Chemosphere 248 (2020) 126001

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Mercury methylation and demethylation potentials in Arctic lake sediments

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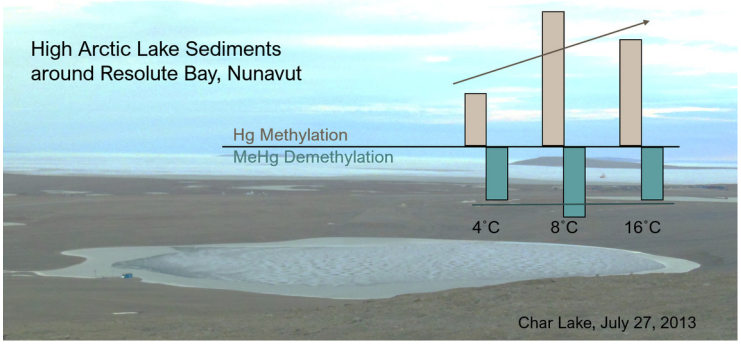
HIGHLIGHTS

- Hg methylation and demethylation potential was measured in four Arctic lake sediments.
- Sediments from the shallowest lake exhibited the greatest methylation potentials.
- Sediments from deep lakes exhibited greater demethylation potentials.
- Methylation potentials were more sensitive to warming than demethylation potentials.
- Warming Arctic lakes may favor Hg methylation over demethylation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 September 2019
Received in revised form
24 December 2019
Accepted 21 January 2020
Available online 23 January 2020

Handling Editor: Martine Leermakers

Keywords:
Mercury methylation
Lacustrine sediments
Biogeochemistry
Isotope amendment
Arctic warming

ABSTRACT

Mercury (Hg) transformations in sediments are key factors in the Hg exposure pathway for wildlife and humans yet are poorly characterized in Arctic lakes. As the Arctic is rapidly warming, it is important to understand how the rates of Hg methylation and demethylation (wich determine Hg bioavailability) change with temperature in lake sediments. Methylation and demethylation potentials were determined for littoral sediments (2.5 m water depth) in two deep and two shallow lakes in the Canadian Arctic using Hg stable isotope tracers at incubation temperatures of 4, 8, or 16 °C for 24 h. Compared to sediments from other regions, Hg methylation and demethylation potentials in these sediments are low. The maximum depth of the lake from which sediment was collected exerted a stronger influence over methylation potential than sediment Hg concentration or organic matter content; the shallowest lake had the highest Hg methylation potential. Sediments from the shallowest lake also demonstrated the greatest response to the temperature treatments, with significantly higher methylation potentials in the 8 and 16 °C treatments. Sediments from the deep lakes demonstrated greater demethylation potentials than shallow lakes. The methylmercury to total Hg ratio in sediments supported the measured transformation potentials as the lake with the greatest methylation potential had the highest ratio. This study supports previous works indicating that Hg methylation potential may increase as the Arctic warms, but

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https://doi.org/10.1016/j.chemosphere.2020.126001

demethylation potential does not respond to warming to the same degree, indicating that Hg methylation may predominate in warming Arctic sediments.

1. Introduction

Warming could lead to the release of accumulated legacy mercury (Hg) stored in Arctic watersheds and lake sediments, which have been shown to be efficient at Hg storage (Semkin et al., 2005; Schuster et al., 2018; Fahnestock et al., 2019). At present, re-released Hg is estimated to account for 60% of atmospheric Hg, compared to the 27% from primary anthropogenic emissions (Amos et al., 2013), and this is likely contributing to the increasing trend in deposition to lake sediments since the industrial revolution (Kirk et al., 2011; Engstrom et al., 2014). According to the theoretical framework for environmental Hg first articulated in Wang et al. (2010), even as global anthropogenic emissions decrease, destabilization of the cryosphere could lead to re-releases of this legacy contaminant from environmental stores is likely contributing to its higher bioavailability in ecosystems linked to these reservoirs. This means that a better understanding of the effects of climate warming on Hg bioavailability in aquatic ecosystems is critical (Chételat et al., 2015).

The main reason for fish consumption advisories around the globe is Hg (WHO/FAO, 2010), which occurs even in remote areas (AMAP 2015), including the high Arctic (Steffen et al., 2015), due to its dispersion via the atmosphere (Travnikov et al., 2017). Environmental Hg occurs in the forms Hg(0) (elemental), Hg(II) (divalent), or organomercury, typically monomethylmercury (MeHg). Elemental and divalent Hg are readily dispersed through the atmosphere (Travnikov et al., 2017) and elemental Hg has atmospheric residence times which allow for global dispersion (Selin, 2009). On Cornwallis Island in the Canadian Arctic, terrestrial watersheds have been shown to retain up to 77% of the atmospherically deposited Hg (Semkin et al., 2005). Once Hg enters aquatic or terrestrial environments it can be methylated, forming MeHg, a potent neurotoxin. Mercury methylation is a key step in the MeHg exposure pathway for wildlife and humans, as it is the form that is bioaccumulated and biomagnified within food webs. It is widely acknowledged that people living at high latitudes have greater exposure to MeHg due to their reliance on local foods and the process of biomagnification (AMAP 2015; UNEP 2013).

Mercury methylation is predominantly a microbiological process in reducing environments (Selin, 2009), involving iron- (Fleming et al., 2006) or sulfate- (Benoit et al., 1999; Gilmour et al., 2011) reducing bacteria and other microbes Desrosiers et al. (2006); Hamelin et al., (2011). Sediment Hg methylation potentials can be affected by the concentration of inorganic Hg(II) and electron donors, such as labile organic carbon, microbial inhibitors, and temperature (St. Pierre et al., 2014; King et al., 1999; Hammerschmidt and Fitzgerald, 2004). A study of tide pool sediment slurries from Allen Bay, Cornwallis Island, found that warming may increase Hg methylation, which was linked to the temperature-dependent sulfate reduction reaction (St. Pierre et al., 2014). In six southern Ontario lakes which ranged in size from 89 to 34690 ha, Hg methylation in sediments was positively related lake temperature and size, while demethylation was negatively related to lake temperature and size (Bodaly et al., 1993).

Demethylation of MeHg can occur through abiotic photodemethylation in lake water columns (Amyot et al., 2004). This transformation was measured in Char Lake, where it was found to be less effectual than in thaw pond systems where dissolved organic carbon is more concentrated, despite the reduced transparency in the thaw pond waters (Girard et al., 2016). Water column demethylation can also occur through microbially-mediated reactions attributed to a diverse group of phototrophic bacteria and sulfate reducers (Grégoire and Poulain, 2014), which may be relevant on surficial sediments in Arctic lakes. Microbial demethylation and reduction of Hg(II) to Hg(0) can be carried out via proteins encoded by the *mer* operon (Boyd and Barkay, 2012) in anaerobic (Compeau and Bartha 1984; Pak and Bartha, 1998) and aerobic (Marvin-DiPasquale and Oremland, 1998) environments.

Sediments are an important environment for MeHg transformations in aquatic systems, but it is important to note that open water environments (Braaten et al., 2014), epiphyte biofilms (Hamelin et al., 2011), and nephiloid layers (Cossa et al., 2009) are also possible sites of MeHg transformation reactions which were not included in this study.

The lakes surrounding the Polar Continental Shelf Project field station on Cornwallis Island have been the sites of pioneering studies of the MeHg bioaccumulation process, including improving understanding of factors influencing uptake of MeHg by primary producers (Chételat et al., 2018), MeHg concentrations in primary consumers (Chételat et al., 2008), and MeHg bioaccumulation across trophic levels, which differs from lake to lake (Lescord et al., 2015). The top predators, Arctic char (*Salvelinus alpinus*) are of particular interest as they contain high concentrations of MeHg and are a small but dependable component of the diet of the local community at Resolute Bay. Mercury concentrations in char differ significantly between populations over a small geographic area (Gantner et al., 2010; Barst et al., 2019). There is some evidence that the study lakes have been affected by climate change at the primary producer level (Antoniades et al., 2011; Michelutti et al., 2003), which may also affect the Hg cycling process in some lakes (Hudelson et al., 2019). Methylation and demethylation are critical links between the Hg pool in the environment and the bioaccumulation and biomagnification processes within the food web, which may be susceptible to climate change influences.

The objectives of this study were to quantify methylation and demethylation potentials under controlled settings for sediments from two shallow and two deep high Arctic lakes to better understand how Arctic warming is influencing Hg fate in cold freshwater systems. Specifically, we determined: 1) the effect of temperature on methylation and demethylation potential; and, 2) which sediment or lake characteristics influence the methylation and demethylation potential.

2. Methods

2.1. Study area, site description, and sampling

Cornwallis Island lies within the polar desert region of the Canadian Arctic Archipelago (75° 08′ N, 90° 00' W). Plant cover is sparse, and soils are rich in carbonates as the parent rock is comprised of dolomite, sandstone, and limestone formations (Cruikshank, 1971) with continuous permafrost of about 0.3–1.0 m below the soil surface, so that ground water flow is essentially nonexistent even during the annual snow melt events (Woo and

Steer, 1982). Two shallow (Meretta and Small) and two deep (Char and Resolute) lakes were selected (Table 1), all within 10 km of each other near the southwest coast of the Island 5 m–25 m asl. The lakes are ultraoligotrophic (0.47 ± 0.52 to 1.38 ± 1.18 μg/L Chl *a*, Hudelson et al., 2019), the shallow lakes are monomictic (stratified under ice cover), and ice covered for the majority of the year, but when ice cover is incomplete the shallow lakes are well mixed. The deep lakes are also monomictic but when ice cover is completely gone (summers of 2011, 2012, and 2015) they showed tendencies toward stratification due to warm air temperatures and efficient thermal heating of the surface waters (field observations).

The study lakes are heated primarily by solar radiation and, when insulating ice cover is absent or incomplete, overlying air temperatures. Lake ice extent is also sensitive to air temperatures and climate warming (Brown and Duguay, 2010), which has induced profound biological effects on many Arctic lakes by reducing ice cover (Smol et al., 2005; Mueller et al., 2009). As deep lakes tend to warm more slowly due to their larger water volume, we expected that the deeper lakes would be cooler than the shallow lakes when air temperatures were >0 °C. In this theoretical framework, shallow lakes are especially sensitive to warmer air temperatures (Antoniades et al., 2005; Schindler and Smol, 2006; Scheffer and van Nes, 2007) and therefore act as sentinels of Arctic lake conditions as climate change progresses.

For each of the lakes, three sediment cores were collected at a water depth of 2.5 m (below the depth of ice scour, the shallowest depth where all lakes contained soft sediments where cores could be collected) in late July of 2013 using a 66 mm diameter gravity corer (HTH70, Pylonex World Class Sediment Corers, Umea, Sweden). Sediment cores for each lake appeared similar. For the shallow lakes, sediment appeared black in color at 2.5–3.3 cm from the surface, but no clear color change indicative of a redox interface was seen in the cores of the deep lakes.

2.2. Experimental manipulation and sample analysis

Sediment manipulations were carried out in a darkened and cool (~4 °C) laboratory to avoid additional environmental effects. Sediment cores were subsampled vertically five times using pre-cleaned 19 mm diameter, 40 mm length Pyrex tubes, creating five replicate "mini cores" for experimental manipulation (Fig. 1). During the insertion of the sub-sampling tubes, care was taken to disturb the sediment as little as possible to preserve redox environments and to retain as much overlying water as possible, with the intention of retaining the redox interface in the upper 4 cm of sediment, where rates of Hg transformations may be at their highest for sediment environments (Regnell and Watras, 2019). These subsamples were capped with pierceable rubber septa and assigned randomly to one of five treatments. One subsample was frozen immediately without further treatment (ambient). The remaining four subsamples were each spiked with 50 μL of 85.1 pg/μL $^{202}HgCl_2$ (methylation tracer) and 100 μL 0.3274 pg/μL of $^{198}MeHgOH$ (demethylation tracer) by injection with 100 μL dedicated syringes inserted through the cap and into the surface of the sediment. Injections were approximately 5% of the expected Hg and MeHg concentrations in the sediments (4253.1 pg of $^{202}HgCl_2$ and 327.4 pg of $^{198}MeHgOH$ per spike), which minimized the experimental impact of changing the concentrations. Care was taken to slowly inject the spiking solutions over the draw depth of the syringe, distributing the spike solution over depth of the subsample. One of the spiked subsamples was then immediately frozen (T_0) and the remaining three spiked subsamples were incubated at either 4, 8, or 16 °C for 24 h. We allowed for longer incubation time than that of similar previous studies (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al., 2006; Lehnherr et al., 2012) because we anticipated these cold sediments with low amounts of organic matter would also have low reaction potentials. Our reasoning for choosing the temperature treatments followed that of St. Pierre et al. (2014) for sediments from a nearby tide pool: one treatment similar to ambient temperatures, one treatment in range with the upper temperatures observed, and one temperature well above the actual observed temperatures which would elicit a temperature effect if detectable effects were present. At the end of the incubations, subsamples were frozen to terminate the incubation (at −80 °C) and were kept frozen (≤−20 °C) during shipping and storage until lyophilization in preparation for analysis.

Methyl-Hg isotopes in sediment distillates were quantified in the Ultra-Clean Trace Elements Laboratory (UCTEL) at the University of Manitoba using US EPA method 1631 (2002) to quantify MeHg, coupled with mass spectrometry. Briefly, 0.25 g of dry sediment (except for Meretta Lake sediments, where 0.125 g of sediment was used) was distilled in a 30 mL solution of 0.2 mL of 20% KCl, 0.4 mL of 9 M H_2SO_4, and 0.4 mL of 1 M $CuSO_4$ at 140 °C for up to 4 h or until a volume of 25 mL distillate was achieved. Each

Table 1
Key characteristics for mercury (Hg) of the four lakes study on southern Cornwallis Island, Nunavut (2013–2014). In the upper panel, letters indicate statistically significant ($\alpha = 0.05$, analysis of variance with Tukey's post hoc separation), difference between lakes for the given measurement. All measurements with three or more observations per lake (N) were tested. In the lower panel (reaction potentials) letters indicate differences in the estimated marginal means by contrasts (see text for details).

Characteristic	N	Meretta	Small	Char	Resolute
Lake					
Surface area (km^2)	–	0.262	0.140	0.526	1.270
Z_{max} (m)	–	9.2	8.2	27.2	22.5
Z_{mean} (m)[a]	–	3.4	–	10.2	8.3
Summer water temp. (°C)[b]	2	[3.0–3.1]	[3.4–3.8]	[1.9–2.9]	[1.8–2.6]
Sediment					
OM (%)	3	18.1 ± 2.0[a]	7.7 ± 1.7[b]	2.3 ± 0.2[b]	7.0 ± 3.3[b]
Total Hg (ng/g dw)	3	46 ± 6[a]	8 ± 2[c]	25 ± 4[b]	7 ± 2[c]
MeHg (pg/g dw)	3	345 ± 42[a]	208 ± 113[ab]	133 ± 23[b]	55 ± 26[b]
MeHg/Total Hg (%)	3	0.1 ± 0.0[b]	0.6 ± 0.2[a]	0.1 ± 0.0[b]	0.2 ± 0.1[b]
Reaction potentials in sediment					
Methylation 4 °C (%/24 h)	3	0.6 ± 0.1[a]	2.8 ± 2.2[a]	n.d.[a]	n.d.[a]
Methylation 8 °C (%/24 h)	3	1.4 ± 0.6[a]	7.3 ± 3.7[b]	n.d.[a]	0.7 ± 1.2[a]
Methylation 16 °C (%/24 h)	3	1.2 ± 0.7[a]	4.8 ± 1.7[b]	n.d.[a]	1.9 ± 0.8[ab]
Demethylation 4 °C %/24 h)	3	n.d.[b]	−0.7 ± 0.6[ab]	−1.3 ± 0.7[a]	−1.4 ± 1.0[a]
Demethylation 8 °C (%/24 h)	3	n.d.[b]	−1.0 ± 0.2[ab]	−1.7 ± 0.9[a]	−1.8 ± 0.4[a]
Demethylation 16 °C (%/24 h)	3	−0.2 ± 0.1[a]	−0.5 ± 0.3[a]	−1.2 ± 0.5[a]	−1.4 ± 0.9[a]

[a] These are taken from those reported in (Welch, 1974). For Meretta this refers only to the larger upper basin.
[b] Water temperatures at 2.5 m below the surface, measured the day of sediment sampling and again 20 days after (July 29th and Aug. 20 th, 2013).

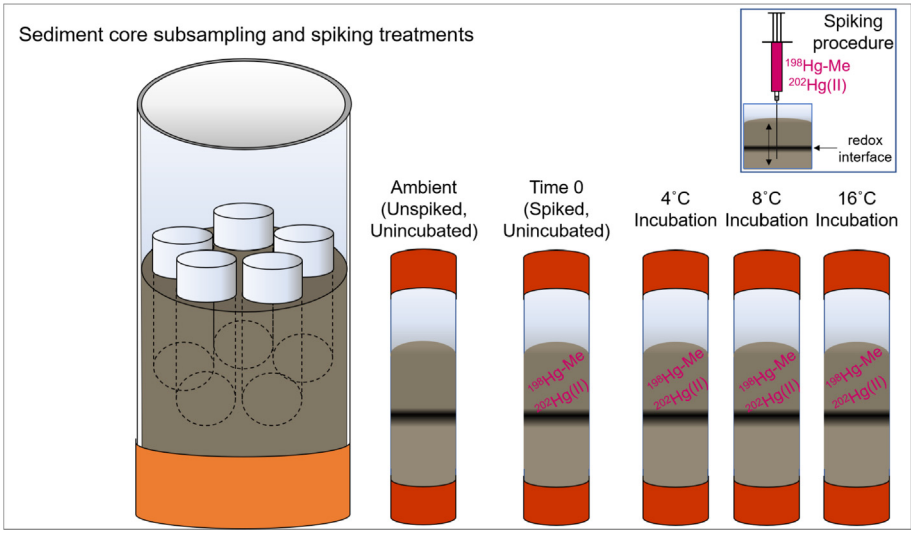

Fig. 1. Sediment core subsampling and Hg isotope spiking procedure schematic. For each of the three sediment cores from each lake, five sub-samples were generated for experimental manipulation.

distillation run included an analytical duplicate, a certified reference material, (TORT-2 from the National Research Council of Canada), and an analytical blank. Blank distillations were performed between runs to eliminate sample carry over. For the MeHg quantification, samples were buffered, pH was adjusted to 4.0 with KOH solution when necessary, 100 μL of 2.5% ascorbic acid was added to increase the reaction efficiency of ethylation of the MeHg upon addition of 40 μL of 1% sodium tetraethylborate (see US EPA method 1631). A Brooks-Rand MERX MeHg analyzer in-line with a Perkin Elmer Elan DRC II inductively coupled plasma mass-spectrometer (ICP-MS), simultaneously quantified MeHg concentration and isotopic composition (also see Wang et al., 2019). The masses (corresponding to Hg isotopes) m/z = 198, 199, 200, 201, 202, and 204 were monitored. When the MeHg concentration of the CRM did not meet the 79% recovery requirement of USEPA method 1631, results were discarded. Mass spectra generated individual peaks for each MeHg isotope, which were quantified by area and converted to pg using a run-specific MeHg standard curve. For the MeHg concentration results, the average percent recovery for the distillation runs was 89%, ranging from 79 to 114%. Similarly, the average percent difference between duplicates was 5 ± 16%.

The methylation and demethylation rate calculations were based on those of Hintelmann et al. (1995). The isotopic signature of the blank was subtracted from the isotopic signature of each sample to eliminate background variability. For each sample, ratios of the tracer isotopes (198 and 202) were calculated with ^{200}MeHg, which (after correction for spike impurities) was not experimentally altered.

To calculate demethylation rates, ambient ^{198}MeHg/^{200}MeHg was subtracted from the spiked sub-samples (T_0 and incubated) prior to conversion to picograms by multiplication by [^{200}MeHg] and conversion to dry wt. concentrations. Then, the change from T_0 during the incubation was found by subtracting the [^{198}MeHg] for the incubated samples from the [^{198}MeHg] in the T_0 samples. This change in the tracer isotope concentration was then multiplied by the [MeHg] for each sample to find the percent demethylation rate for each incubated sample. The methylation rate was calculated in a similar manner using the ^{202}MeHg/^{200}MeHg ratio. The limits of detection for each tracer isotope were calculated after the methods of Hintelmann and Evans (1997) for each core and ranged from 0.021 to 0.76 pg/g^{198}MeHg and from 0.036 to 2.65 pg/g^{202}MeHg.

Each sediment sub-sample was also analyzed for organic matter content (OM) using the loss on ignition method (Heiri et al., 2001), and total Hg (tHg) using a Milestone Direct Mercury Analyzer (US EPA method 7473) at the INRS laboratories.

2.3. Data analysis

All analyses were performed in R version 3.5.1 (R, 2018).

2.3.1. Tests for normality and independence

For each temperature treatment for each lake, we examined the medians and first and third quartiles of the methylation and demethylation potentials using boxplots. Where the quartiles overlapped 0, the value for the methylation or demethylation potential for that treatment was set to 0 for subsequent analyses (Fig. 2). We then tested the potentials for normality using the Shapiro-Wilks test at the level of treatment within lake and found that the treatments which were greater than 0 were normally distributed. We tested for independence between cores using chi-squared tests of independence. For methylation potential and demethylation potential, there was not a significant influence of core ($\chi 2$ = 282, and 348, respectively and p = 0.21 and 0.24, respectively).

2.3.2. Tests for the effect of treatment and differences between lakes

Differences between the incubation temperatures (treatments, Trt) within lakes were tested using linear models with interaction between lake and treatment. For this model, we ran pairwise contrasts on the estimated marginal means (least squares means), first for treatment, then for lake. For the contrasts, we used Tukey's post hoc tests and p value adjustment procedures. In the linear models, the interaction term (Lake*Trt) was not significant for the methylation potential or the demethylation potential, allowing us to run the contrasts for lake and for treatment with the linear model.

Understanding if there are differences between lakes and the effects of the temperature treatments on the methylation and demethylation potentials allowed us to construct models which are informed about these relationships in the next section of the analysis, where relationships between the reaction potentials and other variables in the dataset are described.

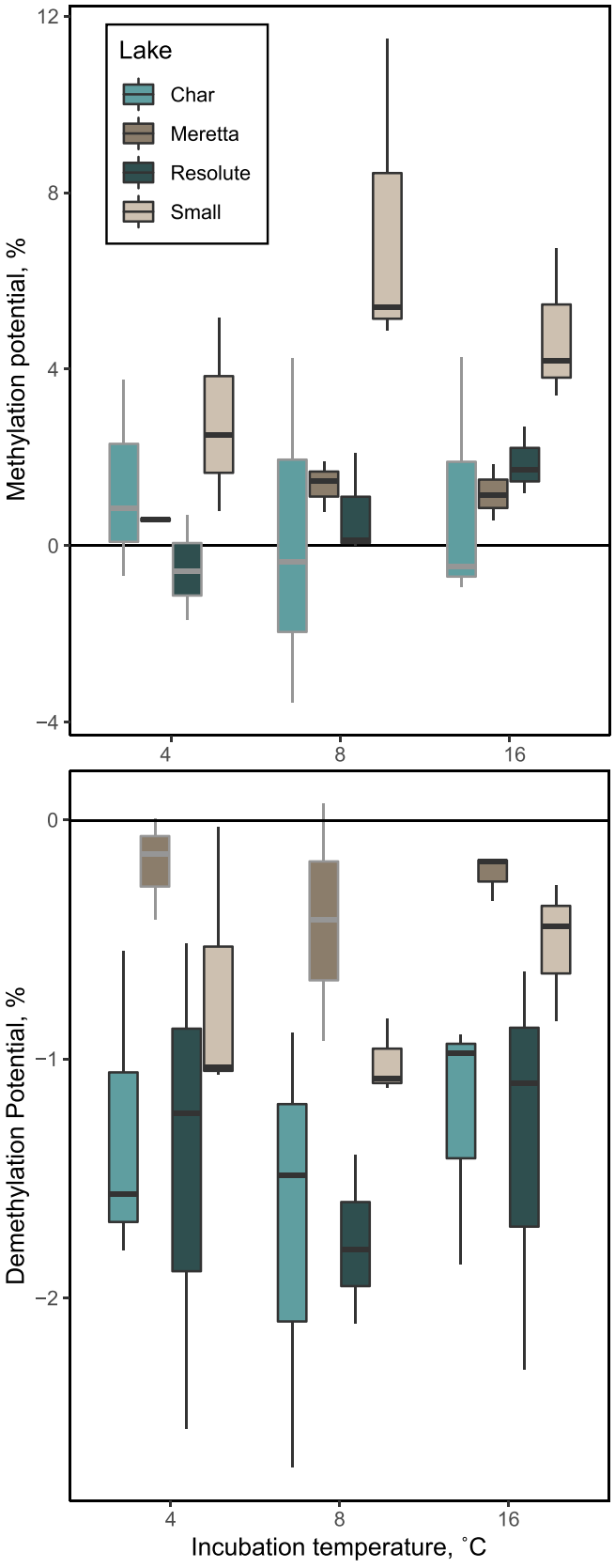

Fig. 2. Boxplots of mercury methylation (upper panel) and demethylation (lower panel) potentials over 24 h in Arctic lake sediments for each of the three incubation temperatures. Note the difference in scales between panels. Where the quartiles of the box plots overlapped 0, the reaction potential was considered 0 in subsequent analyses (outlined in gray).

We also used the estimated marginal means approach described above to determine if there were differences in [MeHg] or the MeHg/tHg between the T_0 samples and the incubated samples.

2.3.3. Models describing reaction potentials, chemical covariates, and temperature

While the contrasts of treatment and lake above indicated that only Small Lake had detectable treatment effects at alpha 0.05, it is yet possible that the small differences between the treatment means could be discerned when the chemical covariates and temperature effects are added in the model. We tested this by constructing a model for methylation potential that included the following terms: maximum lake depth (z_{max}) treatment temperature (Trt) and the interaction between these two temperatures (as per the split-plot experimental design), [tHg], and the interaction of [tHg] with % OM. Organic matter content by itself was not included due to the correlation (Pearson's R = 0.57, p = 2.5e-4) of this variable with [tHg] when all the lakes are pooled together (although there was no consistent correlation within lakes). Lake was included in these models as a random effect, since we detected significant lake effects in the split-plot models (above) but in this part of the analysis lake effects are not of interest. All variables were scaled and centered prior to model construction. The full model was:

Methylation potential = z_{max} + Trt + Trt* z_{max} + [tHg] + [tHg] *OM + Lake (random) [1].

We then sought to simplify the model by dropping extraneous variables based on the chi squared goodness of fit comparison of the Aikake's Information Criterion (AIC) when each term was removed.

To determine if there were chemical or temperature effects on the demethylation potential, we generated the model:

Demethylation potential = z_{max} + Trt + Trt*z_{max} + [MeHg] + [MeHg]*OM + Lake (random) [2].

Organic matter content was not included in the model outside of the interaction term due to significant positive correlation with [MeHg] when all lakes are included in the analysis (though note that this does not hold when lakes this relationship is tested within lake). We simplified this model using the AIC-based chi squared test method described above to determine if any single variables could be dropped from the model. However, even the null (no fixed effects) version of this model failed to converge, indicating that the variation between lakes were not sufficient to support the inclusion of the lake variable as a random intercept. We removed the random intercept but retained all the fixed variables in the demethylation potential model above. In the linear models, treatment and z_{max} were not included outside of an interaction term, since these variables are numeric but essentially act as categorical variables in the absence of the random effect. We then constructed models which included either the [MeHg] or the [MeHg] and OM interaction term and compared successively simple linear models using ANOVA with chi squared tests. Similar comparisons were made between the models which included the [MeHg] or the [MeHg] and OM interaction term.

Finally, we wanted to determine if there was a relationship between demethylation and methylation potential, as methylation provides the reactant for demethylation and therefore could be an important precursory step, although these two processes are generally thought of as separate (Barkay and Poulain, 2007; Eckley and Hintelmann, 2006) and previous research has not

demonstrated a link between the two reactions in sediment (Hintelmann et al., 2000; Hammerschmidt et al., 2006; St. Pierre et al., 2014).

We tested for a relationship between demethylation and methylation potentials using the approach described above, where the initial model was:

Demethylation potential = methylation potential + z_{max} + Trt + Trt* z_{max} + Lake (random) [2], and each variable was tested for exclusion by chi squared tests on the AIC score after the variable's removal. Methylation potential was not retained in the model, indicating that there was no relationship between the two measured potentials. The same result occurred when we tested a simplified version of the model which did not include the random intercepts, z_{max} or treatment: methylation potential was not statistically related to demethylation potential.

3. Results and discussion

3.1. Water temperatures and sediment OM

We expected the deeper Char and Resolute Lakes to be cooler than the shallow Small and Meretta Lakes at 2.5 m depth. However, their mean temperatures while air temperatures were above 0 °C were not statistically different (tested using ANOVA $\alpha = .05$, Table 1), despite Meretta waters warming to 10.7 while Char warmed only to 8.0 °C.

The percentage of OM in sediment was significantly higher in Meretta Lake (18.1 ± 2.0), which has a history of sewage inputs, than in the other lakes (2.3 ± 0.2 to 7.7 ± 1.7, Small and Char Lakes, respectively), but are in the range of previous reports for these lakes (Drevnick et al., 2010; Antoniades et al., 2011).

3.2. Mercury concentrations

The [tHg] and [MeHg] in sediments in this study were in range with previous studies of Arctic lake sediments, which include some of our study lakes (Gantner et al., 2010; Kirk et al., 2011). Total Hg concentration ranged from 5.05 to 51.75 ng/g dry wt., while [MeHg] ranged from 16 to 542 pg/g dry wt. (Resolute and Meretta Lakes, respectively for both measurements). The percentage of the amended (spike additions) MeHg of the total MeHg in the sediment ranged from 1.5 ± 0.4 to 5.4 ± 2.1% (Meretta and Resolute Lakes, respectively) and the percentage of amended tHg (MeHg + Hg(II)) ranged from 2.1 ± 0.2 to 5.5 ± 0.6 (Meretta and Small Lakes, respectively). There were significant differences between [tHg] between lakes, which ranged from 7 ± 2 to 47 ± 6 ng/g dry wt. (Resolute and Meretta Lakes, respectively) with Meretta and Char exceeding the concentrations found in Resolute and Small. Similarly, the [MeHg] in sediments were significantly different between lakes and ranged from 345 ± 42 to 55 ± 26 pg/g dry wt. (Resolute and Meretta Lakes, respectively). Significant differences in [MeHg] and MeHg/tHg were not detected between the T_0 and incubated samples for any of the lakes.

Interestingly, Small Lake had a significantly higher percentage of MeHg/tHg than the other three lakes (0.6 ± 0.2% compared to 0.2 ± 0.1% for the other three lakes combined, Table 1). This is consistent with methylation potentials for these lakes, where Small Lake highest and the other three lakes had lower and relatively similar values (see below). But is not consistent with the sediment concentrations of MeHg and tHg, as Small had lower concentrations of both than Meretta and Char Lakes.

3.3. Methylation and demethylation potentials

The methylation potentials in the sediments ranged from 0 to 7.3 ± 3.7%/day (Char and Small 8 °C treatment, respectively) with an overall mean of 1.7 ± 2.5%/day. While concentrations of the ^{198}MeHg and ^{202}MeHg were well above the method detection limit for all the samples, the change in concentration of the spike amendment (the limit of detection (Hintelmann and Evans, 1997), was below the limit of detection for some samples (Table 1). Methylation of the added ^{202}Hg(II) was not detectable in Char Lake for any of the treatments, this was also true for Resolute Lake 4 °C treatment.

The demethylation potentials ranged from non-detectable to −1.8 ± 0.4%/day (Meretta and Resolute 8 °C treatment, respectively) with an overall mean ± std. deviation of 0.9 ± 0.8%/day. For Meretta Lake sediments, no change in ^{198}MeHg was detectable in the 4 and 8 °C treatments, and thus no demethylation potentials were calculated. Experimentally added Hg(II) has been shown to be more bioavailable than ambient Hg(II) in sediments (Hintelmann et al., 2000) and so demethylation potentials in Hg isotope tracer experiments may be higher than ambient demethylation rates.

The methylation potentials we report (Table 1, Fig. 1) are on the low end of those reported by Lehnherr et al. (2012) in Ellesmere Island wetland pond sediments (median = 5%/day) and Hammerschmidt et al. (2006) for Alaskan Arctic lake sediments. In the former study, organic matter content of sediment was assumed to influence methylation potential, and in the latter study a positive relationship between organic content and methylation potential was demonstrated. The water temperatures of the pond sediments were 11.1–14.9 °C (Lehnherr et al., 2012), much warmer than the maxima in this study, which likely further increased methylation potentials in those sediments. We measured OM content using the same methods as Hammerschmidt et al. (2006), and our sediments were on the low end of those reported in that study, which ranged from 12.9 to 36.6%. Comparing the dissolved organic carbon concentrations in water between the Ellesmere wetland ponds and the lakes in this study (Hudelson et al., 2019), it is evident that the Ellesmere ponds contain much greater amounts of organic carbon in the water column, and it may be assumed that the sediments follow suit. The large difference in OM content of the sediments between these systems may partially account for the low methylation potentials in our study.

Organic matter content has been linked to methylation rate in previous studies (Regnell and Watras, 2019; Watras et al., 1995; Hall et al., 2005), as it generally stimulates microbial activity and by extention, microbial Hg methylation (Frohne et al., 2012). The form and origin of organic matter is also important, as forms which are highly accessible to heterotrophs, such as algally-derived OM (Liem-Nguyen et al., 2016), can stimulate methylation, whereas terrigenous OM may not (Bravo et al., 2017; Herrero Ortega et al., 2018). While previous studies indicate that the food webs of these lakes are benthically based and therefore may have similar sources of OM, we did not characterize the OM quality, and therefore cannot assume it is of similar character, but we recommend this characterization for future studies.

3.4. Effect of temperature treatment and lake of origin on methylation and demethylation potentials

The Lake within treatment contrasts revealed significant differences between the lakes in methylation potential in the 8 and 16 °C treatments, but no difference in methylation potential at 4 °C (Table 1). For the 8 °C treatment, Small Lake sediments demonstrated a significantly higher methylation potential than the other lakes, which did not significantly vary. For the 16 °C treatment, Small sediments were again higher than Meretta and Char sediments but were not higher than Resolute Lake sediments. The higher methylation potentials in Small Lake are consistent with

higher MeHg/tHg percentages in sediment than the other lakes and provide support that the measured methylation potentials are accurate.

For the tests of the effect of treatment within Lake, there was no difference between temperatures for Char Lake (because all these values were non-detectable as described above), Meretta, or Resolute Lakes. For Small Lake, both the 8 and 16 °C treatments demonstrated significantly higher methylation potential than did the 4 °C, indicating that Small Lake sediments were the most responsive to temperature increases. The lack of a temperature effect on methylation potential in three of the lakes may be related to the low Hg-methylating capacity in these systems (see below).

For the demethylation potentials, we found no differences between treatments within lake ($p = 0.422$), indicating that temperature did not affect demethylation potential. There were significant differences between lakes within the 4 and 8 °C treatments but not within the 16 °C treatment. For the 4 and 8 °C treatments, Resolute and Char demonstrated greater demethylation potentials than Meretta. Small Lake was intermediate in both treatments, not being significantly different than any of the other lakes. As Small Lake had the greatest methylating potential, it suggests these processes are decoupled.

Lehnherr et al. (2012) and St. Pierre et al. (2014) report a lower median rate of demethylation potential (median ~ −1.2%/day) than methylation potential. For this study, the difference in methylation potential and the demethylation potential was calculated for each sample. The median of this difference was 0.6 ± 2.5%/day, indicating that methylation potential slightly exceeded demethylation potential. However, when Small Lake was excluded from this calculation, the magnitude of the demethylation potential in general exceeded the methylation potential with a median of −0.5 ± 1.4%/day. In these oligotrophic lake sediments, this dynamic could be attributed to the low density of the microbial community (not measured), which depresses the methylation potential, whereas the demethylation can be carried out as an abiotic or a biological reaction (Grégoire and Poulain, 2014), and therefore could be less affected by the low nutrient conditions.

3.5. Models describing reaction potentials, chemical covariates, and temperature

Simplification of the methylation potential model resulted in the Total Hg * OM and the Trt * z_{max} terms being removed, generating the model equation: Methylation potential = Intercept +0.03 Trt - 0.47 z_{max} − 0.08 [tHg] + Lake (random), (conditional $R^2 = 0.58$, residual degrees of freedom = 30). Of these variables, the intercept (which was allowed to vary for each lake) and z_{max} terms had the largest effect size and had the most significant impact (0.015 and $p = 0.009$, respectively). This result indicates that the most significant effect determining methylation potential was lake depth, which was negatively related to methylation potential. The interaction of treatment and z_{max} was not related to methylation potential, indicating that response to the treatments was similar across lakes. In this model, treatment was retained in the final model but was not significantly related to methylation potential, demonstrating that treatment temperature was influential, but its influence on methylation potential was overridden by lake-to-lake differences in sediment characteristics.

For the demethylation potential models, models which included [MeHg] had a much higher R^2 values than those with the [MeHg] and OM interaction term. There were no significant differences in fit whether the interaction between depth and treatment was included or not. While in the contrast models (above) for demethylation potential, significant differences between lakes and treatments were observed, when these variables are continuous (treatment temperature and z_{max}) they were not significant predictors of demethylation potential. Demethylation potential is therefore best predicted by sediment [MeHg], where the lower [MeHg] sediments from the deep lakes exhibited the highest demethylation potential. Demethylation potentials are highest in the deep lakes, yet there is no discernable pattern between demethylation and OM, [tHg], or [MeHg] (Table 1). This result agrees with St. Pierre et al. (2014) which did not find a significant relationship between demethylation and temperature in coastal marine sediments, and also with Lehnherr et al. (2012) which, though they did not find that demethylation potential was related to [MeHg], did find that demethylation potential was negatively related to % MeHg in pond sediments, demonstrating that demethylation is an important component of Hg biochemistry. The demethylation of Hg likely plays a large role in determining MeHg residence times in sediment, which in turn influences its availability to sediment-dwelling biota.

3.6. Interaction of methylation and demethylation processes

The model detecting an influence of Hg methylation potential on demethylation potential did not detect a statistical relationship between these two processes, whether Lake and Trt variables were included to explain additional sources of variance or not. Previous research has demonstrated that the two Hg transformation steps occur in tandem (Rodrıguez Martı;n-Doimeadios et al., 2004) but a mechanistic link between Hg methylation and demethylation, whether the reactions are microbially-mediated, or abiotic, is lacking (Grégoire and Poulain, 2014). Our results do not support a relationship between these two transformation steps in Arctic lake sediments, but this relationship should be clarified in future research.

4. Summary and implications

The Hg methylation and demethylation potentials we report are among the lowest values for Arctic sediments, reflecting the ultraoligotrophic status and cold temperatures of these polar desert lakes. Mercury methylation potential was highest in Small Lake at 8 °C and in Small and Resolute Lakes at 16 °C. The lake sediments which had the highest percentage of MeHg also exhibited the highest Hg methylation potential, and methylation potential was better explained by lake depth (which corresponds to lake temperature) than [tHg] or OM. Conversely, MeHg demethylation potential was higher in the deeper, colder lakes, where [MeHg] was lowest. This could implicate a microbial demethylation pathway for the colder lakes and an important step in the detoxification of [MeHg], but further research, such as characterization of the microbial community and quantification of *mer* operon expression, is needed to confirm this. Regardless of how the reactions are accomplished, both Hg methylation and demethylation processes appear to be influential for [MeHg] concentrations in sediments of these lakes. Our results for these four lakes combined with the results of previous studies (St. Pierre et al., 2014; Monperrus et al., 2007; Bodaly et al., 1993), demonstrate that warmer sediments will likely lead to enhanced methylation conditions but that demethylation does not demonstrate a temperature dependency. As Arctic warming progresses, the methylation process may dominate over demethylation, although the complex biogeochemistry of Hg may modulate this effect.

Interestingly, Char Lake sediments exhibited non-detectable Hg methylation potentials, and yet Arctic char from Char Lake contain the most Hg (as MeHg) of any of the lakes (Hudelson et al., 2019).

This could be due to differences in MeHg assimilation/accumulation at the base of the food chain between the lakes. Further research is needed to better characterize the bioaccumulation of MeHg between these systems to explain this finding.

Author contribution section

Experimental conceptualization was done by PED and KH. The experimental design, execution of the experiments, data acquisition, and data analysis, interpretation, and writing were performed by the first author, and the contribution of coauthors was through the provision of grant funding, guidance with chemical analyses, and provision of background information. Coauthors provided feedback for the purpose of editing and refining the manuscript

Declaration of competing interest

None.

Acknowledgements

We are deeply grateful to the many contributors to this work. Mercury isotopes were kindly provided by Dr. Carl Lamborg. Robert Currie provided feedback on the manuscript contents and helped with the incubation setup (once). Alicia Manik helped collect sediment and thermistors and introduced KH to the “Lake of Tears”. Dr. Benjamin Barst helped deploy and un-deploy thermistors and contributed several astute observations. Dr. Günter Köck is great at locating buoys 3 m under water on a windy evening. Dr. Derek Muir taught KH to drive a Zodiac and many other aspects of field work in Arctic lakes. The infrastructure provided by Polar Continental Shelf Project facilities and staff made this work possible. Kang Wang was very helpful in the UCTEL facility, both with sample analysis and data analysis. Dr. Martin Horgan provided critical statistical advice. This research was funded by the Northern Contaminants Program (Crown-Indigenous Relations and Northern Affairs Canada) to PED. ATF was supported by Natural Sciences and Engineering Research Council (NSERC) Discovery Program and Canada Research Chairs program. KH was supported by funds from the University of Windsor. Two anonymous reviewers and Drs. Doug Haffner, Jan Ciborowski, Brian Branfireun, and Chris Weisener aided with the interpretation of this work.

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