High Methylmercury in Arctic and Subarctic Ponds is Related to Nutrient Levels in the Warming Eastern Canadian Arctic

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ABSTRACT

Permafrost thaw ponds are ubiquitous in the eastern Canadian Arctic, yet little information exists on their potential as sources of methylmercury (MeHg) to freshwaters. They are microbially-active and conducive to methylation of inorganic mercury, and are also affected by Arctic warming. This multi-year study investigates thaw ponds in a discontinuous permafrost region in the Subarctic taiga (Kuujjuarapik-Whapmagoostui, QC) and a continuous permafrost region in the Arctic tundra (Bylot Island, NU). MeHg concentrations in thaw ponds were well above levels measured in most freshwater ecosystems in the Canadian Arctic (> 0.1 ng L^{-1}). On Bylot, ice-wedge trough ponds showed significantly higher MeHg (0.3 - 2.2 ng L^{-1}) than polygonal ponds (0.1 - 0.3 ng L^{-1}) or lakes (< 0.1 ng L^{-1}). High MeHg were measured in the bottom waters of Subarctic thaw ponds near Kuujjuarapik (0.1 - 3.1 ngL^{-1}). High water MeHg concentrations in thaw ponds were strongly correlated with variables associated with high inputs of organic matter (DOC, a_{320}, Fe), nutrients (TP, TN), and microbial activity (dissolved CO_2 and CH_4). Thawing permafrost due to Arctic warming will continue to release nutrients and organic carbon into these systems and increase ponding in some regions, likely stimulating higher water concentrations of MeHg. Greater hydrological connectivity from permafrost thawing may potentially increase transport of MeHg from thaw ponds to neighbouring aquatic ecosystems.

KEYWORDS

Mercury, Methylmercury, Thaw Pond, Arctic, Subarctic, Lake

INTRODUCTION

The Minamata Convention on Mercury, a global legally-binding treaty designed to reduce the emission of mercury to the environment, has recently been adopted by 198 countries.[1] Nearly a half-century after the discovery of Minamata disease, mercury (Hg) remains a high-

priority global contaminant, especially in the form of methylmercury (MeHg), which bioaccumulates and biomagnifies to high levels in aquatic food webs. Exposure to MeHg can affect the nervous, reproductive, and immune systems of vertebrates, including fish, birds, and humans.[2] Arctic ecosystems are especially vulnerable to Hg pollution due to atmospheric deposition and higher rates of biomagnification in the cold and unproductive food webs of the Arctic.[3–5]

Mercury reaches the Arctic through long-range atmospheric transport in the form of elemental mercury, or Hg(0), where it is deposited into the environment after oxidation into Hg(II).[6] Once deposited, inorganic Hg(II) can be microbially methylated *in situ* to the toxic and biomagnifying form, organic MeHg. A key area of current Arctic research is to establish where Hg(II) methylation occurs in Arctic systems.[7] For inland fresh waters, MeHg is produced in anaerobic sediments and hypolimnia of lakes and ponds or in wetlands.[8,9] Spring snowmelt may also be an important source of MeHg to freshwater ecosystems.[10,11]

In the High Arctic, small ponds have been identified as important sites of microbial Hg(II) methylation.[8,9,12] However, only a few studies have examined the mercury cycle in permafrost thaw lakes and ponds. Although often overlooked, these systems are now considered the most abundant type of aquatic ecosystem at circumpolar Arctic and Subarctic latitudes.[13] They are formed in depressions created by permafrost thawing and may persist from days to hundreds of years, depending on local geomorphology and hydrology.[13,14] Most are small and shallow systems receiving nutrients and organic matter from thawing permafrost and are often colonized by biofilms.[15]

One recent study in the western Canadian Arctic found that lakes affected by the development of retrogressive thaw slumps had lower Hg levels in surface sediments when

compared to reference lakes.[16] In this case, slumping of permafrost soils resulted in high inorganic sedimentation rates and the dilution of Hg in the sediments. However, a study of a peat palsa mire in Norway showed that long-term changes in climate can cause the release of Hg into lake surface waters through increased permafrost thaw depth and thermokarst erosion[17]. Warm and microbially-active thaw ponds receiving inputs from adjacent slumping permafrost soils may in fact be sources of MeHg in the Arctic environment.

Unlike other types of shallow ponds, thaw ponds often show stable thermal stratification in summer with hypoxic to anoxic hypolimnia, some keeping unfrozen bottom waters during the winter months potentially allowing for ongoing microbial activity.[18] In stratified thaw ponds having anoxic bottom waters or sediments, reducing conditions promote microbial Hg(II) methylation. Although many ponds are physically isolated in permafrost landscapes, shifts in the hydrological regime may allow for MeHg to reach surrounding lakes, rivers and marine coastal waters.[17,19–22]

Climate warming and rising permafrost temperatures are increasing the impacts of thermokarst processes on Arctic aquatic ecosystems.[15,23,24] Thawing permafrost may also affect the mercury cycle by modifying hydrological regimes and the transport of mercury from soils and peatlands to nearby aquatic ecosystems.[4,20–22,25,26] The release of nutrients and organic carbon[27,28] and the accelerated microbial transformations of contaminants[29,30] associated with these changes will also likely affect the accumulation or *in situ* production of MeHg in thermokarst aquatic systems.

The main objectives of this study were to assess Arctic and Subarctic thaw ponds as a potential source of MeHg by 1) characterizing MeHg levels encountered in different types of thaw ponds and comparing them to other nearby water bodies, and 2) determining the

81 importance of environmental variables, including nutrients and organic carbon, in explaining
82 among-site differences in MeHg levels in thaw ponds. Two geographic areas were investigated
83 in the eastern Canadian Arctic, one located on a discontinuous permafrost landscape in the
84 Subarctic taiga near Kuujjuarapik-Whapmagoostui, Nunavik (Northern Quebec), and the other in
85 an area of continuous permafrost in the High Arctic tundra on Bylot Island, Nunavut.
86
87 **MATERIALS AND METHODS**
88 **Study Sites**
89 Sampling was conducted in the Qarlikturvik Valley on Bylot Island in Nunavut
90 (73°09'23"N, 79°58'19"W) and in the area surrounding the Kuujjuarapik-Whapmagoostui
91 community in Nunavik (55°16'30"N, 77°45'30"W) (Fig. S1). Sites on Bylot Island were sampled
92 in July and August 2008, 2009, 2010 and 2011, whereas sites near Kuujjuarapik-Whapmagoostui
93 were sampled in July and August 2006, 2009, 2012 and 2013. Bylot Island thaw ponds can be
94 classified into two types: 1) polygonal ponds created by the rise of peat polygon ridges and 2)
95 trough ponds that form over melted ice wedges between the polygon mounds. Trough ponds
96 (elsewhere called runnel ponds[31,32]) are elongated aquatic systems featuring peat erosion and
97 higher turbidity than polygonal ponds, therefore classified as thermokarstic.[33] Both types of
98 ponds examined were no more than a few meters in diameter and generally less than 1.5 m in
99 depth. Seven larger aquatic systems on Bylot Island were categorized as “lakes” for this study,
100 given their much larger surface area and depth. Subarctic sample sites included thermokarst and
101 taiga/rock basin ponds sampled near Kuujjuarapik-Whapmagoostui. Here, thermokarst thaw
102 ponds develop in depressions left after the ice has melted below mineral or besides organic
103 permafrost mounds.[15,34] They are 10 to 30 m in diameter and have a maximum depth of 3.5

m.[15,33] Taiga/rock basin ponds (pooled into one group) are formed on granite or carbonate-derived bedrock respectively and are 10-20 m in diameter with a maximum depth of 1 m. For more information on the formation of study sites see SI.

Physico-Chemical Sampling

Study lakes and ponds were sampled for water chemistry, including dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP), chlorophyll *a* (Chla), anions, cations, major metals, carbon dioxide (CO_2), methane (CH_4) and aqueous total Hg and MeHg concentrations. Additionally, the physico-chemical properties of the water column, including temperature, pH, conductivity, and dissolved oxygen, were measured at the water surface using a YSI 600QS meter (YSI Incorporated). Vertical profiles were also conducted in 3 Subarctic thermokarst ponds. For details on methods, see SI.

Aqueous Total Mercury (THg) and MeHg Concentrations

Water samples were collected for Hg at the surface and 30 cm above the bottom sediments, either from shore or from a raft. Samples were collected using the clean hands, dirty hands sampling protocol for trace metals.[35] Both unfiltered and filtered water samples were taken at each site to determine the proportion of dissolved and particle-bound total mercury (THg or Hg(II) + MeHg) and methylmercury (MeHg). Water samples for total THg and MeHg analyses were pumped through acid-washed Teflon tubing with a peristaltic pump, after the apparatus was flushed with site water for 5 minutes. Samples were stored in acid-cleaned amber glass bottles. Water samples for dissolved Hg and MeHg concentrations were filtered (pore size 0.45 μm) using a peristaltic pump, acid-cleaned Teflon tubing and a GWV High Capacity In-Line Groundwater Sampling Capsule (Pall Corporation) or filtered with pre-ashed glass-fibre filters (0.7 um pore size, Whatman GF-F) on a clean Teflon filtration tower (HCl 10%). All Hg samples

were preserved with ultrapure hydrochloric acid to 0.4% final concentration until laboratory analysis.

Aqueous THg concentration was determined following U.S. EPA method 1631, by bromine monochloride (BrCl) oxidation, tin (II) chloride ($SnCl_2$) reduction, two-stage gold amalgamation and gas-phase detection with a Tekran 2600 Cold-Vapour Atomic Fluorescence Spectrometer (CVAFS) (Tekran Instruments Corporation). The analytical detection limit was 0.04 ng L^{-1}, calculated as three times the standard deviation (SD) of ten blanks. New standards (0.5 ng L^{-1}) were run after each set of 12 samples to test for analytical stability (mean recovery 102.5 ± 9.0%, n = 79). All water samples were run in duplicate or triplicate with a Relative Standard Deviation (RSD) of usually <10% for THg.

Aqueous MeHg concentration was determined following U.S. EPA method 1630, by acid-distillation to remove matrix interferences, derivatization by aqueous-phase ethylation, purging on Tenax (Tenax Corporation) and separation by gas chromatography, before detection with either a Tekran 2500 or Tekran 2700 CVAFS (Tekran Instruments Corporation). The analytical detection limit was 0.02 ng L^{-1} and 0.01 ng L^{-1} respectively for the Tekran 2500 and Tekran 2700, calculated as three times the SD of ten blanks. New standards (0.5 ng/L) were run after each set of 10-12 samples to test for analytical stability (mean recovery 104.2 ± 17.3%, n = 53). Analyses were accepted when recovery of certified trace metal reference materials was in the certified range (152 ± 13 ng/g for TORT-2 lobster hepatopancreas, National Research Council of Canada) and the mean (± SD) recovery was 99.5 ± 8.4% (n = 97). All water samples were run in duplicate with a Relative Standard Deviation (RSD) of <12% for MeHg. Hg analyses met the criteria of a Canadian Association for Laboratory Accreditation (CALA) inter-calibration

149 exercise and an Interlaboratory Quality Assurance Program administered by the Northern
150 Contaminants Program (Government of Canada) (see SI).

151 **Statistical Analysis**

152 For all statistical analyses, among-year averages were calculated for each site (from
153 2008-2011 for Bylot and 2006-2013 for Kuujjuarapik) although not all variables were measured
154 at each site for each year. All of the variables were normalized in order to reduce skewness and
155 the effects of outliers using either log transformations (Temp, pH, Cond, DOC, Chla, Cl, Fe, Mg,
156 Mn, Na, SO_4^{2-}, TN, TP, THg, MeHg, %MeHg,), square root transformations (Ca, K) or power
157 transformations (square) (DO). Inorganic Hg(II) concentrations were estimated by the difference
158 between THg and MeHg concentrations at each site. Normalized data were used to perform all
159 analyses with the R statistical package (R Development Core Team; http://cran.r-project.org).
160 For comparisons of limnological properties and mercury concentrations, the geometric mean
161 (GM) was calculated to better measure the central tendency, calculated as the antilog of the mean
162 of the logarithmic values of the data set. Sites with missing data for multiple variables were not
163 included in the regression analysis, and replacement values were calculated for four sites (each
164 with one missing variable) by imputing the overall variable mean for the type of sample site.

165 Comparisons of limnological properties and mean mercury concentrations were
166 conducted with one-way ANOVAs followed by post-hoc pairwise comparisons using the Tukey
167 HSD correction ($\alpha < 0.05$). Sensitivity analysis with a non-parametric approach (Kruskal-Wallis
168 chi-squared, χ^2 rank sum tests) was conducted to test the assumptions of the analysis of variance
169 model and the non-parametric tests gave the same conclusions as the analyses of variance.[36]
170 Gradients in environmental characteristics were examined by principal component analysis
171 (PCA) using the vegan package in R on centered and scaled data (n=40). A non-parametric

multivariate analysis of variance (MANOVA) was also run to determine whether samples sites differed significantly in terms of measured environmental variables (Adonis test, Vegan package in R).[37]k Due to high collinearity between many of the variables, multiple regression models were difficult to interpret and therefore only simple linear regression models are presented for the most highly correlated environmental variables.

RESULTS AND DISCUSSION

Thermal Stratification

The ponds sampled on Bylot Island (trough and polygonal ponds) and near Kuujjuarapik (taiga/rock and thermokarst ponds) varied in their vertical thermal structure. Strong seasonal thermal stratification was not observed in polygonal ponds on Bylot Island. While polygonal ponds had well-mixed water columns, trough ponds showed stratified conditions during a large fraction of the summer due to the surrounding microtopography, their small fetch, and high humic contents (data not presented here). Hence bottom waters of Bylot trough ponds were mainly hypoxic (often < 2 mgL^{-1}) with only occasional mixing of the upper water column.

Taiga/rock ponds sampled near Kuujjuarapik were very shallow (<1 m) and did not show thermal stratification. However, 9 of the 12 thermokarst ponds (1-3 m in depth) sampled near Kuujjuarapik were strongly thermally stratified. Stratification was sufficiently stable over time to cause low oxygen values in bottom waters, ranging from 0.13 – 3.7 mg L^{-1} or less than 2% saturation at most sites (Table 1, Fig. S2). On average, temperature in the hypolimnion (bottom waters) was around 10°C cooler than at the surface and mean dissolved oxygen was only 5% of the surface concentrations for the Kuujjuarapik thermokarst ponds (Table 1). Oxygen depletion in bottom waters is caused by very limited mixing of the water column, including in spring, and

large microbial respiration.[15,18,33] Thermokarst ponds in this region are often formed as a result of lithalsa degradation and are therefore prone to stable thermal stratification and long water residence time due to high turbidity and low percolation in silty clay soils.[22]

Limnological Properties and Dissolved Gases

Geometric means (± standard deviation, GM ± SD) of limnological properties were compared among sites. Trough and polygonal thaw ponds on Bylot Island showed higher nutrient and DOC levels compared to the (ultra)oligotrophic sites more commonly studied in polar regions (Table 1). Nutrient and DOC concentrations for High Arctic lakes and ponds are typically low, with reported means of 148 – 289 μg L^{-1} for TN, 1.3 – 12.0 μg L^{-1} for TP and 1.5 to 2.2 mg L^{-1} for DOC.[38–41] Compared to mean concentrations from 204 lakes across the Canadian Arctic Archipelago, mean nutrient (TN, TP) levels were roughly 2 – 4 times higher for Bylot polygonal and trough ponds respectively, whereas DOC levels were 2 – 3 times higher.[40]

Bylot thaw ponds also had significantly higher concentrations of solutes than sampled lakes, with higher geometric means for conductivity (μS cm^{-1}), chlorine (Cl), and iron (Fe) (ANOVA, Table 1). Trough ponds, in particular, had higher DOC concentrations and significantly darker water colour (a_{320}) than either polygonal ponds or lakes ($p < 0.05$). This supports our field observations of more active peat slumping in trough ponds. Bottom water was not collected in Bylot ponds, but profiles indicated higher specific conductivity and lower oxygen and pH in trough pond bottom waters. Higher levels of lateral erosion in trough ponds result from ice-wedge melting and soil subsidence on the edge of peat polygons leading to higher inputs of organic material. Indeed, a slightly larger fraction of old carbon available for microbial degradation was observed in trough ponds.[31] Polygonal ponds typically show fewer signs of erosion and had lower DOC concentrations.[20,31,42]

Concentrations of dissolved gases (CH_4, CO_2) were also significantly higher in trough ponds when compared to polygonal ponds (respectively 3 and 5 times higher, Table 1). High levels of CO_2 and CH_4 in trough ponds compared with polygonal ponds likely reflect anoxic conditions promoting fermentation and methanogenesis,[31] which may occur in biofilms, sediments or surrounding anaerobic soils.[43] High levels of dissolved gases also indicate strongly reducing conditions in sediments at these sites, leading to the remineralisation and remobilization of ions (such as Mn) from anoxic sediments.

Subarctic thermokarst ponds similarly displayed higher nutrient and DOC concentrations than neighbouring lakes. Lakes sampled near Kuujjuarapik had mean TN of 267 ± 50.5 μg L^{-1}, mean TP of 6.83 ± 3.33 (TP) μg L^{-1} and mean DOC of 4.98 ± 1.38 mgL^{-1} (GM ± SD, G. MacMillan, n = 7, unpublished data 2012). The average concentrations were therefore 1.5 times (TN), 1.7 times (DOC) and 7 times (TP) higher in the surface waters of Kuujjuarapik thermokarst ponds (Table 1). The bottom waters of these thaw ponds also showed distinct water chemistry, with much higher mean specific conductivity (3×), TP (4×), Chla (8×), CO_2 (6×) and CH_4 (95×) than at the surface (ANOVA, Table 1). The low oxygen measured in the bottom waters of these sites may have caused the remobilization of ions from anoxic sediments and therefore led to higher conductivity. Higher concentrations of dissolved CO_2 and CH_4 in Kuujjuarapik bottom waters also indicates anoxic conditions suitable for microbial gas formation, similar to Bylot trough ponds.

Taiga/rock ponds had the highest average concentrations of Na^+, Cl^-, and sulfate (SO_4^{2-}) but had lower TP and Chla than Kuujjuarapik thermokarst ponds. Concentrations of DOC and nutrients (TN, TP) were roughly twice as high as in neighboring lakes, yet TP was significantly

lower than in thermokarst ponds. Taiga/rock ponds also showed higher conductivity likely related to their coastal locations and marine aerosol influence from Hudson Bay.

Total Mercury and Methylmercury Levels

On Bylot Island, trough ponds had the highest mean (and median) water concentrations of both THg and MeHg (Table 1, Fig. 1). Geomeric mean concentrations of THg from trough ponds were 1.5 times the average found in polygonal ponds and 2.6 times the average in lakes (although the difference was not significant for polygonal ponds). Mean MeHg concentrations were highest in trough ponds, being approximately 3.5 times the average in polygonal ponds and 24 times the average found in larger water bodies. Statistical tests showed differences in MeHg concentrations between trough ponds, polygonal ponds and lakes (Table 1, $p < 0.05$). The percentage of THg in the form of MeHg (or %MeHg) was also significantly higher in both types of thaw pond (26.0 ± 9.0% in trough ponds and 12.0 ± 5.1% in polygonal ponds) when compared to the lakes at 1.5 ± 9.5% (GM ± SD). It should be noted that maximum values reported here for Bylot thaw ponds are very high due to the sampling of one extreme site (BYL63) over two consecutive years (reaching 30.2 ng L^{-1} THg and 18.2 ng L^{-1} MeHg in 2009, and respectively 13.4 and 2.97 ng L^{-1} in 2010). However, median values of THg and MeHg followed the same trends among pond types as the means (SI: Table S1) and statistical tests still showed differences between all groups without these extreme values ($p < 0.05$).

Higher levels of MeHg measured in Bylot thaw ponds (particularly trough ponds) may either originate from a) *in situ* methylation in sediments by microorganisms or b) transport from surrounding peaty soils. Our results suggest that *in situ* methylation may be an important source of MeHg in these systems, as high MeHg concentrations combined with high %MeHg often indicates high net methylation rates.[44] A strong positive correlation between MeHg and inorganic

263 Hg(II) concentrations at these sites (R^2adj = 0.53, $p < 0.01$) suggests that they are suitable
264 aquatic systems for *in situ* production of MeHg and are limited by the availability of inorganic
265 Hg(II) (Fig. 2).

266 On the other hand, MeHg may accumulate in these systems due to high rates of
267 production and transport from surrounding anaerobic soils. Mercury binds strongly to DOC,
268 enhancing the mobilization and transport of this metal within a watershed.[45,46] However, recent
269 studies in the High Arctic have found variable and relatively low methylation potentials of
270 wetland soils and low export of MeHg to downstream lakes.[11,47] Reported methylation rates and
271 %MeHg in Arctic soils are also low compared to the MeHg levels measured in Bylot thaw
272 ponds. Since few data are currently available on methylation rates in Arctic soils (and on the
273 soils surrounding our sample sites in particular), the source of MeHg in these Bylot thaw ponds
274 may therefore be either transport from surrounding soils or *in situ* methylation.

275 For stratified Kuujjuarapik thermokarst ponds, both THg and MeHg concentrations were
276 significantly higher in bottom waters than at the surface (Table 1, $p < 0.05$). Bottom water mean
277 concentrations were about 1.7 times higher for THg and 7 times for MeHg compared to surface
278 water concentrations. Taiga/rock ponds showed the highest mean concentrations of THg (6.50 ±
279 2.47 ng L^{-1}) and relatively high concentrations of MeHg (0.33 ± 0.33 ng L^{-1}), although MeHg
280 was much lower than in thermokarst pond bottom waters (Fig. 1). Statistical tests showed
281 differences between all groups for THg and higher MeHg in bottom waters of stratified
282 thermokarst ponds relative to other groups ($p < 0.05$, Table 1). The %MeHg was also
283 significantly higher in the bottom waters of stratified thermokarst ponds (27.2 ± 24%) when
284 compared to surface waters (6.7 ± 22%) or to taiga/rock ponds (5.1 ± 3.7%). It should be noted
285 that one shallow thermokarst pond sampled in 2013 (SAS-1G) showed much higher

concentrations of THg (4.35 ± 0.24 ng L^{-1}) and MeHg (3.56 ± 0.11 ng L^{-1}), as well as higher %MeHg (82%) than neighbouring sites. Statistical tests still showed differences between all groups without these extreme values ($p < 0.05$).

Strong thermal stratification in Kuujjuarapik thermokarst ponds results in low oxygen or anoxic conditions, which are highly conducive for microbial Hg(II) methylation.[48] Other studies have even suggested that year-round stable stratification potentially allows for ongoing microbial activity (hence potentially methylation) in bottom waters during the winter months.[18] Moreover, dark bottom waters in these turbid thermokarst ponds precludes photodemethylation losses at depth.[49] Bottom waters in these ponds have a combination of high MeHg concentrations and high %MeHg suggesting that, as for the Bylot trough ponds, these sites may have high net methylation rates.[44] However, the lack of correlation between Hg(II) and MeHg at these sites ($p > 0.05$) either suggests that 1) MeHg production is not limited by the availability of inorganic Hg(II) or 2) measured Hg(II) concentrations do not reflect the Hg(II) bioavailable to methylating microorganisms (Fig. 2). As for Bylot Island, there are limited data available for MeHg production and transport from Subarctic peatlands. However, high MeHg and %MeHg in strongly stratified bottom waters of Kuujjuarapik thaw ponds suggests *in situ* methylation at these sites.

Shallow Kuujjuarapik taiga/rock ponds had high THg concentrations and relatively high MeHg concentrations compared to the surface waters of thermokarst ponds (Fig. 1). Proximity of these ponds to the coast of Hudson's Bay may lead to marine inputs of MeHg.[50] However, the %MeHg was quite low which suggests that these sites may have lower rates of Hg(II) methylation than thaw ponds. The lack of stratification (and therefore reducing conditions for Hg(II) methylation) combined with low organic matter inputs due to little or no peripheral

vegetation may help explain the lower %MeHg found at these sites. Higher rates of bio- or photodemethylation may also explain the low %MeHg found in well-lit taiga/rock ponds despite the large pool of potentially bioavailable inorganic Hg.

Unfiltered concentrations of THg and MeHg were measured at all sites over all sampling years. For a subset of sites, dissolved (filtered at 0.45 μm) concentrations were also measured at least once over the extended sampling period (2006 to 2013). Overall, both THg and MeHg were primarily in the dissolved phase, with mean ± SD values of 79.0 ± 16.7% for THg and 83.8 ± 25.6% for MeHg on Bylot (n=11), and of 87.0 ± 8.6% for THg and 83.9 ± 10.4% for MeHg in the Kuujjuarapik area (n=16). This suggests that the Hg measured at these sites is mobile, with a higher potential for lateral transport into other aquatic systems than Hg bound to settling particles. Concentrations of MeHg found in the dissolved phase are also more bioavailable for uptake by lower trophic levels (algae).[51]

Environmental Drivers of Methylmercury Concentrations in Arctic and Subarctic Ponds

PCA was used to identify the dominant environmental gradients in the dataset (Fig. 3). The PCA biplot accounted for 51.9% of the total variation among sites from both study areas (Axis 1: 28.5% and Axis 2: 23.4%). The remaining unexplained variability (48%) can be attributed to a number of different factor, for example, local and regional climatic variation (precipitation, temperature), sedimentation rates, heterogeneity in microbial communities and analytical variability. On the correlation biplot, environmental variables are represented by black arrows, whereas sites are represented by coloured points. The angles relative to axis 1 and 2 show the weight of the variable in determining the construction of the ordination axis, and the angles between the arrows are representative of the degree of correlation between variables.[52]

Based on the PCA scores, the distribution of the sites along axis 1 was most strongly driven by environmental gradients in THg, MeHg, TP, TN, Mn, Fe, and DOC. The dominant gradients detected in axis 2 of the PCA were for pH, DO, Chla, SO_4^{2-} and major ions (Ca, Mg, Na, Cl). The Subarctic sites tended to be more productive (higher planktonic Chla) than Bylot sites (Fig. 3), although polygonal ponds had thick cyanobacterial mats.[53] Overall, the PCA analysis shows a clustering of the different types of ponds based on distinct water chemistry conditions and the positive association of mercury (THg, MeHg and %MeHg) with environmental variables indicating inputs of organic matter (DOC, Fe), high nutrients (TN, TP) and reducing conditions in the sediments (Mn, Fe, TP). Strongly reducing conditions in sediments or bottom waters leads to the remobilization of ions (such as Hg and P) bound to Fe and Mn oxides back into the water column.[54] Differences in environmental variables among sample sites (trough, polygonal, subarctic thermokarst and taiga/rock) were evaluated using a permutational MANOVA (Adonis function, Vegan package in R)[37] which showed that physico-chemical characteristics of the water differed between sample sites (np-MANOVA, $F = 20.47$, $R^2 = 0.71$, $p < 0.01$, 999 permutations).

Simple linear regression models were also calculated for THg and MeHg with the most highly correlated environmental variables (SI: Table S4). Surface water THg was significantly correlated with water colour (a_{320}: $R^2adj = 0.57$, $p < 0.01$), DOC ($R^2adj = 0.45$, $p < 0.01$), Fe ($R^2adj = 0.26$, $p = 0.02$) and TN ($R^2adj = 0.33$, $p = 0.01$). MeHg was most highly correlated with TN ($R^2adj = 0.61$, $p < 0.01$), DOC ($R^2adj = 0.57$, $p < 0.01$), water colour (a_{320}: $R^2adj = 0.39$, $p < 0.01$) and CH_4 ($R^2adj = 0.37$, $p < 0.01$) (Fig. 4). Some regressions showed high leverage due to outlying sample sites, however these relationships were still found to be highly significant when these sample sites were excluded (SI: Fig. S3). Simple linear regression models were also

calculated separately for each region (either Bylot: n = 34 or Kuujjuarapik: n = 24) and on a subset of data from the bottom waters of stratified ponds (n = 9). Overall, concentrations of THg and MeHg were correlated with similar (collinear) environmental variables for these data subsets (for R^2adj and *p*-values, see SI: Table S4).

Many of the explanatory variables were collinear and the relative importance of specific correlations is therefore difficult to interpret. For example, DOC, Fe and water colour (log a_{320}) were correlated with each other, as both Fe and DOC concentrations are known to affect water colour.[55] DOC concentrations were also strongly correlated to CO_2, TN, and Mn concentrations in surface waters. Concentrations of Fe and Mn were auto-correlated and were negatively correlated with pH and dissolved oxygen (DO), as these metals are only soluble under anoxic, reducing conditions. This notwithstanding, these correlations indicate that MeHg concentrations are strongly correlated with environmental variables indicating high inputs of organic matter (DOC, a_{320}, Fe), high nutrients (TP, TN), microbial activity (dissolved CO_2 and CH_4 gases) and reducing conditions in the sediments (Mn, Fe, TP) at these sites.

This study confirms our hypothesis that permafrost thaw ponds may be sources of MeHg in the Canadian Arctic and Subarctic. High concentrations of MeHg (ng L^{-1}) and %MeHg were measured in Bylot trough ponds (0.72 ± 2.37, 26% ± 9.0) and in the bottom waters of Kuujjuarapik thaw ponds (0.99 ± 1.17, 27% ± 24). These values are well above the levels typically found in freshwater ecosystems in the Arctic where average MeHg concentrations generally remain below 0.1 ng L^{-1} [56] (and less than 15% of total Hg) with a few exceptions (i.e. Ellesmere Island ponds).[8,9] Thaw pond MeHg concentrations were also high in comparison with temperate lakes and rivers in northeastern North America[57] (n = 277) where they were found to range from 0.01 to 3.12 ng L^{-1} with a mean of 0.30 ng L^{-1}. Interestingly, Bylot polygonal ponds

had lower MeHg (0.21 ± 0.08 ng L^{-1}) and %MeHg (12% ± 5.1) than neighbouring trough ponds. This is may be due to more oxic water columns, lower levels of lateral erosion (and hence inputs of OM and nutrients) and/or lower sediment surface area to water volume ratio in polygonal ponds which leads to greater dilution of MeHg from the sediments. Surface waters from Kuujjuarapik thermokarst ponds also showed much lower levels of MeHg than bottom waters (0.14 ± 3.34, 6.7% ± 2.7). This indicates that thermal stratification and anaerobic bottom waters create favourable conditions for microbial Hg(II) methylation at these sites. High concentrations of MeHg combined with high %MeHg also support the hypothesis of high net methylation rates in Kuujjuarapik thermokarst pond bottom waters.[44]

Furthermore, this study highlights differences in the major environmental variables explaining among-site differences in MeHg levels in small Arctic and Subarctic aquatic systems when compared to more temperate systems. The major variables controlling MeHg production at temperate latitudes are typically temperature, pH, redox conditions, sulfate and DOM.[58,59] Similarly, MeHg concentrations in the present study were positively correlated with inputs of organic matter (DOC) and low redox (anaerobic) conditions in sediments or bottom waters. Positive correlations between MeHg and DOC in freshwaters may indicate the export of Hg bound to DOM from surrounding soils[45,60,61] or alternatively that organic matter limits microbial activity in lake sediments, thus *in situ* methylation rates.[62,63] Anoxic bottom waters or sediments also favour both Hg release from sediments[64] and increased microbial Hg(II) methylation.[48] Yet THg and MeHg concentrations were not correlated with water column temperature, pH, or SO_4^{2-} at these sites, variables which control MeHg production at more temperate latitudes (Fig. 4).[58,59] The production of MeHg typically increases at warmer temperatures due to increased microbial activity[59] yet we found no association between surface water temperature and MeHg

400 concentration. Elevated MeHg concentrations were found in thaw ponds from both study areas,
401 despite their difference in latitude (~20°N) and climate regimes. Lack of correlation between
402 MeHg and SO_4^{2-} concentrations in surface waters may be due to low sulfate concentrations (<10
403 mg L^{-1} or <100 μM), which limit the activity of sulfate-reducing bacteria. Future studies should
404 focus on relationships between sulfate water concentrations and sulfide pore-water
405 concentrations to identify links between the sulfur and mercury cycles at these sites. Lack of
406 correlation between MeHg and SO_4^{2-} may also indicate that other types of bacteria are
407 responsible for Hg(II) methylation in sediments or bottom waters, such as iron-reducing bacteria
408 or methanogens.[64–66]

409 Unlike for temperate aquatic systems, strong positive correlations were found in these
410 Arctic and Subarctic ponds between MeHg, and higher nutrients (TN, TP) and dissolved
411 greenhouse gases (CO_2, CH_4). Only a few previous studies have found positive relationships
412 between MeHg and lake nutrient status[67,68] and the exact relationship between methylation,
413 nutrient status and N availability remains unclear. A previous study in High Arctic ponds also
414 found positive correlations for MeHg concentrations with nitrogen (ratio of ammonium to
415 nitrate, NH_4^+:NO_3^-) and dissolved CH_4 concentrations.[8] These results were explained as
416 indicating the relative importance of anaerobic microbial activity on Hg(II) methylation and
417 higher ratios of methylation to demethylation rates. Other recent studies performed at the same
418 sites near Kuujjuarapik show that thermokarst ponds are methanotroph-rich ecosystems,[69,70]
419 indicating that methane is a potentially important energy source for microorganisms at these
420 sites. In the present study, the lack of correlation between sulfate and MeHg concentrations and
421 the strong correlations found between dissolved CH_4 and MeHg levels may indicate that
422 methane-producing microorganisms (methanogenic archaea) contribute to the production of

MeHg in the sample sites, as has been observed in other aquatic systems.[65] These novel correlations highlight the importance of investigating the role of organic matter erosion and nutrient inputs on the stimulation of anaerobic microbial activity, and hence potential *in situ* methylation by methanogenic archaea, in these ubiquitous aquatic systems.

Ecological Significance

Our findings contrast with the lack of stimulatory effects observed for retrogressive thaw slumps of clay-rich tills entering lakes in western Canadian Arctic,[16] highlighting that permafrost degradation can affect the mercury cycle differently across the Arctic landscape. Permafrost thaw ponds are now considered the most common freshwater aquatic system at circumpolar latitudes[13] and the impacts of thermokarst thawing on arctic aquatic ecosystems is increasing rapidly with climate warming.[15,23,24] Our study strongly suggests that increasing inputs of organic matter and nutrients into arctic surface waters[27,28,71,72] can have potentially major consequences for the transport and/or *in situ* production of MeHg, particularly in these abundant ponds. Small permafrost thaw ponds may play an important role in controlling the local and regional fluxes of contaminants in the warming Eastern Canadian Arctic.

MeHg in thaw ponds may enter aquatic food webs through feeding on zooplankton by migratory bird population or through downstream transport to larger water bodies. On Bylot Island, large-scale thermal erosion has led to drainage of the terrain into a nearby river.[21,73] In ice-rich permafrost areas, thawing may lead to the coalescence of trough and polygonal ponds into larger lakes, which can then be catastrophically drained into nearby rivers by thermal erosion.[20,74,75] In the Subarctic, there are also signs that rapidly degrading discontinuous permafrost can increase hydrological connectivity and potentially the transport of MeHg to the hydrological network. In the Sheldrake River catchment north of Kuujjuarapik, the thermokarst

446 pond area has increased by 96% over the past 50 years, whereas stream and channel drainage has
447 increased by 18%.[22] Sediment and organic material from the degrading permafrost in this area
448 have been tracked many kilometers distant into Hudson Bay, demonstrating the potential for the
449 export of Hg from ponds to coastal waters. On the other hand, Subarctic thaw ponds can be
450 ephemeral and disappear through 'terrestrialization' (encroaching peat cover) over a relatively
451 short time frame,[76] which may not lead to mercury export. Further studies are required in order to
452 understand the large-scale ecological implications of high MeHg concentrations found in thaw
453 ponds in the eastern Canadian Arctic, especially in the context of a rapidly warming North.

Acknowledgements

We would like to thank three anonymous reviewers for their valuable comments. We are grateful to Virginie Roy, Dominic Bélanger, Fréderique Paquin, Thierry Raté, Rébecca Filion, Paschale Noel Bégin, and Marie-Claude Turmel for help with sample collection, preparation and data analysis. Funding for this project was provided through NSERC Discovery and Northern Supplement Grants to M.A. and I.L., Polar Continental Shelf Project (PCSP) grants to I.L. and M.A., a FRQ-NT Équipe grant to M.A. and I.L., a Northern Contaminants Program grant to M.A. and the Northern Scientific Training Program (Aboriginal Affairs and Northern Development Canada) to G.M., as well as FRQ-NT and Richard J. Schmeelk Canada scholarships to G.M. and NSERC summer scholarships to C.G. and V.R. Logistical support was provided by PCSP, Goose Camp on Bylot Island (Université Laval), Sirmilik National Park (Parks Canada) and the Centre d'Études Nordiques.

Author Contributions. M.A. and I.L. designed the experiment and I.L., C.G., and G.M. collected the data. Data were analysed by C.G., J.C., and G.M, whereas G.M. and M.A. prepared the manuscript with all tables and figures. All authors discussed the results and edited the manuscript.

Supporting Information. Details of the experimental design, raw physicochemical data tables, GPS coordinates, simple linear regressions and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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FIGURE CAPTIONS

TABLE 1. Comparison of limnological properties from sampled sites on Bylot Island and near Kuujjuarapik-Whapmagoostui. Surface water geometric mean values (bold) and ranges (min – max) are shown. One-way ANOVA results and post-hoc pairwise comparisons between the 3 groups (Tukey's HSD) are given ($\alpha < 0.05$). *P*-values were corrected for multiple tests (Holm correction) and non-significant tests are shown by n.s. Several variables were not available for the Bylot lakes and for taiga/rock ponds (na) yet with *p*-values for the entire model. Variables include of water temperature (Temp), pH, conductivity (Cond), dissolved oxygen (DO), absorption coefficient of dissolved organic matter at 320 nm (a_{320}), concentrations of dissolved organic carbon (DOC), carbon dioxide (CO_2), methane (CH_4), major ions, total phosphorus (TP), total nitrogen (TN), chlorophyll a (Chla), total mercury (THg), methylmercury (MeHg) and the percentage of MeHg to THg.

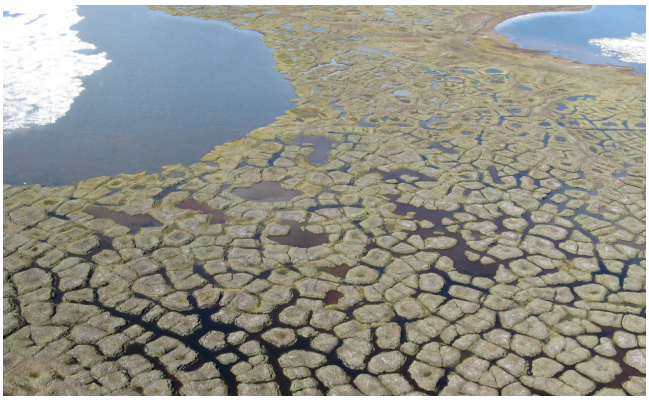
FIGURE 1. Box plots showing concentrations in ng L^{-1} (median ± SD; dots are outliers) for total mercury on the left panel, and methylmercury on the right panel for trough ponds (n=18), polygonal ponds (n=9) and lakes (n=7) on Bylot Island, and for taiga/rock ponds (n=12), thermokarst surface waters (n=12) and thermokarst bottom waters (n=9) near Kuujjuarapik-Whapmagoostui. One trough pond outlier (BYL63) was not included in this figure due to extreme values (21.82 ngL^{-1} for THg, 10.58 ngL^{-1} for MeHg).

FIGURE 2. Principal Component Analysis (PCA) correlation biplot showing 47 sample sites (coloured points) and 21 physicochemical/environmental variables (black arrows) for Bylot and Kuujjuarapik. Site name abbreviations in the legend are BYL for Bylot sample sites and KUUJJ for Kuujjuarapik sites. The PCA accounts for 51.9% of the total variation among sites (Axis 1: 28.5% and Axis 2: 23.4%). The PCA identified the dominant environmental gradient related to THg, MeHg, TN, TP Mn, Fe and DOC concentrations (axis 1) and a secondary gradient of variables including pH, DO, Chla and major ion concentrations (axis 2).

FIGURE 3. Correlations between inorganic Hg(II) and MeHg concentrations in surface and bottom waters from a) Bylot Island ($R^2adj = 0.53$, $p < 0.001$) and b) Kuujjuarapik-Whapmagoostui ($p > 0.05$).

FIGURE 4. Correlations between MeHg concentrations (ngL^{-1}) for surface waters of all samples sites (n = 58) showing significant positive correlations for a) DOC (mgL^{-1}), and b) TN (μgL^{-1}) and no significant correlations for c) pH and d) SO_4^{2-}(mgL^{-1}). All axes are shown on logarithmic scales and regressions were performed on log-transformed data. Bottom waters for stratified Kuujjuarapik thaw ponds were not included to preserve independence of observations.

ABSTRACT ART



Source: Isabelle Laurion, Bylot Island, Nunavut, Canada.

730 **TABLE 1**

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Bylot	a) Trough Ponds (n=18)		b) Polygonal Ponds (n = 9)		c) Lakes (n = 7)		F	*P* - value	Post-Hoc
Temp (°C)	**12.5**	(8.0 – 19.2)	**13.5**	(11.9 – 15.8)	**9.4**	(6.1 – 16.1)	*n.s.*	*n.s.*	*n.s.*
pH	**6.8**	(5.9 – 7.6)	**8.0**	(6.5 – 8.7)	**6.9**	(6.6 – 7.6)	14.54	< 0.001	b > a; b > c
Cond (µS cm^{-1})	**95**	(43 – 448)	**78**	(51 – 119)	**18**	(9 – 90)	15.87	< 0.001	a > c, b > c
DO (mg L^{-1})	**8.90**	(3.81 – 12.25)	**10.46**	(6.75 – 12.09)	**11.52**	(10.43 – 12.85)	*n.s.*	*n.s.*	*n.s.*
a_{320} (m^{-1})	**37.8**	(18.4 – 269.4)	**16.3**	(8.2 – 77.9)	**3.3**	(1.3 – 6.3)	29.34	< 0.001	a > b > c
DOC (mg L^{-1})	**12.4**	(7.7 – 33.0)	**9.0**	(6.6 – 15.2)	**2.3**	(1.0 – 5.3)	36.32	< 0.001	a > c, b > c
CO_2 (µM)	**108.4**	(24.3 – 609.1)	**20.6**	(9.1 – 280.1)	**na**	na	8.206	< 0.01	a > b
CH_4 (µM)	**5.59**	(2.09 – 19.90)	**1.70**	(0.68 – 5.05)	**na**	na	11.58	< 0.001	a > b
SO_4^{2-} (mg L^{-1})	**1.26**	(0.07 – 3.59)	**1.49**	(0.40 – 6.08)	**1.21**	(0.66 – 2.47)	*n.s.*	*n.s.*	*n.s.*
Fe (µg L^{-1})	**90.4**	(11.2 – 1637.5)	**52.9**	(28.68 – 352.4)	**19.9**	(6.06 – 881.6)	38.87	< 0.001	a > c, b > c
Mn (µg L^{-1})	**10.5**	(2.05 – 556.1)	**1.75**	(0.58 – 13.94)	**na**	na	*n.s.*	*n.s.*	*n.s.*
TP (µg L^{-1})	**43.5**	(14.6 – 359.7)	**19.4**	(12.9 – 46.8)	**4.5**	(3.1 – 8.5)	18.68	< 0.001	a > c, b > c
TN (µg L^{-1})	**743.9**	(268.6 – 4366)	**418.7**	(334.3 – 572.3)	**122.8**	(94.8 – 194.5)	19.82	< 0.001	a > c, b > c
Chl*a* (µg L^{-1})	**1.60**	(0.40 – 26.60)	**0.94**	(0.30 – 2.66)	**1.13**	(0.62 – 1.70)	*n.s.*	*n.s.*	*n.s.*
THg (ng L^{-1})	**2.75**	(1.26 – 21.82)	**1.74**	(1.24 – 2.93)	**1.05**	(0.68 – 1.55)	8.34	< 0.01	a > c
MeHg (ng L^{-1})	**0.72**	(0.14 – 10.58)	**0.21**	(0.08 – 0.34)	**0.03**	(0.00 – 0.06)	45.03	< 0.001	a > b > c
MeHg (%)	**26.0**	(11.1 – 48.5)	**12.0**	(4.9 – 18.7)	**1.5**	(0.0 – 5.8)	64.30	< 0.001	a > b > c
Kuujjuarapik	**a) Thaw ponds Surface Waters (n = 12)**		**b) Thaw Ponds Bottom Waters (n = 9)**		**c) Taiga/Rock Ponds (n=12)**		**F**	***P* - value**	**Post-Hoc**
Temp (°C)	**17.8**	(14.4 – 24.2)	**7.6**	(4.9 – 13.1)	**13.5**	(11.4 – 16.3)	50.95	< 0.001	a > c > b
pH	**6.6**	(5.8 – 7.2)	**6.2**	(5.9 – 6.9)	**6.9**	(5.7 – 7.8)	*n.s.*	*n.s.*	*n.s.*
Cond (µScm^{-1})	**52**	(27 – 204)	**188**	(145 – 265)	**77**	(26 – 514)	8.77	0.001	b > a, b > c
DO (mgL^{-1})	**7.76**	(2.49 – 9.81)	**0.41**	(0.41 – 9.31)	**10.41**	(8.34 – 12.73)	33.73	< 0.001	c > a > b
A_{320} (m^{-1})	**31.1**	(12.9 – 53.7)	**48.3**	(19.7 – 106.9)	**na**	na	*n.s.*	*n.s.*	*n.s.*
DOC (mgL^{-1})	**8.71**	(4.0 – 28.0)	**7.3**	(4.2 – 11.9)	**12.5**	(6.8 – 18.3)	*n.s.*	*n.s.*	*n.s.*
CO_2 (µM)	**61.0**	(33.9 – 141.6)	**376.6**	(106.9 – 815.5)	**na**	na	39.78	< 0.001	b > a
CH_4 (µM)	**0.44**	(0.24 – 1.41)	**42.12**	(0.48 – 311.9)	**na**	na	28.05	< 0.001	b > a
SO_4^{2-} (mgL^{-1})	**0.39**	(0.05 – 12.52)	**0.37**	(0.08 – 12.47)	**2.31**	(0.74 – 12.87)	6.03	< 0.01	c > a, c > b
Fe (µgL^{-1})	**357.9**	(45.9 – 2462.3)	**141.4**	(31.6 – 512.3)	**186.4**	(53.6 – 519.7)	*n.s.*	*n.s.*	*n.s.*
Mn (µgL^{-1})	**6.86**	(1.15 – 32.40)	**8.09**	(0.61 – 30.44)	**5.52**	(1.51 – 47.82)	*n.s.*	*n.s.*	*n.s.*
TP (µgL^{-1})	**53.7**	(15.3 – 237.3)	**184.1**	(48.1 – 431.8)	**14.69**	(5.2 – 65.3)	30.53	< 0.001	b > a > c
TN (µgL^{-1})	**409**	(228 – 2899)	**360**	(267 – 496)	**530**	(208 – 804)	*n.s.*	*n.s.*	*n.s.*
Chl*a* (µgL^{-1})	**5.91**	(1.97 – 14.30)	**52.50**	(7.4 – 203.4)	**1.39**	(0.46 – 4.76)	50.30	< 0.001	b > a > c
THg (ngL^{-1})	**2.12**	(0.75 – 4.35)	**3.66**	(1.38 – 8.56)	**6.50**	(3.47 – 11.16)	16.23	< 0.001	c > b > a
MeHg (ngL^{-1})	**0.14**	(0.02 – 3.56)	**0.99**	(0.13 – 3.07)	**0.33**	(0.11 – 1.24)	9.26	< 0.001	b > a; b > c
MeHg (%)	**6.7**	(2.7 – 81.9)	**27.2**	(6.4 – 78.1)	**5.1**	(1.3 – 12.9)	18.33	< 0.001	b > c, b > a

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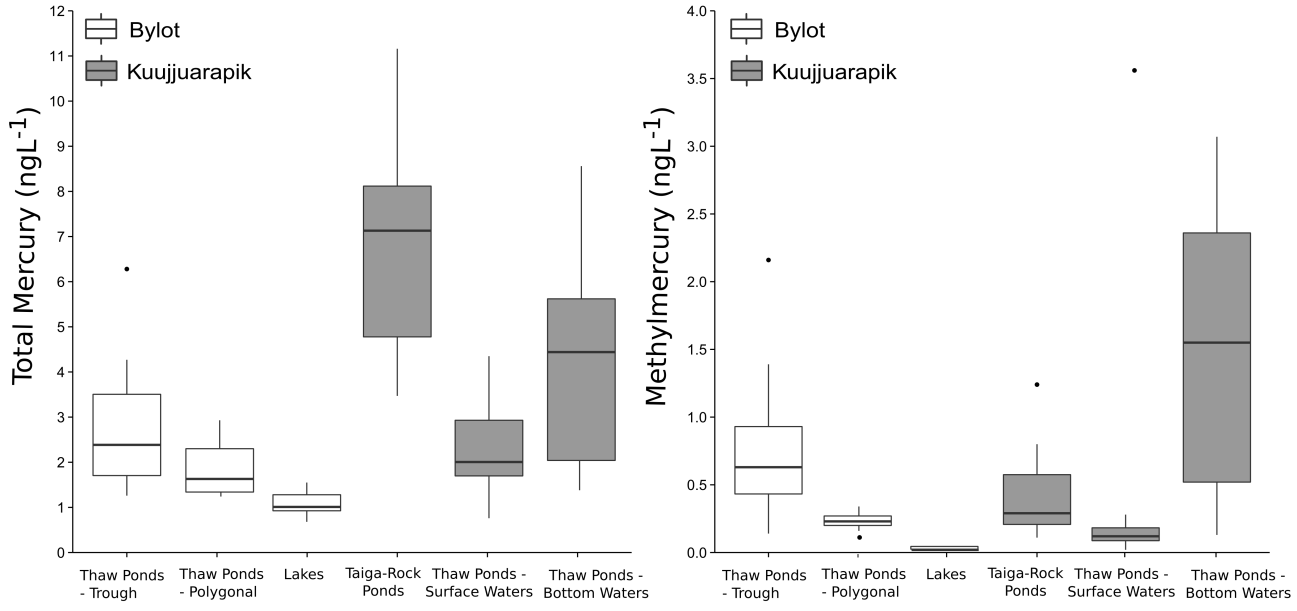

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736 **FIGURE 1**

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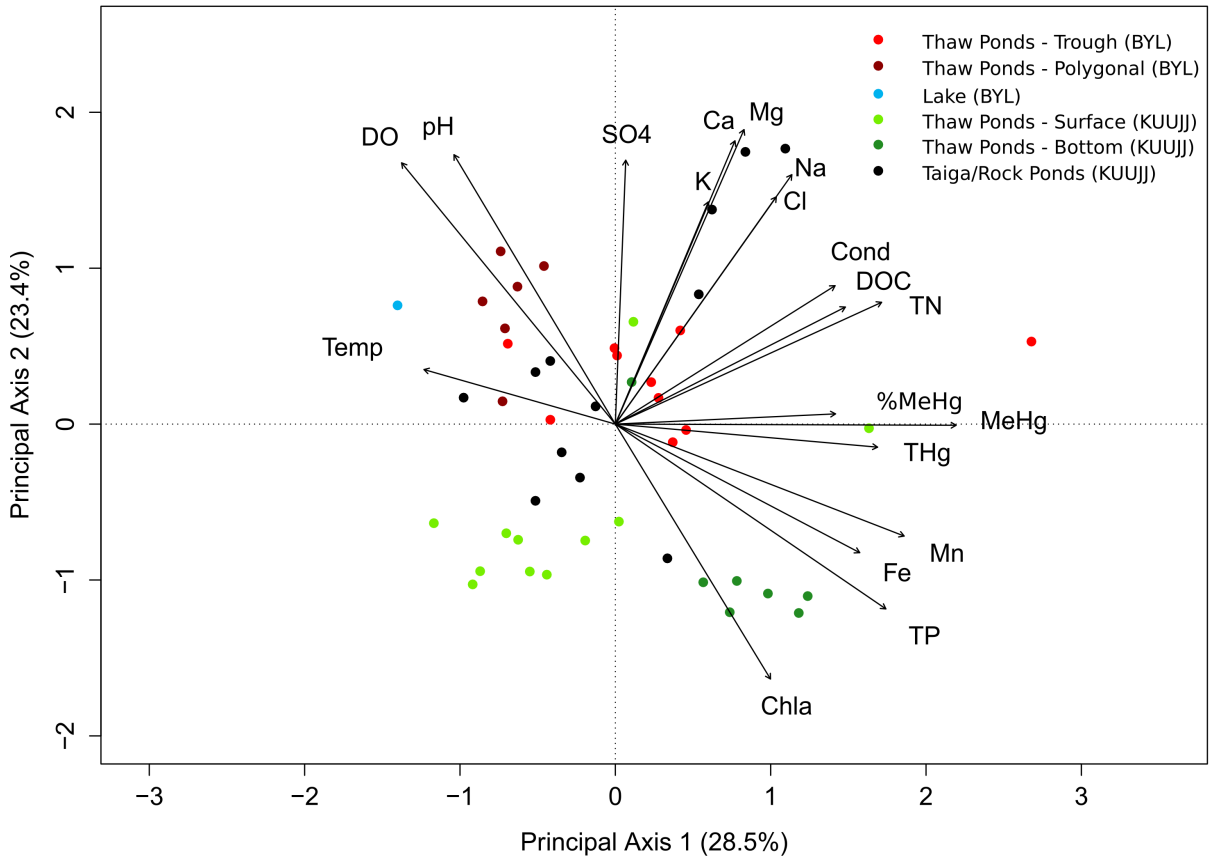

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740 **FIGURE 2**

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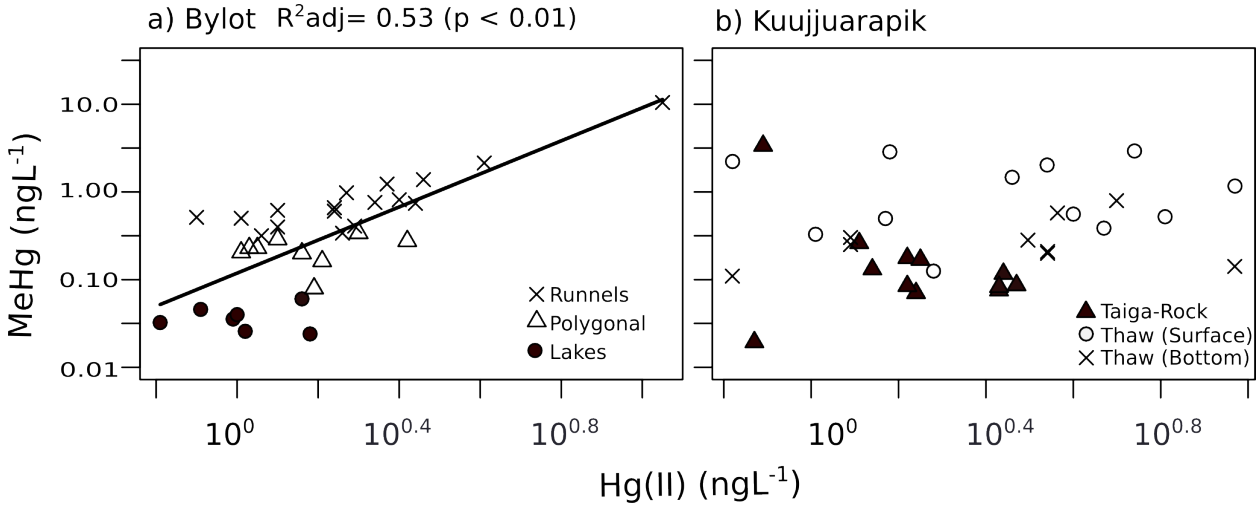

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743 **FIGURE 3**

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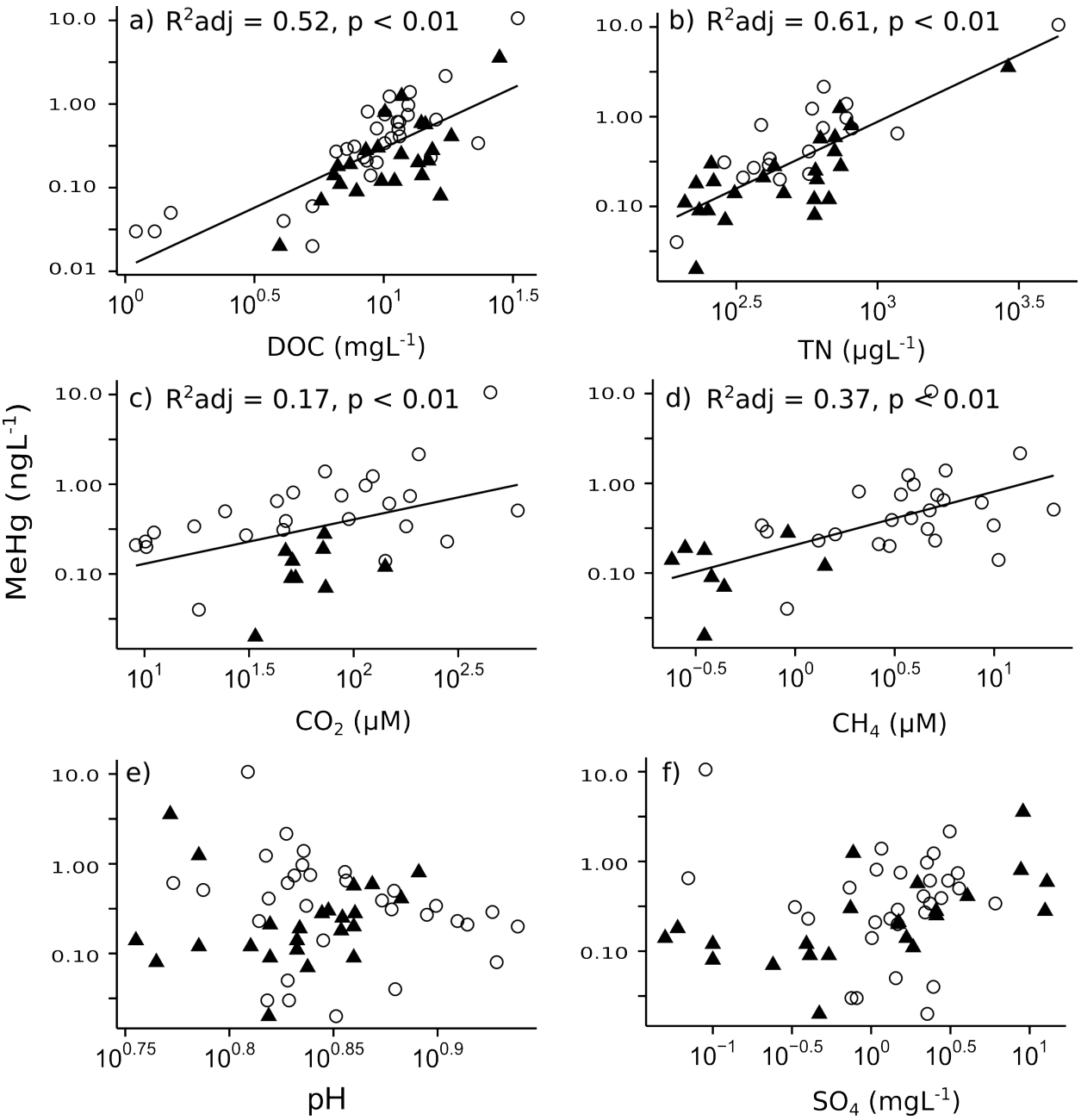

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746 **FIGURE 4**

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