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| Journal: | Arctic Science |
| --- | --- |
| Manuscript ID | AS-2018-0022.R1 |
| Manuscript Type: | Article |
| Date Submitted by the Author: | 12-Nov-2018 |
| Complete List of Authors: | Lescord, Gretchen; Laurentian University, Boreal Ecology; University of New Brunswick, Canadian Rivers Institute and Biology Department Clayden, Meredith; University of New Brunswick, Canadian Rivers Institute and Biology Department Kidd, Karen; McMaster University, Biology; University of New Brunswick, Canadian Rivers Institute and Biology Department Kirk, Jane; National Water Research Institute Wang, Xiaowa; National Water Research Institute, Aquatic Contaminants Research Division O'Driscoll, Nelson; Acadia University Department of Biology Muir, Derek; Environment and Climate Change Canada, Aquatic Contaminants Research Division |
| Keyword: | Sulfate, food webs, methylmercury, oligotrophic, bioaccumulation |
| Is the invited manuscript for consideration in a Special Issue?: | Not applicable (regular submission) |
Assessing the utility of sulfur isotope values for understanding mercury concentrations in water and biota from high Arctic lakes

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Abstract:

Methylmercury (MeHg) biomagnifies through aquatic food webs resulting in elevated concentrations in fish globally. Stable carbon and nitrogen isotopes are frequently used to determine dietary sources of MeHg and to model its biomagnification. However, given the strong links between MeHg and sulfur cycling, we investigated whether sulfur isotopes (δ34S) would improve our understanding of MeHg concentrations ([MeHg]) in Arctic lacustrine food webs. Delta34S values and total mercury (THg) or MeHg were measured in water, sediments and biota from 6 lakes near Resolute Bay, Nunavut. In two lakes impacted by historical eutrophication, aqueous sulfate δ34S was ~8‰ more positive than sedimentary δ34S, suggestive of bacterial sulfate-reduction in the sediment. In addition, aqueous δ34S showed a significant positive relationship with [MeHg] across lakes. Within taxa across lakes, [THg] in Arctic char muscle and [MeHg] in their main prey, chironomids, were positively related to their δ34S values across lakes, but inconsistent relationships were found across entire food webs among lakes. Across lakes, nitrogen isotopes were better predictors of biotic [THg] and [MeHg] than δ34S within this dataset. Our results show significant linkages between Hg and S biogeochemistry in high Arctic lakes which is an important consideration given anticipated climate-mediated changes in nutrient cycling.

Key words: Sulfate, food webs, methylmercury, oligotrophic, bioaccumulation
1. Introduction:

Methylmercury (MeHg) is a neurotoxin and has been considered a contaminant of concern in Arctic aquatic systems for many years (e.g., Chételat et al. 2015). Due to its tendency to bioaccumulate in biota and biomagnify through food webs, MeHg has been detected in Arctic char (Salvelinus alpinus, herein referred to as char), the top predator and only fish species in remote high Arctic lakes, sometimes at concentrations in excess of governmental guidelines for safe consumption (e.g., 0.5 ppm, Health Canada 2002; Gantner et al. 2010; Lescord et al. 2015a). These char are an important subsistence food for members of Inuit communities across the Canadian Arctic and a better understanding of [MeHg] in these fish and the food webs that support them is therefore vital (Muir et al. 2009; Lescord et al. 2015a). However, Hg cycling in Arctic lakes is complex and many biological and biogeochemical processes affect its eventual uptake into organisms and biomagnification through food webs. Mercury in Arctic systems is a largely result of long-range atmospheric transport of elemental and inorganic Hg (Hg(II)) from distant sources; this Hg(II) is readily deposited across the Arctic (Angot et al. 2016) and can enter freshwater systems directly during annual spring melting of ice and snow-packs. Inorganic Hg can subsequently be converted to MeHg during the oxidation of organic matter by anaerobic sulfate-reducing and other anaerobic bacteria (SRBs; Gilmour et al. 2013).

The formation of MeHg is tightly linked to sulfur (S) cycling and studies in more southerly freshwater ecosystems have shown that increasing amounts of aqueous sulfate result in higher rates of bacterial Hg methylation (Gilmour et al. 1998) as well as [MeHg] in water (Myrbo et al. 2017) and biota (Sumner 2016). However, this trend is complicated by complexation of the produced MeHg with sulfides, a process known as sulfide inhibition, as this
limits bioavailability to food webs and has been linked to lower [MeHg] in water (Benoit et al. 1999; Bailey et al. 2017) and fish (Sumner 2016). Overall, far less is known about the Hg-S relationship in high Arctic freshwater ecosystems, where aqueous S concentrations can be very low, depending on local sources, when compared to those in temperate regions. Various species of Hg form strong complexes with S-containing compounds, including reduced sulfur functional groups within dissolved organic matter (DOM), which enhances DOM-facilitated transport of Hg from upstream or riparian areas to downstream sites (Haitzer et al. 2002; Paranjape and Hall 2017). Within biota, MeHg binds to the sulfur-containing amino acid cysteine in proteins, a process which partly accounts for its biomagnifying and neurotoxic characteristics (Clarkson and Magos 2006; Larose et al. 2008). Changes to the S cycle could therefore impact MeHg formation (i.e., via bacterial-sulfate reduction), uptake, and concentrations in top predator fishes and a better understanding of Hg-S relationships in aquatic systems is needed. This is particularly true in the Arctic where evidence from lacustrine sediment cores suggests that warmer temperatures have enhanced algal productivity and the sedimentation of detrital carbon, which accelerates the S cycle and fuels dissimilatory sulfate reduction and, therefore, Hg methylation (Drevnick et al. 2010; Michelutti et al. 2007). These and other climate-related changes anticipated to impact remote Arctic lakes could alter both S and Hg cycling and, therefore, uptake into the food webs supporting Arctic char (Macdonald et al. 2005; Power et al. 2012).

Stable isotope values of S in sediments and water are related to sulfate-reduction (and therefore likely MeHg formation) in both the catchment and lake system, can help delineate food web structure, and may improve our understanding of MeHg uptake in aquatic biota. More specifically, microbial sulfate (SO$_4^{2-}$) reduction in hypoxic or anoxic sediments and waters results in sedimentary S that is depleted in $^{34}$S (i.e., low in $\delta^{34}$S values) when compared to that of
water column SO$_4^{2-}$ (Canfield 2001; Proulx and Hare 2014). Furthermore, since the $\delta^{34}$S values in a predator generally reflect that of its diet (McCutchan et al. 2003), this isotope allows one to distinguish the relative importance of sediment versus open water sources of S to consumers, assuming the original compartment values are distinct (Croisetière et al. 2009). As a result, within a given ecosystem, sediment-feeding organisms can have relatively low $\delta^{34}$S values compared to those that feed on particles suspended in the water column (Proulx and Hare 2014) and $\delta^{34}$S values can identify within-lake energy sources to consumers (Croisetière et al. 2009; Karube et al. 2012).

Despite the links between Hg and S cycling, few studies have used $\delta^{34}$S to assess MeHg bioaccumulation in aquatic ecosystems. Sulfur isotopes have mainly been used to quantify marine versus freshwater-derived S in migratory fish diets (e.g. Fry and Chumchal 2011) and to determine whether these different sources of energy affect total [Hg] in Arctic lacustrine fishes (Swanson et al. 2010a, 2011). Other related studies have occurred in more southerly estuaries or temperate lakes (e.g. Ethier et al. 2008; Schmitt et al. 2011; Clayden et al. 2017), which have drastically different limnological properties when compared to high Arctic systems (e.g., higher nutrient and DOC concentrations, lower pH, see Clayden et al. 2017). In this study we used $\delta^{34}$S, along with the more commonly-used stable isotopes, nitrogen ($\delta^{15}$N, a measure of relative trophic position) and carbon ($\delta^{13}$C, a measure of littoral vs. pelagic energetic sources), to study Hg bioaccumulation and biomagnification in simple food webs of 6 high Arctic lakes. Specifically, our goals were to: 1) evaluate $\delta^{34}$S as a means of distinguishing between energy sources in the diets of food web organisms against previously-published data on $\delta^{13}$C (Lescord et al 2015a); and 2) determine whether [MeHg] was related to tissue $\delta^{34}$S in individual groups of organisms (i.e., fishes, invertebrates) and through food webs.
2. Materials & Methods

2.1. Study sites

The 6 lakes were located on Cornwallis Island in the central Canadian Arctic Archipelago near the hamlet of Resolute Bay, Nunavut, Canada; a map is provided in the Supplemental Information file (SI file; Figure SI-5). This region has a polar desert climate, with low mean annual precipitation and temperature (150 mm and -16.5°C; Antoniades et al., 2011). Detailed water chemistry and lake morphological characteristics are reported in Lescord et al. (2015a). Briefly, these lakes range in size from 39 to 130 ha and in maximum depth from 8 to 27 m, and they are ultra-oligotrophic, with mean chlorophyll-a, total phosphorus (TP), and dissolved organic carbon (DOC) concentrations ranging from 1.28 to 2.23 µg/L, 3.6 to 8.0 µg/L, and 0.5 to 1.9 mg/L, respectively. Dissolved oxygen and temperature profiles showed no thermal or oxygen stratification in the water columns of these systems (Lescord et al. 2015a). Mean pH was similar across the lakes, ranging from 7.9 to 8.1, whereas mean aqueous SO$_4^{2-}$ in surface waters were low but varied by approximately 6-fold (0.23 to 1.35 mg/L across lakes). The food webs have low biodiversity; Arctic char are the only fish species, while the benthic invertebrate community consists mainly of chironomids and the zooplankton community is dominated by copepods (Chételat and Amyot 2009). The lakes from this study (and therefore the char that reside in them) were assumed to be land-locked with no direct marine connection (Lescord et al. 2015a).

Four of the lakes are generally considered un-impacted by human activity (Char, Small, North and 9-Mile lakes), whereas the catchments of Meretta and Resolute Lakes include the Resolute Bay airport and a former military air base; from 1949 to 1998, untreated waste water from the air base was released directly into the catchment of Meretta Lake (Antoniades et al.
2011) that then flows into Resolute Lake. Although recovery from this eutrophication has occurred, these inputs affected both the chemical and microbial characteristics of Meretta Lake (Antoniades et al. 2011). Furthermore, the proximity of both Meretta and Resolute Lakes to the local airport has altered their organic contaminant profiles when compared to more remote lakes in the area (Lescord et al. 2015b; Cabrerizo-Pastor et al. 2018).

2.2. Field sampling

All field sampling was conducted between July and August of 2010 and 2011. Details of sampling for water chemistry (e.g. MeHg, total Hg (THg, all forms of Hg in a sample), nutrients, pH), biota (Arctic char, larval and adult chironomids, zooplankton) and sediments are reported in Lescord et al. (2015a). Briefly, water samples were collected weekly above the deepest part of each lake, approximately 1 m below the surface using a Niskin bottle. Larval and adult chironomids were collected by kick sweeping shore lines and aspiration from the ice surface, respectively. Periphyton scrapings were taken from littoral rocks in triplicates. Bulk zooplankton samples were collected by towing a net (80 μm mesh) for 3-5 minutes on each lake; these samples were then size filtered at <250 μm, 250-500 μm, and >500 μm. Large char (>18 cm total length) were collected using gill nets and small char (<18 cm total length) were electrofished along shorelines; these size categories of fish were kept separate for all laboratory and statistical analyses. Fish sampling was done using protocols approved by the Animal Care Committee of the University of New Brunswick (#2010/11-1D-01). For δ^{34}S analysis, water samples were collected from the surface and deep point of each lake (n = 1 replicate per lake per depth, in each of 2010 and 2011); these data were averaged across depths and years (n = 4 per lake). Samples were kept cool in the field and sulfate was extracted within 6 hours of collection at the Polar
Continental Shelf (PCSP) base by ion-exchange as barium sulfate (Carmody et al. 1998). Surface sediment samples from the Arctic lakes were taken from the top 0.5 cm slice of cores (n = 18, 3 replicates per lake in 2011) that were collected in the littoral zone of each lake as part of other studies (Lescord et al. 2015a; Lescord et al. 2015b).

2.3. Laboratory analyses

All laboratory analyses were performed on individual muscle subsamples for large char, whole body homogenates for small char, bulk zooplankton (pooled by sample date, location, and filtration size, n = 2-5 per lake) and benthic invertebrates (all in the family Chironomidae and pooled by sample date and location for adults and larva separately, n = 1-5 per lake). Biotic samples were freeze dried and hand-ground to a fine powder before all analyses.

Biotic sulfur stable isotope analysis was conducted at the Colorado Plateau Stable Isotope Laboratory (Northern Arizona University, Flagstaff, AZ, USA). For these samples (n = 157), certified reference materials (International Atomic Energy Agency IAEA S1, S2, S3, S4, S05, S06) were used and percent differences from expected values (ranging from -34.05‰ for IAES S06 to 22.67 ‰ for IAEA S2) averaged 0.82 ± 22.8% (total n = 21). Duplicate samples were also run and the average percent difference between duplicates was 4.21 ± 2.2% (n = 11). Sulfur isotopes (n = 20) and the percentage of sulfur (%S; n = 23; see Table SI-1) in sediments were measured at IsoAnalytical (Crewe, U.K.). The percent difference from certified reference materials (CRMS, International Atomic Energy Agency IA-R061, IAEA-SO-5, NBS-1577B) averaged 8.49 ± 18.2% (n = 15) and sample duplicates averaged 1.31 ± 3.42% (n = 5). Delta $^{34}$S signatures in aqueous sulfate were measured as barium sulfate at the University of Waterloo
Environmental Isotope Laboratory (Waterloo, ON, Canada; average percent difference between duplicates = 0.41±7.9%).

Procedures for δ¹³C, δ¹⁵N and Hg analyses in water, sediments and biota are reported in Lescord et al. (2015a), along with associated quality assurance measures. Briefly, stable C and N isotopes were analyzed at the Stable Isotopes in Nature Laboratory (University of New Brunswick) via Continuous Flow-Isotope Ratio Mass Spectrometry (CF-IRMS). Data on elemental content of carbon, nitrogen, and sulfur of biota and sediment samples (as percentages of dry weight) were obtained in association with stable isotope analyses for each element.

Percent recoveries of CRMs during CN isotope analysis ranged from 97.5±5.8% to 105.1±4.6% (n = 162) and duplicates were <1% different from each other.

Water samples were analyzed for THg and MeHg at the Low-Level Mercury Analytical Laboratory at the Canadian Centre for Inland Waters (CCIW, Environment Canada) following US EPA Method 245.7 and 1630 methods, respectively (EPA 1998; 2005). All chironomids and zooplankton were analysed for [MeHg] using a potassium hydroxide (KOH) digest and detected using Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS) at the Center for Analytical Research on the Environment (CARE) at Acadia University. Methyl Hg concentrations in blanks were low and consistent (average concentration = 0.01±0.09 ng/g, n = 17) and percent recoveries of CRMs were high (101.1±18.9%, n = 33). Small and large char were measured for [THg] (92-99% of which was MeHg; Lescord et al. 2015a) using a Milestone Direct Mercury Analyzer (DMA-80) at the University of New Brunswick. Blanks were also low during THg analysis (average concentration = 0.002±0.002 µg/g, n = 66) and 97.5±11.8% of CRMs were recovered (n = 108). Total [Hg] in muscle from large char were converted to whole-body equivalent concentrations as per (Peterson et al. 2005).
2.4. Statistical analyses

All statistical analyses were conducted using R v. 3.4.3 and SigmaPlot v. 11 and alpha (α) was set at 0.05 for all tests. Although zooplankton were separated by size factions (<250 μm, 250-500 μm, and >500 μm) in the field, samples were pooled for analysis due to biomass constraints. To account for potential variation in baseline δ¹⁵N values (Jardine et al. 2006), δ¹⁵N values were adjusted (δ¹⁵N_adj) for each biotic sample by subtracting the mean δ¹⁵N value of periphyton from a given lake (Lescord et al. 2015a, n = 3-5 per lake). Delta³⁴S values were not baseline-adjusted. Because elemental composition has been shown to affect MeHg accumulation in Arctic biota (Chételat et al. 2012), we also considered the percentage of S, C and N (%S, %C and %N) of biotic samples in subsequent statistical analyses.

Log₁⁰-transformed [Hg] (MeHg in invertebrates, THg in fish) were regressed against corresponding δ³⁴S values within biotic groups as well as in surface waters (MeHg and THg, separately). These relationships were tested using a linear mixed effect model (LME) through the nlme package in R (Pinheiro et al. 2018) including lake as a random factor to account for site-specific variability in the data. To compare the regression slopes of biotic [Hg] versus δ³⁴S between the 6 lake food webs, analysis of covariance (ANCOVA) models (Log₁⁰ Hg [THg (fish, whole-body estimates) and MeHg (invertebrates), dry wt.] = lake + δ³⁴S + δ³⁴S*lake) were run, using biotic Hg as the dependent variable.

To further assess how biotic Hg concentrations related to sulfur isotopes in combination with other elemental measures (δ¹⁵N_adj, δ¹³C, %N, %C, and %S), penalized regression modeling was performed. Specifically, we used the Least Angled Shrinkage and Selection Operator (LASSO) method through the R package lars (Hastie and Efron 2013), similar to Lescord et al. (2018).
Four sets of analyses were run; [Hg] in either chironomids (MeHg), zooplankton (MeHg), small char (THg), or large char (THg) were used as dependant variables with 6 elemental or isotopic predictor variables ($\delta^{15}N_{\text{adj}}$, $\delta^{13}C$, $\delta^{34}S$, %N, %C, and %S). LASSO, a form of least angle regression, performs forward selection of predictors by incrementally reducing a penalty parameter (lambda, $\lambda$), allowing more variables to enter the model. Predictors with less influence on a dependant variable retain a coefficient of zero, excluding them from the final model estimates (see Lescord et al. 2018 for full description of the LASSO method). We chose to use the LASSO method because elemental measures in this study were somewhat correlated (e.g., variance inflation factors of 1.5-27.9 in linear models) and LASSO has been shown to produce more accurate models when sample sizes are low and predictor variables are correlated compared to other linear methods (Dormann et al. 2013; Hebiri and Lederer 2013; James et al. 2013). Mallow’s Cp values, an information theory measure similar to Akaike Information Criterion (AIC), was used to select the final LASSO models; the model with the lowest Mallow’s Cp value (>2, to prevent overfitting models) was chosen (James et al. 2013). While the inclusion of a predictor variable in a final LASSO model indicates an effect on the dependent variable (i.e., [Hg] in this study), the R package selectiveInference was also used to estimate the significance of each predictor included in a given model at the corresponding level of $\lambda$. (Tibshirani et al. 2017). LASSO path plots as well as correlation matrices are included in the supplementary information (SI) file.

3. Results & Discussion

3.1. $\delta^{34}S$ values in water and sediments
Average values of $\delta^{34}\text{S}$ in sediment and aqueous $\text{SO}_4^{2-}$ ranged from -13.04 to -3.43‰ and from -10.03 to -3.10‰, respectively, and absolute differences between these compartments were not consistent across lakes (Figure 1). The values for Arctic lake sediments overlapped with those of boreal lakes (~5 to -2‰, Quebec lakes; Croisetiere et al., 2009), but not with those of coastal hemiboreal systems (9.6 to 12.5‰, Nova Scotian lakes; Clayden et al. 2017). In addition, $\delta^{34}\text{S}$ values of aqueous sulfate in the Arctic systems fell within the typical range of terrestrial biogenic and anthropogenic sulfur emissions (Wadleigh et al. 1996) and did not overlap with those from either boreal or temperate systems (~4 to 10‰ and 10.4 to 10.7‰, respectively), the latter of which more closely matched that of $\text{SO}_4^{2-}$ in precipitation (Croisetiere et al., 2009; Clayden et al., 2017). Mean annual precipitation near these temperate lakes is almost 10-fold higher than at the Arctic lakes (1332 mm versus 150 mm, respectively Zhang et al. 2010; Antoniades et al. 2011); therefore it is likely that sulfur in precipitation influences $\delta^{34}\text{S}$ values of aqueous $\text{SO}_4^{2-}$ in more southerly lakes. Differences in aqueous $\delta^{34}\text{S}$ values may also be related to differences in bedrock geology among regions (Hitchon and Krouse 1972).

In 3 of our pristine study lakes, mean $\delta^{34}\text{S}$ values in sediments were more positive than those measured in the water column (Figure 1). However, in the wastewater-impacted Meretta and Resolute Lakes, aqueous $\delta^{34}\text{S}$ values of sulfate were 8.4 and 7.9‰ more positive than sedimentary values, respectively (Figure 1). At low temperatures (i.e., 5°C), $\delta^{34}\text{S}$ values of sediments where sulfate reduction occurs are expected to be 8-14‰ lower than those of water sulfate values due to bacterial fractionation (Canfield 2001); our results may therefore indicate enhanced SRB activity in these two systems, possibly due to the historical wastewater inputs altering the bacterial communities and cycling of nutrients (Antoniades et al. 2011). Indeed, the %$S$ in the sediments were higher in Meretta and Resolute Lakes (0.19-0.30%) when compared to
three of the remote lakes (0.1-0.12%), but not 9-Mile Lake, which had sediments with >0.4% (see Table SI-1). Changes to the microbial community can alter sulfur cycling and different strains of SRB fractionate S isotopes at different rates (Wing and Halevy 2014; Bradley et al. 2016). While the anthropogenic changes to bacterial communities in Meretta have been relatively well-studied, any changes to the microbial community in Resolute Lake have not. Furthermore, the historical eutrophication of Meretta Lake may have created more favorable redox condition in its sediments, enhancing sulfate reduction (Holmer and Storkholm 2001). An increase in SRB activity may explain why [MeHg] and % MeHg were 2-6 times higher in water samples from Meretta Lake when compared to the remote lakes and to downstream Resolute Lake (see Figure 1 and Lescord et al. 2015a). While [MeHg] in fish and chironomids were not higher in Meretta or Resolute Lakes compared to the remote lakes (Lescord et al. 2015a), levels of MeHg in zooplankton from Meretta were 4-fold higher than in all other lakes (Table 1 of the Supplemental Information). This, in combination with the higher aqueous δ³⁴S values of sulfate and [MeHg], as well as more negative sediment δ³⁴S values, suggest that there could be enhanced Hg(II) methylation in Meretta Lake (Canfield 2001; Alpers et al. 2014). However, recent studies suggest that the rates and degree of fractionation of S isotopes due to SRBs vary among bacterial strains/species (Bradley et al. 2016). Little is known about SRB communities in these high Arctic lakes where aqueous sulfate concentrations are very low (i.e., 0.23 to 1.35 mg/L across lakes and highest in the unaffected Small Lake); it is therefore likely that other processes (e.g., sulfurization; Werne et al. 2008) and bacteria are also affecting S and Hg cycling, respectively, in these systems.
3.2. The use of $\delta^{34}S$ to differentiate between pelagic and benthic energy sources in Arctic lakes

Although $\delta^{13}C$ values indicated differences in the habitat use of zooplankton and chironomids in our study lakes (see Lescord et al. 2015a), there was no consistent difference in $\delta^{34}S$ values between these groups (Figure 2A) which precluded the use of isotope mixing models to assess their relative importance in the diets of Arctic char. $\Delta^{34}S$ values were also not useful in distinguishing between benthic invertebrates and zooplankton as prey for fish in temperate coastal lakes (Clayden et al. 2017). In our Arctic lakes, $\delta^{13}C$ values were more negative in pelagic zooplankton than benthic invertebrates in each lake (Figure 2B) and mixing models indicated that most or all of the carbon ($\geq$76\% across lakes) in the diet of char in these systems is derived from benthic rather than pelagic sources (Lescord et al. 2015a), agreeing with the results of Muir et al. (2005) and Gantner et al. (2010) from the same lakes, and of Swanson et al. (2010a) for resident fishes from other coastal Arctic lakes. Our current results therefore suggest that $\delta^{13}C$ is a more useful indicator of diet sources for biota from high Arctic lakes than $\delta^{34}S$, which contrasts with results from lakes in boreal Québec, Canada (Croisetière et al., 2009) and those of estuaries in the western United States (Willacker et al. 2017). Overall, far less is known about how $\delta^{34}S$ values respond to changes in S cycling and biogeochemical conditions when compared to $\delta^{13}C$ and carbon cycling. It is possible that physico-chemical factors such as temperature and dissolved oxygen concentrations (and, therefore, thermal and oxic stratification patterns), which vary greatly among temperate, boreal, and Arctic regions, influence S isotope fractionation and therefore its applications to food web delineation. Indeed, these ultra-oligotrophic lakes likely do not undergo seasonal stratification, which would change the anoxic cycling of S, Hg, and other variables when compared to more southerly systems.
3.3. Relationship between $\delta^{34}$S values and Hg concentrations in Arctic water and biota

Across all 6 Arctic lakes, average [MeHg] in surface waters were positively related to the corresponding $\delta^{34}$S values of aqueous SO$_4^{2-}$ (LME p = 0.022; Figure 3), which implies that lakes with $^{34}$S-enriched SO$_4^{2-}$ had higher production of MeHg due to enhanced SRB activity using more of the $^{32}$S isotope, as discussed in section 3.1. MeHg concentrations from deep water samples, however, were not significantly related to their corresponding $\delta^{34}$S values (p =0.645 and 0.487, $r^2$ = 0.027 and 0.049, respectively; data not shown). Because of their oligotrophic nature and lack of riparian cover, these high Arctic lakes do not stratify during the summer months (Lescord et al. 2015a), resulting in less anoxia in deep waters when compared to more temperate systems (Snucins and Gunn 2000). It is possible that the relationship between $\delta^{34}$S and [MeHg] in surface (but not deep) waters is due to the influence of spring snow- and ice-melt, which are important sources of MeHg to high Arctic systems and alter SO$_4^{2-}$ concentrations and $\delta^{34}$S values in receiving waters (Loseto et al. 2004; Mörth et al. 2008; Giesler et al. 2009). Our water samples were collected after the annual spring melt so it is possible the relationship between aqueous [MeHg] and $\delta^{34}$S values of sulfate would change if samples were collected before ice-off. It is also unclear how photochemical reactions in snow or surface waters, which affect Hg retention and loss (Mann et al. 2014), may affect SO$_4^{2-}$ concentrations and $\delta^{34}$S values of spring melt-water.

Total [Hg] in water showed no significant relationship with $\delta^{34}$S values of aqueous SO$_4^{2-}$ (LME p = 0.129; Figure 3). However, this relationship is largely influenced by Meretta Lake and when removed, the negative relationship between aqueous THg concentrations and $\delta^{34}$S became significant (LME p = 0.040, $r^2$ = 0.506; not shown). Because the number of lakes examined in
this study was low, we were not able to determine whether Meretta Lake’s influential data were
indeed statistical outliers. Studies have shown that the lighter $\delta^{34}S$ of DOM complexes are
reflective of a terrestrial-based carbon source and to aerobic conditions in riparian soils and
limited S isotope fractionation by shoreline plants (Giesler et al. 2009). DOM complexes are
important transporters of Hg in aquatic systems; therefore terrestrial organic matter increases
aqueous [THg] in boreal streams and lakes presumably due to enhanced transport from riparian
areas (Teisserenc et al. 2011, 2014; Eklöf et al. 2012). The negative relationship between $\delta^{34}S$
values of sulfate and aqueous THg in the current study may therefore reflect higher Hg input
with greater terrestrial DOM. However, sulfur compounds, DOM, and Hg have complex
biogeochemical interactions (e.g., Haitzer et al. 2002; Ravichandran 2004) and further study is
warranted to understand how these processes alter $\delta^{34}S$ values, particularly in ultra-oligotrophic
Arctic systems.

Relationships between [MeHg] or [THg] and $\delta^{34}S$ values in biota varied among organisms in
these high Arctic lakes. Benthic chironomids had positive relationships between their tissue
[MeHg] and $\delta^{34}S$ (LME p = 0.008; Figure 3), which is in contrast with the negative relationships
between [MeHg] and $\delta^{34}S$ for several benthic macroinvertebrate taxa from temperate systems
(Clayden et al. 2017). However, zooplankton from these Arctic lakes showed a negative
relationship between their [MeHg] and $\delta^{34}S$ values (Figure 3D). This relationship was significant
after the removal of Meretta Lake, where large Daphnia sp. have been detected, which elevate
the MeHg composition in bulk zooplankton (Chételat and Amyot 2009). Daphnia sp. are only
found in higher-nutrient Arctic systems and likely thrive in Meretta because of the historical
anthropogenic eutrophication (Chételat and Amyot 2009; Lescord et al. 2015a).
Similar to benthic chironomids, both large and small char showed positive relationships between [THg] and δ^{34}S (LME p = 0.008 and 0.027, respectively; Figures 3E and 3F). Other fish studies showed opposing log-THg versus δ^{34}S relationships between species from the same streams (Schmitt et al., 2011), no relationships between these variables across lakes (Ethier et al., 2008; Clayden et al., 2017), or that δ^{34}S was a strong positive predictor of [THg] in fishes in estuarine wetlands (Willacker et al. 2017). In the latter study, the authors attribute the positive relationship to the influence of marine S values as well as the presumed higher rates of Hg methylation and ^{34}S enrichment due to SRB activity in impounded sites (Willacker et al. 2017).

The consistent, positive relationships between water [MeHg], invertebrate [MeHg], or fish [THg] and δ^{34}S values may also be related to SRB activity and suggest linkages between Hg and S cycling in these remote high Arctic systems. Studies examining the mechanisms behind these positive relationships are warranted and sampling of additional Arctic lakes would help determine whether the positive trends between biotic [THg] or [MeHg] and δ^{34}S found in this study occur more broadly.

The relationships between log_{10}[THg or MeHg] versus δ^{34}S values of food web organisms varied among lakes (ANCOVA: Lake* δ^{34}S interaction term p = 0.002, F = 4.240), with a positive slope in North Lake, a negative slope in Meretta Lake, and no significant slopes in the other four systems (Figure 4). These mixed relationships contrast with our previous findings in seven coastal temperate lakes, where relationships were consistently negative (Clayden et al., 2017). It is important to note that the δ^{34}S values in temperate coastal lakes were generally more positive than those presented herein (see section 3.1 for comparisons), which would alter the range in values on the x-axis assessed. However, the mixed Hg-δ^{34}S relationships herein also contrast with the strong and consistent relationships between log-THg or MeHg and δ^{15}N.
through these food webs (Lescord et al., 2015a) and other aquatic food webs worldwide (Lavoie et al., 2013). Few studies have related [Hg] to $\delta^{34}$S values in biota across a range of trophic levels and, in those that have, both the direction and strength of the relationships vary, particularly among regions. Our results from Arctic systems add to this mixed body of evidence and show that the [Hg]-$\delta^{34}$S relationships in food webs can differ between similar lake ecosystems within a relatively small geographic area (i.e., ~12 km). It is possible that various physical and chemical factors (e.g., stratification and anoxic habitat) may contribute to these differences, and more work is needed to investigate these effects. Interestingly, the two lake food webs that showed the strongest relationships between [Hg] and $\delta^{34}$S had considerably different morphology: Meretta Lake was one of the smallest (0.39 km$^2$) and shallowest lakes (max depth = 9.2 m), while Resolute Lake was the largest (1.3 km$^2$) and one of the deepest systems (14.7 m) in our dataset.

### 3.4. Multiple isotopes as predictors of Hg concentrations in Arctic biota

Overall, the predictive models showed that various combinations of isotope and elemental measures (including the commonly used $\delta^{15}$N$_{adj}$, and $\delta^{13}$C as well as $\delta^{34}$S, %N, %C, and %S) had a significant relationship with [THg] or [MeHg] in biota from these Arctic lakes. Not surprisingly, $\delta^{15}$N values were a consistent positive predictor of all biotic [Hg], though this relationship was only significant in zooplankton and large char (Table 1). In both large and small char models, the %S in biotic tissue was a positive predictor of [THg] (Table 1, Figure SI-2), which may be related to the amount of S-containing amino acids, the dominant S-containing compounds in organisms, (Schlegel 1981) as they are strong protein-based binding sites for MeHg in tissues (Peng et al. 2016; Bradley et al. 2017). In addition, [THg] or [MeHg]
concentrations were positively related to %S through the food webs of 5 lakes (linear models, p<0.001 to 0.003, r² = 0.396 - 0.894; SI file); the sixth lake, Small Lake, showed no significant relationship between [THg] or [MeHg] and %S (p = 0.130, r² = 0.162; Figure SI-4).

Interestingly, δ¹⁵N values were positively related to %S measures in each of the 6 food webs (p<0.001 to 0.003, r² = 0.375 to 0.660; Figure SI-3), implying higher S-containing amino acid content with increasing trophic level. Delta³⁴S values were identified as predictors of [MeHg] or [THg] in invertebrates and small char, though their effect was weak (i.e., coefficients were small) and varied in direction (Table 1). For example, [MeHg] in chironomids and small char were positively related to their tissue δ³⁴S, while zooplankton showed a negative relationship between the two variables (Figure 3). Other elemental measures were excluded from all models (i.e., %N; Table 1) or had mixed relationships between models. Delta¹³C values, for example, were only predictive of fish Hg, with higher [THg] in large char with more positive δ¹³C values; this suggests increased Hg uptake in individuals with more benthic feeding.

Overall, these results imply that [Hg] in Arctic biota are most strongly related to an organism’s trophic position (i.e., δ¹⁵N) but that measures of S content and δ¹³C also influence [Hg] in some groups of organisms. They further demonstrate the utility of modeling trophic interactions and contaminant transfer using multiple isotopic and elemental tracers, as they simultaneously suggest an increase in %S and [Hg] with trophic level, as well as the influence of S-cycling on Hg bioaccumulation in food webs of high Arctic lakes.

3.5. Conclusions

In this study the δ³⁴S of benthic invertebrates and zooplankton across our Arctic study lakes were not significantly different, in contrast to what has been observed in boreal lakes. As
such, tissue $\delta^{34}S$ values did not help to distinguish between dietary sulfur derived from sediments versus aqueous $SO_4^{2-}$ in these food webs. These results suggest that SRB activity is likely not the primary driver of $\delta^{34}S$ values in these ecosystems. However, $\delta^{34}S$ values were consistently and positively related to $[\text{THg}]$ or $[\text{MeHg}]$ in benthic invertebrates and fish, linking S isotope fractionation and Hg bioaccumulation. The mechanisms behind these relationships warrant further study, particularly in high Arctic systems where primary productivity is increasing (Michelutti et al. 2007) and changes to microbial S cycling have been reported (Drevnick et al. 2010).

Acknowledgements

Funding and logistical support for this study was provided by the Natural Sciences and Engineering Research Council of Canada through their Canada Research Chair (# 950-203477 and # 950-211803) and Discovery (#341960-2013 and #312237) Programs, the Northern Contaminants Program of Indigenous and Northern Affairs Canada, Environment and Climate Change Canada (Water Science and Technology Directorate, #1114181), the Stephen A. Jarislowsky Foundation, and the Polar Continental Shelf Program (#M26) in Resolute, NU. The authors sincerely thank Debbie Iqaluk, Brandy Iqaluk, Angella Mercer, Amber Gleason, Greg Lawson, Sam Edmonds, Paul Drevnick, Benjamin Barst, and Günter Köck for assistance with field work and laboratory analyses.
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Table 1: A summary of LASSO regression results of isotopic and elemental predictors of log$_{10}$ THg or MeHg concentrations in biota across six lake food webs near Resolute, Nunavut, Canada. Variables included in the models were carbon, nitrogen, and sulfur isotopic and elemental measures ($\delta^{34}$S, $\delta^{15}$N$_{adj}$, $\delta^{13}$C, %S, %N, %C). The results presented are considered the best-fit model parameters and were selected based on Mallow’s Cp values at a given level of the penalty parameter ($\lambda$).

| Dependent Variable  | n  | Mallow's Cp | Penalty ($\lambda$) | R$^2$ | Standardized coefficients | p-values |
|---------------------|----|-------------|---------------------|------|----------------------------|----------|
|                      |    |             |                     |      | $\delta^{34}$S (%o) | %S | $\delta^{15}$N$_{adj}$ (%o) | %N | $\delta^{13}$C (%o) | %C |
| Chironomids [MeHg]  | 25 | 2.83        | 1.36                | 0.10 | 0.020 | --- | 0.036 | --- | --- | --- |
| p-values            |    |             |                     |      | 0.560 | --- | 0.331 | --- | --- | --- |
| Zooplankton [MeHg]  | 24 | 3.17        | 0.71                | 0.34 | -0.079 | --- | -0.167 | --- | --- | 0.221 |
| p-values            |    |             |                     |      | 0.327 | --- | 0.044 | --- | --- | 0.017 |
| Small Char [MeHg]   | 24 | 10.23       | 0.19                | 0.59 | 0.061 | 0.061 | 0.103 | --- | -0.023 | 0.091 |
| p-values            |    |             |                     |      | 0.115 | 0.017 | 0.139 | --- | 0.406 | 0.065 |
| Large Char [THg]    | 59 | 3.17        | 1.04                | 0.52 | ---   | 0.110 | 0.171 | --- | 0.063 | --- |
| p-values            |    |             |                     |      | ---   | <0.001 | <0.001 | --- | 0.013 | --- |
Figure 1: Mean values (± one standard deviation, SD) of δ³⁴S in aqueous sulfate (SO₄²⁻) and sedimentary sulfur (S) from six lakes near Resolute Bay, Nunavut, Canada. Lakes are arranged on the y-axis in order of increasing mean SO₄²⁻ concentration in surface water (i.e., 1.35±0.22, 0.85±0.10, 0.56±0.14, 0.31±0.12, 0.71±0.09, and 0.23±0.05 mg/L, respectively; Lescord et al. 2015a) within groups (remote versus impacted). Total sulfur content in North Lake was too low to obtain δ³⁴S values. MeHg percentages and concentrations (mean ± SD) in surface waters of these lakes are also plotted (data from Lescord et al. 2015a).
Figure 2: A comparison of mean $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ values (±SD) in chironomids and zooplankton from six lakes near Resolute Bay, Nunavut, Canada. Shaded and white areas show impacted and remote lakes, respectively.
Figure 3: Relationships between log_{10} mercury concentrations (\([\text{MeHg}]\) in invertebrates, \([\text{THg}]\) in fish) and sulfur stable isotope values (\(\delta^{34}\text{S}\)) in A-B) surface waters (\([\text{MeHg}]\) and \([\text{THg}]\)), C) chironomids, D) zooplankton, E) small char, and F) large char from six lakes near Resolute Bay, Nunavut, Canada. The shaded area around regression lines represents 95% confidence intervals. Note the differences in scale on the x-axis. Data points for surface waters (A and B) represent one value taken per-lake in 2010 and 2011 for Hg and \(\delta^{34}\text{S}\) simultaneously.
Figure 4: Relationships between log$_{10}$ Hg concentrations ([MeHg] in chironomids and [THg] in fish) and $\delta^{34}$S values through food webs from six lakes near Resolute Bay, Nunavut, Canada. Note the differences in scale among lakes. Only organisms that are involved in aquatic food webs should be included in biomagnification models (Borgå et al. 2012); as such, zooplankton were not included in these analyses. Within food-web regressions including zooplankton are shown in Figure SI-6.