g).[30] Similarly, our estimates of MMHg in Arctic seston were lower than values reported for sites in the Great Lakes Region

(which often exceeded > 10 ng/g).[31] There was no difference in mean biofilm MMHg concentrations among our three Arctic study areas (one-way ANOVA, $p = 0.51$, $n = 25$ lakes), while significantly higher seston MMHg concentrations were measured in polar desert lakes compared to tundra and sub-Arctic lakes (one-way ANOVA, $p < 0.001$, $n = 22$ lakes) (Supplemental Figure S6).

BAFs between dissolved water MMHg and basal organic matter sources suggested there was greater accumulation of MMHg in higher latitude lakes at Iqaluit and Resolute Bay. BAFs for MMHg in both seston and rock biofilms were negatively correlated with water quality variables, mainly DOC (Figure 5), but also Chl ($p < 0.002$) and TN ($p < 0.001$ for biofilms; $p>0.05$ for seston). Watras et al.[13] similarly measured higher partitioning of MMHg between water and seston in Wisconsin lakes that had lower DOC concentrations. Our observations for Arctic lakes indicate a more efficient uptake of MMHg from water to benthic and plankton organic matter in ultra-oligotrophic, low DOC systems, which could explain the greater lake sensitivity to MMHg bioaccumulation observed for aquatic invertebrates (Figure 2, 4).

Estimates of MMHg in basal organic matter should be interpreted with caution because these bulk samples contained a mix of organic matter types—namely algae, detritus, bacteria and protozoa—and their complex composition likely varied among lakes. Future research on Arctic seston quality and potential influences on MMHg accumulation seems warranted. Similarly, zooplankton and chironomids are selective feeders, and the MMHg estimates may not accurately reflect dietary exposure for those aquatic invertebrates. Additional measurements of seston MMHg in different size fractions and over the growing season may better characterize trophic transfer of MMHg to Arctic zooplankton. Few published measurements of MMHg in lake seston

exist, and our estimates are among the first for Arctic fresh waters. There were technical challenges in obtaining sufficient sample from some oligotrophic lakes, and seston MMHg concentrations were below analytical detection at several sites. Despite these limitations, we found consistent patterns for two independent measurements on organic matter (biofilms, seston), suggesting greater uptake of MMHg occurred at the base of benthic and planktonic food chains in unproductive, low-DOC lakes in the Canadian Arctic.

Potential Mechanisms Controlling Lake Sensitivity to MMHg. On a broad geographic scale, climate controls the biological production of lakes and their watersheds in northern Canada.[10] We found that latitudinal variation in water DOC, TN and Chl resulted in changes to lake sensitivity to mercury. Enhanced MMHg bioaccumulation in our study lakes may have resulted from greater bioavailability of dissolved MMHg in low DOC waters[13-15] or a lack of biodilution in waters with little algal biomass, a process that reduces MMHg exposure to invertebrate grazers in more productive temperate systems.[16, 32] Concentrations of DOC in some polar desert lakes are so low as to be insufficient to catalyze photochemical breakdown of MMHg[33], and lower turnover of water MMHg may have also played a role in enhancing MMHg bioaccumulation, if this loss process was insignificant. Likewise, phytoplankton production in polar desert lakes is extremely low due to poor nutrient availability and cold temperatures.[34] Given the strong collinearity between water DOC and algal biomass (estimated by Chl) among the study lakes, our models could not distinguish the contributions of each of those environmental drivers. Further, lakes were sampled on one occasion, and seasonal variation in water quality (particularly algal biomass) and MMHg bioaccumulation was not constrained. Future controlled experiments are recommended to test independent and interactive effects of

DOC and primary productivity for MMHg bioaccumulation since climate warming during the 21st century will stimulate both watershed loadings of DOC and algal growth in Arctic lakes.[35]

The bioaccumulation of MMHg was negatively correlated with water DOC across our latitudinal gradient, in contrast with results from Scandinavia[36] and north-temperate lakes of North America[13, 37, 38] where positive correlations between DOC and mercury levels in biota have been reported. In those regions, the positive association is related to mercury transport from watersheds to lakes that is facilitated by downstream flow of mercury-bound DOC[11], resulting in more aqueous inorganic and methyl mercury in higher DOC lakes.[36, 39] In Arctic lakes with snow-dominated hydrology, mercury transport to lakes occurs largely via snowmelt runoff in spring when soils are still frozen.[40] DOC also affects mercury cycling through complexation processes that mediate cellular uptake of inorganic mercury or MMHg by bacteria[12] and algae[14]. The source of DOC (e.g., humic acids from terrestrial soils, *in situ* algal production) can also affect mercury bioavailability.[41] Our measurements of water DOC did not take into account the complexity of organic matter sources. The diversity of watershed vegetation, soil and permafrost conditions as well as variable contributions of autochthonous primary production likely resulted in DOC of different chemical composition among study lakes across the latitudinal gradient. Future research is recommended to examine the role of DOC source and composition in enhanced mercury bioaccumulation in the high Arctic.

The species composition of aquatic invertebrates differed among study areas, which may have influenced the observed MMHg bioaccumulation patterns. Zooplankton diversity declines with latitude in Canada,[42] and large-sized *Daphnia* (water flea) or anostracans (fairy shrimp) can be a significant component of Arctic zooplankton, particularly in small fishless lakes. Those taxa

bioaccumulate more MMHg than copepods[43], and their presence may have contributed to the trend of higher MMHg concentrations at more northern latitudes (Figure 2). In a temperate lake, Todorova et al.[44] similarly observed that shifts in species composition towards larger *Daphnia* species increased the MMHg concentrations of bulk zooplankton. Little information is available on taxonomic differences in MMHg bioaccumulation among chironomids although most in our samples were from one grouping (subfamily Chironominae).

Our Arctic study lakes were located in coastal areas, which receive enhanced deposition of inorganic mercury from spring atmospheric mercury depletion events (AMDEs)[45, 46] as well as MMHg deposition following atmospheric breakdown of volatile dimethylmercury of marine origin.[47-49] Considerable polar research has demonstrated that much of the inorganic mercury deposited onto snow during AMDEs quickly revolatilizes back to the atmosphere within a few days.[50, 51] We observed low THg concentrations in water and sediment from the Arctic lakes, including declining trends with latitude, suggesting that AMDEs were not a major source of inorganic mercury. Water MMHg concentrations in polar desert lakes at Resolute were low but slightly higher than in tundra lakes at Iqaluit relative to the amount of water THg present (mean %MMHg of 6% at Resolute vs 2% at Iqaluit). Given the slow rates of sediment mercury methylation in polar desert lakes[52] and their low sediment MMHg concentrations[29], a marine source of MMHg (via breakdown of evaded dimethlymercury) may have contributed to bioaccumulation in those food chains. Microbially-mediated production of MMHg also occurs in in sediments of Arctic lakes and is controlled by redox conditions, sulfate and DOC concentrations, and temperature.[53] Irrespective of unique mercury biogeochemical processes that

389 occur in Arctic coastal areas, water DOC, TN, and Chl were important environmental variables
390 explaining MMHg bioaccumulation.

391 **Implications for the Fate of Mercury Deposition in Arctic Lakes.** Our research
392 demonstrates that Arctic lakes with very low DOC, TN and algal biomass are more sensitive to
393 mercury contamination despite low levels of inorganic mercury loading. The Arctic Archipelago,
394 which covers 1.4 million km^2 of northern Canada, is largely polar desert, and there are numerous
395 unproductive lakes that are potentially sensitive. The MMHg:DOC ratio in surface waters may
396 be useful as a preliminary indicator of enhanced MMHg bioaccumulation across this vast
397 territory. Long-term climate warming in the Arctic will likely alter MMHg bioaccumulation in
398 lakes, and our findings indicate that reductions in food chain accumulation may occur in polar
399 desert lakes if there is increased production and transport of DOC or greater algal growth.
400 Indeed, long-term monitoring of landlocked Arctic char from polar desert lakes at Resolute Bay
401 indicates that their mercury concentrations have been declining over the last decade.[54] However,
402 mercury levels in fish have been recently increasing in other regions of the Canadian Arctic[55, 56],
403 potentially reflecting an increase in global mercury emissions, or climate-related changes in
404 watershed mercury transport (including from permafrost melt) and MMHg production.[57] Further
405 effort is needed to synthesize the various contributions of changing environmental processes on
406 MMHg accumulation in Arctic lake food chains. Over the last century, the anthropogenic
407 mercury flux to Canadian Arctic lakes has increased by an estimated 3.5 fold.[2] Our findings
408 emphasize the importance of continuing global efforts under the UNE Minamata Convention on
409 Mercury to reduce anthropogenic mercury emissions because of their significant impact on
410 sensitive ecosystems even at lower levels of atmospheric deposition.

411 ASSOCIATED CONTENT

412 **Supporting Information**

413 Locations and morphometry of the study lakes; details of water sampling methods; details of
414 methods and QA/QC for mercury analyses; latitudinal trends of sediment THg; comparison of
415 mercury in surface and bottom waters of Gatineau Park lakes; multiple regression models for
416 MMHg in aquatic invertebrates; chironomid MMHg in relation to water MMHg:DOC ratio for a
417 published dataset; MMHg in rock biofilms and seston from Arctic lakes.

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421 **Notes**

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434 for assistance in the laboratory.

435 **Table 1. Spearman rho coefficients for correlations between surface water chemistry and**
436 **MMHg concentrations in chironomids (*n* = 35) and zooplankton (*n* = 34). Partial Spearman**
437 **rho coefficients were also determined after controlling for the effect of water MMHg.**

	Spearman rho		Partial Spearman rho	
Explanatory Variable	Chironomid MMHg	Zooplankton MMHg	Chironomid MMHg	Zooplankton MMHg
Chl (µg/L)	-0.34*	0.07	-0.68***	-0.29
DOC (mg/L)	-0.37*	0.03	-0.77***	-0.40*
pH	0.18	-0.14	0.19	-0.15
Conductivity (µS/cm)	0.31	-0.05	0.26	-0.17
Temperature$^{\alpha}$ (°C)	0.12	-0.16	-0.22	-0.28
TN (µg/L)	0.01	0.11	-0.51***	-0.56***
Water MMHg (ng/L)	0.45**	0.61***	---	---

438 * $p < 0.05$, ** $p < 0.01$*** $p < 0.001$

439 $^{\alpha}$ Surface water temperature for zooplankton, bottom water temperature for chironomids

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617

Figure Headings

Figure 1. Latitudinal trends in modelled atmospheric mercury deposition (top panel; data from Muir et al.[2]) and lake-mean concentrations of water THg and MMHg and sediment THg in the four study regions. Box plot colours correspond to locations on the map. Water THg and MMHg concentrations are from the surface layer except for thermally-stratified Gatineau Park lakes where the mean of surface and bottom water concentrations for each lake are presented.

Figure 2. Lake-mean concentrations of MMHg in benthic chironomid larvae and zooplankton in the four study regions. Box plot colours correspond to locations on the map in Figure 1.

Figure 3. PCA correlation biplot showing dominant gradients in surface water chemistry and physical characteristics of lakes spanning 30° of latitude in eastern Canada. Lakes are identified by study region (Gatineau Park = yellow, Kuujjuaraapik = blue, Iqaluit = orange, Resolute Bay = green). See methods for abbreviations.

Figure 4. The MMHg:DOC ratio of surface water strongly explained the sensitivity of lakes to MMHg bioaccumulation in chironomid larvae (r^2_{adj} = 0.70, p < 0.001, n = 35) and zooplankton (r^2_{adj} = 0.38, p < 0.001, n = 34). Note the MMHg:DOC ratio in the right panel is log-transformed.

Figure 5. Relationship between water DOC and MMHg bioaccumulation factors (BAFs) for basal organic matter sources of sub-Arctic and Arctic lakes: rock biofilms (r^2_{adj} = 0.51, p < 0.001, n = 24) and seston (r^2_{adj} = 0.43, p < 0.001, n = 22). Note water DOC in the right panel is log-transformed.

Figure 1

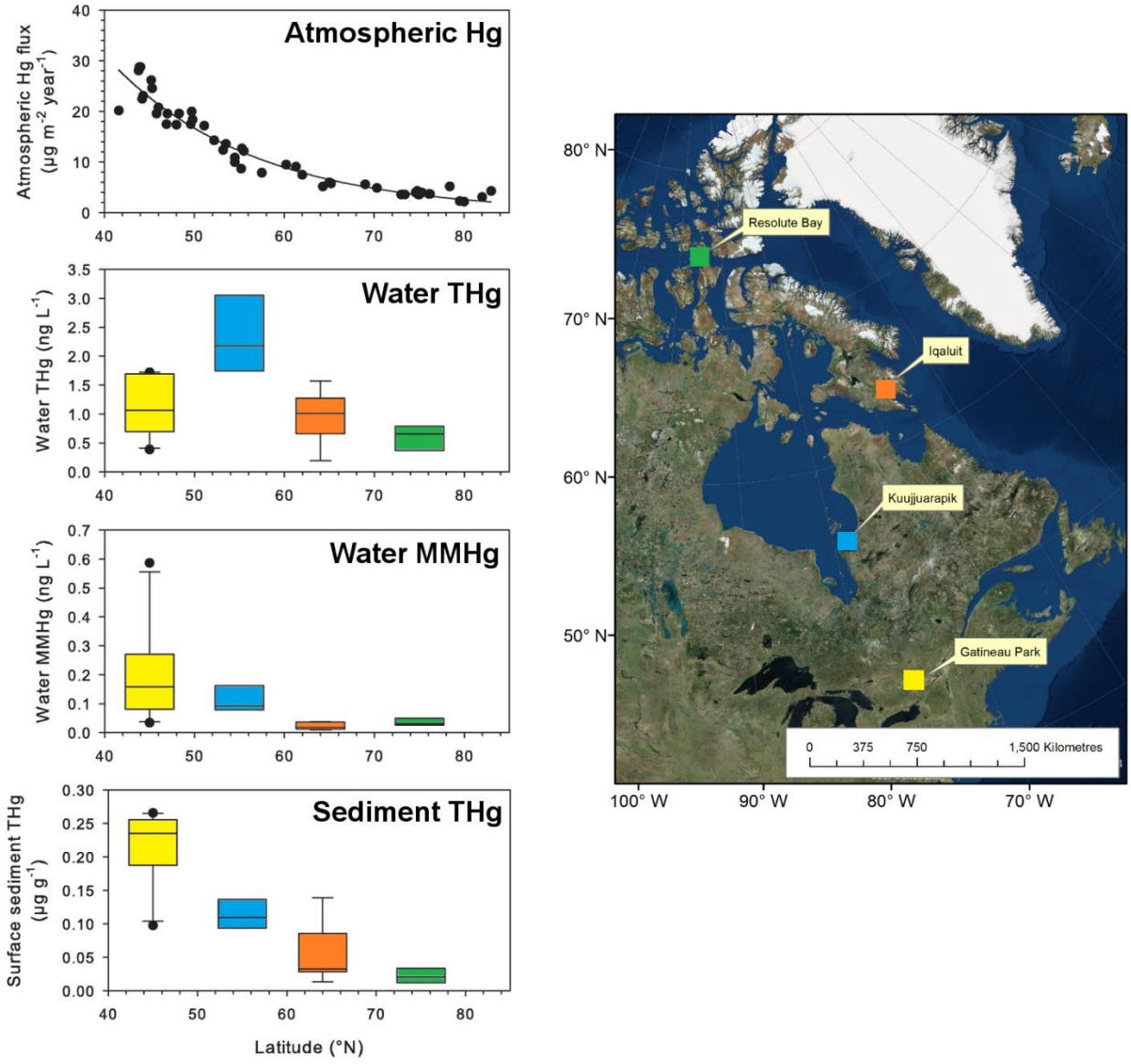


Figure 2

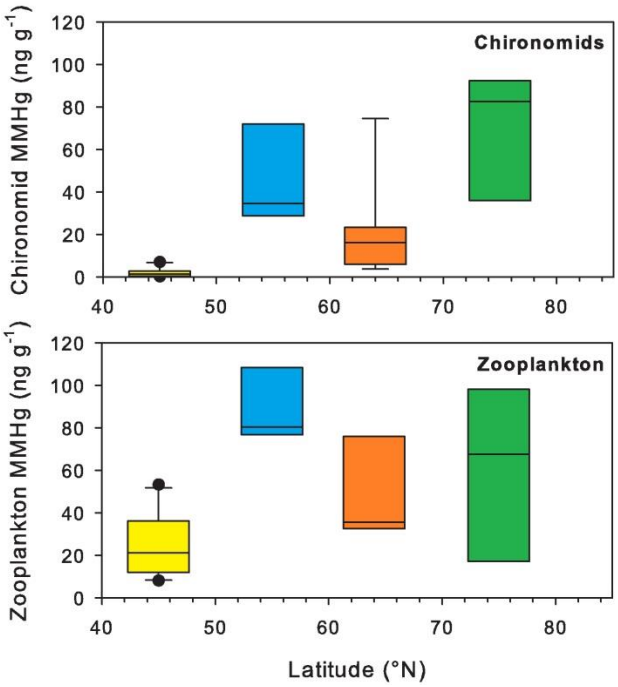
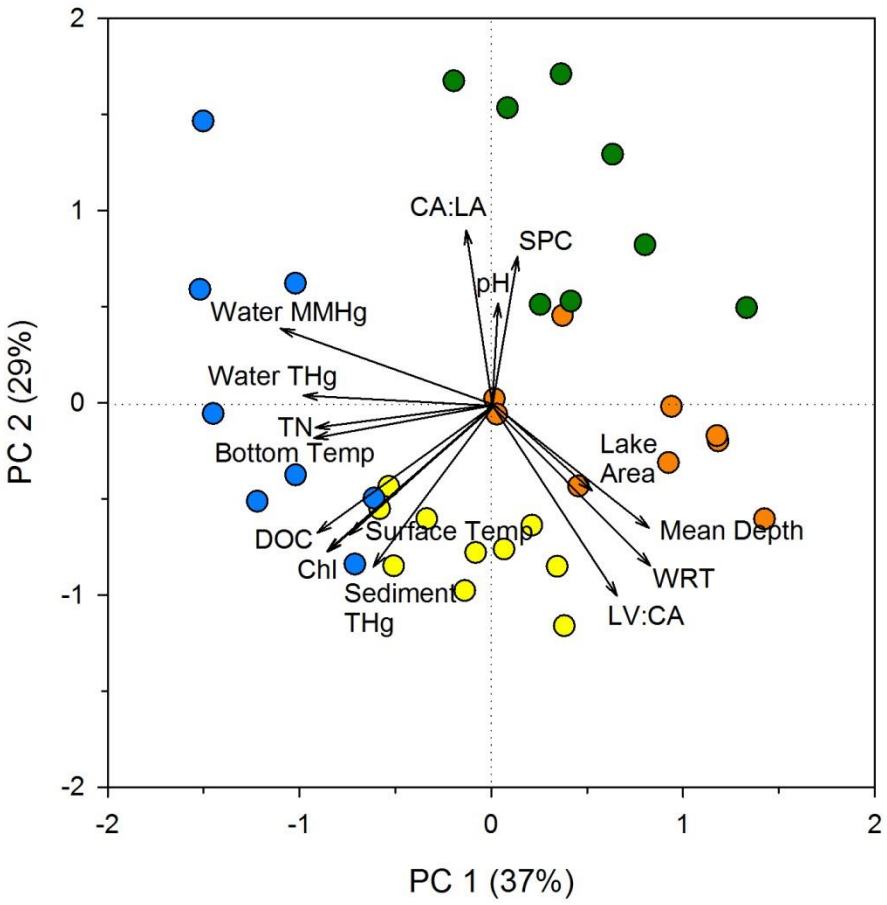


Figure 3



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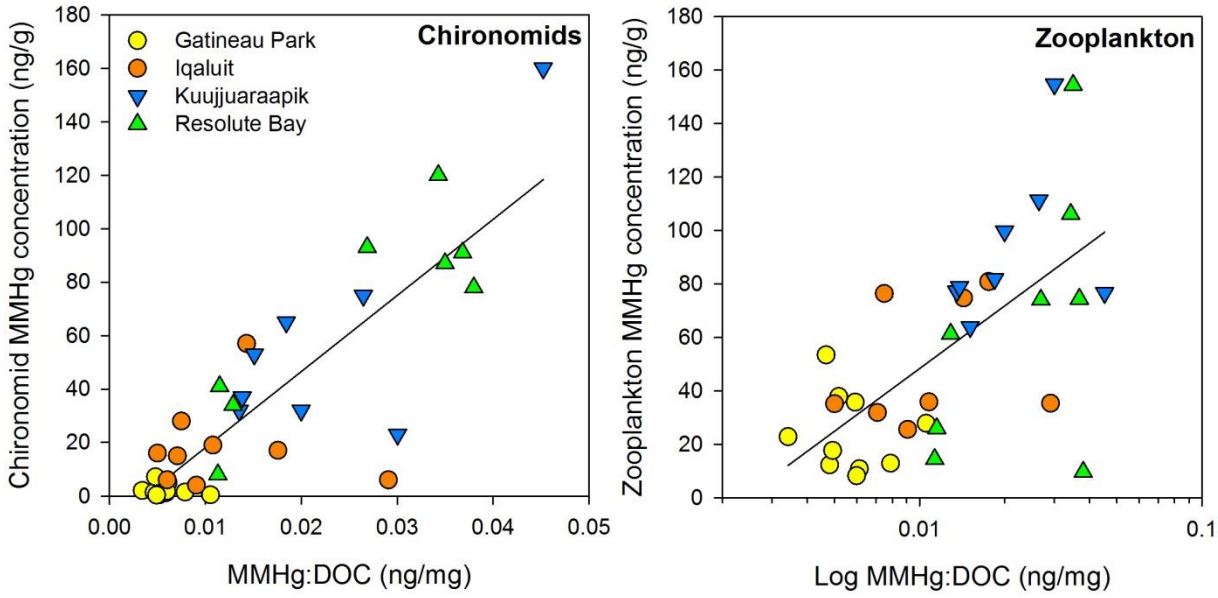
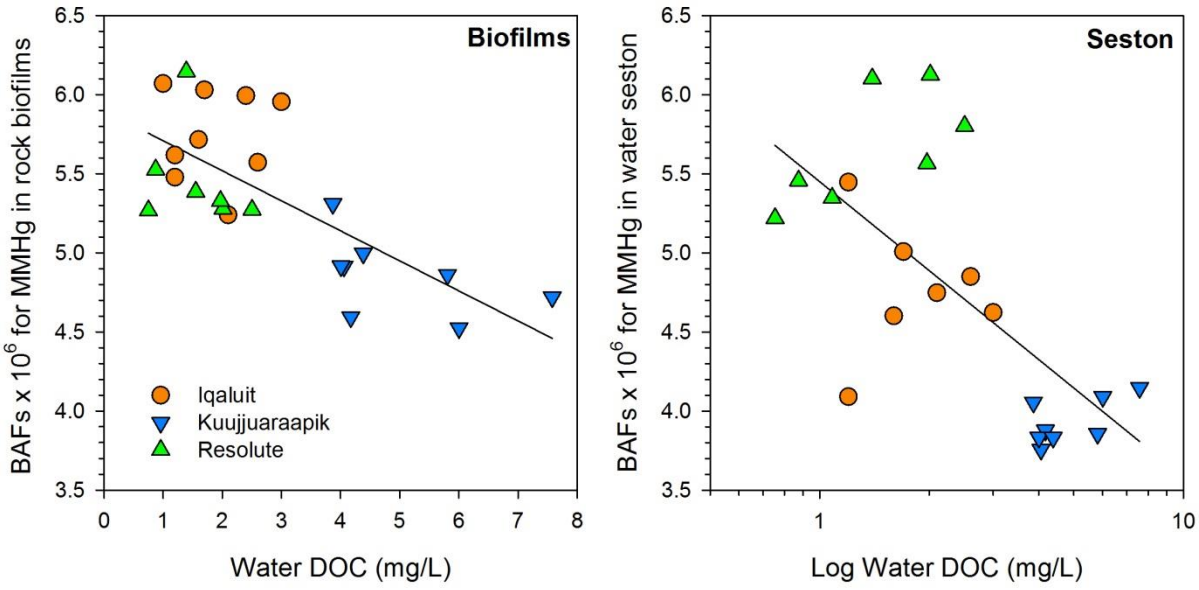


Figure 5



Supporting Information for:

The ratio of methylmercury to dissolved organic carbon in water explains methylmercury bioaccumulation across a latitudinal gradient from north-temperate to Arctic lakes

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Table S1. Location, sampling year, and size of the 35 study lakes.

Study Area	Lake	Year	Latitude	Longitude	Lake Area (km^2)	Catchment Area (km^2)	Mean Depth (m)
Gatineau Park (mixed forest)	Black	2011-12	45°29'30"	75°51'51"	0.02	0.10	5.8
	Brown	2011-12	45°36'33"	75°55'56"	0.27	6.24	2.9
	Clair	2011-12	45°35'46"	76°03'29"	0.11	0.5	13.7
	Kidder	2011-12	45°36'17"	76°05'19"	0.06	1.78	9.9
	La Pêche	2011-12	45°37'23"	76°11'07"	7.06	49.4	5.7
	Meech	2011-12	45°32'07"	75°53'24"	2.89	60.2	13.3
	Phillipe	2011-12	45°36'15"	76°00'05"	1.75	18.1	9.1
	Pink	2011-12	45°28'05"	75°48'28"	0.11	0.92	11.7
	Ramsay	2011-12	45°35'54"	76°05'58"	0.11	2.71	7.1
	Taylor	2011-12	45°36'17"	76°03'04"	0.30	3.82	8
Kuujjuaraapik-Whapmagoustui (sub-Arctic taiga)	Site 1	2012	55°19'11"	77°42'41"	0.08	2.70	0.7
	Site 2	2012	55°22'10"	77°37'04"	0.11	3.35	1.0
	Site 3	2012	55°18'16"	77°42'56"	0.01	0.62	0.3
	Kachishayoot	2012	55°20'03"	77°37'31"	0.29	1.78	1.9
	Site 5	2012	55°17'26"	77°43'08"	0.05	1.00	1.3
	Site 6	2012	55°19'12"	77°38'32"	0.08	0.39	0.6
	Site 7	2012	55°20'01"	77°35'48"	0.39	2.31	0.9
	Site 8	2012	55°20'14"	77°36'42"	0.10	0.19	1.2
Iqaluit (tundra)	Site 1	2013	63°47'49"	68°32'46"	0.03	0.21	1.8
	Site 2	2013	63°45'29"	68°26'38"	0.08	2.00	6
	Site 3	2013	63°39'07"	68°17'49"	0.28	4.03	12
	Site 4	2013	63°47'53"	68°32'17"	0.09	0.37	5
	Site 5	2013	63°44'56"	68°23'53"	0.36	1.87	6
	Site 6	2013	63°54'58"	68°34'23"	0.42	12.5	3
	Iqalugaajuruluit	2013	63°41'06"	68°22'34"	0.54	3.74	8
	Site 8	2013	63°49'30"	68°36'14"	0.56	14.2	12
	Tasirluk (Crazy)	2014	63°52'29"	68°28'40"	4.5	41.1	7.5
Resolute Bay (polar desert)	Ruins	2014	74°40'48"	94°54'52"	0.13	20.2	1.8
	Meretta	2014	74°41'24"	94°59'24"	0.27	5.18	3.1
	RZ2	2014	74°43'15"	94°51'42"	0.03	1.51	0.8
	Teardrop	2014	74°41'03"	94°59'22"	0.04	0.42	4.3
	Small	2014	74°45'33"	95°03'37"	0.15	1.56	2.7
	North	2014	74°46'37"	95°05'47"	0.63	83.7	6. 7
	Resolute	2014	74°41'15"	94°56'33"	1.21	19.8	9
	RZ-P3	2014	74°44'38"	94°57'18"	0.04	1.40	0.8

Water Sampling Methods:

At each lake, *in situ* water temperature, specific conductivity, pH, and dissolved oxygen were measured with a YSI multi-parameter sonde (YSI Inc., Yellow Springs, Ohio, USA). In Gatineau Park lakes, *in situ* chlorophyll (Chl) was measured with a YSI fluorescence probe, validated with Chl analyses by ethanol extraction of filtered seston in the laboratory for a subset of six lakes (Supplemental Figure S1). Water for mercury analysis was collected using clean protocols for trace metals (e.g., clean hands/dirty hands method, acid washing of sampling equipment). Surface water was collected as sub-surface grabs in Nalgene® PETG bottles for mercury analysis and in HDPE bottles for analysis of dissolved organic carbon (DOC), total nitrogen (TN), and Chl. Lakes in the Arctic study areas were not stratified or only weakly stratified, and surface grab samples were representative of water column concentrations. Five lakes at Resolute Bay were partially ice covered during sampling in July 2014. For those lakes, water was collected as surface grabs from the ice moat (open water area) and under the ice pan by drilling a hole through the ice to collect water at 4 m depth with a peristaltic pump and acid-washed teflon tubing. Water THg and MMHg concentrations reported for those partially ice-covered lakes are the means of the surface grab and under ice measurements, which were similar in concentration. In thermally stratified lakes at Gatineau Park, deep hypolimnetic waters (1 m above the sediments) were sampled for water chemistry by peristaltic pump and acid-washed teflon tubing or by acid-washed teflon Kemmerer bottle. Total and filtered (0.45 or 0.7 µm) water samples were collected for mercury analysis, preserved with ultra-pure HCl (0.4% by volume) and refrigerated.

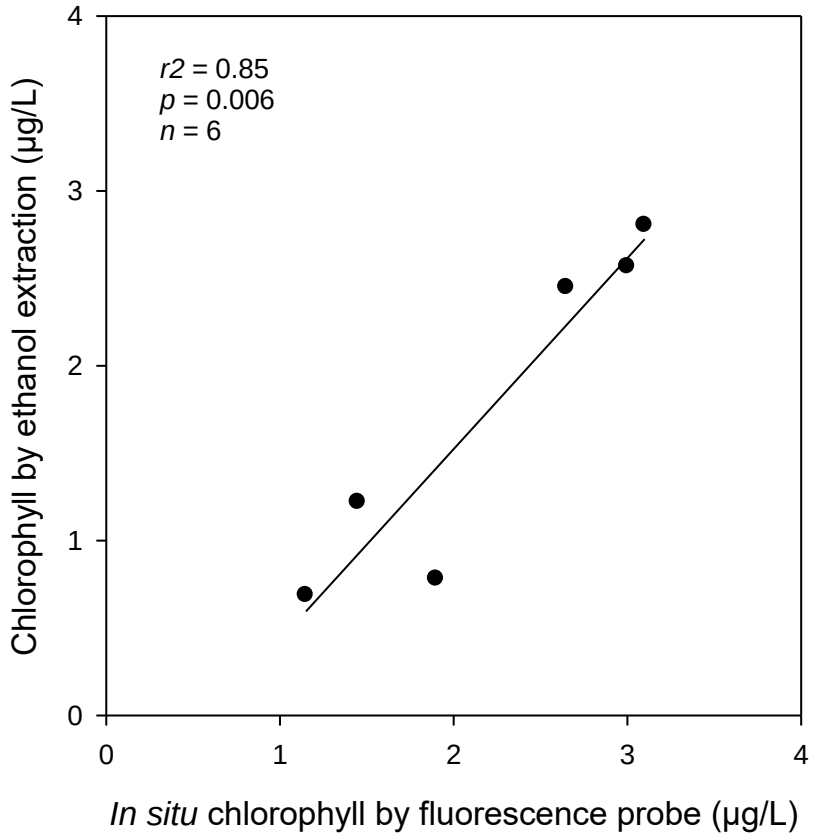

Figure S1. Comparison of two methods for measurement of chlorophyll concentration in surface water using either an *in situ* chlorophyll probe or ethanol chlorophyll extraction from filtered seston of six lakes in Gatineau Park. Data points are lake-mean estimates of surface water chlorophyll concentration that were calculated with 2 to 10 measurements in each lake.

Derivation of Lake and Watershed Morphometrics

Lake and watershed morphometrics including lake area, lake depth, catchment area to lake area ratio (CA:LA) and water residence time (WRT) were determined using GIS-based terrain analysis methods. The bathymetry of each water body was measured in a boat using a GPS-linked echosounder. Lake areas were obtained from 1:50,000 scale CANVEC National Vector hydrography dataset and the catchment area (or gross drainage area) for each water body was extracted from a hydrologically pre-processed, 1:50,000 Canadian Digital Elevation Data (CDED) Digital Elevation Model using well-established methods within the System for Automated Geoscientific Analysis (SAGA) GIS software.[1] The water residence time of a water body is determined by the ratio of annual discharge volume (q, m^3 yr^-1) entering or exiting the lake to the total volume (V, m^3) of the water body itself.[2] Since data on annual discharge were not available for the study lakes, we estimated it using mean mean annual runoff (MAR) from the landscape for each of the four study regions combined with the catchment area of each lake. MAR was estimated using Water Survey of Canada discharge records for nearby rivers at each site and normalizing to the associated catchment area. Combining this estimate with watershed area (A_ws), lake area (A_lk) and average lake depth (D_lk) for each waterbody (all in units of m or m^2), WRT in days was calculated as follows):

WRT (days) = (V/q) = ((A_lk*D_lk)/((A_ws+A_lk)*(MAR)/1000))*365

LV:CA is a proxy for WRT that assumes constant MAR. Within any one of the four study regions, the information content of LV:CA is equivalent to WRT since MAR is a constant. Across the four study sites, the estimation of MAR is incorporated to improve the estimate of WRT. Finally, CA:LA is a simpler, and more commonly used morphometric that can be calculated in the absence of both MAR and lake depth.

Analytical Methods for Water Mercury: Water samples for MMHg analysis were predistilled with additions of KCl and H_2SO_4 to remove matrix interferences. MMHg extract was derivatized by aqueous ethylation using $NaBEt_4$, trapped with Tenax and measured with a Tekran 2700 (Tekran® Instruments Corporation, Toronto, Canada) cold vapor atomic fluorescence spectrometer (CVAFS) with a detection limit of 0.01 ng L^{-1}. Relative standard deviations (RSDs) for field and analytical duplicates were 5.5 ± 5.8% (*n* = 64) and 7.5 ± 5.8% (*n* = 13), respectively. A MMHg standard spiked in Milli-Q water was analyzed after every 12 samples during water MMHg analyses with a recovery of 97.6 ± 11.6 % (n=37). Tort-2 was used as a standard (added to Milli-Q water) to verify the distillation method and potential matrix interferences associated with the presence of organic matter in the water. Recoveries of the distilled Tort-2 additions in water were 103 ± 7.8 % (n = 43).

Water total mercury (THg) was determined on 50 mL samples by BrCl oxidation, $SnCl_2$ reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 CVAFS with a detection limit of 0.05 ng L^{-1}. RSDs of field and analytical duplicates were 2.12 ± 3.2% (*n* = 64) and 1.9 ± 5.0% (*n* = 14), respectively. The average recovery of a standard spike for total mercury was 100% ± 4.2% (n = 43). In addition, internal reference waters of known concentration (inter-laboratory calibration solutions) were analyzed for total mercury after every 12 water samples with a recovery of 105% ± 10.7% (n = 34).

Analytical Methods for Solid-Phase MMHg: Freeze-dried and homogenized samples of chironomid larvae (*n* = 84) and biofilm organic matter (*n* = 70) from Arctic lakes were analyzed for MMHg at the Laboratory for the Analysis of Natural and Commercial Environmental Toxins (LANCET, University of Ottawa, Ottawa, Canada). Sample masses of 1–10 mg (chironomids) or 30–100 mg (biofilm organic matter) were pretreated with an alkaline digestion in KOH followed by acidic digestion in KBr and CuSO4. Bromide derivative of MMHg was extracted in dichloromethane, isolated with sodium thiosulfate and back extracted in dichloromethane for determination by capillary gas chromatography coupled with atomic fluorescence spectrometry. Concentrations of MMHg in chironomid larvae from Gatineau Park (*n* = 38) and all seston (*n* = 48) and zooplankton (*n* = 55) samples were determined at the Laboratoire de biogéochimie environnementale (Université de Montréal, Montreal, Canada). For those samples, MMHg was extracted from sample masses of 1–10 mg (chironomids), 0.5–2 mg (seston) or 3-30 mg (zooplankton) by digestion in 4 M HNO_3 at 55°C for 16 h, derivatized by aqueous ethylation using $NaBEt_4$, trapped with Tenax and measured with a Tekran 2700 CVAFS.

Table S2. Recoveries for THg or MMHg from certified reference materials, precision of duplicate samples (relative standard deviation, RSD), and method detection limits for solid-phase Hg analysis of various environmental matrices.

Sample Type	Hg Analysis Method	CRM Analyzed	% Recovery of Hg	Sample Duplicate RSD	Method Detection Limit
Sediment	Direct mercury analyzer	MESS-3	THg: 97 ± 7% (n = 12)	2 ± 2% (n = 8)	0.2 ng of Hg
Chironomid (Arctic), rock biofilm	Alkaline digestion in KOH followed by acidic digestion in KBr and CuSO4, extraction with dichloromethane, detection by GC-AFS	TORT-2 DORM-4	MMHg: 100 ± 5% (n = 17) MMHg: 94 ± 7% (n = 17)	5 ± 4% (n = 19)	3 ng/g (for 5 mg invertebrate sample)
Seston	Nitric acid digestion, aqueous ethylation, detection by CVAFS	TORT-2	MMHg: 100 ± 13% (n = 12)	Insufficient sample to do analytical duplicates	0.4 ng/g (for 1 mg of seston sample)
Zooplankton, chironomid (north-temperate)	Nitric acid digestion, aqueous ethylation, detection by CVAFS	TORT-2	MMHg: 113± 7% (n = 22)	13 ± 10% (n = 22)	0.09 ng/g (for 5 mg invertebrate sample)

Latitudinal Trend of Surface Sediment THg

Surface sediment THg concentrations were normalized for organic matter content using percent nitrogen (%N), which declined with latitude. Means (± 1 standard deviation) of %N in surface sediment from each study area were: 1.9 ± 0.5 % (Gatineau Park), 1.8 ± 0.3 % (Kuujjuaraapik), 0.7 ± 0.4 % (Iqaluit), and 0.6 ± 0.5 % (Resolute Bay). After normalizing for organic matter content (%N), lake-mean concentrations of sediment THg were positively correlated with lake depth (Figure S2).

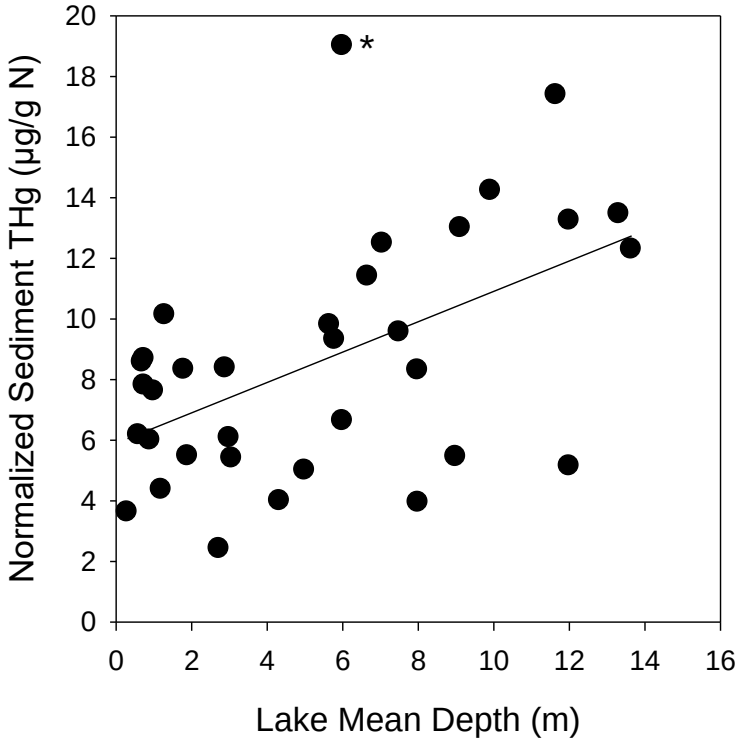

Figure S2. Relationship between lake mean concentration of sediment THg (normalized for nitroge content) and lake depth (regression model: THg/N = 5.900 + 0.501 * Mean Depth; r^2_{adj} = 0.31, $p < 0.001$, n = 33 lakes). Note that 1 outlier (identified by the asterix) was removed for the regression model.

After controlling for both organic matter content (%N) and lake mean depth, surface sediment THg concentrations declined with latitude (Figure S3), similar to the trend for uncorrected THg concentrations presented in Figure 1. A multiple regression model including both lake mean depth and latitude was highly significant (regression model: THg/N = 13.902 + (0.391 * Mean Depth) - (0.132 * Latitude); r^2_{adj} = 0.44, p < 0.001, n = 33 lakes).

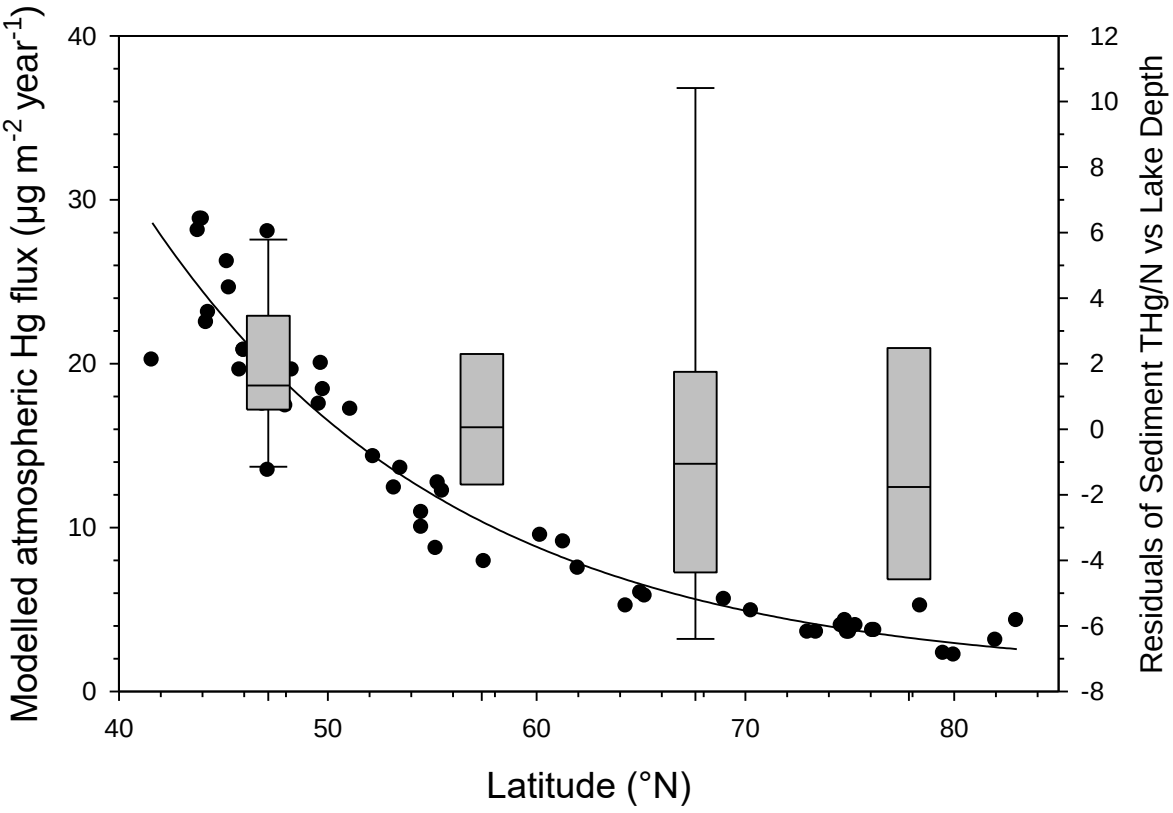

Figure S3. Latitudinal trends in modelled atmospheric mercury deposition (solid circles; from Muir et al.[3]) and normalized concentrations of THg in surface sediment from lakes in the four study regions.

Table S3. Means and ranges of chemical variables of surface waters, and mercury concentrations of surface sediment and aquatic invertebrates in lakes in the four study regions.

		Surface Water							Sediment	Biotic MMHg	
Region	Descriptor	DOC (mg/L)	TP (µg/L)	TN (mg/L)	Chl (µg/L)	THg (ng/L)	MMHg (ng/L)	% MMHg	THg (µg/g)	Chironomids (ng/g)	Zooplankton (ng/g)
Gatineau Park (46°N)	Mean	4.9	---	0.21	1.8	0.83	0.03	4	0.22	2	24
(*n* = 10 lakes)	Range	3.2–6.7		0.14–0.29	1.2–3.0	0.38–1.37	0.01–0.07	2–9	0.10–0.27	0.3–7	8–53
Kuujjuaraapik (55°N)	Mean	5.0	6.3	0.27	1.9	2.30	0.11	5	0.11	60	93
(*n* = 8 lakes)	Range	3.9–7.6	3.1–8.7	0.21–0.34	0.8–2.9	1.23–3.09	0.06–0.18	3–6	0.05–0.14	23–160	64–155
Iqaluit (64°N)	Mean	1.9	4.7	0.08	0.5	0.95	0.02	2	0.06	19	49
(*n* = 9 lakes)	Range	1.0–3.0	1.2–9.6	0.04–0.17	0.2–1.2	0.19–1.57	<0.01–0.04	1–4	0.01–0.14	4–57	26–81
Resolute Bay (75°N)	Mean	1.5	4.5	0.17	0.3	0.62	0.03	6	0.03	69	65
(*n* = 8 lakes)	Range	0.8–2.5	2.8–5.6	0.07–0.26	0.1–0.6	0.28–0.95	0.02–0.05	4–10	0.01–0.09	8–120	10–154

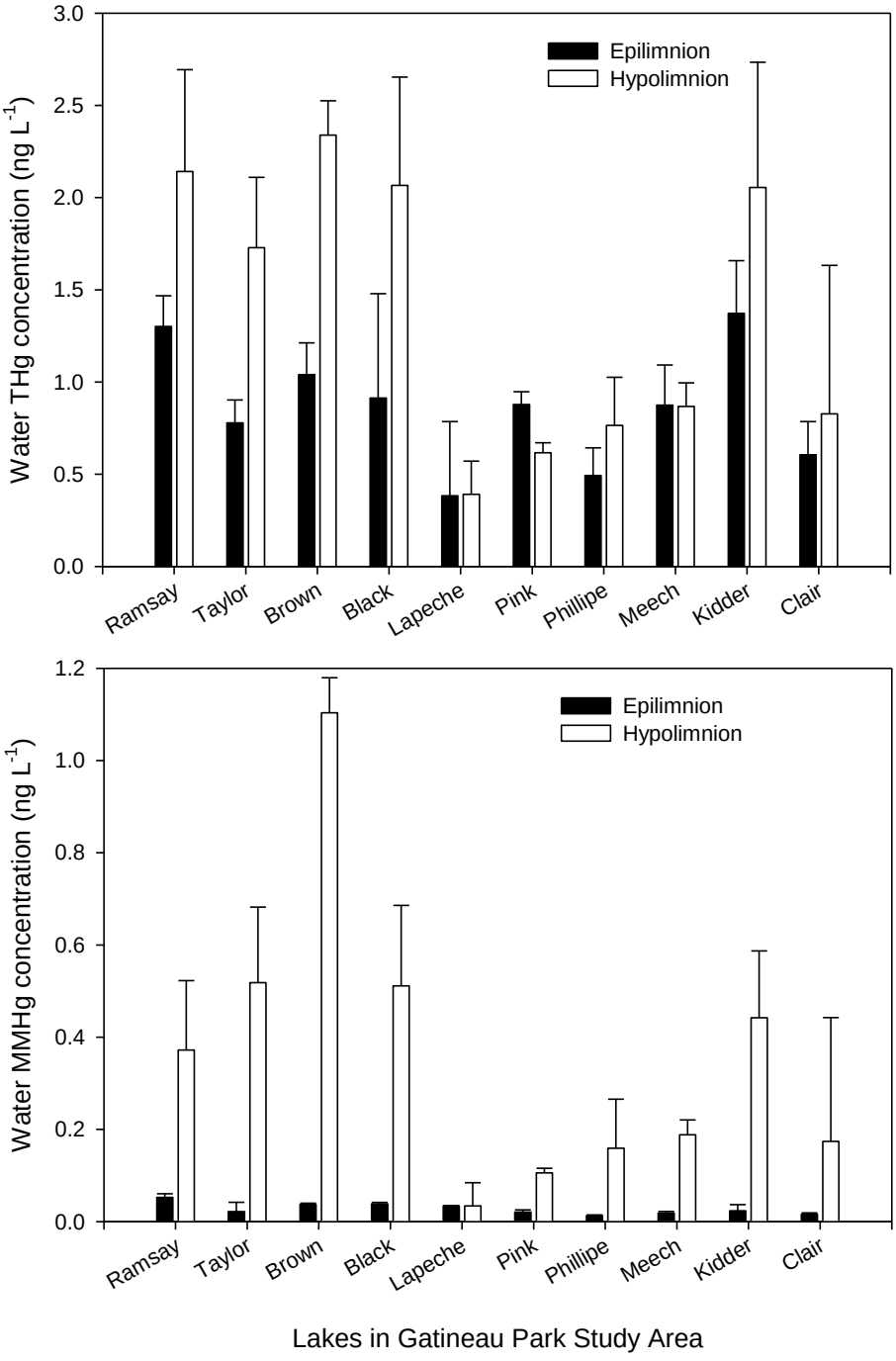

Figure S4. Comparison of surface water (epilimnion) and bottom water (hypolimnion) concentrations of THg (top panel) and MMHg (bottom panel) in stratified Gatineau Park lakes. Values are means (± 1 standard error) of early summer and fall measurements in 2011 and 2012 (3-4 sampling dates).

Table S4. Multiple regression models explaining MMHg concentrations of aquatic invertebrates in relation to surface water concentrations of MMHg, DOC, Chl and TN.

Response Variable	Model Equation	Model r^2_{adj}	Model p
Log Chironomid MMHg (n = 35)			
Model 1	= 1.408 + 13.113 $MMHg_{water}$*** – 2.049 log DOC***	0.55	<0.001
Model 2	= 0.459 + 10.995 $MMHg_{water}$*** – 1.121 log Chl***	0.44	<0.001
Model 3	= -0.374 + 10.877 $MMHg_{water}$*** – 1.211 log TN*	0.22	0.007
Zooplankton MMHg (n = 34)			
Model 4	= 45.676 + 723.733 $MMHg_{water}$*** – 54.798 log DOC*	0.45	<0.001
Model 5	= -19.543 + 720.888 $MMHg_{water}$*** – 51.391 log TN*	0.41	<0.001
Model 6	= 21.699 + 649.684 $MMHg_{water}$*** – 26.005 log Chl	0.39	<0.001

log = log-transformed

Significance of individual variables: * $p < 0.05$, *** $p < 0.001$

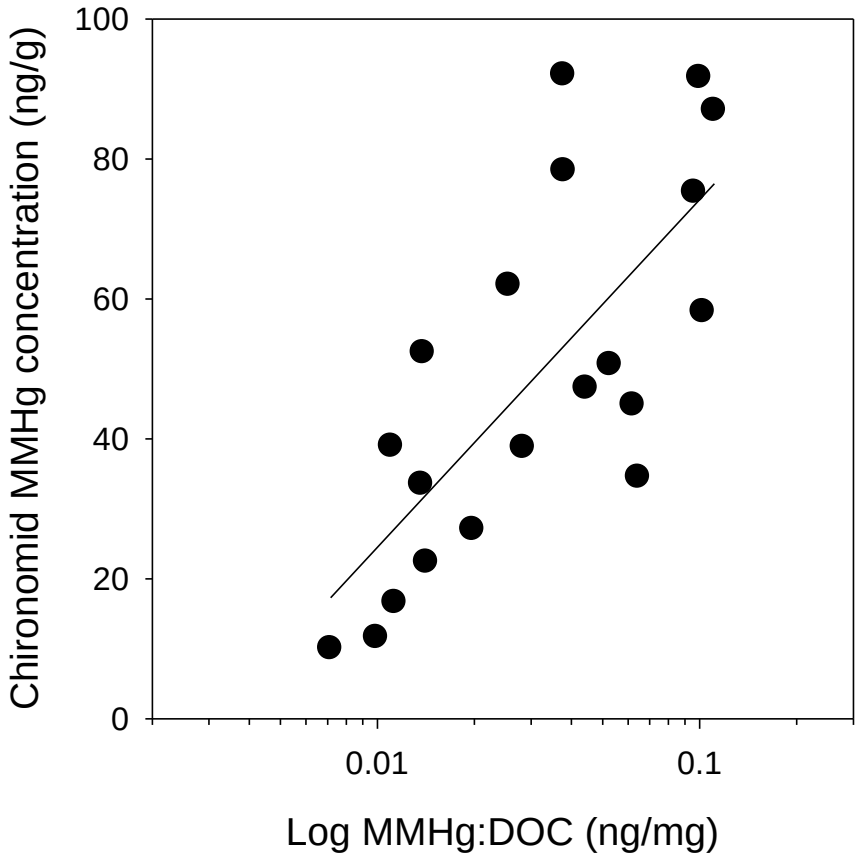

Figure S5. Relationship between MMHg concentration in chironomid larvae and the surface water MMHg:DOC ratio (r^2_{adj} = 0.52, p < 0.001, n = 20 lakes), following re-analysis of a previously published dataset for the Canadian high Arctic. Data points are lake-mean concentrations measured on 1 or 2 occasions in 2005 and/or 2006. An outlier lake with only 1 chironomid MMHg measurement was excluded from the regression. Ranges of surface water concentrations of DOC (< 0.6 – 7.4 mg/L) and MMHg (< 0.02 – 1.5 ng/L) were observed among high Arctic study lakes because more productive polar oasis sites on Devon Island were sampled in addition to polar desert sites on Cornwallis and Somerset Islands. See Chetelat et al.[4] for more detail on methods used to generate the dataset.

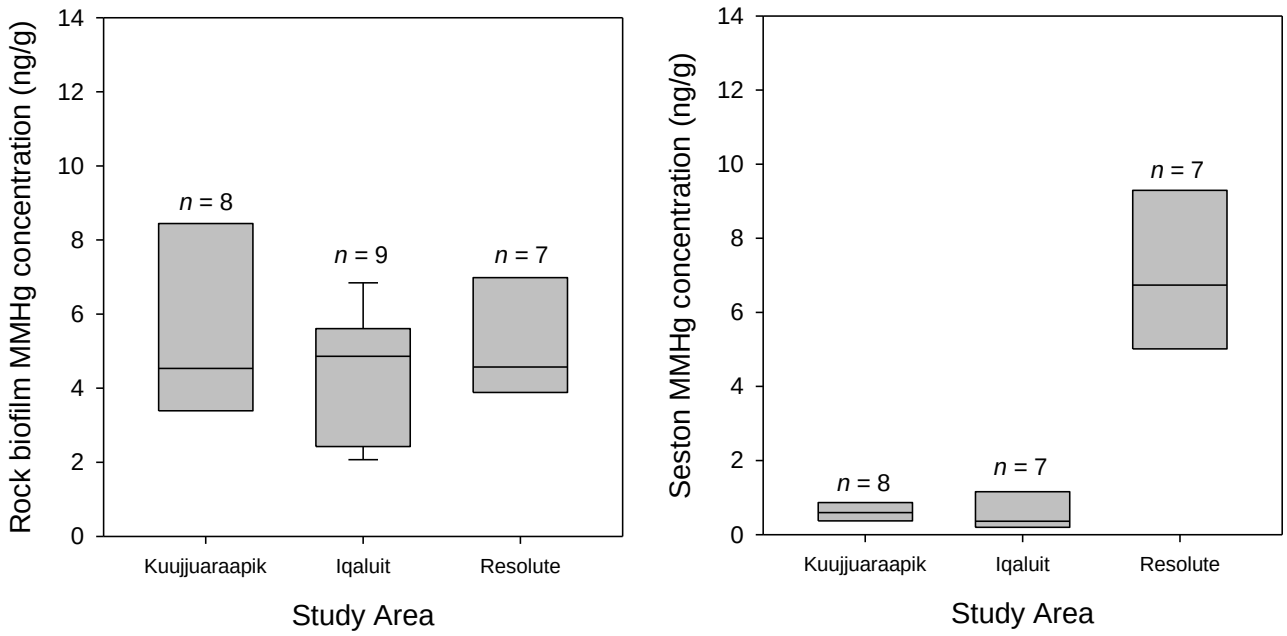

Figure S6. Boxplots of MMHg concentrations in rock biofilms and water seston from lakes in the three Arctic study areas.

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