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Comparison of Mercury Dynamics in High Arctic Lakes

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By

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Comparison of Mercury Dynamics in High Arctic Lakes

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DECLARATION OF CO-AUTHORSHIP / PREVIOUS PUBLICATION

I. Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows:

Chapter 2 was coauthored with Paul E. Drevnick, Feiyue Wang, Deborah Armstrong, and Aaron T. Fisk. 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.

Chapter 3 was coauthored with Derek C.G. Muir, Paul E. Drevnick, Günter Köck, Deborah Iqaluk, Xiaowa Wang, Jane L. Kirk, Benjamin D. Barst, Alice Grgicak-Mannion, Rebecca Shearon, and Aaron T. Fisk. The data analysis, interpretation, and writing were performed by the first author, and the contribution of co-authors was through the provision of grant funding, experimental design, sample and data acquisition, and for AGM and RS, geospatial analysis. Coauthors provided feedback for the purpose of editing and refining the manuscript.

Chapter 4 was coauthored with Paul E Drevnick, Derek C.G. Muir, Günter Köck, Benjamin D. Barst, Niladri Basu, and Aaron T. Fisk. The key ideas, data analysis, interpretation, and writing were performed by the first author, and the contribution of coauthors was through the provision of grant funding, sample collection and some sample analyses, . Coauthors provided feedback for the purpose of editing and refining the manuscript.

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II. Previous Publication

Dissertation Chapter	Publication Title /Full Citation	Publication Status
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ABSTRACT

Arctic lakes and their watersheds are being simultaneously subjected to the deposition of atmospheric pollutants such as mercury (Hg), and warming. Once Hg enters an ecosystem, it may become methylated, greatly increasing its toxicity and reducing organisms' ability to eliminate it. Mercury is bioaccumulative and thus found at high concentrations in land-locked Arctic char (*Salvelinus alpinus*) and other top predators. In sediment, Hg methylation rate is temperature-dependent, and [Hg] in Arctic predatory fish has been correlated with trends in air temperature. Despite reductions in Hg emissions in North America and Europe, [Hg] continues to rise in some Arctic species. The purpose of this study was to better understand how climate change may influence Hg flow through Arctic lake food webs. The effect of temperature differences on Hg methylation and dynamics were examined in laboratory-based temperature manipulation experiments and by studying natural variation in temperature between shallow and deep lakes. Additionally, time-series of [Hg] in Arctic char were characterized and relationships between these time-series and climate trends were examined. The sediments of the shallow, warmer lakes demonstrate higher Hg methylation potentials than those of the cooler, deeper lakes, but differences between lakes were small, possibly due to the ultraoligotrophic nature of the sediments. Additionally, the midge larvae (Diptera: Chironomidae; which represent the bulk of the invertebrate biomass and the bulk of Arctic char diet) and Arctic Char) of the two shallow lakes exhibited lower methyl-Hg (MeHg) bioaccumulation factors than larvae and Arctic Char of the two deep lakes . The results of the analysis of time-series of [Hg] trends in Arctic char indicate that differences between the shallow and deep lakes Arctic char populations were sustained over time. Considered together, these findings indicate that while Hg methylation and MeHg demethylation influence

concentrations of MeHg in sediment, differences in the MeHg bioaccumulation appear to account for differences in [Hg] between chironomid and Arctic char in the lakes, with deeper lakes exhibiting higher bioaccumulation factors. The higher bioaccumulation ratios observed in colder lakes is likely the result of less primary production on surface sediments leading to less secondary production (chironomid biomass) and therefore less food and greater retention of MeHg by both chironomids and Arctic char. The analysis of the time-series of Arctic char [Hg] in relation to climate variables failed to reveal any single climate variable that significantly influenced all six populations. However, for three of the populations, trends were positively related to sea ice duration. and in the lake whose Arctic char had the highest [Hg], there was a positive correlation with snowfall. This is consistent with prior research demonstrating the importance of snow pack and snow melt to influx of Hg to polar desert lakes. Three of the six Arctic char populations exhibited significant declines in [Hg] over time, consistent with reduced bioaccumulation factors associated with lake warming, but in one of the lakes, interpretation of this trend is confounded by recovery from historical waste-water inputs. Taken together, the results indicate that a warming Arctic should result slightly increased accumulation of MeHg in sediments, but, paradoxically, less Hg in biota because temperature-dependent faster growth rates result in biomass increases that exceed the increased rates of Hg methylation in sediments. However, the complex biogeochemistry of Hg prevents any further interpretation or accurate prediction of future effects.

DEDICATION

I dedicate this work to my family, Robert Currie, Sol Hudelson Currie, Emilie Stahler, Mary, Austin, Anna, Addison, Jameen, William and Scott Hudelson.

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TABLE OF CONTENTS

LIST OF TABLES

Chapter 2

Chapter 3

Chapter 4

LIST OF FIGURES

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

CHAPTER 1 INTRODUCTION AND BACKGROUND

1.1 Mechanisms and Processes Determining the Fate of Mercury in Aquatic Systems

1.1.1 Chemical forms of Mercury in the Environment

Mercury (Hg) has an electron configuration (a $6s^2$ orbital subshell) that strongly resists electron donation, imparting a behavior similar to that of the noble gases. These characteristics indicate that Hg forms weak intermolecular bonds (typically covalent rather than ionic), melts at low temperatures, and volatilizes readily at room temperature, forming a monomeric gas. The behavior and reactivity of Hg in the environment is dependent on its oxidation state, which are elemental Hg^0 (0), mercurous Hg^+ (+I) and mercuric Hg^{2+} (+II). In the environment, Hg+ can form Hg_2^{2+} , which is unstable and rapidly forms Hg^{2+} and Hg^0, with Hg^0 being highly volatile and Hg^{2+} being more prevalent in aquatic systems (Boszke et al. 2002). Elemental Hg is the predominant form of Hg in the atmosphere, while Hg^{2+} is also detected and Hg^+ is essentially non-detectable (Schroeder and Munthe 1998). The most reactive environmentally relevant Hg species are Hg^{2+}, HgX^+, HgX_2, HgX_3^-, and HgX^{2-} (where $X = OH^-$, Cl^-, or Br^-), Hg^0 in the form of an aerosol (i.e., $Hg^0_{aqueous}$ in air), and Hg^{2+} bound to water-soluble organic acids (Boszke et al. 2002). Mercury readily dissolves some other metals, including gold, silver, and aluminum to form amalgams, but notably does not dissolve iron. Less reactive environmental species include mercury organic compounds such as $Hg(CN)_2$, HgS and compounds thereof, particularly in the form of humic substances, and CH_3Hg^+, or methylmercury (hereafter MeHg) and compounds thereof, including CH_3HgCl, and CH_3HgOH (Boszke et al. 2002). Methylmercury is a relatively unreactive form of Hg, yet it can be highly dynamic and can undergo bioaccumulation as well as biotransformation to more reactive forms listed above (Clarkson and Magos 2006). While exposure to inorganic forms of Hg pose human health risks, the primary concern with regards to

human Hg exposure is with the highly neurotoxic MeHg, which occurs primarily through the consumption of fish (Clarkson and Magos 2006).

Mercury is the most genotoxic naturally occurring element (Lindström et al. 2019), with a concentration of approximately 80 μg / kg in the Earth's crust (Gonzalez-Raymat et al. 2017). In bedrock, it is primarily found in the mineral form cinnabar (HgS), but is also found in minor quantities in the sulfur-bearing minerals livingstonite ($HgSb_4S_8$) and corderite ($Hg_3S_2Cl_2$) (Gonzalez-Raymat et al. 2017). Due to its chalcophilic and organophilic nature, Hg is found in high concentrations in rock formations of volcanic origin, and Hg emissions from rocks and soils has been used to detect ores and petroleum deposits (Fitzgerald and Lamborg 2013). Cinnabar is extremely insoluble in natural waters, and yet Hg is mobile in surface (i.e., terrestrial, freshwater, and marine) environments, both through weathering of cinnabar deposits and volatilization (Fitzgerald and Lamborg 2013). Mercuric mercury chemistry is largely controlled by its strong affinity for thiol groups, particularly $R\text{-}S^-$ (Clarkson and Magos 2006). Sulfide (S^{2-}) and organic carbon are the primary environmental ligands for Hg in surface environments.

1.1.2 Mercury in Aquatic Environments: A Watershed Perspective

1.1.2.1 Deposition of Mercury and Formations of Complexes with Environmental Ligands

Due to weathering and volatilization, Hg is naturally released into the Earth's atmosphere. Mercury is also released from the Earth's crust to the atmosphere (or to surface environments) via metal smelting, Hg mining, iron, steel, cement, and caustic soda (at chlor-alkali plants) manufacturing, and coal, oil, and waste combustion (Giang et al. 2015; Streets et al. 2017; 2019) When elemental Hg is in the gas phase, it is inert allowing for a long residence time in the atmosphere, but it can interact with terrestrial biomes in a variety of ways (Schroeder and

Munthe 1998). Divalent Hg and particulate bound-Hg are also found at measureable levels in the atmosphere, but their concentrations are typically lower than that of elemental Hg due to their shorter atmospheric residence times (Selin 2009). Deposition (exchange from the atmosphere to land-, sea-, snow-, or ice-scapes) can occur via wet or dry processes, after which re-emission or interactions which generate the variety of chemical species and oxidation states listed above can occur. The characteristics of the landscape, deposition route, and environmental conditions such as temperature and UV will determine the fate of Hg in each unique biome. As divalent and particulate bound-Hg are more water soluble, these forms deposit more readily than elemental Hg (Selin 2009). Atmospheric transformation between these three forms can greatly affect their depositional availability and can be facilitated by the presence of ligands in the form of sulfide, halides, hydroxyl groups, and water, all of which can be found in clouds as aerosols (Fitzgerald and Lamborg 2013). Overall, the primary sink of atmospheric elemental Hg is oxidation to divalent Hg, which precedes deposition (Selin 2009).

As land masses tend to have low Hg concentrations, terrestrial environments on a global scale act as Hg sinks with a total deposition of ~3200 Mg/ year and re-emission of 1700-2800 Mg/ year (Selin 2009). With the exception of geologically enriched areas, most Hg in terrestrial and freshwater environments is deposited as Hg(II) from the atmosphere (Selin 2009). Prompt (within days) recycling to the atmosphere may then occur, with an estimated 5 – 60 % of deposited Hg returning to the atmosphere, depending on the deposition surface (Harris et al. 2007; Steffen et al. 2002; Ariya et al. 2004). Recyling to the atmosphere is predominantly due to oxidation to elemental Hg, which can be microbially- (Brazeau et al. 2013), chemically- (Brooks et al. 2006) , or photo- (Haverstock et al. 2012) mediated.

Newly deposited Hg becomes preferentially associate with vegetation (Harris et al. 2007) or is directly taken up by vegetation (Obrist et al. 2017; Graydon et al. 2009). Forested landscapes have greater surface area than non-vegetated landscapes, which greatly increases Hg deposition to those landscapes (Driscoll et al. 2007) as well as providing additional Hg ligands in the form of organic material (Kolka et al. 2001). In terrestrial systems, much of the mercury (as Hg(II) and MeHg) is in the soil, associated with organic matter, where it binds tightly to sulfide groups (Skyllberg et al., 2003). Leaflitter is an important conduit of Hg (to soil and aquatic habitats) in forested systems, generally contributing greater amounts of Hg than dry and wet deposition directly to the soil Hg pool, although this can vary with forest type (Grigal 2002). Once in the soil, Hg can become adsorbed and remain in the soil, or, if Hg is in the aqueous phase, within the porespaces of soil (Skyllberg et al., 2003), it may be methylated, or could runoff into lower areas of a watershed (Selin 2009) in association with particulate matter or organic carbon complexes (Kolka et al. 2001; Boszke, et al. 2002).

Natural organic matter (NOM, both dissolved and particulate forms) is made up of complex molecules which include a variety of moieties and functional groups (Wang and Mulligan 2006) which can act as ligands for inorganic and organic Hg (Miller et al. 2009; Hintelmann et al. 1997). In particular, reduced sulfur moieties (sulfides and thiols) can form ionic bonds with Hg resulting in strong complexation (Ravichandran 2004). Trace metal binding sites on NOM are hydrophilic or hydrophobic acid moieties including carboxylic acids, phenols, ammonium ions, thiols, and alcohols (Ravichandran 2004). However, because Hg is a soft metal with a highly polarizable outer electron shell, it demonstrates a stronger affinity for less electronegative halides (sulfur and nitrogen) than ligands containing more electronegative oxygen (Asaduzzaman and Schreckenbach 2011). Bond dissociation energy for free Hg (II) is

highest for sulfur, followed by selenium and tellurium regardless of the type of organic molecule in which the ligands are complexed (Asaduzzaman and Schreckenbach 2011). However, MeHg has a stronger affinity for selenium than for sulfur (Sugiura et al. 1978). In oxic freshwater environments, both Hg (II) and MeHg demonstrate strong binding capacities with components of dissolved organic matter (DOM) such as humic and fulvic acids (Hintelmann et al. 1997; Miller et al. 2009). While sulfur is a minor constituent of NOM, reduced sulfur groups are a key ligand for Hg and MeHg in terrestrial and aquatic environments (Ravichandran 2004; Skyllberg and Drott 2010). In most natural waters, Hg concentrations are low relative to DOM concentrations, conditions which favor Hg-thiol bonds (Haitzer, Aiken, and Ryan 2002). Complexation with DOM facilitates the movement of Hg from soils and sediments (Wallschläger et al. 1996) into aquatic environments via runoff (Canário, Vale, and Nogueira 2008; Han et al. 2006). The composition of NOM varies widely within and between ecosystems, and that binding affinity of Hg to DOM can vary with factors such as pH and ion (such as Cl^-) concentration (Chen et al. 2013; Ravichandran 2004).

1.1.2.2 Complexation Effects on Bioavailability of Environmental Hg

As discussed, the composition and structure of NOM in natural environments varies greatly, but, the relationship between DOM and Hg bioavailability is similar across many aquatic ecosystems.

Both laboratory and field studies demonstrate that dissolved organic carbon (DOC, a way of quantifying DOM) facilitates Hg uptake, while field studies demonstrate that increased DOM or DOC is associated with Hg uptake, and while there are patterns among ecosystem types, both high DOC and low DOC systems can exhibit efficient Hg uptake resulting in higher Hg bioaccumulation or high concentrations in biota. First, a laboratory study found that Hg(II)

complexed with DOM of marine origin was up to 2.7 fold more available for methylation by marine sediment microbes than was inorganic Hg(II) (*aq*) (Mazrui et al. 2016). Dissolved organic carbon has also been shown to influence MeHg and Hg(II) uptake by diatoms even in chlorine-rich waters, where it is unlikely that MeHg complexed with DOC (Zhong and Wang 2009). Across a spectrum of DOC concentrations, bioavailability of MeHg and Hg(II) to the freshwater alga *Selenastrum capricornutum* was greatest at low DOC concentrations (Gorski et al. 2008). However, Hg(II) bioavailability to gram-negative bacteria followed a bell shaped curve as DOM increased in natural waters, indicating a threshold effect (Chiasson-Gould, Blais, and Poulain 2014). Experimental evidence suggests that DOM likely shuttles Hg(II) into bacterial cells and alters the cell wall to facilitate Hg(II) internalization (Chiasson-Gould, Blais, and Poulain 2014). In natural settings, concentrations of MeHg and total Hg increased with increasing DOC concentrations in a survey of remote Adirondack lakes which were influenced by wetland runoff (Driscoll et al. 1995). Similarly, a review of MeHg in fish in streams and lakes demonstrated that low rates of primary production and connection to wetlands were positively associated with higher MeHg levels in fish (Ward, Nislow, and Folt 2010). In areas less influenced by wetlands, a survey of 26 tundra lakes which span a large DOC gradient, DOC was found to enhance total Hg bioaccumulation by aquatic invertebrates up to concentrations of 8.6 mg C/L, but at higher DOC concentrations, bioaccumulation decreased (French et al. 2014). In estuarine food webs of the Northeast U.S.A., higher organic carbon was linked to lower MeHg bioaccumulation in fish (Taylor et al. 2019). Mesocosm studies of estuarine amphipods demonstrated a similar relationship between bioaccumulation of MeHg and DOC (Curtis et al. 2019). Across a 30˚ latitudinal gradient, Arctic lakes with high MeHg concentrations in invertebrates had either high water MeHg concentrations or high ratios of MeHg:DOC,

indicating that low DOC lakes are more sensitive to MeHg contamination (Chételat et al. 2018). Higher DOC concentrations associated with flooding enhanced Hg methylation rates (see below for more information on Hg methylation) in Swedish beaver ponds of varying ages (Herrero Ortega et al. 2018).

Additional descriptions (aromaticity, protein content) of DOM can also be predictive of fish Hg concentrations, demonstrating greater predictive power than DOC concentration alone (Lescord et al. 2018). While the nature of the relationship between DOC and Hg varies based on environmental factors, the role of DOC as a shuttle for importing Hg into the base of food webs is established from studies which directly examine bacterial or algal uptake, and from studies which link DOC or DOM to fish or invertebrate Hg levels. While it is clear that reduced sulfur groups are a critical ligand of Hg within organic matter (see section 1.1.2.1), most studies linking Hg to the base of food webs do not include direct measurements of sulfur within the organic matter or often even sulfates or sulfites in water, but rather rely on DOC or DOM measurements.

1.1.2.3 Mercury Methylation and Demethylation in Watersheds

In most freshwaters, Hg(II) is the predominant form of Hg, whereas in fish, the predominant form is MeHg. As discussed, MeHg in aquatic food webs poses the largest risk to human and wildlife health; therefore, understanding the processes preceding Hg methylation and bioconcentration is imperative. It has been established that atmospheric Hg(0) can travel great distances before being oxidized to Hg(II) and undergoes wet and dry deposition onto terrestrial and aquatic biomes. After deposition, Hg(II) can be reduced and revolatilized or become sorbed, predominantly to sulfide or thiols. Prior to and after sorption to a S group or other ligands, Hg methylation is possible. Here I will outline factors contributing to the methylation reaction.

In the environment, Hg methylation is carried out largely by sulfate- (Benoit et al. 1999; Gilmour et al. 2011) or iron-reducing (Fleming et al. 2006) bacteria as well as methanogens (Hamelin et al. 2011) in wetlands (St. Louis et al. 1994) and sediments (Hammerschmidt et al. 2006) and in biofilms (Hamelin et al. 2011). The reduction of SO_4 is a redox sensitive reaction and therefore tends to occur in low dissolved O_2 environments. However, abiotic Hg methylation in oxic sea water has also been documented (Munson et al. 2018). Sulfate reducing bacteria expressing both the *hgcA* and *hgcB* genes demonstrate Hg methylation (Parks et al. 2013). *HgcA* encodes a corrinoid iron-sulfur protein known to act as a methyl-transferase and with a similar structure to a protein which performs the same function in acetyl-CoA synthesis (Parks et al. 2013). Similar proteins are produced by methanogenic bacteria, all containing a cobalt molecule surrounded by a ring structure resembling hemoglobin (Matthews 2009). *HgcB* encodes a protein with a ferrodoxin structure capable of reducing the corrinoid structure after the methyl-transferase reaction is completed (Parks et al. 2013). The methyl (CH_3^+) group donor is likely methyl-H_4 folate (as $CH_3\cdot$ or CH_3^-), and Hg methylation then proceeds on an Hg(II) thiol complex involving either free thiols or cysteine residues (Parks et al. 2013). The reduction of Co(II) to Co(I) is then completed by the ferrodoxin protein encoded by *hgcB* (Parks et al. 2013). Since the sequencing of the *hgcAB* genes, their expression has been linked to Hg methylation across diverse environments, including on floating *Sphagnum* moss mats (as biofilm) (Yu et al. 2010), the human gut microbiome (Rothenberg et al. 2016), tropical wetland and temperate swamp soils (J. K. Schaefer et al. 2014), rice paddy soils (Liu et al. 2018), and Antarctic sea ice (Gionfriddo et al. 2016). Mesocosm experiments indicate that MeHg which originated from terrestrial or atmospheric sources bioaccumulated more readily than MeHg formed *in situ* in sediment (Jonsson et al. 2014).

Methylmercury demethylation is an important regulator on MeHg in ecosystems and can be accomplished via microbial and abiotic pathways. Microbial demethylation and subsequent reduction of Hg(II) to Hg(0) can be accomplished by proteins encoded by the *mer* operon, which can be found in a variety of aerobic microbial genomes as a chromosomal or plasmid element and is thought to be a detoxification mechanism (Boyd and Barkay 2012). Anaerobic bacteria also carry out demethylation (Compeau and Bartha 1984; Pak and Bartha 1998), but in freshwaters, the majority of bacterially mediated demethylation appears to be under oxic conditions (Lehnherr 2014). Reductive demethylation is favored at high redox conditions and high Hg concentration (Schaefer et al. 2004) while at lower redox conditions oxidative demethylation, a more ubiquitous process, has been documented (Marvin-DiPasquale and Oremland 1998). Both types of microbial demethylation are associated with elements of the *mer* operon, which is highly variable and may encode several enzymes (Boyd and Barkay 2012). Abiotic demethylation is accomplished through photodemethylation (Klapstein et al. 2018), which is thought to be the predominant abiotic demethylation pathway (Barkay and Poulain 2007), but abiotic demethylation in dark conditions has also been observed (Munson et al. 2018).

1.1.3 Mechanisms of MeHg absorption from food

Fish consumption is the primary route of Hg (predominantly as MeHg) exposure to humans, which occurs worldwide. In environmental as well as biological (i.e., within the gut) conditions (Bradley et al. 2017), Hg(II) and MeHg are bound to ligands when exposure occurs. Methylmercury in fish muscle is almost exclusively bound to cysteine (Cys) residues of proteins (Lemes and Wang 2009), which are abosorbed in the gut via L-type neutral amino acid transporters in the intestinal epithelium (Yin et al. 2008). Methylmercury-chloride also enters cells by non-specific active uptake and diffusion (Bridges and Zalups 2017). The pathway for

Hg(II) uptake is less clear, as this chemical has multiple potential absorption routes. Hoyle and Handy (2005) found that Hg(II) is taken up via voltage-gated Na^+ or Ca^{2+} channels, through Na^+K^{2+} Cl^- cotransporter, as well as, for $HgCl_2$, diffusion. The gut mucus lining has a high affinity for Hg(II) ions, which limits their uptake (Pärt and Lock 1983).
Researchers have been using the work of Bloom (1992) to assume that >95% of the Hg in predatory fish is MeHg.

1.2 Introduction to Study

Climate change is decreasing lake ice extent and increasing water temperatures and primary productivity in Arctic lakes. Simultaneously, Hg deposition across the Arctic increased. Despite reductions in Hg emissions in North America and Europe, Hg continues to rise in some Arctic species across large areas of the Arctic. "Legacy" Hg may become dynamic with increasing temperatures promoting methylation conditions. Once Hg is deposited, it may be methylated, greatly increasing its toxicity and reducing organisms' ability to eliminate it. Mercury is bioaccumulative and therefore found at high concentrations in land-locked Arctic char (*Salvelinus alpinus*) and other top predators. Because methyl-Hg is difficult for organisms to eliminate, it accumulates in biota relative to the surrounding environment (bioaccumulation) and higher trophic level organisms have higher amounts (biomagnification). In sediments, Hg methylation rate is temperature-dependent (St. Pierre et al., 2014), and Hg levels in Arctic predatory fish have been tied to trends in air temperature (Evans et al., 2013). The purpose of this study is to better understand the impacts of climate change on Hg dynamics in high Arctic lakes. This will be accomplished by 1) studying the effect of temperature on Hg methylation and demethylation bioavailability (Chapter 2) 2) lake-to-lake comparision of Hg

bioaccumulation by benthic invertebrates (Chapter 4) and 3) associating the temporal trends and among-lake variation of Hg in the top predator, Arctic char with climate variables (Chapter 3).

1.3 Polar Desert Climate and Environment

Northern ecosystems are characterized by low biodiversity, and their inhabitants are adapted to tolerate extreme cold, seasonally variable energy inputs, and oligotrophic conditions (Vincent et al., 2008). Cornwallis Island, Nunavut, Canada, is very dry and cold, with a mean annual temperature of -16.4 °C, and the average precipitation is approximately 150 mm annually (Environment Canada, 2016). June and July are the warmest and wettest months, with temperatures at 4.5 and 2.0 °C on average and the total precipitation 28.1 and 33.1 mm, respectively (1981 – 2010 normals, Environment Canada, 2016). While there is typically some snow during these months, the majority of the precipitation occurs as rain, and June, July, and August are the only months where snow accumulation is negligible. January and February are the coldest months, with average temperatures of -32.2 °C, and precipitation only 4 mm (1981 – 2010 normals, Environment Canada, 2016). The island lies within the polar desert ecozone (Cruikshank 1971), in which cold temperatures limit plant growth to the brief summer, during which "air temperatures remain far below the optimum level for life processes" (Schultz and Halpert 1995). The active layer of the underlying permafrost is approximately 0.5 m deep (Schindler et al. 1974a). Plant cover is sparse and the soils are almost ahumic but rich in carbonates due to the dolomite, sandstone, and limestone formations that make up the parent rock (Cruikshank 1971). Temperature is thought to be the main constraint on plant growth (Arkay, 1972).

The Inuktitut name for the community on Cornwallis, Qausuittuq (ᖁᑲᐅᓪᓗᖅ), translates to "place with no dawn". Solar radiation is extremely limited from the September to June solstice and from early November to early February the area experiences polar night (Schindler

et al. 1974a). Conversely, the midnight sun remains in the sky from late April to mid-August, when it dips below the horizon for the first time, after which the length of the days rapidly decreases.

In the polar desert ecozone of the high Arctic, lakes make up <2% of the landscape (Walker et al. 2005), yet they are hot spots of biological production (Williamson et al. 2009), supporting relatively dense vegetation growth compared to their almost un-vegetated catchments. The lakes of Cornwallis are classified as ultraoligotrophic, characterized by a short growing season (2 - 2.5 months of open water, if at all), limited nutrient availability, linear food web structure, low productivity (Rigler 1978) and correspondingly low sedimentation rates (Whalen and Cornwell 1985). During the initial limnological assessment of Char Lake, one of the study sites (Figure 1), phosphorus and nitrogen inputs were reportedly 0.016 and 0.314 g/m^2 annually to the lake (Schindler et al. 1974). Mean summer chlorophyll *a* concentration in Char Lake was 0.4 mg/m^3 and the annual planktonic primary production was 4.1 g C /m^2·yr (Welch and Kalff 1974). More recent studies report chlorophyll a concentrations between <0.1 and 0.6 µg/L (Michelutti et al. 2003) and 0.7 µg/L (Gantner et al. 2010a). The low rates of nutrient influx to the lake are likely due to the lack of vegetation in its catchment. By contrast Toolik Lake, an Arctic lake with a well-vegetated catchment in the North Banks region of Alaska, has annual inputs of 4.06 g TN /m^2·yr, 0.148 g TP/m^2·yr, and 136.9 g OC/m^2·yr, and chlorophyll *a* concentration is about 5 µg/L (Whalen and Cornwell 1985).

The lake ice typically thaws in late July or August, but it is not uncommon for some ice cover to persist throughout the summer (Douglas and Smol 2000); in fact, this occurred twice during this study (2013 and 2014). During the "open" season, the water is isothermal and well oxygenated (Rigler 1978). In the early 1970s, Char Lake typically froze on approximately

September 18 (Schindler et al. 1974a). Ice cover reached its maximum (2.2-2.4 m) in late May (Schindler et al. 1974a). The ice rapidly became snow covered, preventing solar radiation from reaching the lake (Schindler et al. 1974a).

The pelagic zone of the study lakes reflects the paucity of nutrients and extreme variation in solar radiation of their catchments. For instance, Char Lake has dissolved organic carbon (DOC) concentrations reported from 0.043 ± 0.06 (Lescord et al., 2015) to 0.90 mg/L (Laurion et al., 1997). The 435 ha catchment was estimated to be 7% vegetated; meanwhile 23% of the bottom area of Char lake is covered in a thick layer of mosses (Welch and Kalff, 1974). This benthic production is in part possible because of the high water clarity due to the oligotrophic nature of these lakes (Laurion et al., 1997).

Six lakes were chosen for this study (Figure 1) based on available historical data, ongoing research, and proximity to the Resolute Bay weather station and the Polar Continental Shelf Project field station (Nunavut, Canada). Char and Meretta Lakes were studied intensely during the first International Polar Year, in a study called the Char Lake Project, conducted from 1969 – 1972 (see references from Schindler et al. 1974a and 1974b, Welch and Kalff 1974). Meretta Lake received waste water from the North Base, a Canadian Department of Transport base from 1949 – 1998, through a series of ponds and streams in its watershed (Schindler et al. 1974, Douglas and Smol 2000). This resulted in an increase in benthic production and planktonic primary production, but in recent years the lake demonstrates a turn towards pre-enrichment conditions (Antoniades et al. 2011). This lake has reduced water clarity relative to the other lakes in the area, and less compact, darker sediments (field observations). Uniquely, Meretta Lake also has a population of Daphnia (Chételat & Amyot, 2009).

Small, Resolute, Amituk, and North Lakes, which have also been included in several studies in recent years (Muir, et al. 2009; Drevnick et al. 2010; Gantner et al. 2010a and 2010b; Lescord et al. 2015) are included in the study. Most importantly, these six lakes are part of a long-term monitoring study, the Char Monitoring Project, being conducted by Derek Muir, Günter Köck, and collaborators. This research group has been studying Arctic char in the study lakes since 1989.

1.4 Biology of High Arctic Lakes

The bulk of the biomass and productivity in high Arctic lakes occur on the surface of the sediments, where nutrient concentrations are enhanced by sedimentation from the water column and released from the decomposition occurring in the sediments, and the physical environment is stable (Douglas and Smol 2000; Bonilla et al. 2005; Vadenboncoeur et al. 2008; Vincent et al. 2008; Chételat et al. 2010). During the Char Lake Project, Welch and Kalff (1974) estimated that 80% of the total respiration in Char Lake is benthic. The benthic consumer population of Char Lake consists of "oligochaetes, cyclopoid and harpacticoid copepods, cladocerans, ostracods, *Mysis relicta*, aquatic mites, nematodes, and the caddisfly *Apatania zonella*", as well as 7 species of Chironomidae (Welch 1976). Chironomids have four life stages: egg, larva, pupa, and adult. Eggs are laid at the end of the adults' life, (Thorp and Covich 2010), and hatch in late summer (Welch 1976). Typically, the *Heterotrissocladius*, *Orthocladius*, and *Paracladius* genera in Char Lake have a three-year life cycle, while the *Pseudodiamesa*, *Trissocladius*, and *Lauterbornia* species have a two-year cycle (Welch 1976). At the end of the pupal stage, the pupae emerge from the sediments and swim to the surface of the lake, where they undergo their final molt and become adults. Mating occurs on the ice or near the shore from mid-July to September (Welch 1976).

A study of chironomid diets in 22 Arctic lakes and ponds, including all of the sites in this study, found that the most common items found in chironomid gut tracts were diatoms and sediment detritus, although algal filaments and invertebrates were also detected, and stable isotope data from the study indicate that most of the carbon assimilated originated in the benthos (Chételat et al. 2010), which was confirmed by a more recent study (Lescord et al. 2015). The sole species of fish inhabiting the study lakes are lacustrine (non-anadromous) Arctic char. Arctic char are long-lived, have low feeding rates, grow slowly, and do not spawn every year (MacCallum and Regier 1984). The average age of Arctic char from the study lakes is 16.9 ± 4.8 (mean ± std dev, n = 725, Char Monitoring Project, unpublished data). A recent study which included five of the six study lakes confirmed that the char consumed mostly benthic carbon as opposed to pelagic (Lescord et al. 2015). Lengthening of the food chain by cannibalism was indicated for Char and Resolute lakes (Gantner et al. 2010b).

The character of the lake sediments is determined by factors such as how much light penetrates to the sediment, whether it is within the ice scour zone (0-3 m) and the amount of nutrients in the watershed and lake waters. The bottom of Char lake was characterized as having five zones: the rocky zone (0-3 m), shallow sediment zone (3-4 m), the moss zone (3-19 m), bare depressions within the moss zone, and the deep sediment zone (19-27 m) (Welch and Kalff 1974). The bare patches within the moss zone were 0.2-0.4 m in depth and filled with "turbid or milky" fluid, which was attributed to the presence of anaerobic bacteria as the fluid was anoxic (Welch and Kalff 1974), which may bear characterisicts of a nephiloid layer, a high turbidity hotspot of elevated nutrient and natural organic matter content found in low mixing zones of lakes and oceans (Blees et al. 2014). Respiration was measured for each zone and it was determined that the thickly vegetated moss zone had the greatest respiration rate: although it

covered only 23% of the bottom area it performed 48% of the respiration ((as annual respiration over 3 years) Welch and Kalff 1974). Each zone was found to be inhabited by distinct populations of Chironomidae, with *Heterotrissocladius and Trissocladius* species dominating the deep sediment zone, while *Orthocladius Pseudodiamesa, Paracladius, and Lauterbornia* sp. were restricted to the rocky and moss zones (Welch 1974). In the last 4 years of larval life, mortality due to Arctic char predation was evident (Welch 1974).

1.5 Climate Change in the Arctic

The Arctic is experiencing well-documented unprecedented warming, leading to a cascade of events that directly impact Arctic food webs (Michelutti et al. 2007). Observations of shifts in climate patterns were first observed in the 1970s and 1980s (National Snow and Ice Data Center, 2016), when increases in surface air temperatures were first observed (Moritz et al., 2002). Since the 1980s, sea ice extent has significantly decreased across the Arctic, indicating a period of active climate warming (Markus et al., 2009). From 1982 – 2002, north of 60°N, surface temperatures increased 0.54°C per decade, while surface albedo decreased -1.4% (Wang and Key, 2003).

Data from the Environment Canada weather station near Resolute Bay supply more evidence for the warming trend, especially during the fall season. Since the weather station began recording data daily in 1955, there has been a significant increase in all average seasonal temperatures, with the greatest increase occurring in the fall season (slope = 0.063 °C/year, R^2 = 0.32, $p < 0.0001$), leading to an increase of 3.79 °C over 60 years. Snowfall during the fall season, typically the season of heaviest snowfall, has slightly but significantly increased (slope = 0.0047 cm/year, $R^2 = 0.084$, $p = 0.024$), leading to an increase in annual snowfall of 0.29 cm over 60 years; however, snow depth has significantly decreased for the winter, spring, and

summer seasons, and annual snow depth (slope = -0.149 cm/year, R^2 =0.24, $p < 0.0001$) has decreased as well. The decrease in snowpack after an increase in snowfall could be due to the slight (and not statistically significant) increases in rain during the fall and summer seasons.

As stated above, low temperatures are thought to be the main factor limiting plant growth in the Arctic (Arkay, 1972). At low temperatures, small temperature increases can have large effects on plant production and water absorption so the slight increases in temperature described here could potentially result in real increases in vegetation in the lake catchments.

1.6 Potential Effects of Climate Change on Lakes

In aquatic systems, opaque ice and snow cover inhibits photosynthetic primary producers, and longer ice-free seasons can result in greater abundance and diversity of algae (Smol et al. 2005). Algae are often the "first responders" to changing environmental conditions, as they are ecologically sensitive and omnipresent. The remains of diatoms (Class Bacillariophyceae), a diverse group of siliceous algae present in almost all aquatic ecosystems, are ideal biomonitors for environmental perturbations such as climate change (Smol and Stoermer, 2010). A study of the diatom chronology in Meretta Lake sediments revealed an increase in overall diatom diversity which closely tracked the trend of increased mean annual air temperatures in the Resolute area (Michelutti et al. 2002). In another of the study lakes, Char Lake, the diatom community has historically been dominated by benthic *Fragilaria* species, and only recently (since approximately 1987) have planktonic diatoms been detected in the diatom record, and then only to a minor degree (Michelutti et al., 2003). It is important to note the difference between the responses of algal communities in different types of water bodies. Specifically, small, shallow water bodies possess less thermal inertia due to their greater surface area to volume ratio, and therefore they more closely track climate events than larger, deeper lakes, making

them excellent bellwethers for high-resolution climate studies (Pienitz et al., 2004). The thermal inertia of deeper lakes increases their tendency towards thermal stratification, which leads to a divergence between benthic and pelagic habitats, promoting growth in the pelagic zone and inhibiting growth in the benthos (Rühland et al., 2003; Pienitz et al., 2004).

In addition to the chronology of siliceous fossils, the chitinous remains of invertebrates, particularly chironomids (Diptera: Chironomidae) are also useful as bioindicators in Arctic lakes (Smol et al., 2005), where they are one of the major constituents of the total invertebrate biomass (Namayandeh and Quinlan, 2011) and present in almost all lake types up to the extreme high Arctic (Vincent et al., 2008).

The duration of ice cover is probably one of the main factors stabilizing energy flow in Arctic lakes (Douglas and Smol 2000; Smol et al. 2005). Warmer fall seasons with less snow fall, the predominant trend of the past 25 years, will delay the formation of opaque lake ice. Lake ice forms in the autumn and begins to break up in the spring or summer, so changes in temperature during those times have the greatest influence on lake ice dynamics.

Lake ice cover responds to changes in climate, particularly during spring break up (Duguay et al. 2006). The sites chosen for this study are all relatively close together, and therefore are subjected to similar solar radiation, wind, snow cover, and air temperature conditions (all of which play an important role in determining lake water temperatures (Duguay et al. 2006)). This allows for the assumption that differences in lake water temperatures are largely due to lake-to-lake differences, and not to differing weather patterns between sites. Although the weather factors which influence freeze-up and ice-off conditions are made up of several variables, air temperatures alone can be a very reliable predictor of ice conditions

(Duguay et al. 2006), and indeed recent warming air temperatures have had dramatic effects on the mixing dynamics of lakes on Ellesmere Island (Mueller et al. 2009).

Historically, Char Lake and Meretta Lake had similar mixing regimes (monomictic), however, recent measurements reveal that Char Lake can stratify when air temperatures are very warm, as in the summer of 2011 (and possibly the summers of 2008, 1999, and 2012, when mean summer temperature was 4.4, 4.7, and 5.9 °C, respectively), leading to dimictic classification. Summer stratification could also occur in other deep lakes in the area. The thermal regime directly effects productivity and food web dynamics in nutrient-poor Arctic lakes, and is one of the most important factors shaping the ecology of those systems (Michelutti et al. 2003; Schindler and Smol 2006; Amyot and Chételat 2009). Increased primary productivity can potentially also increases the flux of carbon and other nutrients to lake sediments, a phenomenon which could be responsible for stimulation of sulfur reduction in Amituk and Char lake sediments among others (Drevnick, et al. 2010).

1.7 Atmospheric Mercury Deposition in the High Arctic

Levels of mercury (Hg) circulating in the environment have dramatically increased since the Industrial Revolution, and risk of exposure to humans and sensitive ecosystems is a concern across the Canadian Arctic (AMAP 2011). Volatilized Hg is predominantly in the elemental form (Hg^0), but can be oxidized to Hg^{+2} and Hg^{+1}, more hygroscopic forms (Ariya et al. 2004). Because Hg can be transported by air and ocean currents and by rivers, and it can persist in the atmosphere for up to two years (in the gas phase) before being deposited, emitted Hg can be deposited in remote regions such as the Arctic (Ariya et al. 2004; AMAP 2011). Emissions from the United States and Europe are declining, but emissions from Asia (responsible for 50% of global emissions) continue to increase (Selin 2009). The largest anthropogenic source of Hg to

the Canadian Arctic appears to be East Asia, followed by Europe and Russia, North America, and South Asia (Dastoor et al. 2015). Worldwide measurements of gaseous elemental Hg and studies of firn air (air bubbles trapped in ice) indicate increasing concentrations from the 1940s until the 1970s, peaking 1980s, and then decreasing to a plateau around 1996-2001 (Steffen et al. 2015). A study of particulate and reactive gas phase Hg conducted at Resolute Bay reports a decrease of 3% / year from 1983 – 1995, consistent with the worldwide decrease from anthropogenic sources (Steffen et al. 2015).

Much of the Hg deposited across terrestrial landscapes accumulates in lakes, as they are topographical focal points. In the water column, Hg can be revolitalized to the atmosphere, taken up by biota, or deposited to the sediments (AMAP 2011). In the sediments, Hg can remain in the ionic form or it can be transformed into MeHg. The methylation reaction is thought to be carried out predominantly by sulfate-reducing bacteria, but iron-reducing bacteria and phytoplankton have also been implicated and photomethylation has also been documented (Fleming et al. 2006; Barkay and Poulain 2007). Methyl mercury is not a highly water-soluble species (Goyer et al., 2000), but it has high affinity for biological molecules, including dissolved organic carbon (Wyn et al. 2010), proteins (especially to cysteine residues) (Clarkson and Magos 2006), and thus it tends to concentrate in the biological compartments of the ecosystem. In a variety of food webs, MeHg consistently biomagnifies (Campbell et al., 2005) and is toxic. The main route of exposure is through the diet (AMAP 2011). Long-lived predators at the top of the lacustrine food chain are therefore at the greatest risk for MeHg toxicity effects (Engstrom 2007). Concentrations of MeHg in fish can exceed those in surface waters by 10^6 to 10^7 fold (Sandheinrich and Wiener 2011). A close relationship exists between δ15N and MeHg concentrations in fish from the study lakes (Barst et al., 2016), likely due to the fact that MeHg

has a high affinity for protein, which is also tracked by δ15N (Campbell et al., 2005). Mercury is difficult to detoxify metabolically, and is likely associated with observed histological damage to liver tissue in Arctic char from the study sites (Barst et al., 2016).

The indigenous people of Canada have one of the highest exposures to Hg in the world because of their reliance on traditional foods (Chan and Receveur 2000). While a majority of Hg exposure occurs due to consumption of marine animals, high levels of Hg are also found in land-locked fish populations, especially when the fish are piscivorous (Chételat and Braune, 2012).

1.8 Mercury Availability and Methylation in a Warming Arctic

Although in general Arctic lakes seem less biologically complex than temperate lakes, the cycling of Hg through Arctic ecosystems is not straightforward when complex climate-related factors are considered. Concerns about Hg contamination in the Arctic are amplified when climate warming is considered. As stated previously, the majority of MeHg originates in the lake sediments, and is generated by microbial processes (Selin, 2009). As sediments warm, microbes tend to increase their metabolic rate. *Sediment Hg methylation rates increase with increasing temperatures* (King et al., 1999; Hammerschmidt et al., 2006). Also, as the water column and sediments warm, primary productivity will likely increase, resulting in greater sedimentation of detritus to the sediments and further stimulating the metabolic rate of sediment microbes, resulting in greater MeHg production (Hammerschmidt et al., 2006; Selin 2009; Drevnick et al., 2010). As the watershed weathers, legacy Hg could be released into the watershed as well, adding to the pool of dynamic Hg (Hammerschmidt and Fitzgerald, 2004). Further, as warming increases metabolic rate of microbes, it also increases metabolic rate of poikilotherms like fish and insects, which could increase their MeHg burden by increasing food intake (Dijkstra et al., 2013). There are therefore multiple ways in which continued climate

warming could affect the Hg levels in biota: increased or decreased amount of Hg (II), altered methylation, or altered bioaccumulation rates or processes, or some combination of these effects. Lake depth, which influences temperature and therefore productivity, will likely be an important differentiator in which of these effects dominate the Hg movement. As MeHg formation influences Hg availability to the food web, it is critical that we understand factors controlling this process.

While [MeHg] in sediments plays a role in determining [MeHg] in biota, it is not always correlated to [MeHg] in biota or [MeHg] in water (Buckman et al., 2019; Gantner et al., 2010a). This is due to differences in bioaccumulation processes at the base of the food web. In order to compare the bioaccumulation process between organisms within a system or between systems, factors describing bioaccumulation from water, pore water, and sediment can be calculated as ratios of [MeHg] in biota over in the appropriate substrate (Gobas, 2001). Generally, bioaccumulation rates tend to increase with latitude (Lavoie et al., 2013; Chételat et al., 2014). In summary, Arctic lakes have short food webs or chains (Vincent et al. 2008) with three trophic levels, algal primary producers, chironomid primary consumers, and Arctic char (Gantner et al. 2010b; Lescord et al. 2015). The bulk of the primary production occurs on the benthos, and the benthos is also the primary site of Hg methylation (Hammerschmidt and Fitzgerald 2004). Chironomids link the MeHg source to the biological compartment with highest MeHg concentration, Arctic char (Gantner et al. 2010b). Methylation is a biological and the reaction rate is temperature-dependent. As warming continues, there is potential for 1) increased diversity and biovolume of primary producers, 2) thermal stratification, changes in mixing dynamics, changes in ice extent, 3) enhanced methylation rates in sediments which are warmer

and richer in organic carbon, leading to 4) increased contaminant burden in the top predator, Arctic char.

1.9 Thesis objectives

The focus of this research was Hg dynamics in High Arctic lakes by specifically examining key mechanisms that influence Hg dynamics in these freshwater ecosystems. This study focused on the shallow sediment zone (Welch and Kalff 1974) of the lakes, but it is important to note that the moss zone is likely another very important environment for Hg and nutrient storage and cycling but was not examined here. Also, while Resolute and Char lakes appear to have similar sediment zones (field observations), less is known about sediment zones of Small and Meretta lakes. In Small Lake, light penetration reaches the deepest lake sediments while in Meretta Lake the decreased water clarity prevents light from reaching the bottom of the lake in the open water season (field observations).

Amounts of Hg and MeHg will be related to other factors in each lake, including total Hg and MeHg concentrations in sediment, methylation rate, and lake temperature to determine to what degree the Hg/MeHg concentrations in each compartment are linked. Deep lakes with larger watersheds are expected to have greater amounts of Hg, but warmer lakes are expected to have higher methylation rates. These factors will both contribute to the amount to Hg/MeHg in the chironomids, and their relationship is the crux of this research project.

In Chapter 2, I determined the methylation and demethylation potentials of sediments from the shallow sediment zone of each lake using stable Hg isotope incubations and a novel sediment core subsampling technique designed for compact sediments and related the potentials to lake characteristics including temperature/depth, organic matter, and tHg and MeHg concentrations. I hypothesized that warmer incubations would have increased methylation

potentials for all lake sediments, but that there would be little or no effect of temperature on demethylation potentials.

Chapter 3 statistically linked climate trends to temporal trends in Arctic char Hg concentration over time. I hypothesized that warmer, wetter conditions would uniformly affect the lakes and lead to increased Hg concentration in Arctic char. I length-adjusted the Arctic char Hg concentrations so that they were comparable between lakes and between years. Then, I found the linear trends in char Hg concentration over time for each population using regression, and grouped the populations according to these trends. I used both non-linear correlation and mixed model regression to relate the Arctic char Hg concentrations over time for each population with concurrent precipitation, temperature, wind speed, and climate oscillation measures.

With Chapter 4, I followed the biomagnification process up the base of the food chain, linking the methylation rate to the concentration of MeHg in the chironomid larvae,adults,, and Arctic char. I hypothesized that the shallow lakes would have higher bioaccumulation factors than the deeper lakes. I used bioaccumulation factors, a ratio of the MeHg concentration in biota (chironomid larvae and adults and Arctic char) and environmental media (lake water, pore water, and sediment) to describe bioaccumulation differences between the lakes. Further, I used trophic transfer factors, ratios of MeHg concentrations between predators and prey, to describe the efficiency of transfer between trophic levels.

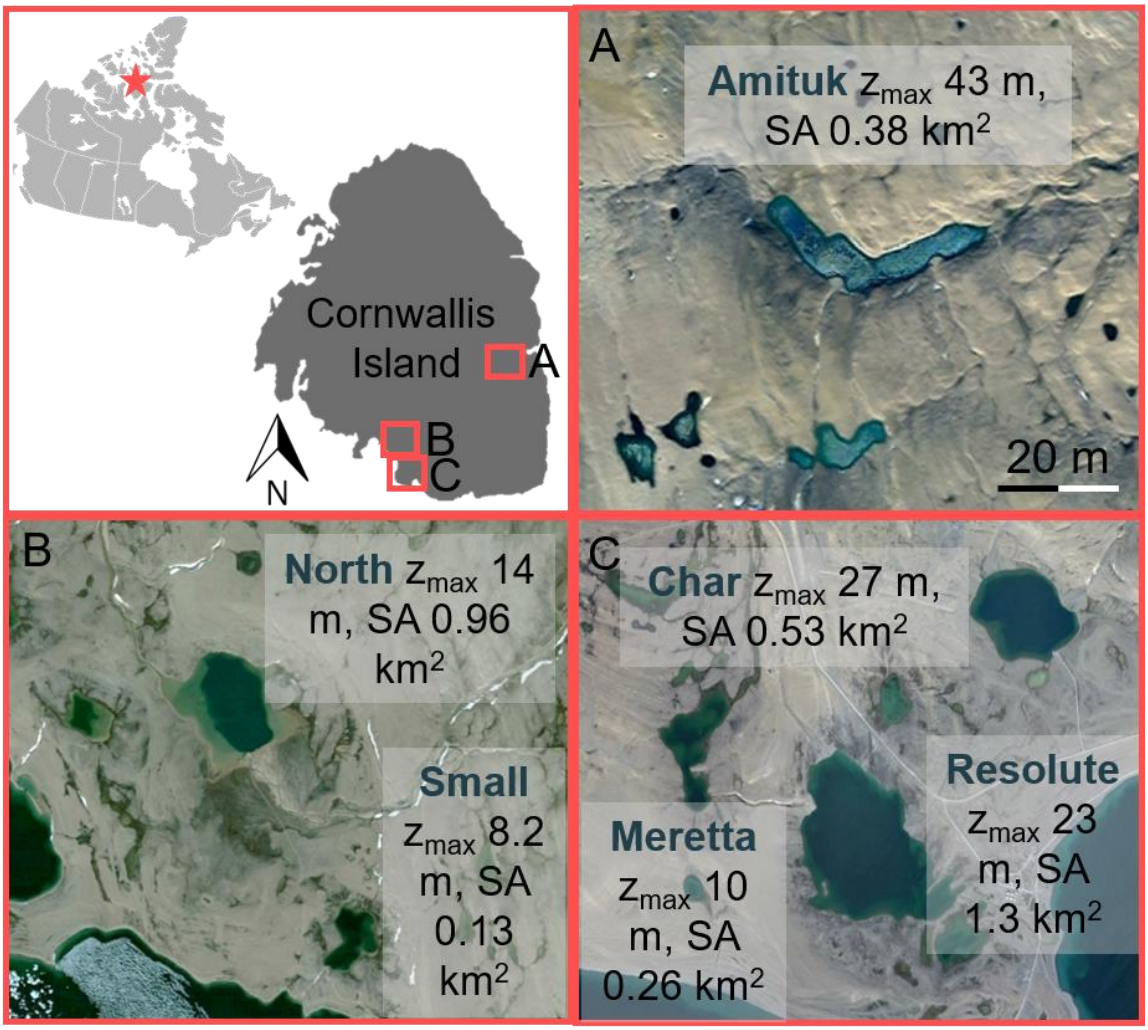

Figure 1: Map of study area depicting each lake on Cornwallis Island, NU, Canada. Scale is the same for all insets. SA equals surface area. Imagery copyright Landsat/Copernicus (A) and Maxmar Technologies (B and C), all accessed via GoogleEarth, Sep. 23rd 2019

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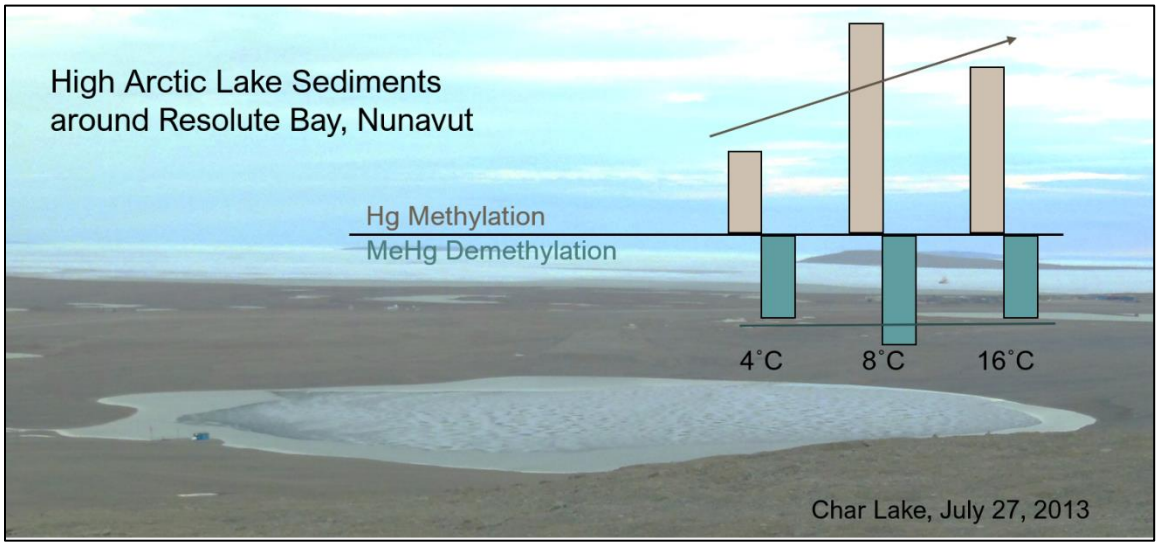
CHAPTER 2 MERCURY METHYLATION AND DEMETHYLATION POTENTIALS IN LAKE SEDIMENTS IN A WARMING ARCTIC



Graphical Abstract

2.1 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, Mierle, and Neureuther 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, 2011), 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 directly 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 photo-demethylation 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, Averty, and Pirrone 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, Douglas, and Smol 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.

2.2 Methods

2.2.1 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 to 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 to 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, Douglas, and Smol 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 7 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.

2.2.2 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 (Figure 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 hrs. 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 grams 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 9M H_2SO_4, and 0.4mL of 1M $CuSO_4$ at 140 °C for up to 4 hrs or until a volume of 25 mL distillate was achieved. Each 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 uL of 2.5% ascorbic acid was added to increase the reaction efficiency of ethylation of the MeHg upon addition of 40 uL 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, Lotter, and Lemcke, 2001), and total Hg (tHg) using a Milestone Direct Mercury Analyzer (US EPA method 7473) at the INRS laboratories.

2.2.3 Data Analysis

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

2.2.3.1 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 (Figure 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).

2.2.3.2 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.

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.

2.2.3.3 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, Keppel-Jones, and Evans 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:

$$\text{Demethylation potential} = \text{methylation potential} + z_{max} + \text{Trt} + \text{Trt}^* z_{max} + \text{Lake (random)} \quad [2],$$

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.

2.3 Results and Discussion

2.3.1 Water temperatures and sediment OM

We expected the deeper Char and Resolute Lakes to be cooler than the shallow Small and Meretta Lakes at 7 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).

2.3.2 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 – 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.

2.3.3 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, Keppel-Jones, and Evans, 2000) and so demethylation potentials in Hg isotope tracer experiments may be higher than ambient demethylation rates.

The methylation potentials we report (Table 1, Figure 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. We measured organic matter 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. The water temperatures of the wetland pond sediments were 11.1 – 14.9 °C, much warmer than the maxima in this study, which likely further increased methylation potentials in those sediments.

2.3.4 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). 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.

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 a abiotic or a biological reaction (Grégoire and Poulain 2014), and therefore could be less affected by the oligotrophic low nutrient conditions.

2.3.5 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.

2.3.6 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 (Rodríguez Martín-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.

2.3.7 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.

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CONFLICTS OF INTEREST

None.

Table 1: Key characteristics for mercury (Hg) of the four lakes 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[1]	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)[1]	--	3.4	--	10.2	8.3
Summer water temp. (°C)[2]	2	[3.0 – 3.1]	[3.4 – 3.8]	[1.9 – 2.9]	[1.8 – 2.6]
Sediment					
TOC (%)	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 hrs)	3	0.6 ± 0.1^{a}	2.8 ± 2.2^{a}	n.d.[a]	n.d.[a]
Methylation 8 °C (% / 24 hrs)	3	1.4 ± 0.6^{a}	7.3 ± 3.7^{b}	n.d.[a]	0.7 ± 1.2^{a}
Methylation 16 °C (% / 24 hrs)	3	1.2 ± 0.7^{a}	4.8 ± 1.7^{b}	n.d.[a]	1.9 ± 0.8^{ab}
Demethylation 4 °C % / 24 hrs)	3	n.d.[b]	-0.7 ± 0.6^{ab}	-1.3 ± 0.7^{a}	-1.4 ± 1.0^{a}
Demethylation 8 °C (% / 24 hrs)	3	n.d.[b]	-1.0 ± 0.2^{ab}	-1.7 ± 0.9^{a}	-1.8 ± 0.4^{a}
Demethylation 16 °C (% / 24 hrs)	3	-0.2 ± 0.1^{a}	-0.5 ± 0.3^{a}	-1.2 ± 0.5^{a}	-1.4 ± 0.9^{a}

[1]These are taken from those reported in (Welch 1974). For Meretta this refers only to the larger upper basin.

[2]water temperatures at 7 m below the surface, measured the day of sediment sampling and again 20 days after (July 29th and Aug. 20th, 2013).

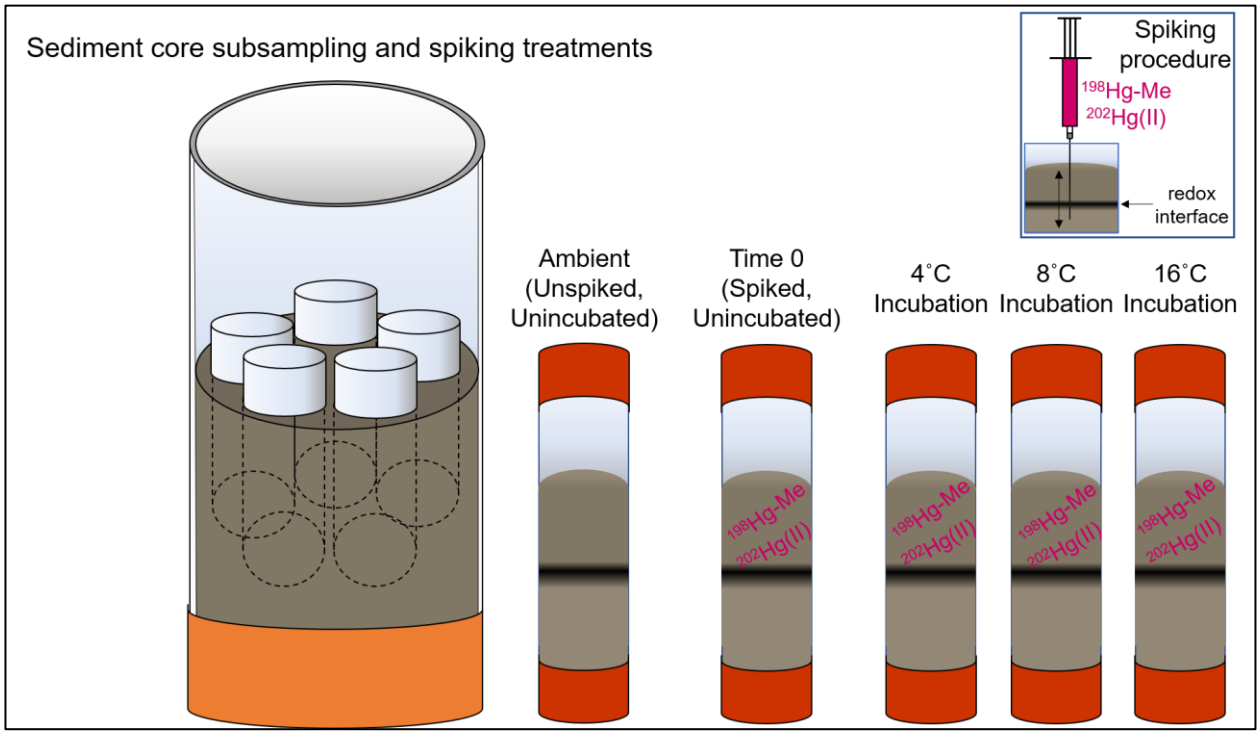

Figure 1: Sediment core subsampling and Hg isotope spiking procedure schematic. For each of the three sediment cores from each lake, five sub-samples were generated for experimental manipulation.

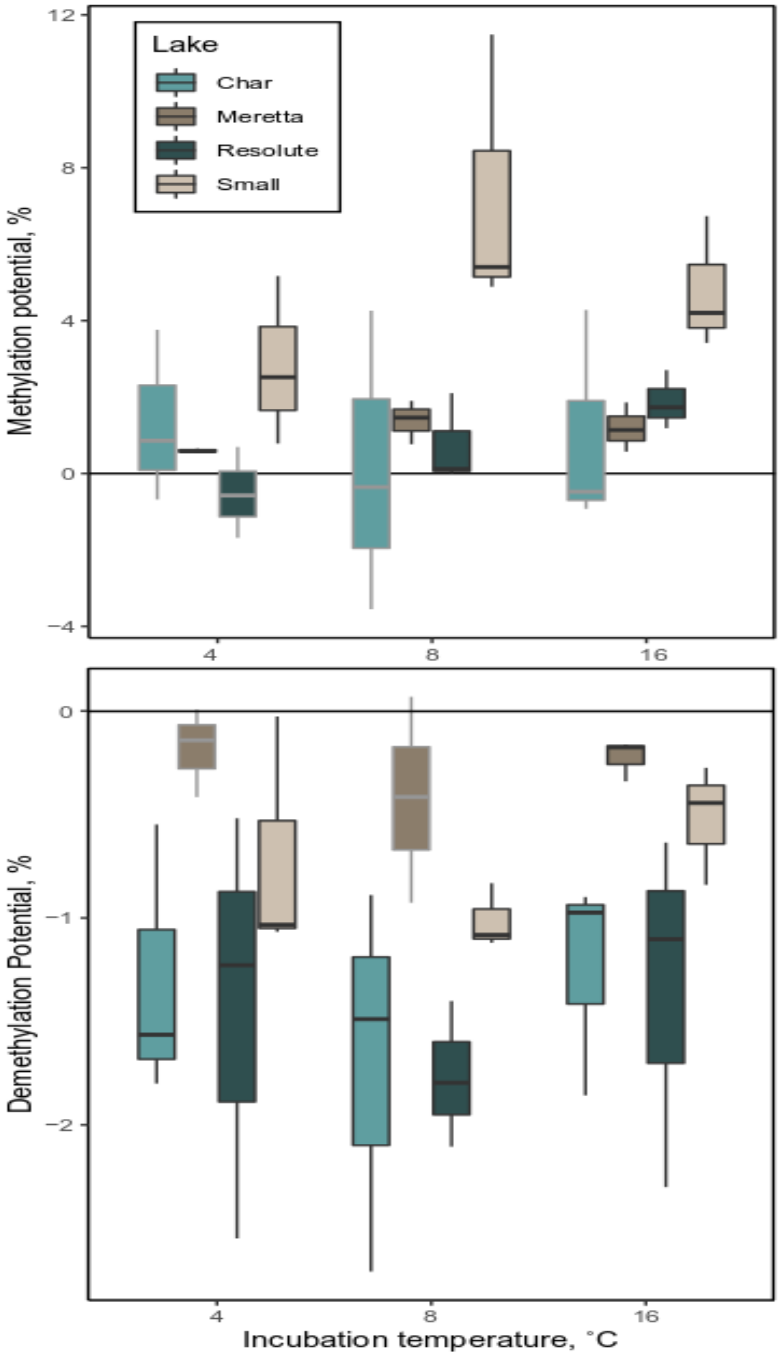

Figure 2: Boxplots of mercury methylation (upper panel) and demethylation (lower panel) potentials over 24 hrs in Arctic lake sediments for each of the three incubation temperatures. Note the difference in scales between panels. Where the quartiles of the box plots overlapped 0, the reaction potential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

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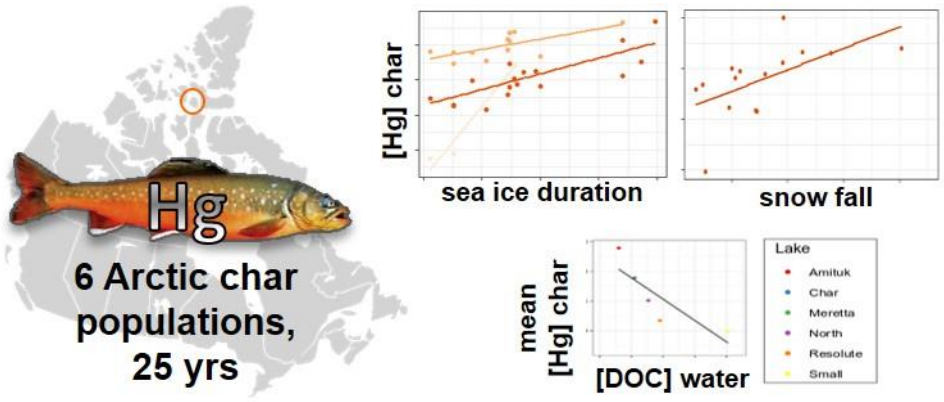
CHAPTER 3 TEMPORAL TRENDS, LAKE-TO-LAKE VARIATION, AND CLIMATE EFFECTS ON ARCTIC CHAR (SALVELINUS ALPINUS) MERCURY CONCENTRATIONS FROM SIX HIGH ARCTIC LAKES IN NUNAVUT, CANADA



Graphical Abstract

3.1 Introduction

The amount of mercury (Hg), a persistent and neurotoxic contaminant, circulating in the environment has increased 3-5 fold since the industrial revolution (Selin 2009), concurrent with increases in global CO_2 emissions (Lamborg et al., 2002). Much of the Hg is released directly into the atmosphere (Streets et al., 2017), which, through natural circulation processes, acts as a conduit for contaminants to high latitude environments (Shindell et al., 2008). The reactivity of atmospheric Hg increases in high latitude environments due to low temperature halogen chemistry, promoting oxidation to water soluble and divalent species which readily deposit onto environmental surfaces (Angot et al., 2016). Consequently, the Arctic acts as a global sink for Hg, with an estimated 117 tonnes deposited annually (Dastoor et al. 2015). This generates a disproportionately high risk of Hg exposure for Arctic indigenous people and wildlife (NCP, 2012; Dietz et al., 2009; AMAP 2015), despite its great distance from the major Hg emission sources.

Once deposited, Hg toxicity is greatly increased by methylation, which occurs primarily in aquatic and semi-aquatic environments (Morel et al., 1998, Selin 2009). Fish and top predators are especially prone to high levels of Hg due to bioaccumulation and biomagnification of methyl Hg (MeHg), and fish consumption is a major human exposure route (Selin 2009). Mercury poses health risks to wildlife (Scheuhammer et al., 2015) and people (Ha et al., 2017), which led to the development of the *Minamata Convention on Mercury*, a voluntary global treaty to reduce Hg pollution (UNEP 2013). The preamble to the convention stresses the greater risk to Arctic Indigenous communities due to their reliance on wild foods.

At the same time, global climate change is also disproportionately impacting the Arctic. As climate change progresses, there is a need to better understand the dynamics of Hg in

sensitive biota, as well as how climate change will affect the role of Arctic ecosystems as Hg sinks (Alava et al., 2017). For example, in two high Arctic sites, increased Hg deposition from the atmosphere occurred at higher temperatures (Cole & Steffen, 2010) and warming and decreased ice extent could promote the production of MeHg (AMAP 2011). Field measurements of Hg in Arctic air exhibit recent declines (Steffen et al., 2015); with declines of 0.9% / year from 2000 – 2009 of gaseous elemental Hg in air at Alert (Cole et al., 2013). However, due to changes in snow pack and sea ice characteristics, the Global/Regional Atmospheric Heavy Metals model predicts that Hg deposition in the Arctic is increasing, and that the Arctic remains a net sink for Hg (Dastoor et al., 2015). More recently, the projected 30-99% decline in permafrost due to thawing was predicted to release a portion of the estimated 793 ± 461 (mean ± SD) gigagrams of Hg stored in northern hemisphere permafrost over the next century (Schuster et al., 2018).

Methyl Hg concentrations in Arctic animals vary greatly across species, time, and location (AMAP, 2011). The concentration of MeHg in fish in any given aquatic system is influenced by Hg inputs to the body of water and its watershed, water chemistry, methylation rates, and food web structure within the lake (Rypel, 2010). Across North America, trends in predator fish Hg concentrations over time vary by region (Zhou et al., 2017; Eagles-Smith et al., 2016; Gandhi et al., 2014; Gantner et al., 2009; Rennie et al., 2005) but do not necessarily reflect Hg deposition in many cases due to variation in Hg post-depositional processing. In the Arctic, post-depositional processing strongly influences population-level trends in biota [Hg]; although Hg deposition across the landscape is assumed to be similar (due to atmospheric transport), there are large differences in biota [Hg] at the population level (also see Pelletier et al. 2017).

Non-migratory, or landlocked Arctic char (*Salvelinus alpinus*) are excellent biomonitors for freshwater ecosystems in the Arctic, because they are long-lived aquatic top predators, remain in a single ecosystem, are sensitive to environmental changes, and are a minor but dependable food source for some Arctic communities (Power et al., 2012, Barst et al., 2018). Mercury cycling is sensitive to meteorological drivers (Dastoor et al., 2015) which, in the Arctic, are undergoing rapid shifts due to climate change (Hinzman et al., 2005; Polyak et al., 2010). For example, warming may increase Hg methylation rate (Hammerschmidt and Fitzgerald, 2004, 2006; Lehnherr et al., 2012). Increased temperature has been shown to increase MeHg bioaccumulation in coastal marine killifish (*Fundulus heteroclitus*) attributed to increased metabolic rate (Dijkstra et al. 2013). Evans et al. (2013) reported higher [Hg] in lake trout (*Salvelinus namaycush*), northern pike (*Esox lucius*), and burbot (*Lota lota*) associated with cooler temperatures in Great Slave Lake (though they find no evidence of a direct effect of temperature), while Carrie et al. (2010) report increasing [Hg] in burbot in the neighboring Mackenzie River which the authors linked to warming-induced ice loss and increased primary productivity. In 90 large natural lakes of Québec, warmer temperatures were associated with higher growth rates resulting in lower [Hg] in walleye (*Sander vitreus*), while the warm temperatures were associated with increased [Hg] in northern pike from the same lakes (Lucotte et al. 2016). A study of landlocked Arctic char in a small lake in Greenland linked increasing [Hg] with increased temperatures, which was attributed to increases in primary production, similar to the logic of Carrie et al. (2010). In small southern Ontario lakes, a negative relationship was observed between temperature and [Hg] in largemouth and smallmouth bass (*Micropterus salmoides* and *M. dolomieu*, respectively) which was attributed to growth dilution (Chen et al., 2018). Ward et al. (2010) did not detect a temperature-dependent bioaccumulation

effect in Atlantic salmon (*Salmo salar*), but rather, found that [Hg] in salmon was dependent on growth rate and prey [Hg], with fast-growing fish exhibiting growth dilution, and slow growing fish having higher [Hg]. The effect of temperature on Hg bioaccumulation in fish can therefore be said to be species- and habitat-specific, and to be modulated by atmospheric and biogeochemical processes prior to the biological transformations (methylation) preceding bioaccumulation in fish. Though Hg bioaccumulation is modulated by habitat-specific effects, biomagnification of Hg through aquatic food webs is a generally consistent process, exhibiting similar rates when diverse food webs are compared, but tending to be higher in oligotrophic, cold systems (Lavoie et al. 2013). As hypothesized by several of the researchers cited in the Hg bioaccumulation literature above, differences in aquatic predator [Hg] between populations is largely due to processes occurring at the base of the food web, which may or may not also influence fish growth rate (also see Pućko et al. 2014). Studies of Hg concentration in Arctic animals over time indicate that trends vary widely between and within taxa, with the majority reporting non-significant temporal trends (Rigét et al., 2011). The lack of consistency in trends underscores the importance of continued research of contaminants in Arctic animals, as it is thus far difficult to forecast changes in Hg dynamics and concentrations in organisms. In some locations of the Canadian Arctic, Hg concentrations are increasing in anadromous Arctic char, while other populations are declining or exhibiting no change (Evans et al. 2015; Brown et al., 2018). Likewise, the Hg trends in ringed seals (*Pusa hispida*) in the Eastern Canadian Arctic generally increased from the early 1970s to 2009 (Brown et al., 2018), but in polar bears (*Ursus maritimus*) current levels are not different from those in the 1980s (Brown et al., 2018). In five species of seabird eggs from the Canadian Arctic, Hg concentrations were increasing in the 1970s and 1980s before plateauing and then exhibiting declines from 1993-2013 (Braune et al.,

2016). For example, a study of museum specimens of ivory gulls (*Pagophila eburnea*) reported a dramatic 45x increase in MeHg concentrations from 1877 to 2007 without any indication of a dietary shift (Bond, et al., 2015).

Currently, our understanding of temporal trends and climate effects on [Hg] in animals is confounded by the complex biogeochemistry of Hg and differences in reported trends across and within geographic areas and over time. This study seeks to gain insight on how population-level (ie., lake-to-lake) differences influence the current understanding of predator [Hg] temporal trends and the influence of climate by focusing on multiple populations of a single species in neighboring small lakes with similar food webs and a single species of fish. The objectives of this study were to describe temporal trends and lake-to-lake variation of [Hg] in landlocked Arctic char and determine if climate influenced the temporal trends. We analyzed [Hg] in char over a period of up to 29 years from six lakes on Cornwallis Island, Nunavut, Canada.

3.2 Methods

3.2.1 Site Description

Char, Resolute, North, Meretta, Small, and Amituk Lakes are located on Cornwallis Island (75.105° N, -94.828° W), Nunavut, Canada (Figure 1), home to the second most northerly community in the world, Resolute Bay (Qausuittuq, ᖁᑲᐅᓴᐃᑦᑐᖅ). The island lies within the polar desert ecozone of the high Arctic, where lakes make up <2% of the landscape (Walker et al. 2005). The lakes of Cornwallis are classified as ultra-oligotrophic, characterized by a short growing season (2 - 2.5 months of open water, occasionally retaining some ice cover throughout), limited nutrient availability (Schindler et al., 1974a), benthic based food webs (Welch and Kalff, 1974), low productivity (Rigler, 1978) and correspondingly low sedimentation rates (Whalen and Cornwell, 1985).

Arctic char are the only fish species in the study lakes. The Arctic char are landlocked due to the shallow depth of lake outflows resulting from isostatic rebound (Power et al. 2012). North and Small Lakes have adjoining watersheds, as do Resolute, Char, and Meretta Lakes. These five lakes range from 1 to 12 km from Resolute Bay on the southwestern coast of Cornwallis Island, while Amituk Lake is on the eastern edge of the island 48 kilometers north of Resolute Bay. Ponds in the catchment of Meretta Lake received waste water draining from the Canadian Department of Transport Airport Base, the 'North Base', via a utilidor and a 1.6 km stream system from 1949 – 1998 (Schindler et al. 1974b; Douglas and Smol, 2000). The lake responded primarily by increasing benthic planktonic diversity and biomass, contributing to anoxia in the hypolimnion, with a very slight increase in phytoplankton production, and in recent years shows signs of recovery (Antoniades et al., 2011).

3.2.2 Arctic Char Sampling and Hg Analysis

Arctic char collections began in 1989 and have been described in detail previously (Gantner et al., 2010a, b; Lescord et al., 2015a; Muir et al., 2005). Briefly, annual char collections were carried out in late July or early August using gill nets (mesh size 36 and 42 mm). Conditions permitting, nets were set in the same area and orientation each year. Total and fork lengths (cm) and weight (g) were measured for each fish and a skinless dorsal muscle sample was collected and kept frozen prior to total Hg analysis. Fulton's condition factor (K) was calculated as ($100 \times wt \cdot fork\ length^{-3}$) (Froese, 2006). Muscle samples were analyzed for total Hg by cold vapor atomic absorption spectrometry or by USEPA method 7473 (USEPA, 2007). DORM-3 (fish muscle protein) and DOLT-4 (dogfish liver) certified reference materials (National Research Council of Canada) were analyzed with samples to assess accuracy and precision. Recovery of the certified reference materials were 99.8% for DORM-3 (n = 42) and 97.5% for DOLT-4 (n =

41) for samples analyzed from 2011-2018. For samples analyzed prior to 2012, measurement accuracy was previously reported and achieved acceptable levels (see Gantner et al., 2010a; Lescord et al., 2015a). Blanks had non-detectable concentrations or levels <5% of measured values, and therefore no blank correction was used. The analytical laboratories (National Laboratory for Environmental Testing (NLET) and the Muir analytical group, Canada Centre for Inland Waters, Environment and Climate Change Canada, Burlington, ON) have successfully participated in the annual Northern Contaminants Program Quality Assurance program (NCP, 2012). The annual means for these measurements are provided in Tables A-1-6.

3.2.3 Statistical analyses

Alpha was set at 0.05 for statistical analyses, which were performed with R version 3.5.1 software (Copyright 2018, The R Foundation for Statistical Computing).

3.2.3.1 Fish population characteristics

Fish total length (cm), weight (g), and age (years) data for the six char populations were normally distributed and their means were compared by analysis of variance (ANOVA) and Tukey's post-hoc tests. Linear regression was then used to determine if these characteristics changed over time within each population.

3.2.3.2 Arctic char Hg concentrations – temporal trends and lake-to-lake variation

Arctic char muscle total [Hg] were log transformed to achieve normality for each lake for each year, based on Shapiro-Wilk's tests. Because fish size varied significantly within lakes between years, and across lakes, a single length-adjusted annual log [Hg] was generated. This was achieved using a regression between log [Hg] and fish total length at the mean total length for all the fish (40.1 cm, Figure A-1) for each year and lake, a method of length adjustment used in previous studies (Evans et al., 2005; Miller et al., 2013). Our *a priori* requirements for an

adjustment variable were that the variable exhibit a consistent relationship to log [Hg] among populations, and that the same adjustment method be applied to all lakes and all years. For comparison, log [Hg] by age relationship for each lake is presented in Figure A-2 but was not found to be better than length. Another approach to size adjustment is to use an analysis of covariance approach (AMAP 2011, section 5.3.3.4), however, this approach was not feasible for this data set due to the significant change over time exhibited by the biological variables (Table A-7). Length was selected as the adjustment variable over other characteristics, such as age, $\delta^{15}N$, and weight, because for these populations log [Hg] it exhibited the most consistent relationship (both among and within-lakes). Though there are other significant differences in the other biological characteristics between populations (Table 1), once the adjustment was made for fish length, the significance of other biological variables for predicting log [Hg] greatly decreased, indicating that much of the variability in log [Hg] both within and among lakes was explained by fish length. The annual length-adjusted log [Hg] was used for the temporal and climate analyses; while the mean of the annual length-adjusted log [Hg] was used for the lake-to-lake comparisons (Table A-8).

To assess the temporal trends in [Hg] in the Arctic char, linear regressions were run for each lake with length-adjusted log [Hg] versus year. There was an eight-year gap between the earliest samples and more recent samples collected from Amituk Lake, which could lead to errors in interpretation of the temporal trend. Therefore, separate regressions were run with all the data (1989 – 2018, 18 years) and with only recent data (2001 – 2018, 16 sampling years).

To compare [Hg] in Arctic char between lakes, we first used length-adjusted log transformed [Hg] and year as the experimental unit to compare lakes by an ANOVA and Tukey's post-hoc test. Because there were significant temporal trends in [Hg] in three of the

lakes according to the linear regressions described above, the differences detected by this approach may not be persistent over time. To assess the current state of Hg in Arctic char in these lakes, we used Hg data from all fish collected in 2017 and 2018. The [Hg] were log transformed, and we used an ANCOVA with fish length as a co-variate to remove the effect of size, and Tukey's post-hoc tests to compare between lakes. The results of the ANCOVA confirmed that the lake-to-lake differences from the initial ANOVA approach were persistent for the 2016 - 2018 Arctic char.

3.2.3.3 Influence of watershed, lake and climate characteristics on Hg temporal trends

The three types of variables known to influence [Hg] in fish (geographic i.e., watershed; lake, i.e., depth and water chemistry; and climate) were tested against the length-adjusted [Hg] of Arctic char using Spearman correlations. The watershed and water chemistry analyses used Spearman's rank comparisons because the mean length-adjusted [Hg] was compared to single means for these measures, making lake the experimental unit. For the climate analysis, multiple measurements per lake and per climate variable over time were tested, making year the experimental unit. Because multiple comparisons were made, p values were corrected to prevent test-wise type 1 error inflation using the false discovery rate method (Benjamini and Hochberg, 1995). Details on the variable used for each Spearman correlation analysis are provided below.

3.2.3.3.1 Watersheds

Fourteen watershed variables, several of which have been previously shown to influence Hg in lakes or in fish, were tested against Hg concentrations in Arctic char. A land cover shapefile derived from Landsat 5 and 7 ortho-images (4) describing vegetation cover types (Land Cover Circa 2000), the Canadian Digital Elevation Model raster and National Hydro Network polyline and polygon shapefiles were all used to generate maps of each of the lake watersheds;

all data were retrieved from the NRCan OpenData portal (http://geogratis.gc.ca). Geographic analyses were performed in ArcMap 10.3.1 (Esri, Redlands, CA, USA). Watershed delineation using the elevation and stream network data was carried out for each of the study lakes by using a digital elevation model to locate pour points and flow direction of streams within the watersheds using the Hydrology toolbox in the Spatial Analyst extension. The land cover polygon shapefile describing vegetation cover types was clipped to each delineated watershed in order to calculate the area of each vegetation type in each watershed (Figures A-3-5, Table A-9). The surface area of each lake and the maximum depth (z_{max}) were also included.

3.2.3.3.2 Water chemistry

Six water chemistry variables were tested against [Hg] in Arctic char. Water sampling for this dataset has been described elsewhere (Cabrerizo et al., 2018a; Lescord et al., 2015a). Briefly, water samples were collected annually concurrent with fish sampling (but less frequently), from mid-lake or as near to mid-lake as ice cover would permit. When ice cover prevented boat access to the deepest area of the lake, only surface samples were collected. Using a pre-cleaned 2 L Niskin sampler, water was collected from 0.5 – 1 m in depth, and from 1 m above the deepest depth for each lake (see Kirk and St. Louis, 2009). Samples were stored in pre-cleaned brown glass bottles at 4˚C, and filtered using GF/C (47 mm, pore size 1.2 µm for chlorophyll *a* (Chl *a*) and particulate organic carbon (POC); 25 mm, pore size 0.7 µm for dissolved organic carbon (DOC)) within 24 hrs. The filters were wrapped in aluminum foil and frozen until analysis. Unfiltered subsamples for analysis of total dissolved nitrogen (TDN), nitrite/ nitrate (NO_3/NO_2), total dissolved phosphorus (TDP), were stored at 4 ˚C until analysis. Water samples and filters were analyzed at NLET within 28 days of collection. Chlorophyll *a* was extracted with acetone and measured using spectrophotometry at wavelengths 663, 645, and

630 nm (NLET method 01-1100, Environment Canada, 2010). Means for this dataset are presented in Table A-10.

3.2.3.3.3 Weather and climate data

Climate variables were tested against [Hg] in Arctic char. Daily and hourly weather data (temperature (°C), snow fall (cm), rain fall (mm), accumulated snow (cm), and wind speed (km/h) were collected by Environment and Climate Change Canada weather stations near Resolute Bay. The Resolute CARS weather station provided data from 1988 to 2013 and the Resolute CS weather station provided data from 2013 to 2015. Differences in temperature and snow depth between weather stations were not significant for overlapping years (t-test), so no distinction was made when combining station data. Sea ice thickness (cm) and duration (days) provided by the Canadian Ice Service was also included because sea ice is both sensitive to climate and weather and plays a large role in determination of climate and weather through feedback mechanisms (Curry et al., 1995). Sea ice measurements were made through the ice in Resolute Bay about 1 km from Resolute Lake. Repeating patterns in sea surface temperature or height (which is related to pressure and temperature of the water mass) that influence global weather patterns are known as climate oscillations. Weather in the Canadian Arctic is influenced by several of these oscillations (AMAP, 2011), and trends in oscillation values have been associated with contaminant transfer to the Arctic (Eckhardt et al., 2003; Octaviani et al., 2015). The indices of the Pacific North American Pattern (PNAP), the Arctic Oscillation (AO), the Pacific Decadal Oscillation (PDO) and the North Atlantic Oscillation (NAO) provided by the National Weather Service Climate Prediction Center of the National Oceanic and Atmospheric Administration) were included in the analysis. Air temperatures, climate oscillation indices, and ice data were compiled into annual measures. For temperature, wind speed, oscillations, and sea

ice thickness, annual means were calculated. For the precipitation measures (rain fall, snow fall, and snow accumulation depth) annual totals were calculated. When more than 10% of any measurements were missing for the year, the annual summaries were not calculated. For this analysis, both the corrected p values and the uncorrected p values are presented in the results because, while we acknowledge the possibility that some of the significant correlations may be due to type I error, the cost of type I error in an exploratory statistical study is sufficiently low to balance the risk of type II error in favor of detecting a biologically significant result (see Cabin and Mitchell, 2000). For additional interpretation of these tests we provide plots of each significant relationship in Figure A-6.

3.2.3.4 Modeling length-adjusted Hg concentration using climate

After the analyses of temporal trends in [Hg], lakes were divided by trend type (i.e., decreasing (3 lakes) or no change (3 lakes)). The length-adjusted log [Hg] in Arctic char of the three declining lakes (46 total sampling events) were subjected to a mixed model and stepwise selection procedure: a mixed model was constructed with all of the 11 annual climate variables and included lake as a random variable using the lme4 package (Bates et al., 2015) before applying a stepwise backward selection process on the fixed effects, using the cut-off for significance (α) of 0.05 and estimating degrees of freedom using the Kenward-Roger estimation method available in the MuMin package (Bartoń, 2018). This procedure selects variable sets which do not exhibit correlation among variables. We performed the same analysis for the length-adjusted log [Hg] in Arctic char from the three lakes which did not exhibit a linear trend ($n = 40$ observations). Then, to better understand the importance of each lake's record in the selection process and the relationship of the selected climate variables on each of the study populations [Hg], this model was applied to each of the lakes separately.

3.3 Results

3.3.1 Arctic char samples

Arctic char sampling occurred most often in Resolute Lake (22 sample years and 299 fish) and least in Meretta Lake (8 years of sampling and 111 fish) (Table 1). The goal of each sampling was to catch 10 or more adult (> 200 g) fish, which was achieved in all but Char Lake, where yields were usually below 10 (see Tables SI 1-6 for annual means of the char population characteristics).

3.3.2 Change over time in population characteristics

The regressions of the annual means of the char population characteristics revealed that, for at least one population, each of the annual mean population characteristics changed over time (Table A-7). In North, and Resolute Lakes, annual mean fish total length significantly increased with time, while in Small Lake, length significantly decreased. Similarly, the Resolute char increased in mean weight over time while weights in Small Lake decreased. For the Amituk, Meretta, and Small Lake char populations, annual mean K significantly declined over time.

3.3.3 Size – Hg relationships of Arctic char populations

The majority (51 of 87) of the annual log Hg-fish length regressions had significant p-values (Figure A-1); in general, only years which had very low or negative slopes did not have significant relationships. Regardless of significance, all regressions were retained for subsequent analyses. The mean slope of the log Hg and length regressions for each lake (mean ± standard deviation) ranged from 0.016 ± 0.018 in Char Lake to 0.039 ± 0.012 in Small Lake.

3.3.4 Lake-to-lake variation in Arctic char Hg

Using length-adjusted of [Hg] over the entire collection period to compare lakes, concentrations in the Small Lake char were the lowest but not significantly different than Meretta and Resolute Lakes (Table 1). Amituk Lake char had significantly higher [Hg] than the other lakes; the next highest lake-mean [Hg] were those in Char Lake which were nearly three times lower (Table 1). When the length-adjusted mean [Hg] were compared (Tables 1 and A-8), the grouping assignments were similar to the groupings for the non-length-adjusted [Hg], with Amituk, Char, and North populations significantly higher than the others.

3.3.5 Temporal trends in Arctic char Hg by lake

Based on linear regressions, length-adjusted log [Hg] in char did not significantly change in North, Small, or Char Lakes ($p = 0.73$, 0.58, and 0.07, respectively), and significantly decreased in Resolute (slope = -0.005, $R^2 = 0.33$, p = 4.9e-3) and Meretta (slope = -0.015, $R^2 = 0.88$, p = 6.0e-4), over time (Figure 2). For the Amituk Lake char, length-adjusted log [Hg] decreased over the period 2001 to 2018 (slope = -0.016, $R^2 = 0.35$, N=14, p = 0.016), but was not significant (slope = -0.005, $R^2 = 0.081$, N=16, p = 0.252) when the two early sampling years were included. When the slope values are back-transformed from the log, the change over time for the significantly decreasing lakes are -1.94 % for Amituk, -3.5% for Meretta, and -1.1% ng/g wet wt. for Resolute.

3.3.6 Influence of water chemistry, lake and climate characteristics on Hg trends

None of the watershed characteristics were significantly correlated to the lake-to-lake variation in length-adjusted log [Hg] in Arctic char (Table 2). For water chemistry data, DOC in both surface and profundal waters, and POC in profundal waters were significantly correlated with Arctic char [Hg] (adj. p = 0.019 for each measure, Table 2, Figure A-6), although the lakes

are well mixed and so differences in water chemistry over depth may be biologically insignificant. Among the climate variables, sea ice duration in nearby Resolute Bay was significantly positively correlated to the [Hg] over time for Resolute Lake (adj. p = 0.041, Table 3, Figure 3) and snow fall was significantly positively correlated to Amituk Lake char [Hg] (adj. p = 0.024).

3.3.7 Models of length-adjusted log Hg over time vs. climate

The stepwise selection procedure generated the following model equation for the declining [Hg]lakes:

Length-adjusted log [Hg] = (Intercept) + 0.170 Snow fall – 0.242 Rain fall - 0.553 NAO, for which, the marginal (fixed effect) R^2 was 0.035 and the conditional (fixed and random effects) R^2 was 0.942. As seen in Table 4, the 2.5% confidence intervals for the variables did not overlap 0, therefore the effect is significant, which is confirmed by the p values for the model variables (Table 4). The very small marginal R^2 (especially in comparison to the larger conditional R^2) indicates the poor fit of the model when all lakes are included, and the small contribution of the fixed climate factors to overall fit relative to the contribution of "population". For the lakes which did not exhibit significant temporal trends for Hg, the selection process yielded an intercept-only model as no climate variables were significant predictors of length-adjusted log Hg in char for these lakes (data not shown). When the three selected variables were used to model each lake separately, the model exhibited a significant fit with Resolute Lake, but not with any of the other lakes (Table A-11); significance of each of the climate variables for each of the lakes are presented in Table A-12. The p values indicate that the selected climate variables generally fit better with the declining Hg populations, but that Resolute and Amituk

Lakes appear to have driven the selection process for these variables (Table A-12). The fit of the model is very poor for the no-trend populations.

3.4. Discussion

Temporal trends in Arctic char muscle length-adjusted [Hg] in six small high Arctic lakes either decreased or did not significantly change. Mercury concentrations in char differed widely between the lakes despite their geographic proximity and similar food webs, and the relative differences have persisted throughout the 25 years of sampling (1993-2018). The best explanatory variables for lake-to-lake differences were POC and DOC concentrations in profundal waters near the site of methylation in the sediments, but watershed variables were not significant. Although there was no single climate variable that was related to char [Hg] across all populations, sea ice duration was significantly positively related to [Hg] in three populations (two populations were not significant after p value correction), two of which are likely also impacted by recovery from historical waste water pollution. The mixed model analysis generated a similar result: NAO and rain fall were significant predictors in Resolute but not strong predictors in other lakes, while snow fall was significant for Amituk Lake in the correlation and modeling analyses. The Resolute Lake population with the most complete sampling history (n = 22), exhibited significant results in both the correlation and the mixed model analyses, highlighting the importance of high-resolution biological data for monitoring and modeling studies. However, spurious results are also possible as more data is acquired. Our results confirm that [Hg] in Arctic char can vary widely between lakes, even over a relatively small geographic area that likely receives similar atmospheric deposition of Hg, and the influence of a changing Arctic climate has not created clear trends but appears to manifest in a system-specific

manner. Therefore, it is recommended that larger-scale temporal trend and climate analyses consider populations as distinct experimental units within a geographic area.

3.4.1 Mercury in Arctic char: Comparison between lakes and influence of water chemistry and watersheds

Arctic char muscle [Hg] increased with body length, which is consistent with a recent study documenting a positive relationship between length and [Hg] for 59 populations of non-anadromous Arctic char (Barst et al., 2018). The relative ranking by lake of Hg concentrations did not vary when concentrations were corrected for length, which reflects the effort of this monitoring program to collect similar size fish from all lakes, reducing the impact of size differences from year to year.

Mercury concentrations in the Arctic char varied widely between the six lakes sampled in this study, despite their geographical proximity and the similarity of their predominantly benthic food webs (Lescord et al. 2015, Gantner et al. 2010a). These concentrations were in range of other reports for landlocked Arctic char from the eastern Canadian Arctic (Gantner et al., 2009, van der Velden et al., 2015, Barst et al., 2018), although [Hg] in Amituk Lake char exceeded most other reports. These concentrations essentially mirrored those reported in Gantner et al. (2010b) for the same populations from 1999 – 2007, consistent with temporal trends observed in this study. The char in Amituk Lake had almost three times higher [Hg] than fish from the other study lakes, perhaps because it was the only lake that contained a wetland within the watershed. Wetlands are productive features in terms of vegetation, and wetland soils, including those in the Arctic, and are known to be important sources of MeHg (Loseto et al., 2004a; St. Louis et al., 1994). The small wetland area, or the reported potential geological Hg in Amituk Lake's watershed (Semkin, et al., 2005), are potential reasons why this lake is higher in [Hg] in char

than the other Cornwallis Lakes; however; our results below indicate that water chemistry differences are a more likely explanation.

Char, Resolute, and Meretta Lakes are intermittently hydrologically linked and have adjoining watersheds, and yet trends in the Arctic char [Hg] differ between the lakes. Meretta Lake is upstream of Resolute Lake, and there is some evidence that Resolute Lake was also affected by the waste water inputs based on elevated perfluorooctane sulfonate (PFOS) concentrations in water (Lescord et al., 2015b) and in catchment soils (Cabrerizo-Pastor et al., 2018b). The history of contamination of the Meretta Lake catchment by waste waters may be a factor in the observed decline of [Hg] in char over time although [Hg] in the char were similar to North and Resolute lakes when sampling began in 2006. Meretta is in the process of returning to the pre-waste water reference state (Antoniades et al., 2011) and its current water chemistry is similar to that of North and Resolute Lakes (Table A-10; Lescord et al. 2015a). The nutrient and contaminant signature of sewage or waste water can have long lasting effects in Arctic lakes due to slow turnover (Hermanson 1998). Waste water or the nearby airport may have been sources of Hg, PFOS, and other contaminants. Regarding Hg, it is likely that the nutrients in the waste water stimulated methylating bacteria in the lake sediments, increasing the dynamic Hg in Meretta, especially under the reported anoxic conditions (Antoniades et al., 2011). As the lake returns to oligotrophic status, MeHg production in the sediments could be rapidly declining, and the [Hg] in the char may reflect this decline.

Previous research demonstrates that lake and watershed factors play a large role in determining the condition of individuals (Munkittrick and Dixon, 1989), as well as the mercury burden of the fish (Munthe et al., 2007; Chen et al., 2005; Johnston et al., 1991). Previous studies which included the current study lakes found that the watershed area: lake area ratio was

correlated to [Hg] in Arctic char (Gantner et al., 2010b) and watershed area was important for Hg in char (Lescord et al., 2015a); however watershed size was not a significant factor in this study. We found that lake-to-lake variation in char [Hg] is better explained by water chemistry features than watershed features or the lake morphology attributes, although lake morphology can influence water chemistry and aspects of the char populations therein (Riget et al., 2000). A study of land-locked monomorphic Arctic char morphological variants in 35 Icelandic lakes found that the underlying geology, water source (spring-fed or runoff), and fish community structure were more influential than other physical factors (lake area, depth, or volume) but that these physical factors were nonetheless correlated to char morphological characteristics (Kristjánsson et al. 2011). In the absence of geological, community, or water source differences, it is likely that lake dimensions play a large role in shaping the benthic community of the lakes, which influences both the water chemistry properties and the char populations. A survey of land-locked char populations in 27 Greenland lakes ranging from >200 to 3.3 m in depth found that lake volume and depth were significantly positively correlated with the maximum size of char (Rigét et al. 2000). Further, Rigét et al. found that decreased water transparency due to glacial runoff led to fewer char compared to a similar sized, but not glacially-influenced lake in the same watershed. The Rigét et al. study demonstrates that both lake size and water transparency shape char populations.

Inputs of terrestrial organic matter to polar desert lakes are minimal, and food webs are supported largely by benthic primary production (Chételat et al., 2010), which could contribute to the relative importance of in-lake processes rather than watershed processes. Our water chemistry values were consistent with the findings of Michelutti et al. (2003) and Lescord et al. (2015a) for the study lakes and typical for ice-dominated oligotrophic Arctic lakes (Chételat et

al., 2015). The relationship between DOC and Hg or MeHg in fish across lakes has been well studied (Driscoll et al., 1995). Typically, as lake DOC concentration increases, so do Hg or MeHg concentration in water (Watras et al., 1998; MacMillan et al., 2015) leading to greater Hg bioaccumulation (O'Driscoll et al., eds, 2005), although the inverse relationship has also been reported (Kamman et al., 2005). This relationship holds up to a point: a study in tundra lakes the Mackenzie River Delta (Northwest Territories, Canada) region demonstrated that there is a concentration threshold of 8.5 mg C /L, and higher concentrations beyond this inhibit Hg bioaccumulation in amphipods (French et al., 2014). The oligotrophic study lakes are well below this threshold, and yet, our findings demonstrate the opposite relationship expected for DOC concentrations in water and [Hg] in biota. Recent work which included four of the lakes in this study demonstrated that MeHg bioaccumulation in lake food webs is strongly influenced by the MeHg:DOC ratio, with primary producers in low DOC lakes exhibiting greater uptake of MeHg along a DOC gradient (Chételat, et al., 2018). Lakes which had low concentrations of DOC and MeHg in the waters were found to be more sensitive to MeHg contamination, resulting in increased [MeHg] in biota when DOC was lowest. This was attributed to more efficient uptake of MeHg from water and organic matter in oligotrophic systems where organic matter concentrations are low. Our findings support this: DOC and POC were negatively related to [Hg] in Arctic char. Overall, we found only slightly tighter relationship between profundal water chemistry and char [Hg] than surface water chemistry; probably in part due to the well-mixed nature of the lakes. This finding indicates that Hg monitoring programs would be better served by monitoring profundal water chemistry than surface water chemistry, particularly in systems where the food web is benthically based or in stratified systems. Additionally, in areas where the DOC concentrations are below the threshold of 8.5 mg C/L, it may be advisable to avoid

consuming fish from the lakes with the clearest water. This "rule of thumb" warrants further investigation and if it holds true, would be a simple way to assess the potential Hg levels in char providing a guide for fish consumption and inform monitoring programs.

3.4.2 Temporal trends in Arctic char Hg concentrations and the influence of climate

There were two types in temporal trends in the total [Hg] in Arctic char from the six study lakes: three of the lakes significantly decreased, while three others did not exhibit a significant linear trend. In a small lake in southwest Greenland, [Hg] in landlocked Arctic char increased from 1994 – 2008 (Rigét et al., 2010). For both anadromous and non-anadromous Arctic char in Labrador, researchers report significant increases, decreases, and non-significant trends for 1977-78 to 2007-09, but this was based on only two time points, and in general, concentrations were largely unchanged over time (van der Velden et al., 2015). The mismatch of trend directions for [Hg] in Arctic char, amid dramatic climate changes and decreased concentrations of gaseous elemental Hg in the Arctic atmosphere demonstrates the complexity of the Hg biogeochemical cycle and its impact on fish [Hg].

Mercury concentrations in Arctic char from Resolute Lake were positively correlated to (after corrections for multiple testing) sea ice duration in Resolute Bay. When p values were not adjusted, sea ice duration was positively correlated to Meretta and North Lake char [Hg] as well (Figure 3). During the period of this study, a rapid decline in sea ice duration in Resolute Bay was observed (-3.1 days / year, $p = 0.00001$, cumulative decrease of 62 days). In the Alaskan Arctic, declines in lake ice have been linked to concurrent sea ice declines due to more open ocean area and warmer temperatures (Arp et al., 2015), and lake ice extent decline has been documented in other Arctic lakes over a wide geographical area (Šmejkalová et al., 2016; Smol et al., 2005). Lake ice can greatly influence productivity in Arctic lakes (Smol et al., 2005;

Williamson et al., 2009) and may also influence Hg chemistry by reducing photoreduction of Hg^{+2} and MeHg, reducing evasion of gaseous Hg (Soerensen et al., 2016), and stabilizing the water column and reduced mixing, promoting anoxic (i.e., methylating) conditions near the sediment (Eckley and Hintelmann, 2006). The impact of declining lake ice may not influence char in a uniform manner across lakes because lake ice extent varies widely due to factors such as lake depth and wind fetch.

Snow fall was positively correlated to Amituk Lake char [Hg] (before and after p value adjustment). Similarly, in the modeling analysis, snow fall significantly predicted char [Hg] for Amituk. This relationship is supported by experimental evidence which demonstrated that snowmelt and the spring freshet are the primary source of total Hg (Semkin et al. 2005) and MeHg (Loseto et al., 2004b) to Amituk Lake. Topography, prevailing wind direction, and the course of snowmelt reaching the lakes play important roles in snow accumulation patterns in the polar desert and may be of interest for further investigation which make Amituk Lake unique among the study lakes. Amituk Lake is of interest due to the exceptionally high concentration of Hg (and other metals) in Arctic char from this lake (Muir et al. 2005; Barst et al., 2016). In this study, we found that the water of this lake has low concentrations of dissolved and particulate organic carbon (even when compared to the other oligotrophic lakes), which likely increases the susceptibility of biota to Hg contamination (Chételat et al., 2018). This sensitivity, when combined with the demonstrated importance of snow melt as a source of Hg and MeHg to this lake (Semkin et al. 2005; Loseto et al., 2004b) are likely factors which set this Hg "hot spot" apart from the other lakes in the study and warrant further investigation.

The mixed modeling analysis indicated that for the Resolute Lake char, the NAO index was significantly negatively related to [Hg], The NAO was weakly positively correlated to POPs

in char from three of the study lakes in a previous analysis (Cabrerizo et al., 2018a). The statistically weak findings in both studies could indicate that NAO is important for these char populations, but differences in contaminant pharmacokinetics may drive the inverse relationship indicated by the coefficients between the two studies. In its positive phase, the NAO is important for movement of air masses from lower latitudes poleward; it can therefore be associated with warmer temperatures in the Arctic and cooler temperatures at lower latitudes, as air masses overlying these two regions mix (Ambaum et al., 2001). The NAO exerts strong control over the transport of atmospheric contaminants poleward (Eckhardt et al., 2003; Octaviani et al., 2015), consistent with previously reported positive relationships to POPs in Arctic char. It is noteworthy that NAO was not a significant explanatory variable with any char population Hg concentration in the correlation analysis. In the modeling analysis, its significance is reliant on the presence of the variable rain fall, without which it is no longer a significant predictor for Resolute Arctic char Hg (though rain and NAO are not correlated), further demonstrating that the relationship is statistically weak.

Environmental conditions have been shown to influence temporal trends in predatory fish growth and [Hg] in small lakes, both winter temperature (-) and mean annual temperature (+) were implicated as drivers (Lucotte, et al., 2016). Evans et al. (2013) found that temperature was the most consistent explanatory variable of [Hg] in predatory fish in Great Slave Lake although inclusion of the PNAP improved explanatory power for trends of Hg in lake trout. Here we did not find a consistent significant effect of temperature on [Hg] in the study populations, despite steadily increasing mean annual temperatures during most of the study period. In contrast to previous studies for persistent organic pollutants on the same char populations (Cabrerizo et al., 2018a), precipitation and sea ice were stronger predictors of char Hg than climate oscillations,

but the same oscillation was weakly implicated for the Cornwallis Island char populations in both studies.

The correlations of climate variables between Resolute Lake and Amituk Lakes, which have the longest sampling history, indicates that additional sampling years may reveal additional climate effects using statistical analyses. This exploratory analysis has demonstrated strong statistical links between two of the six monitored populations and two rapidly changing climate variables but did not detect any variables which were significant across all the lakes. Further work is warranted to investigate the effects of ice extent on contaminant burdens in Arctic char in additional populations and continued study of the populations described here.

3.4.3 Summary

This statistical analysis found that in six neighboring high Arctic lakes with significantly different mean [Hg] in char, trends in [Hg] in landlocked Arctic char over time either decreased, or exhibited no clear linear trends amid concurrent declines in atmospheric gaseous [Hg] , (Steffen et al. 2015). Lake-to-lake differences are likely due to organic carbon content and Hg processing of each of the lakes; watershed characteristics were not correlated to [Hg] in fish. No single climate factor influenced all populations consistently, but local sea ice duration was significantly positively correlated to [Hg] for the Resolute population, and snow fall was positively related to [Hg] in the Amituk population. The study lakes with the most complete sampling history, Resolute and Amituk Lakes, had the strongest relationships with climate variables. This highlights the need for continued monitoring and high-resolution sampling to better understand the roles of multiple stressors on biomonitoring targets while demonstrating that “hot spots” of Hg contamination may respond differently to the changing climate. Overall, we demonstrate that population-level differences in animal [Hg] temporal trends and climate

influences can occur even at very fine geographic scales, and that oversimplification of these trends should be avoided for larger-scale studies.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ASSOCIATED CONTENT

Open data portal links:

Contaminant and biological data on landlocked Arctic char

https://open.canada.ca/data/en/dataset/44319e2b-135c-4585-a6ab-87cb29ee2acf

Mercury in landlocked Arctic char

https://open.canada.ca/data/en/dataset/90e55c10-6fef-4387-a03f-6cd1a644e8b3

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Table 1: Selected descriptors (mean ± 1 SD, unless otherwise stated) of landlocked Arctic char from the six study lakes on Cornwallis Island, Nunavut, Canada.
Letters indicate significant differences in the annual means among lakes for each descriptor (ANOVA with Tukey's test, $\alpha = 0.05$). See Tables SI 1-6 for annual means. See Table 2 for length-adjusted means over time. Lower panel, selected descriptors of each lake.

	Amituk	Char	Meretta	North	Resolute	Small
No. of years	18	13	8	14	22	14
Catch/year	10 ± 6	7 ± 2	14 ± 4	13 ± 5	14 ± 4	16 ± 6
No. of fish	184	85	111	181	299	220
Total length (cm)	44.3 ± 5^{a}	39.4 ± 5.2^{ab}	43 ± 5^{ab}	39.3 ± 5^{ab}	40.7 ± 5^{ab}	37.1 ± 5^{b}
Weight (g)	701 ± 273^{a}	756 ± 284^{a}	721 ± 273^{a}	494 ± 273^{ab}	537 ± 286^{ab}	357 ± 273^{b}
Fulton's condition	0.89 ± 0.12^{ab}	0.94 ± 0.15^{a}	1.01 ± 0.09^{a}	0.91 ± 0.06^{a}	0.94 ± 0.07^{a}	0.81 ± 0.07^{b}
Age (y)	18 ± 3^{ab}	17 ± 3^{bcd}	7 ± 3^{d}	16 ± 2^{bc}	19 ± 2^{a}	14 ± 2^{c}
$\delta^{13}C$ (‰)	-22.3 ± 0.9^{a}	-23.8 ± 0.9^{b}	-22 ± 0.8^{a}	-23.7 ± 0.8^{b}	-22.3 ± 0.8^{a}	-23.4 ± 0.8^{b}
$\delta^{15}N$ (‰)	11.9 ± 0.9^{a}	11.4 ± 0.9^{a}	11.7 ± 0.9^{a}	11.7 ± 0.9^{a}	11.7 ± 0.9^{a}	9.4 ± 0.9^{b}
Hg (µg/g, wet wt.), all years	1.28 ± 0.23^{a}	0.43 ± 0.23^{b}	0.14 ± 0.23^{bc}	0.28 ± 0.23^{bc}	0.18 ± 0.23^{c}	0.12 ± 0.23^{c}
Hg (µg/g, wet wt.), 2016 and - 2018 only	1.09 ± 0.11^{a}	$0.71 - 0.66^{b}$	0.08 ± 0.11^{c}	0.33 ± 0.11^{c}	0.17 ± 0.11^{c}	0.11 ± 0.11^{c}
Hg (µg/g wet wt.) for a 40.1 cm char	0.90 ± 0.28^{a}	0.47 ± 0.13^{b}	0.12 ± 0.07^{e}	0.26 ± 0.05^{c}	0.17 ± 0.06^{d}	$0.13 \pm 0.03^{d,e}$
Lake surface area (km^2)	0.378	0.526	0.262	0.957	1.27	0.140
Lake depth (m)	43	27	10	14	22.5	8.2
Watershed area (km^2)	31.1	3.32	6.15	97.0	11.6	0.878
Watershed: lake area ratio	0.012	0.16	0.043	0.010	0.109	0.159

Table 2. Spearman's rho rank correlations for length-adjusted Hg concentrations in Arctic char and each watershed or lake feature for the 6 lakes from Cornwallis Island, Nunavut. Ties in rank (due to measures of 0 area for the given cover type in multiple watersheds) are indicated in the last column. P values are corrected for multiple comparisons using the Benjamini-Hochberg false discovery rate procedure (1995). See Table A-10 for watershed feature data.

Feature	Rho	P	Ties
% Water	-0.314	0.957	
% Barren	-0.086	0.957	
% Till/colluvium	-0.086	0.957	
% Gramminoid shrub tundra	-0.030	0.957	tie
% Snow/Ice	0.638	0.749	tie
% Bare soil with cryptogram crust	0.029	0.957	
% Dwarf shrub	0.131	0.957	tie
% Tussock tundra	0.034	0.957	tie
% Wet sedge	-0.270	0.957	tie
% Wetland	0.655	0.749	tie
% No data	0.655	0.749	tie
Lake Surface Area, km^2	0.371	0.957	
Max. Depth Z_{max}, m	0.886	0.339	
Watershed Area, km^2	0.429	0.957	
Surface water [Chl *a*]	-0.600	0.499	--
Surface water [DOC]	-0.886	0.055	--
Surface water [POC]	-0.943	0.019*	--
Surface water [NO_2]	0.314	0.816	--
Surface water [SRP]	-0.087	0.873	--
Surface water [NO_3/NO_2]	-0.087	0.873	--
Profundal water [Chl *a*]	0.371	0.803	--
Profundal water [DOC]	-0.943	0.019*	--
Profundal water [POC]	-0.943	0.019*	--
Profundal water [NO_2]	-0.100	0.873	--
Profundal water [SRP]	-0.371	0.803	--
Profundal water [NO_3/NO_2]	-0.200	0.873	--

Table 3: Spearman correlation coefficients (rho) of climate variables and oscillations with the length-adjusted log Hg concentration in Arctic char over time for each of the study lakes. Significant correlation coefficients after application of the Benjamini-Hochberg false discovery rate p value correction are indicated with *, those that were significant before p value correction are italicized. See Figure A-5 for plots of significant relationships. AO = Arctic Oscillation, PNAP = Pacific North American Pattern, NAO = North Atlantic Oscillation, and PDO = Pacific Decadal Oscillation.

Climate Parameter	Amituk	Char	Meretta	North	Resolute	Small
Snow Fall	*0.718**	-0.573	0	-0.082	0.397	0.198
Wind Speed	-0.088	0.145	*-0.786*	-0.064	*-0.478*	0.336
Rain Fall	-0.382	-0.027	-0.286	-0.088	*-0.480*	-0.176
Snow Accum. Depth	-0.038	0.091	-0.200	0.236	0.212	-0.227
Temp.	-0.121	0.245	*0.821*	0.368	-0.290	-0.011
Sea Ice Thickness	-0.027	-0.300	-0.429	-0.294	-0.358	-0.063
Sea Ice Duration	-0.200	0.075	*0.829*	*0.591*	*0.727**	-0.236
AO	0.218	-0.064	-0.286	0.033	-0.071	0.187
PNAP	0.075	0.600	-0.321	0.434	0.309	-0.302
NAO	0.175	0.227	-0.500	0.055	-0.090	0.495
PDO	0.343	0.390	-0.643	0.181	0.103	0.462

Table 4: Fit statistics, degrees of freedom, and p values of the linear models generated for length-adjusted log Hg concentration from each Arctic char population using the three climate variables (NAO, rain fall and snow fall) selected in the stepwise selection process. The coefficients for these models are presented in A-12.

Variable	Coefficient ± SE	2.5% CI	97.5% CI	DF	t value	p value
Intercept	0.053 ± 0.82	-1.83	1.93	2	0.064	0.950
Snow Fall	0.17 ± 0.074	0.026	0.31	36	2.29	0.028
Rain Fall	-0.24 ± 0.069	-0.374	-0.11	36	-3.53	0.0012
NAO Index	-0.55 ± 0.16	-0.86	-0.24	36	-3.46	0.0014

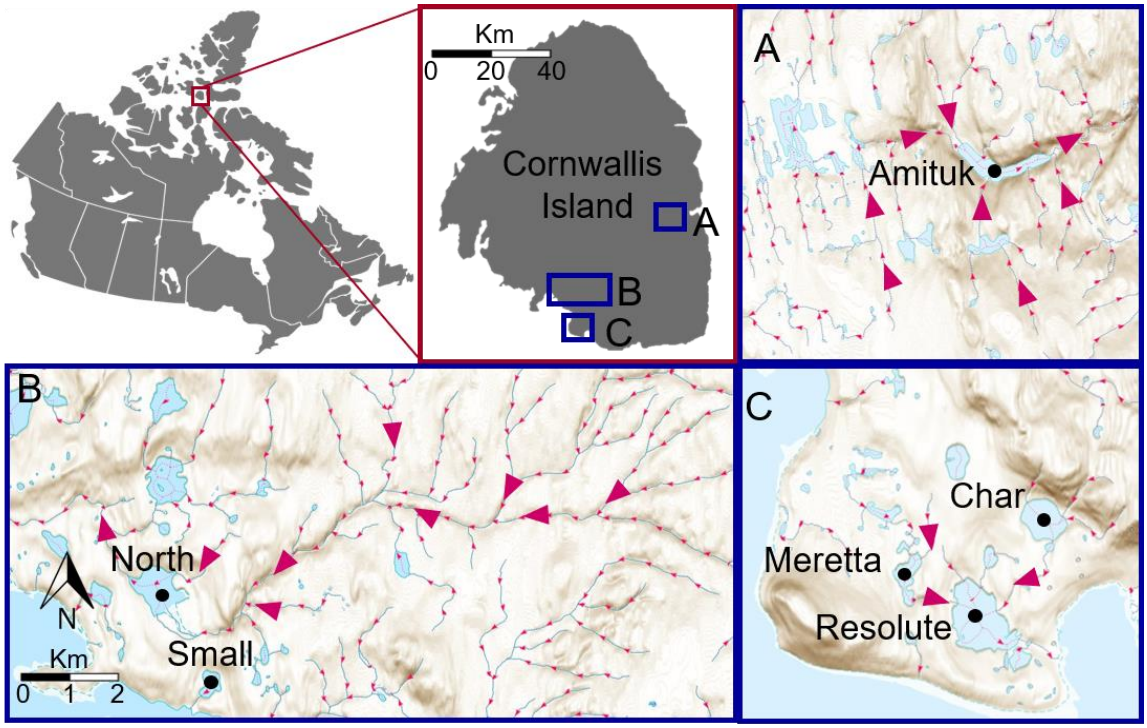

Figure 1: Study location in six lakes on Cornwallis Island, NU, Canada where Hg in Arctic char muscle was monitored over time. Pink arrows indicate water flow direction. Scale bar on inset B also applies to insets A and C.
Inset maps retrieved from GeoGratis Toporama (Natural Resources Canada, 2019).

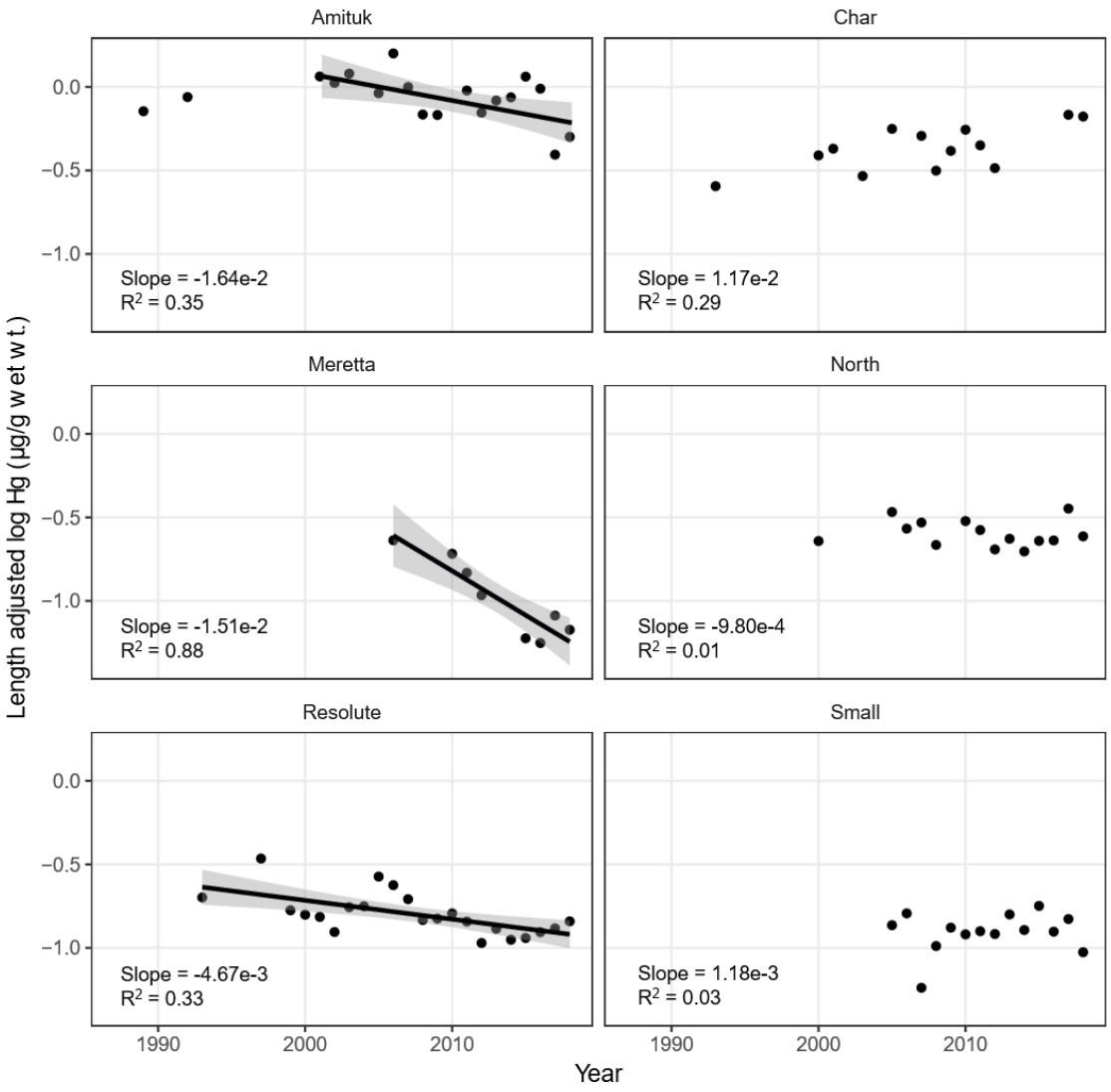

Figure 2: Regression lines of the log Hg:length relationship for Arctic char for each year of collection in six lakes from Cornwallis Island, NU, Canada.
The mean total length (40.1 cm) of all Arctic char used in this study is indicated by the vertical dashed line. Regression lines are shaded by Year; dashed regression lines indicate non-significant relationship. The point at which each regression line crosses the mean length is presented in Table 2. See Figure A-1 for the log Hg:age relationship.

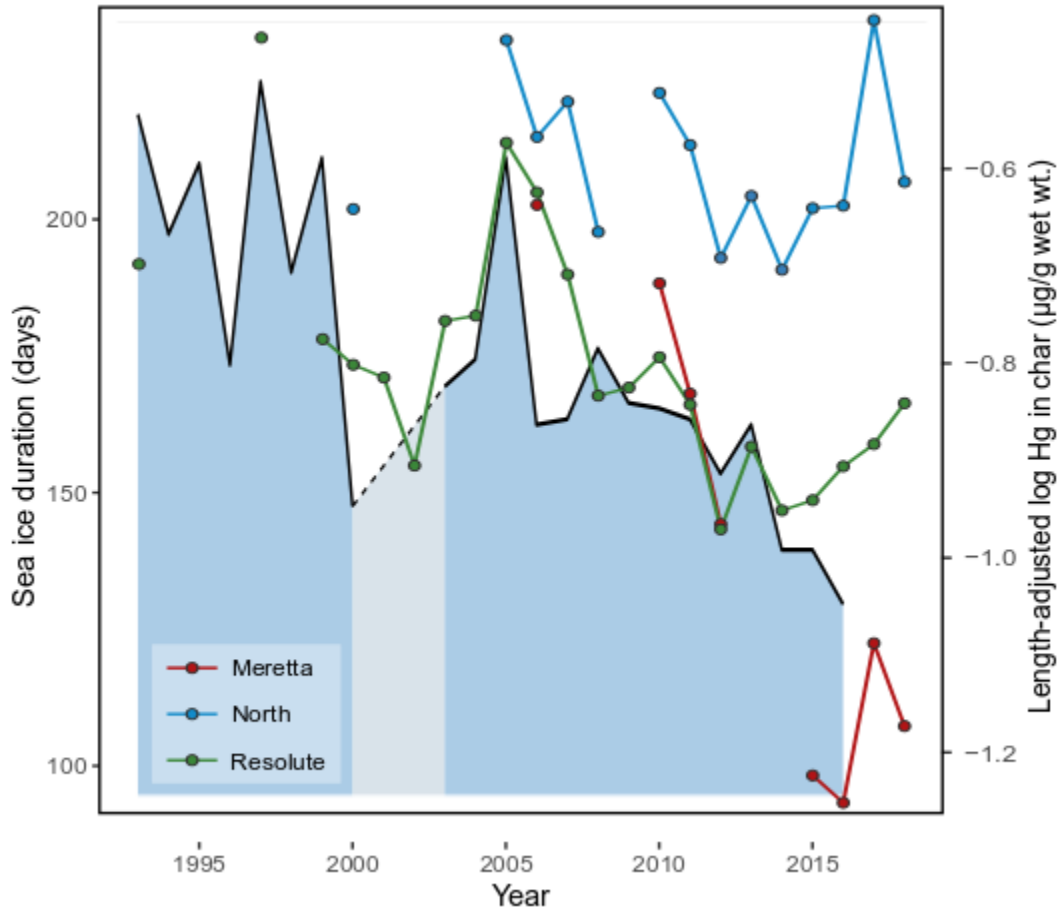

Figure 3: Temporal relationship between sea ice duration in Resolute Bay (left axis) and length-adjusted Hg concentration in Arctic char from Meretta, North, and Resolute Lakes (right axis) on Cornwallis Island, NU, Canada.
Where sea ice duration data was missing, a dotted line was drawn in to complete the shape.

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CHAPTER 4 INFLUENCES ON BIOACCUMULATION AND BIOTA-SEDIMENT ACCUMULATION FACTORS FOR METHYL-MERCURY IN HIGH ARCTIC LAKES

4.1 Introduction

Human activities have altered the natural biogeochemical cycling of mercury (Hg) (Fitzgerald & Lamborg, 2013) by releasing large amounts into earth's atmosphere, both indirectly, through coal burning, and directly, by mining and refining Hg for manufacturing or other uses (Streets et al., 2017). Some Hg species are relatively inert and can persist in the atmosphere for up to a year before reacting with ions or particles and depositing on Earth's surface, allowing for long-range atmospheric transport of Hg (Angot et al., 2016; Fitzgerald, et al., 1998). Due to the natural flow of hemispheric convection currents, the Arctic acts as a sink for atmospheric Hg emitted the northern hemisphere (Angot et al., 2016; Ariya et al., 2004; Dastoor et al., 2015). The increased concentrations of atmospheric Hg due to anthropogenic releases, which have more than tripled natural atmospheric Hg concentrations (Streets et al., 2017), mean that large amounts of Hg have been deposited across Arctic land, sea, and ice since the industrial revolution (Dastoor et al., 2015;. Muir et al., 2009).

Once deposited in an ecosystem, a portion of the Hg is subjected to methylation, usually (but not exclusively, see Munson, 2014) by sulfate-reducing, iron-reducing, or methanogenic bacterial processes (Gilmour et al., 2011; Parks et al., 2013). Methylation usually occurs in aquatic or semi-aquatic environments (Chen et al., 2014) and results in the formation of CH_3-Hg (MeHg), a more toxic form of Hg which most organisms have limited ability to metabolize or eliminate (Bradley et al., 2017). Because MeHg ishas high affinity for proteins , it accumulates in organisms leading to bioaccumulation (increased concentrations in biota relative to environment) and biomagnification (increased concentrations with increased trophic level). Therefore MeHg accounts for the majority of Hg in many aquatic invertebrates, fish (Sandheinrich & Wiener, 2011), and top predators (Campbell et al., 2005; Lavoie et al., 2013).

For large predatory fish, the majority of Hg in the tissues is MeHg, and measurement of total Hg is essentially the same as MeHg (Bloom, 1992, but see Lescord et al., 2018). The most common exposure route in aquatic organisms is through diet (Hall et al., 1997), and variation in [Hg] is well explained by the feeding behavior of organisms (Chen et al., 2014), but other life history traits, such as size and age in fish, are also influential (Gantner et al., 2010; Muir et al., 2005).

Although [MeHg] consistently increases with trophic level (Campbell et al., 2005; Lavoie et al., 2013), its concentrations in top predators can differ greatly between systems even when life history characteristics are accounted for (Barst et al., 2019; Gantner et al., 2010). Further, [MeHg] in sediments are not necessarily correlated to [MeHg] in biota or water (Buckman et al., 2019; Gantner et al., 2010). Bioaccumulation factors (BAF) and sediment bioaccumulation factors (BSAF) are contaminant concentration ratios that relate an organism's tissue concentration relative to that of the sediments in its surroundings (Gobas, 2001). These ratios are used because they allow researchers to standardize the bioavailability of contaminants and allow for comparisons between ecosystems. Methylmercury bioaccumulation tends to be higher in Arctic lakes relative to lower latitude systems for both primary consumers (Chételat et al., 2014) and fish (Lavoie et al., 2013). Polar desert lake benthos act as control points of primary production (Schindler et al., 1974; Welch & Kalff, 1974) and Hg methylation (Semkin, Mierle, & Neureuther, 2005; Vandal, Mason, McKnight, & Fitzgerald, 1998). In the study lakes near Resolute Bay, Nunavut, Canada (Figure 1), the sediments are the site of primary and secondary production (Chételat, Cloutier, & Amyot, 2010), which support the sole fish species, Arctic char (*Salvelinus alpinus*) (Lescord et al., 2015) as well as Hg methylation and demethylation (Hudelson et al. 2020 methylation).

Generally, increased primary production leads to increased Hg methylation (King et al., 1999; Ullrich et al., 2001) but can also lead to biodilution (Mackay et al. 2016). Temperature is a major factor limiting primary production in Arctic landscapes (Arkay, 1972) and one of the major controls of primary production in lakes (Antoniades et al., 2011). Increasing temperatures associated with climate change could stimulate both primary production and Hg methylation in Arctic environments (AMAP 2011) leading to higher MeHg concentrations in biota (Bodaly et al., 1993). Mercury methylation has been shown to increase with increasing temperature (St. Pierre, et al., 2014; Yang et al., 2016) (Chapter 2) while demethylation does not exhibit a similar response to temperature. However, the fish of warmer lakes do not always have higher [Hg]; in fact, arctic char from deeper, colder polar desert lakes have greater [Hg] than char from neighboring warm lakes (Chapter 3). Increased temperature has been shown to increase [Hg] in fish (Carrie et al., 2009; Dijkstra et al., 2013; Rigét, Vorkamp, & Muir, 2010), but increased temperatures have also been linked to decreased [Hg] in fish (Chen et al., 2018; Evans et al., 2013), and in one study, warmer temperatures were associated with both increased [Hg] in northern pike (*Esox lucius*) and decreased [Hg] in walleye (*Sander vitreus*) from the same 90 Québec lakes (Lucotte, Paquet, & Moingt, 2016).

Models of fish bioaccumulation of MeHg from diet and gill-uptake (Gewurtz et al., 2006; Gobas, 1993; Hrenchuk, 2010; Trudel & Rasmussen, 1997) indicate that increasing the water temperature (thereby increasing the metabolic rate) of Arctic char increases their [MeHg] only slightly, but large increases in [MeHg] in fish are observed when the [MeHg] in food is increased (bioaccumulation model and estimates provided in Appendix B). This is due to the consistent nature of bioaccumulation, while bioconcentration efficiency varies greatly among lakes. The model results also reflect the findings of Ward et al. (2010), who found that [MeHg] in food and

growth rate exerted stronger effects on [MeHg] in Atlantic salmon (*Salmo salar*) than temperature. Therefore, it is likely that lake-to-lake differences in Arctic char [MeHg] in these populations can be attributed to differences in [MeHg] in prey. Warmer waters and sediments can lead to increased Hg methylation, and primary and secondary production, and the differences between these rates should be reflected in the Arctic char [MeHg].

The Arctic char collected in this study are a subset of those presented in Hudelson et al. (2019) and are discussed at length therein. Briefly, that study found that lake-to-lake differences in Arctic char [Tot. Hg] were best explained by [DOC] in profundal lake waters, which in turn were related to lake depth. There was a significant negative relationship between Arctic char [Tot. Hg] and [DOC] in lake waters, which had been previously documented by Chételat et al. (2018) in invertebrates. As [DOC] was negatively related to lake depth, there was a positive relationship between Arctic char [Tot. Hg] and lake depth. The objective of the current study was to quantify BAFs and BSAF in the dominant invertebrate and vertebrate in four high Arctic lakes, and examine the influence of key factors that influence these metrics to better understand Hg and MeHg bioaccumulation in cold freshwater ecosystems. The factors include Hg methylation rates, water chemistry and lake characteristics. We selected two deep lakes and two shallow lakes to determine if the greater thermal inertia of the deeper lakes, resulting in cooler water and sediment temperatures, significantly influenced BAF and BSAF relative to their shallow counterparts, which warm more quickly. By comparing the processes in deep, cooler lakes to the shallow, warmer lakes, these results will provide some insights into how climate change could impact MeHg bioaccumulation in Arctic lake food webs.

4.2 Methods

4.2.1 Study Area and Site Description

Cornwallis Island lies within the polar desert ecoregion of the Canadian Arctic Archipelago, just north of the Northwest Passage. The annual average temperature is -15.7 ± 1.4 ˚C, with 161.2 mm of precipitation (1981-2010 climate normals, Environment & Climate Change Canada). The underlying geology is carbonate based and alkaline, dominated by limestone and dolomite (Edlund, 1991). The island has a shallow active layer underlain by continuous permafrost (Cruickshank, 1971), which is reported to thaw under lakes and down to depths of 1 m in late summer (Semkin et al., 2005). Soil is thin, patchy, and generally poorly developed (Edlund, 1991), with sparse vegetation consisting of graminoids and tussock grasses, and dwarf shrubs (Hudelson et al., 2019). The second most northernly community in Canada, Resolute Bay, and the Polar Continental Shelf Research Station are near the southeast coast of the island, and the study lakes are within 5.0 kilometers of the research station (Figure 1).

The lakes on Cornwallis are characterized by ultraoligotrophy, low biodiversity at the species level, and benthically based food webs (Welch & Kalff, 1974), where the top predator and only fish is Arctic char (*Salvelinus alpinus*) (Hobson & Welch, 1995). We selected two shallow (Meretta and Small, 9.2 and 9.8 m, respectively) and two deep (Resolute and Char, 22.5 and 27.2 m, respectively) lakes in order to compare the two types of systems. One of the study sites, Meretta Lake, was the final receptacle for waste water from the North Base from 1949 to 1998 (Douglas & Smol, 2000; Schindler et al., 1974). The waste water was comprised of cooking, washing, and sewage effluent, which was collected into holding tanks before being discharged into a 1.6 km watercourse, consisting of streams and lagoons, before draining into Meretta Lake (Douglas & Smol, 2000; Schindler et al., 1974). The nutrient inputs resulted in the

lake's trophic status shifting from oligotrophic to mesotrophic (Schindler et al., 1974), with evidence of hypolimnetic anoxia and drastic changes in the benthic community composition (Antoniades et al., 2011); but after the base was dismantled and the waste water inputs ended, the lake quickly began transitioning back to its pre-enrichment condition. The zooplankton community in the Cornwallis Lakes is usually dominated by *Limnocalanus macrurus*, a calanoid copepod, but this species disappeared from Meretta during the North Base years, and was replaced by *Daphnia* species and *Cyclops scutifer*, a cyclopoid copepod (Chételat & Amyot, 2009). Meretta Lake has two basins: a larger basin to the north and a smaller to the south; sampling for this study was carried out in the larger basin.

4.2.2 Sampling

For each lake, water, sediment, sediment cores (for methylation experiments and pore water collection), and chironomids were collected between July 20th and August 10th of 2013, with additional chironomids collected in the same period in 2014, when the lakes had either moated or were clear of ice. Sample collection targeted areas in the photic zone of each lake but below the depth of ice scour along the shoreline (7 m), sediments in this zone were dense, with sparse filamentous algae on the surface, except for in Meretta Lake where the upper layers were more flocculent. At a depth of 2.5 to 3 cm below the sediment surface, most cores turned from gray/brown to black in color, likely signifying the location of the oxic/anoxic interface below which the majority of methylation activity is expected (Lehnherr, St. Louis, & Kirk, 2012). Sediment cores, surface sediments, and chironomid samples were all collected in the same area of the lake in order to characterize this zone, which is assumed to be important for these lakes for primary and secondary production and Hg transformation.

4.2.2.1 Water and Pore Water

Lake water samples were collected from just below the surface of the water near the deepest point of each lake using a pre-cleaned Niskin sampler. All lake water and pore water samples were collected, handled, and stored according to established methods for low-level Hg analysis, including the "clean hands, dirty hands" protocol (U.S.E.P.A Method 1631, 2002).

Three sediment cores were collected from the photic zone below the depth of ice scour (7 m) of each lake for pore water extraction. Acid-cleaned Rhizons (Rhizosphere Research Products, Wageningen, The Netherlands) were then carefully inserted vertically into the top of the sediment cores until the porous probe was fully submerged in sediment. During the insertion the sediment structure was disturbed as little as possible (after the method of Shotbolt, 2010, but the tubes were pushed vertically into the sediment instead of horizontally). Gentle suction was then initiated in the syringes attached to the Rhizon samplers until 30 mL of pore water was collected from each sediment core. Aliquots were injected into pre-cleaned amber glass bottles and preserved with 5% HCl. Bottles were double bagged, and kept cool prior to analysis.

Methyl-Hg in the pore water and lake water samples was measured using U.S.E.P.A. Method 1631 with a Brooks Rand distillation block and MeHg Analyzer (cold vapor atomic fluorescence spectrometry). In each distillation, one sample was spiked with MeHg standard reference material TORT-3 (lobster hepatopancreas) to assess spike recovery. Spike recovery was 80-92%, well above the 65% acceptance criteria. The mean percent difference between duplicates was 9.17% (maximum percent difference was 14.53%), also within the acceptance criteria (<35%). Dissolved organic carbon was measured using standard methods.

4.2.2.2 Sediment

In a previous study, sediment cores were collected from the same area and at the same time as those used for pore water extraction (above) and for collection of chironomids (below) in each lake in order to determine methylation and demethylation potentials in the sediments (Hudelson et al. 2019b). Here, we use the reaction potentials of the 4 ˚C treatment, as the water temperature during these sample collections was nearest to 4 ˚C (Table 1).

4.2.2.3 Chironomids

In each of the study lakes, an Eckman grab or a sediment corer was used to collect sediment from which chironomid larvae were removed. At least 30 individuals were collected from each lake each year, washed with distilled water to remove adhering sediment, and frozen in individual tubes. Adult, emerged chironomids were collected by aspirator from the ice and snow surrounding/ covering each lake and frozen until subsequent sample processing. In the laboratory, samples were lyophilized and homogenized prior to digestion in a methanolic (25% KOH) solution at 135 ˚C for four hours (USEPA Method 1630). Methyl-Hg quantification was carried out on a Tekran 2700 GC-CVAFS unit (Tekran Instruments Corporation, Toronto, Canada) using purge and Tenax trap followed by thermal desorption, pyrolosis at 800 ˚C, and detection by CVAFS at 253.7 nm. With each run, standard reference material DORM 4 was co-analyzed. Recovery of the DORM 4 standard reference material indicated that recovery was 103.8 ± 0.52%, and precision between duplicate samples was 21.5%, both well within the acceptance criteria for the method.

Additional subsamples of lyophilized chironomids were used to quantify total Hg. A Nippon NIC MA-3000 was used in accordance with USEPA Method 7473, and DORM 4 was

the standard reference material. Recovery of the DORM 4 was 97.3 ± 3.24% and precision between duplicate samples was 7.7%, which are within the acceptance criteria for the method.

Only two chironomid samples were available for the analysis of total mercury in larval chironomids and thus concentrations could not be statistically compared between lakes. For each life stage and population, two sample t-tests ($\alpha = 0.05$) were used to determine if there were significant differences between sampling years for total Hg and MeHg concentration. Because there were no significant differences between years, we did not incorporate a term for year in subsequent analyses.

4.2.2.4 Arctic char

Collection and analysis of arctic char used in this study has been previously described (Hudelson et al., 2019) as they are part of an ongoing monitoring project (Gantner et al., 2010; Lescord et al., 2015; Muir et al., 2005). Briefly, Arctic char were collected by gill netting (mesh size 36 and 42mm) in late July - early August each year, conditions permitting. Total length (cm) and weight (g) were measured prior to dissection. Total Hg analysis was performed on skinless dorsal muscle using USEPA method 7473, as in large predatory fish, most of the Hg is MeHg (Bloom, 1992). Fulton's condition factor was calculated using the formula: $100 \times wt \times fork\ length^{-3}$ (Froese, 2006). Age determination was carried out on otoliths using the break and burn method (John Babaluk, Freshwater Insitute Manitoba, MB).

Water, sediment and chironomid samples were collected in 2013-2014 at all the study lakes. However, Arctic char were not collected in 2013-2014 from all the lakes, and so it was necessary to use an average over years before and after the collection of the other biota to estimate the what char from the lakes with missing data would be. Throughout the char monitoring project, yields from Char Lake have been lower than the other lakes, and it was

decided to pause sampling from this lake in 2012 to allow the population to recover (see Hudelson et al. 2019). When the population was sampled again in 2017 and 2018, the char were larger and in better condition than the preceding sampling years. There were also no char collected from Meretta Lake in 2013-2014, but there were in 2010-2012 ad 2015-2018. Because of these gaps in the sampling record and the known trend in [Hg] in char from Meretta and Resolute Lake populations (Hudelson et al. 2019), the average of 2013-2014 ± 3 years (2010-2017) was used for this analysis, as this was the shortest time increment which included Arctic char sampled both before and after the other types of samples in this study were collected.

To better compare and describe the populations, length at age was calculated for the mean age (13), and the mean ± the standard deviation (8 and 18) for each lake.

Arctic char [Hg] were log transformed to achieve normality. To adjust for differences in [Hg] due to size, we used a regression-based length-adjustment procedure for each population, where the regression coefficients of log [Hg] and length were calculated, and then the overall mean length (39.4 cm) was used to find the log [Hg] concentration for the average fish from each lake (Figure 2, Table 3). In order to verify that the length adjusted means for the time period of 2010-2017 are near the same as they would be for 2013 and 2014 only, we calculated the length adjusted means for 2013 and 2014 only in the lakes which had data in those years, Resolute and Small. The length adjusted [Hg] and 95% confidence intervals are 0.137 ± 0.020 and 0.115 ± 0.016 for Small and Resolute, respectively. As these estimates are similar to those generated using the 2010-2017 data (Table 1), we are confident that our estimates are appropriate.

4.2.3 Bioaccumulation Factors

BAFs and BSAFs for MeHg were calculated for the mean larval and adult chironomid [MeHg] and Arctic char adjusted [tot. Hg] for each lake using the following equations:

$$BAF_{water} = [MeHg_Y]_X / [MeHg_Y]_{water} \quad [1],$$

$$BSAFs = [MeHg_Y]_X / [MeHg_Y]_{sediment} \quad [2],$$

Where X = larval, adult chironomid or Arctic char, Y is total Hg or MeHg, $[MeHg_Y]_X$ is concentration in ng/g wet weight, $[MeHg_Y]_{water}$ is the mean lake or pore water concentrations in µg/L, and $[MeHg_Y]_{water}$ is sediment concentrations in ng/g (all units in ppb).

Additionally, the ratio describing the difference between Arctic char and chironomids (trophic transfer factor or TTF, see DeForest et al. (2007)) were also calculated, where

$$TTF_x = [MeHg_Y]_{Arctic\ char} / [MeHg_Y]_{chironomidX} \quad [3]$$

Where X = either larval or adult chironomids, and Y is either total Hg or MeHg.

Statistical analysis

Normality of data was tested using the Shapiro-Wilks test. Where applicable, analysis of variance tests (ANOVA) with Tukey's post hoc separations were used to determine if differences between lakes were significant. For all tests $\alpha = 0.05$.

4.3 Results and Discussion

4.3.1 Mercury and organic carbon in water, pore water, and sediments

Concentrations of MeHg in the water column were significantly different between lakes, with Meretta Lake having the highest concentration 0.06 ± 0.02 and Char having the lowest 0.01 ± 0.01 ng/L (Table 1). Concentrations of MeHg in pore water were not significantly different between lakes: Small Lake had 0.3 ± 0.1 and Char had 0.2 ± 0.1 ng/L.

In whole sediment, Meretta Lake's historical organic enrichment is evident: TOC was more than twice the percentage of the next highest lake, Resolute (17.7 ± 1.7 and 8.5 ± 1.8%, respectively, Table 1); Char Lake had the lowest amounts of organic carbon at 2.3 ± 0.2%. The

high to low ranking of lakes for organic carbon in pore water and whole sediments were identical, but the differences between lakes were greater for organic carbon in whole sediment.

Total Hg in whole sediments was also highest in Meretta (345 ± 42 pg/g), followed by Small (208 ± 113 pg/g), nearly double that of Char and Resolute (133 ± 23 and 55 ± 26 pg/g, respectively). Concentrations of MeHg in sediments were higher in the shallow lakes, with Meretta being the highest (56 ± 12 pg/g) followed by Small (51 ± 20 pg/g) and Char (31 ± 4 pg/g), and Resolute (23 ± 9 pg/g), but only Meretta and Resolute were significantly different.

Organic carbon, [Tot. Hg], and [MeHg] were higher in pore water than in lake water, but no differences between lakes for pore water were statistically significant, likely due to the high variation between measurements (Table 1).

In the studied lake sediments, OC% was positively correlated to [MeHg] ($R = 0.71$, $p < 0.001$, 95% CI = 0.49 – 0.84) and to [Tot. Hg] ($R = 0.57$, $p < 0.001$, 95% CI = 0.30 – 0.76). When Meretta Lake is removed, there is no longer a significant correlation between MeHg concentration and % OC in lake sediments. For [tot. Hg] and % OC when Meretta Lake is removed, there is a significant negative correlation ($R = -0.82$, $p = 1.24e-7$, 95% CI = -0.92 – 0.65). Because of historical pollution in Meretta Lake, the sediments are greatly enriched in OC and Hg relative to the other lakes. The long-term monitoring study of Arctic char [total Hg] in these lakes indicates that Hg has declined over time in Meretta (2006 – 2018), declined more slowly in Resolute Lake (1993 - 2018), and has not significantly changed in Char (2000 - 2018) or Small (2005 - 2018) Lakes with time (Hudelson et al. 2019). The rapid decline in Meretta char Hg in that study was attributed to recovery from the waste water and sewage inputs and a return to more natural levels. The shallower lakes contained greater [OC] and [total Hg], in part due to the nutrient enrichment in Meretta Lake. Methylmercury represented only a fraction of the

total Hg, and this was particularly apparent in sediment. Meretta Lake sediments and lake water contained the highest [MeHg], while the non-point source polluted lakes contained less of the bioaccumulative form of Hg.

4.3.2 Sediment methylation and demethylation

Methylation and demethylation potentials were calculated on the same sediment cores here (Hudelson et al. 2020). We used the results of the 4 ˚C treatment because that is the most relevant *in vivo* temperature for the study period (2013-2014). The methylation potential (change in [^{202}Hg-Me] in 24 hrs) was highest in the shallow lake sediments (0.59 ± 0.06 and 2.82 ± 2.21 % in Meretta and Small Lakes, respectively) and below the detection limit in the deep lakes. The reaction potentials do not reflect the [OC] or the [Tot. Hg], but rather appear to be differentiated by the depth-temperature gradient between lakes.

4.3.3 Chironomids

There were no significant differences in larval or adult MeHg concentrations in 2013 and 2014 (consistent with findings of Lescord et al. 2015), so further analyses pooled these samples. Concentrations of MeHg in chironomids from each lake were higher in adults than in larvae (Table 1), reflecting the findings of Chételat et al. (2008). Each population was similar in MeHg concentration in larvae, ranging from 32.6 ± 8.6 to 51.8 ± 17.4 ng/g wet wt. (Meretta and Resolute, respectively). For the adult chironomids, MeHg was significantly higher in Small Lake and lower in Meretta Lake (98.7 ± 44.5 and 55.1 ± 24.2 ng/g wet wt., respectively), but Resolute and Char were similar in concentration (76.0 ± 26.3 ng/g wet wt.).

Chironomid [MeHg] in this study were in range of those from previous studies for adults and larvae (Lescord et al. 2015 and Chételat et al. 2014, larvae only, Chételat et al. 2008, larvae and adults). In the study by Lescord et al., the reported standard deviations for chironomid

larvae are large: the mean and standard deviation for Meretta in 2010 was 131.7 ± 121.9 ng/g dry wt. for three samples in 2010. In this study, we again found wide variation, particularly in Small Lake 104 ± 61 ng/g dry wt. for three samples over 2013 and 2014. This could be due to the difficulty in collecting sufficient numbers of chironomids to generate a sample for MeHg analysis, necessitating pooling larvae which may be different instars or have different feeding habits, both of which should affect [MeHg]. Chételat et al. (2008) separated the chironomid larvae by removing predatory Tanypodinae from larval samples in which they were present, but no attempt to separate the predatory taxa was made by Lescord et al. or this study. No taxonomic separations were attempted by Chételat et al. (2008) or in this study for the adult samples.

4.3.4 Arctic char

The length at age for the three ages varied greatly between lakes (Table 2). As there were no fish younger than 11 caught from Resolute Lake, the length at age 8 years could not be calculated. For Meretta Lake, the oldest fish caught was 11, so there were no results for the length at ages 13 and 18. The ages of fish caught from Char Lake were 7-19 years, but there were none that were aged 13 years. Fish at each age were caught from Small Lake, and at each age, fish from Small Lake were the smallest (27.6 cm, 39.2 cm, and 39.8 cm for 8, 13, and 18 years, respectively). Char caught in Meretta were the largest at 8 years (43.8 cm). For 18 year old char, those caught in Char Lake were the largest at 57.3 cm.

The length adjustment procedure used to standardize [Tot. Hg] (which is assumed to be equivalent to [MeHg] in large predatory fish) changed the relative rank order of [Tot. Hg] of the populations. The Char Lake char have the highest unadjusted and adjusted [Tot. Hg] (0.36 ± 0.24 and 0.33 ± 0.03 µg/g wet wt., respectively), while the unadjusted Resolute [Tot. Hg] is

higher than the shallow lakes, the length-adjusted [Tot. Hg] in Resolute is less than the length-adjusted [Tot. Hg] for the Small Lake population (0.12 ± 0.15 and 0.13 ± 0.02 µg/g wet wt., respectively).

4.3.5 Bioaccumulation factors

Bioaccumulation factors are presented both log transformed (Table 3) and without transformation (Table 4) for consistency with other studies. All bioaccumulation factors here are based on wet weights. As expected, BAFs are higher in char than in adult and larval chironomids regardless of the denominator.

Values of BAF_{water} in this study relative to those in temperate top predator fish are high: Scudder Eikenberry report that for the top predators in stream systems, $\log_{10}$ BAFs approached 6.6, while in this study, $\log_{10}$ BAF_{water} for the top predator ranged from 14 – 17 (Scudder Eikenberry et al., 2015).

A literature review which compiled 43 BAFs for MeHg in freshwaters (where the denominator in the factors was unfiltered water [MeHg]), including numerous macroinvertebrates, zooplankton, prey fish and game fish (DeForest et al., 2007). The study areas ranged from a small hypereutrophic lake in New York (Becker & Bigham, 1995), reservoirs within the Guadalupe River watershed in California (Kuwabara et al., 2005), tributaries in the the Cache Creek watershed (California), an area impacted by Hg mines and geothermal Hg releases (Slotton, Ayers, Suchanek, Weyand, & Liston, 2004), and the Florida Everglades (Cleckner, Garrison, Hurley, Olson, & Krabbenhoft,1998). In this study, the mean BAF_{water} for chironomid adults, larvae, and Arctic char was 4.0×10^6, exceeding the geometric mean BAF_{water} (2.3×10^6) reported by the literature review, but not approaching the maximum of 4.8×10^7. In the Northwater Polynya (off the coast of Nasaruvaalik Island, ~130 km north of

Resolute Bay), Clayden et al. report the mean BAF for Arctic alligatorfish (*Ulcina olrikii*) and Arctic cod (*Boreogadus saida*) was $2.8x10^6$ and for a range of invertebrates, the BAF_{water} ranged from 0.20 – 2.3 $x10^6$, with a mean of 0.77 $x10^6$ (Clayden, Arsenault, Kidd, O'Driscoll, & Mallory, 2015). The overall mean BAF_{water} for the Clayden et al. study was 1.3 $x10^6$, which is again lower than the mean BAF_{water} we report. The mean BAF_{water} for fish in the Clayden et al. study and in this study are the same order of magnitude, but we find greater overall value: 2.7 $x10^6$ and 8.8 $x10^6$ for the Clayden et al. study and for this study, respectively. Chételat et al. (2018) generated BAFs for biofilms/lake waters across a large latitudinal transect and found that BAFs are higher for higher latitude lakes, and attributed this difference to the gradient in [MeHg]/DOC in water with latitude. Moving northward, decreased [DOC] resulted in more efficient uptake of MeHg by biofilms (i.e., primary producers).

As expected based on previous reports, accumulation factors generally increased with trophic status regardless of the substrate used to calculate the factors, so that those for Arctic char were higher than those in adult chironomids, which were in turn higher than the larval chironomids. For example, for Char Lake, the $BAF_{porewaters}$ were 1.88 $x10^5$, 2.68 $x10^5$, and $1.35x10^6$ for larval chironomids, adult chironomids, and Arctic char, respectively. Accumulation factors were fairly consistent among lakes but not without some important differences. Comparing the BAF_{water} between the study lakes, for larval and adult chironomids and for Arctic char, Meretta Lake had the lowest values (6.16×10^5, 1.04×10^6, and 1.93×10^6, respectively), while the other lakes exhibited values ranging from 1.19×10^6 to 2.58 $x10^7$ (for Small Lake larval chironomids and Char Lake Arctic char, respectively). Char Lake had the highest BAF_{water} for larval chironomids and for Artic char (1.44×10^6 and 2.58×10^7, respectively), while Small Lake had the highest for adult chironomids at 2.58×10^6.

The $BAF_{porewater}$ results were similar to those of the lake water in that Meretta was again low relative to the other lakes. The $BAF_{porewater}$ for larval and adult chironomids were lowest in Meretta (1.33×10^5 and 2.24×10^5, respectively), but for Arctic char, the lowest was in Small Lake (4.12×10^5, compared to Meretta which was 4.80×10^5). Resolute Lake demonstrated the highest $BAF_{porewater}$ for larval and adult chironomids (2.76×10^5 and 4.82×10^5, respectively), while Char Lake again had the highest for Arctic char (1.35×10^6).

A similar pattern is born out in the BSAF results, with Meretta again showing the lowest values (5.80×10^2, 9.79×10^2, and 1.61×10^3 for larval and adult chironomids and Arctic char, respectively) , then Small Lake (8.90×10^2, 1.92×10^3, and 2.28×10^3 for larval and adult chironomids and Arctic char, respectively), and then Resolute having the highest values for chironomids (2.26×10^3 for larvae and 3.95×10^3 for adults) and Char again having the highest values for Arctic char (1.04×10^4).

Overall, when bioaccumulation factors are compared among the lakes, the results indicate that the shallow lakes, Meretta and Small, have lower values than the deeper lakes Char and Resolute, and this is consistent regardless of the substrate type used to calculate the bioaccumulation factor.

DeForest et al. (2007, and references therein) report MeHg TTFs ranging from ~1.3 to 6.6 for rainbow trout and fathead minnows, respectively, with finescale dace being intermediate (note that these results are from laboratory studies and the factors are based on dry wts). The majority of MeHg TTFs in that review study were ~2.5. In this study, we found a similar range of TTFs for MeHg, which ranged from 1.31 (Resolute adult chironomids) to 7.2 (Char larval chironomids), with higher TTFs for larval than for adult chironomids. DeForest et al. note that for low food concentrations, TTFs tend to be disproportionately high, and then drop in value

when food concentrations are higher, suggesting a limit to MeHg assimilation from the diet. The mean [MeHg] in chironomids ranged from 32.6 ± 8.6 to 98.7 ± 44.5 (for Meretta larvae and Small adults, respectively), which is near the lower limit in the DeForest et al. review, suggesting that the trophic transfer of MeHg in these systems would be highly efficient. When MeHg TTFs are compared among the lakes of this study, the most striking aspect is that they are much higher in Char Lake than in the other lakes, with the factors in Char Lake being well over double the values of the next highest lakes for each chironomid life stage (7.20 for larvae and 5.05 for adult chironomids). Small and Resolute Lakes were remarkably similar for TTFs (2.89 and 2.29 for larvae, respectively; 1.33 and 1.31 for adults, respectively) and Meretta TTFs were slightly higher (3.61 for larvae and 2.14 for adults). These results indicate that the trophic transfer process is much more efficient in Char Lake than in the other three lakes, which are more similar. When this is put into the context of the bioaccumulation factor results, we see that Resolute Lake tended to have the highest bioaccumulation factors for chironomids, but the lowest for trophic transfer to Arctic char, and for the shallow lakes which tended to have the lowest bioaccumulation factors for chironomids, the TTFs were intermediate. Char Lake had the highest adj. [Hg] in Arctic char and the highest TTF, indicating that the difference in Char Lake Arctic char was not related to higher [MeHg] in chironomids, but is due to other life-history differences between the Arctic char in Char lake and the other populations.

4.3.6 Summary of factors influencing BAFs with emphasis on comparing deep and shallow lakes

Mean MeHg concentration in water was higher in the shallow lakes but was not significantly different from the deep lakes. DOC in 2013 and 2014 was higher in the shallow lakes than the deep lakes, and this is typical (over time) for these lakes (Hudelson et al. 2019).

Total Hg and MeHg in water were lowest in Char Lake, as was DOC. The MeHg/DOC ratio, which is useful for predicting MeHg bioaccumulation across a latitudinal gradient (Chételat et al. 2018) did not predict MeHg concentration in the lakes.

In sediments, Meretta's historical waste water influence increased the TOC in sediments well above the other lakes. As Resolute is downstream from Meretta, and previous studies have indicated that the waste-water contamination may have also influenced Resolute Lake, the TOC in Resolute Lake may be increased over its natural levels, although further characterization of the organic material is necessary to support or refute this comparison.

The shallow lakes had the highest DOC, tHg, and MeHg in pore water, though these differences were not significant. In the case of MeHg, Meretta and Char had the same mean concentration.

Adult chironomids had higher [MeHg] than larval chironomids, as expected. While the mean [MeHg] in larvae was higher in the deep lakes, it was not significantly so. In adult chironomids, both the highest and lowest [MeHg] were in the shallow lakes, with the deep lakes being intermediate.

Unadjusted char [Hg] were significantly lower in the shallow lakes. After adjustment for length, [Hg] in Char lake was around 3-fold higher than the other lakes, which were similar. BAF_{water} were lower in the shallow lakes than in the deep lakes. Char Lake had the highest values for BAF_{water}. Resolute Lake had the highest $BAF_{porewater}$, Meretta the lowest.
The BSAFs were lower in Meretta and Small than in Char and Resolute Lakes.

The TTFs did not differentiate on the basis of depth, but were the highest in Char Lake and lowest in Resolute Lake. This could be due to the larger size range of fish in Char Lake, which could encompass fish which are more piscivorous/cannibalistic than the other lakes,

driving up the [Hg] with size. While the mean size of char from Char Lake was intermediate, the largest char of the study were found in that lake, and contained the highest [Hg] (Fig. 2). This in part drove the strong regression relationship between log[Hg] and length in the Char Lake char population, which was not found in the other lakes, where the R^2 values indicate the relationship between [Hg] and length weaker (Fig. 2). The length adjustment procedure we employed reduced differences in [Hg] between lakes but Char lake remained higher than the other lakes in part due to high [Hg] in the larger than average fish from this lake. Therefore, it is likely that the high TTFs and BAFs in Char lake are influenced by the large and likely piscivorous char from that lake and that the very large values likely indicate another trophic step and not a difference in the biomagnification process itself.

4.3.7 Synthesis

Overall, differences in concentration of [MeHg] in sediments, lake waters, or pore waters alone did not explain differences in chironomid [MeHg] length adjusted char [Hg], indicating that concentrations of chemical species alone are an oversimplification of the Hg dynamics in the lake systems. Rather, Hg dynamics may be better understood when population densities and biomass estimates are also considered. Sediments and lake waters in the shallow lakes were generally enriched in organic carbon and MeHg relative to the deep lakes, but, in the shallow-water sediments sampled in this study, chironomid larvae tended to have lower [MeHg] than those in the deep lakes. This could be due to the slightly warmer temperatures in the shallow lakes (Table 1) and the relationship between temperature and maturation rates of chironomids: in warmer sediments chironomids mature and emerge faster (Eggermont & Heiri, 2012), and may have less time to absorb MeHg from the sediments than their counterparts in deeper, colder lakes. Further, the sediments of the shallow, warmer lakes may support a larger density of

chironomid larvae than deep cold lakes. The lack of data regarding chironomid uptake of MeHg over temperature gradients and lack of data regarding chironomid maturation rate or voltinism (generations per year) inhibit better understanding of these dynamics, as does the lack of data regarding chironomid biomass in Arctic lakes. Slow-growing chironomids in colder waters could provide higher [MeHg] to predators (similar to slow-growing fish, see Ward et al. 2010) when they are consumed in the pupal or adult phases. As the Arctic continues to warm and the growing season in these lakes is extended, primary and secondary production in the sediments and eventually in the water columns should also increase. This increase in production will likely result in decreased [Hg] in Arctic char as indicated by the lower bioaccumulation factors in the shallow lakes relative to the deep lakes. In a study of climate effects on Arctic char [Hg] over time, three of the six Arctic char populations demonstrated significant temporal declines in [Hg] (Hudelson et al. 2019a), consistent with reduced bioaccumulation factors in response to lake warming. The bioaccumulation and trophic transfer factors presented in this study indicate that as Arctic warming continues, [Hg] in Arctic char should decline as bioaccumulation becomes less efficient, but other factors such as enhanced deposition of Hg as snowfall increases, or changes in food web structure in the lakes, may influence MeHg bioaccumulation.

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CONFLICT OF INTEREST

None.

ASSOCIATED CONTENT

Open data portal links:

Contaminant and biological data on landlocked Arctic char

https://open.canada.ca/data/en/dataset/44319e2b-135c-4585-a6ab-87cb29ee2acf

Mercury in landlocked Arctic char

https://open.canada.ca/data/en/dataset/90e55c10-6fef-4387-a03f -6cd1a644e8b3

Table 1: Key characteristics (mean ± SD) of the four lakes study on southern Cornwallis Island, Nunavut. Sediment, chironmid, and Arctic char [MeHg] and [Total Hg] are in wet weight, sediment TOC is based on dry weight.
Letters indicate statistically significant difference between lakes for the given measurement (ANOVA with Tukey's post hoc separation). All measurements with three or more observations were tested. For concentration measurements, $\alpha = 0.05$.

Characteristic	N[1]	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
Summer water temp. (˚C)	2	[3.0 – 3.1]	[3.4 – 3.8]	[1.9 – 2.9]	[1.8 – 2.6]
Sub-surface MeHg (ng/L)	3	0.06 ± 0.02^{a}	0.04 ± 3.0e-6^{ab}	0.01 ± 0.01^{b}	0.03 ± 0.02^{ab}
Sub-surface Tot. Hg (ng/L)	3	0.8 ± 0.1^{a}	0.8 ± 0.1^{a}	0.4 ± 0.2^{b}	0.7 ± 0.1^{a}
Sub-surface DOC (mg/L)	1	[2.0 – 2.1]	[2.2 – 2.8]	0.8	[1.4 – 1.7]
MeHg / DOC (ng/mg)[2]	--	0.028	0.016	0.016	0.017
Sediment					
TOC (%)	3	17.7 ± 1.7^{a}	7.5 ± 2.3^{b}	2.3 ± 0.2^{b}	8.5 ± 1.8^{b}
Tot. Hg pg/g wet wt.	3	345 ± 42^{a}	208 ± 113^{ab}	133 ± 23^{b}	55 ± 26^{b}
MeHg pg/g wet wt.	3	56 ± 12^{a}	51 ± 20^{ab}	31 ± 4^{ab}	23 ± 9^{b}
MeHg / Tot. Hg %	3	16 ± 2^{b}	26 ± 4^{b}	24 ± 2^{b}	45 ± 11^{a}
Methylation potential (%/day)[3]	3	0.6 ± 0.1^{a}	2.8 ± 2.2^{a}	n.d.^{a}	n.d.^{a}
Demethylation potential (%/day)[3]	3	n.d.^{b}	-0.7 ± 0.6^{ab}	-1.3 ± 0.7^{a}	-1.4 ± 1.0^{a}
Pore water					
DOC (mg/L)	6	4.3 ± 0.7^{a}	3.7 ± 1.3^{a}	2.5 ± 2.0^{a}	3.3 ± 1.1^{a}
Tot. Hg (ng/L)	6	2.6 ± 1.4^{a}	2.4 ± 1.7^{a}	2.0 ± 1.5^{a}	2.3 ± 1.4^{a}
MeHg (ng/L)	5	0.25 ± 0.09^{a}	0.32 ± 0.13^{a}	0.25 ± 0.13^{a}	0.19 ± 0.08^{a}
Chironomids					
Larvae MeHg (ng/g wet wt.)	3	32.6 ± 8.6^{a}	45.7 ± 26.6^{a}	46.2 ± 26.3^{a}	51.8 ± 17.4^{a}

Characteristic	N[1]	Meretta	Small	Char	Resolute
Adult MeHg (ng/g wet wt.)	7	55.1 ± 24.2[b]	98.7 ± 44.5[a]	65.9 ± 26.1[ab]	90.5 ± 20.4[ab]
Arctic char					
Unadjusted Hg (µg/g wet wt.)	29[4]	0.13 ± 0.06[c]	0.11 ± 0.05[c]	0.36 ± 0.24[a]	0.16 ± 0.08[b]
Length adjusted Hg (µg/g wet wt.)[5]	--	0.12 ± 0.03	0.13 ± 0.02	0.33 ± 0.03	0.12 ± 0.15

[1]N refers to the minimum number of observations from each lake for a given measurement. Means and std dev are calculated for n ≥ 3, otherwise a range or the value is given.
[2]see Chételat et al. 2018.
[3] reaction potential at 4˚C, reproduced from Hudelson et al. 2019b. n.d. indicates non-detectable rate.
[4]see table 2 for number of Arctic char from each lake.
[5]estimated using the length adjustment procedure, and therefore are estimates ± standard error.

Table 2: Means and std dev. of Arctic char from the four study lakes near Resolute Bay, NU caught in the years 2010-2017. CF: Fulton's condition factor. Letters indicate difference between lakes for each measure (ANOVA with Tukey's post hoc, α= 0.05).

	Meretta	Small	Char	Resolute
N	90	148	29	130
Total Length (cm)	42.2 ± 4.1[a]	35.9 ± 3.2[b]	35.6 ± 15.3[b]	42.3 ± 4.7[a]
Weight (g)	645.1 ± 190.3[a]	292.9 ± 69.5[b]	637.6 ± 847.5[a]	592.4 ± 242.9[a]
CF	0.84 ± 0.08[a]	0.63 ± 0.1[c]	0.74 ± 0.13[b]	0.75 ± 0.08[b]
Age (yrs)	6.6 ± 1.8[c]	13.5 ± 2.7[b]	12.5 ± 3.5[b]	17.3 ± 4.1[a]
Length at Age 8	43.8	27.6	30.3	NA
Length at Age 13	NA	35.2	NA	37.5
Length at Age 18	NA	39.8	57.3	44.0

Table 3: Log transformed bioaccumulation factors and trophic transfer factors (from wet wts.) for methylmercury from lake water, pore water, and sediment for larval chironomids, adult chironomids, and Arctic char (length adjusted) from lakes near Resolute Bay, NU.

	Meretta	Small	Char	Resolute
$BAF_{lake\ water}$				
Larval chironomids	5.79	6.08	6.16	6.13
Adult chironomids	6.02	6.41	6.31	6.37
Arctic char	6.29	6.51	7.41	6.64
$BAF_{pore\ water}$				
Larval chironomids	5.12	5.15	5.27	5.44
Adult chironomids	5.35	5.49	5.43	5.68
Arctic char	5.68	5.61	6.13	5.8
BSAFs				
Larval chironomids	2.76	2.95	3.17	3.35
Adult chironomids	2.99	3.28	3.32	3.6
Arctic char	3.21	3.36	4.02	3.78
Arctic Char TTFs				
Larval chironomids	1.10	1.08	1.13	1.06
Adult chironomids	1.06	1.02	1.10	1.02

Table 4: Bioaccumulation factors and trophic transfer factors (from wet wts.) for methylmercury from lake water, pore water, and sediment for larval chironomids, adult chironomids, and Arctic char (length adjusted) from lakes near Resolute Bay, NU.

	Meretta	Small	Char	Resolute
$BAF_{lake\ water}$				
Larval chironomids	6.16×10^5	1.19×10^6	1.44×10^6	1.34×10^6
Adult chironomids	1.04×10^6	2.58×10^6	2.05×10^6	2.35×10^6
Arctic char	1.93×10^6	3.25×10^6	2.58×10^7	4.36×10^6
$BAF_{pore\ water}$				
Larval chironomids	1.33×10^5	1.43×10^5	1.88×10^5	2.76×10^5
Adult chironomids	2.24×10^5	3.08×10^5	2.68×10^5	4.82×10^5
Arctic char	4.08×10^5	4.12×10^5	1.35×10^6	6.32×10^5
BSAFs				
Larval chironomids	5.80×10^2	8.9×10^2	1.47×10^3	2.26×10^3
Adult chironomids	9.79×10^2	1.92×10^3	2.10×10^3	3.95×10^3
Arctic char	1.61×10^3	2.28×10^3	1.04×10^4	6.09×10^3
Arctic Char TTFs				
Larval chironomids	3.61	2.89	7.20	2.29
Adult chironomids	2.14	1.33	5.05	1.31

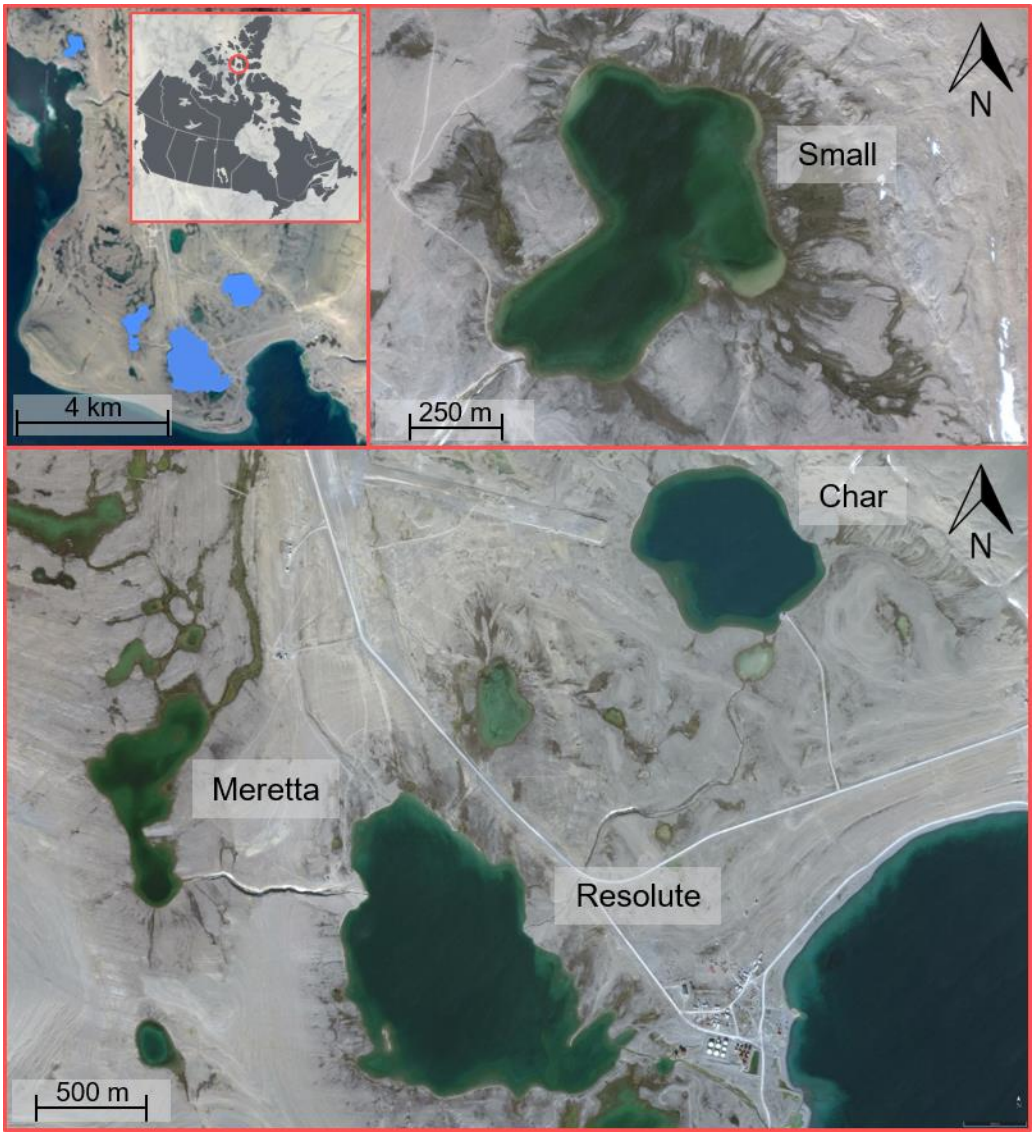

Figure 1: Study area on Cornwallis Island, NU, Canada. Inset 1 depicts relative locations of the study lakes, other insets show detail. Imagery from GoogleEarth 2019 DigitalGlobe.

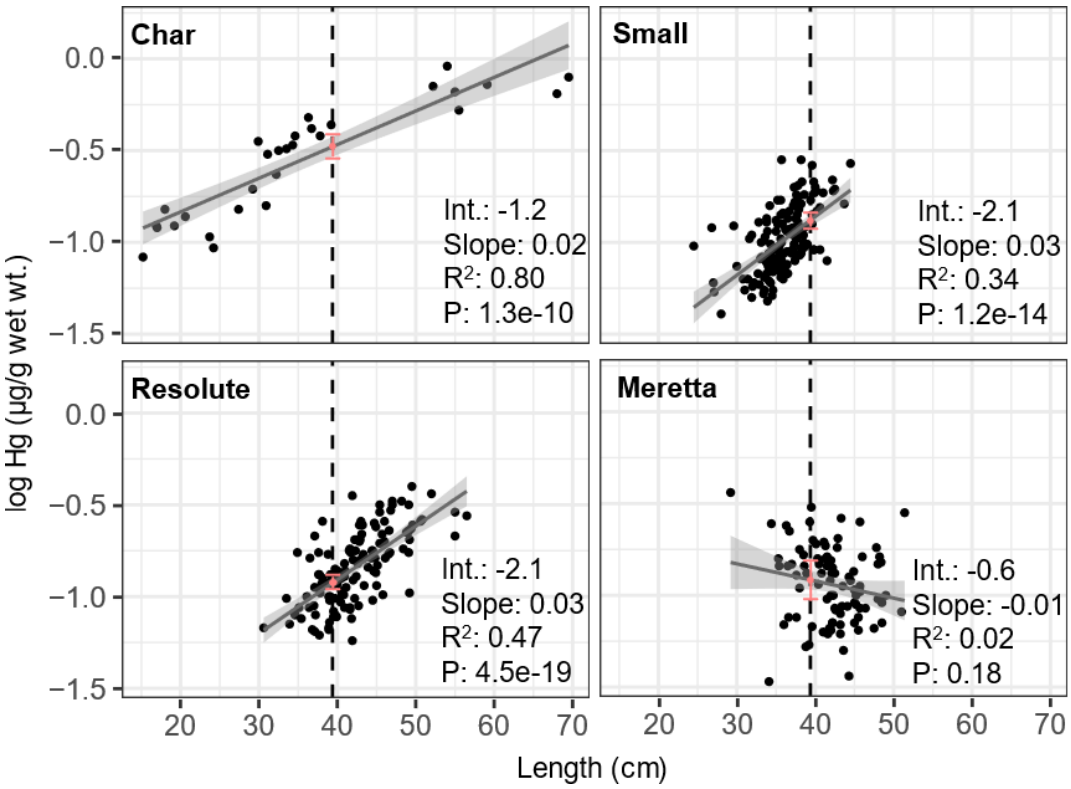

Figure 2: Regression of log [Hg] by length for each population. Mean length is indicated by dashed line, pink error bars indicate 95% confidence interval for regression estimated value of log [Hg] at mean length.

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CHAPTER 5 DISSERTATION CONCLUSION

5.1 General Discussion

As climate change continues to warm the Arctic, there is potential for large pools of environmental mercury (Hg) to be released (Schuster et al. 2018; Soerensen et al. 2016), potentially increasing risk of exposure to methylmercury (MeHg) globally (Amos et al. 2013). The study of small Arctic lakes, which are generally, relative to nearby marine and lower-latitude lake ecosystems, species-poor and biologically less complex (Welch 1991; Hobson and Welch 1995), can provide insights into how Hg moves through aquatic ecosystems. Further, the comparison of shallow, warmer lakes to deep, colder lakes provides insight into how the movement of Hg may be affected by warming (as in Taylor et al. 2019). High latitude lakes present a paradox in the current understanding of how Hg loadings reach biota: while atmospheric deposition and lake sediment [Hg] decline as latitude increases (Muir et al. 2009; Dastoor et al. 2015), high Hg levels (above 0.5 µg/g wet wt.) are reported in non-migratory fish from remote Arctic lakes (Barst et al. 2019), indicating that Arctic lakes are more "sensitive" to Hg contamination than other ecosystems (Chételat et al. 2018; 2014). Therefore, the benefits of addressing the knowledge gap of Hg movement in lakes on Cornwallis Island, NU, are three-fold: 1) the intrinsic importance of understanding Hg movement in sensitive lakes, 2) an improved understanding of how Hg may move through more complex aquatic systems, and 3) an improved understanding of how Hg loadings in aquatic ecosystems will respond as global warming progresses. This thesis addresses several key aspects of the Hg bioaccumulation cycle in high Arctic lakes both prior to biotic uptake and at each trophic level (Figure 1) and improves the scientific understanding of how climate change has impacted and will impact Hg in aquatic ecosystems.

5.2 Contributions to the Field

5.2.1 Why does mercury concentration in fish differ spatially and temporally?

The only fish species and top predator in the study lakes are Arctic char (*Salvelinus alpinus*), a cold-water specialist in the Salmonidae family. Arctic char [Hg] in these sensitive lakes has been monitored since 1989 to determine why Arctic lakes particularly sensitive to Hg loadings, as this remains poorly understood. Previous studies established that the food chain in the lakes is based in the benthos (Lescord et al. 2015; Welch and Kalff 1974) and that trophic level and food chain length are influential in determining lake-to-lake differences in Hg biomagnification between Arctic char populations (Gantner et al. 2010a), but food chain length did not explain lake-to-lake differences in length-adjusted [Hg] (Gantner et al. 2010b). Rather, catchment-to-lake area ratio was the best explanation of between population differences in [Hg], but this relationship does not bear out when only Cornwallis Island populations are considered (Lescord et al. 2015). Length, age, and $\delta^{15}N$ (i.e., trophic level) best explained differences in [Hg] within populations, but large differences remained even after adjustment for covariates (Muir et al. 2005). Length-at-age has been shown to be important for explaining population level differences in Arctic char Hg concentrations (Swanson and Kidd 2010, Swanson et al. 2011). Fourteen years ago, in one of the first temporal trends studies of Hg in the Arctic char, no significant trend was found for the Resolute population and nonsignificant increases in were reported for the Amituk and Char Lakes populations. Additionally, that study reported that "elevated Hg in char from Amituk Lake relative to the other lakes in the region cannot be readily explained by the available information on lake characteristics" (Muir et al. 2005).

High latitude lakes are characterized by low nutrient input and low biodiversity (for metazoans; Vincent et al. 2008) and in the case of lakes in polar deserts benthically-based

(Quesada et al. 2008) food chains as opposed to food webs (Power et al. 2008). Fish in such lakes are shown to have much higher [Hg] than expected based on environmental (i.e, atmospheric, water, and sediment) [Hg]. The results from Chapter 4 provide a crucial insight into this phenomenon: lakes with the lowest [DOC] in water had the highest [Hg] in fish. This could be tied to the lower growth efficiency (Ward et al. 2010a; Ward et al. 2010b; Baumann et al. 2017) in the colder deeper lake Arctic char populations compared to the shallower lakes which likely have longer and more frequent ice-free (i.e., growing) periods. In ice-dominated or benthically-based aquatic systems, organic carbon content of the water column may be an indicator of the system's primary productivity levels and not directly related to the transfer of Hg to biota, as it is in other ecosystems (O'Driscoll et al. 2005; Driscoll et al. 1995; Mazrui et al. 2016; Ravichandran 2004).

5.2.2 Mercury in warming Arctic lakes

Arctic warming has in many lakes lengthened the ice free period and thereby increased the length of the growing season (Ruhland et al. 2008; Brown and Duguay 2011) which our results indicate should reduce fish [Hg] by increasing growth efficiency. Further, as lake ice extent decreases, phytoplankton and zooplankton production will likely become more prevalent, providing a lower [Hg] food source for fish. However, our results also demonstrate that Hg methylation will likely increase as water and sediment temperatures increase, which may counteract this effect. Crucially, the liberation of the large pools of legacy Hg to the atmosphere could greatly increase Hg loading to the lakes and their watersheds. As Arctic warming progresses, snowfall is projected to increase (Krasting et al. 2013), which our results indicate could also increase fish [Hg]. As these changes co-occur in the future, lake-to-lake differences

will likely dominate, and we should not expect similar effects across fish populations in either direction or magnitude.

5.2.3 Overall Conclusions

Taken together, the results of these three studies help to elucidate 1) why lake-to-lake differences in [Hg] occur: growth efficiencies which are tied to primary and secondary production in the benthos, which are in turn partially controlled by temperature 2) whether or not these differences in [Hg] in biota are linked to methylation and demethylation in sediments: methylation potentials are generally higher in sediments from shallow, warmer lakes, and these sediments demonstrate greater response to warming temperatures than colder, less productive lakes. The shallow lakes demonstrate greater methylation potentials but do not demonstrate higher [Hg] in the chironomids or in char; actually, unadjusted and length-adjusted [Hg] in char are lower in the shallow lakes.

5.3 Future Research

This work has progressed our understanding of Hg in biota in Arctic lakes and given indications of how Hg in the lakes has responded over time and what we can expect in the future. However, like most investigations, it led to more questions than it answered. In order to better contextualize Hg in the lakes and how it relates to the organic carbon, collection of water samples over depth for determination of the optical properties, (i.e., protein content, aromaticity) of the available carbon (Lescord et al. 2018; Williamson et al. 1999) could determine the "quality" of the material and determine if it is a vector for Hg in waters, which could then be integrated into lake food chains. This would help to determine if the Hg in fish: productivity of lake relationship is due to reduced organic carbon content of the water in cold water lakes, and is therefore a stoichiometric relationship, or if measurement of organic carbon in the water is a

proxy for the productivity of the lake system (benthos and water column) which is not directly related to Hg transport or bioavailability. In the Cornwallis Island lakes there is no clear relationship between Hg or MeHg in water and DOC content (this thesis), but at larger scales, relationships between DOC and MeHg in water have been related to MeHg bioaccumulation (Chételat et al. 2018). This could have to do with the origin and the affinity of Hg or MeHg with the molecules making up the DOC. While it is clear that DOC affects Hg dynamics and bioaccumulation in lakes, there is a gap in the knowledge as to exactly why that is (French et al. 2014). In ice-dominated, benthically based lakes, DOC in water columns is dominated by more bioaccessable fulvic acids and the larger, less labile humic acids are more rare (French et al. 2014; McKnight et al. 1991).

The Northern Contaminants Program of Aboriginal Affairs and Northern Development Canada seeks to provide information to Northeners about contaminants in traditional/country foods. The Char Monitoring Project is supported by this program because the char act as biomonitors for Hg trends in the High Arctic region. Mercury trends in these char are not simply a product of Hg deposition but also of lake conditions, and are thereby affected by ice cover, primary productivity, and temperature. This thesis demonstrates some of ways that long-term contaminants records can aid in understanding not just contaminant dynamics but also other important changes that char demonstrate and the variation in those changes between ecosystems. These records are a valuable asset to Canadians and other Northeners and I recommend that monitoring continue in all the lakes included in this study. Further, I recommend that efforts are made to compare and contrast the temporal trends in Hg with PCBs and emerging contaminants in order to gain insight about the different processes governing these trends (for example, the methylation step for Hg which does not have an analogous step for PCB uptake). Finally, I

recommend that an analysis of temporal trends in growth and stable isotopes in the char is conducted which may aid in understanding the contaminant trends and reveal important biological differences between lakes and over time.

5.4 Limitations

Limitations on the interpretability of this work include a lack of ability to put the work in context of the wider food web, which includes more diversity than the samples collected for these studies. Also present in this food web are immature char which serve as predators of larval chironomids and prey for the larger char. Further, the biofilms on the moss beds and the mosses themselves play an important role in primary production, chironomid and probably larval char habitat, and likely Hg cycling in these lakes. However, samples of these mosses were not included in these studies. Future work should include characterization of the role of the moss beds in carbon, sulfur, and Hg cycling in these lakes.

Lake-to-lake variation is the driving factor in determining Hg dynamics in these lakes and therefore prevents extrapolations between systems. Further studies should better characterize the lake-to-lake variation and not attempt to generalize between lakes.

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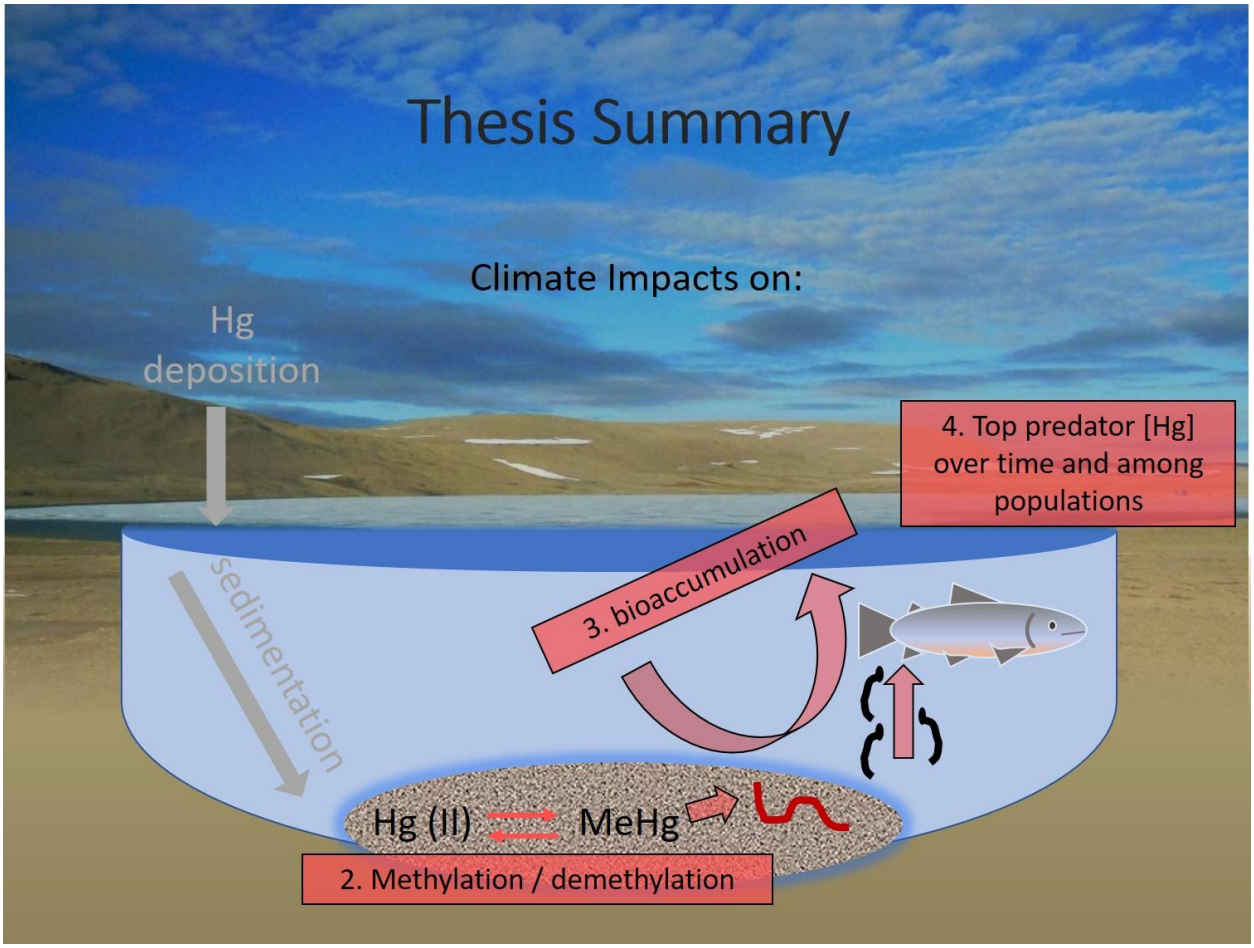

Figure 1: Summary of thesis data chapter contents in the context of Hg movement through an Arctic lake (Photo: Char Lake, Aug. 2013).

APPENDICES

Appendix A Supplemental Material for Chapter 3

Supporting Information for Hudelson et al. (2019)

1.1 Additional Data and details of Hg analysis in char

Table A-1 Annual averages and standard deviations of measurements of char Hg concentration from Amituk Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
1989	26	0.85 ± 0.56	39.2 ± 6.9	0.82 ± 0.10	528 ± 277	--	--	--
1992	14	0.91 ± 0.67	38.6 ± 4.9	0.93 ± 0.14	534 ± 142	--	--	--
2001	4	2.20 ± 1.31	46.4 ± 6	0.71 ± 0.08	755 ± 352	20 ± 3	--	--
2002	4	1.52 ± 0.77	48 ± 6.8	0.70 ± 0.12	844 ± 467	18 ± 2	12.1 ± 0.6	-20.9 ± 0.4
2003	5	1.86 ± 0.72	46 ± 4.2	0.72 ± 0.06	728 ± 223	19 ± 1	11.7 ± 0.7	-20.7 ± 0.5
2005	6	1.05 ± 0.70	36.3 ± 9.7	0.83 ± 0.08	476 ± 478	18 ± 3	10.5 ± 1.1	-21.1 ± 0.5
2006	7	2.13 ± 0.88	45.3 ± 9.3	0.88 ± 0.11	875 ± 538	22 ± 5	--	--
2007	10	1.63 ± 0.89	44.1 ± 6	0.73 ± 0.05	660 ± 302	21 ± 2	11.8 ± 1.1	-21.3 ± 0.5
2008	2	1.20± 0.25	54.9 ± 8.6	0.75 ± 0.00	1284 ± 591	--	12.1 ± 1.3	-21 ± 0.2
2009	13	1.12 ± 0.71	44.6 ± 8.9	--	--	22 ± 4	11.7 ± 1.3	-21.7 ± 0.8
2011	9	1.07 ± 0.45	39.9 ± 7.4	0.71 ± 0.06	497 ± 308	16 ± 5	12.2 ± 0.4	-23.1 ± 1.1
2012	10	0.88 ± 0.45	42.3 ± 8.2	0.62 ± 0.10	523 ± 330	17 ± 4	12 ± 1	-23.1 ± 0.8
2013	8	0.94 ± 0.44	49.2 ± 8.5	0.73 ± 0.07	975 ± 566	16 ± 4	12.3 ± 0.4	-22.8 ± 1.2
2014	11	1.50 ± 0.55	50.5 ± 3.9	0.75 ± 0.07	998 ± 307	16 ± 4	12.5 ± 0.5	-23.2 ± 0.3
2015	20	1.23 ± 0.26	44.7 ± 4.6	0.68 ± 0.04	629 ± 196	16 ± 3	12.7 ± 0.6	-23.5 ± 0.4
2016	15	1.33 ± 0.56	44.9 ± 5.4	0.68 ± 0.05	644 ± 248	15 ± 4	12.3 ± 0.6	-23.5 ± 0.4
2017	5	0.86 ± 0.5	46.3 ± 13.2	0.67 ± 0.07	801 ± 484	16 ± 4	11.8 ± 2	-24 ± 0.8
2018	3	1.08 ± 0.26	49.6 ± 2.6	0.78 ± 0.01	959 ± 155	--	--	--

Table A-2 Annual averages and standard deviations of measurements of char Hg concentration from Char Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
2000	4	0.55 ± 0.27	36.6 ± 2.8	0.67 ± 0.07	329 ± 80	19 ± 7	11.9 ± 0.7	-23.6 ± 0.3
2001	3	0.49 ± 0.10	43.1 ± 2.7	0.98 ± 0.11	785 ± 76	18 ± 5	--	--
2003	6	0.53 ± 0.22	50.5 ± 8.9	0.88 ± 0.20	1286 ± 762	26 ± 5	11.5 ± 1.9	-24 ± 0.8
2005	7	0.60 ± 0.21	45.1 ± 9.9	1.07 ± 0.18	1173 ± 936	19 ± 4	11.9 ± 1	-23.9 ± 0.4
2007	4	0.62 ± 0.18	41.7 ± 4.8	0.81 ± 0.05	609 ± 241	22 ± 8	12.4 ± 0.4	-23.7 ± 0.4
2008	3	0.57 ± 0.04	57.2 ± 4.6	0.91 ± 0.08	1744 ± 539	--	12.6 ± 0.1	-24.1 ± 0.6
2009	5	0.44 ± 0.28	38.6 ± 6.7	--	--	--	11.2 ± 1.1	-23.4 ± 0.5
2010	6	0.31 ± 0.1	34 ± 2.9	0.73 ± 0.07	296 ± 109	9 ± 1	11.5 ± 0.6	-23.7 ± 0.6
2011	4	0.41 ± 0.05	35.2 ± 3.6	0.78 ± 0.07	345 ± 90	13 ± 1	11.5 ± 0.3	-23.3 ± 0.2
2012	2	0.23 ± 0.13	27.1 ± 9.1	--	--	14 ± 1	10.5 ± 2.3	-25.8 ± 0.1
2017	7	0.71 ± 0.12	59 ± 7	0.91 ± 0.04	1944 ± 713	17 ± 1	13.1 ± 0.2	-25.3 ± 1
2018	9	0.66 ± 0.18	56.1 ± 5.6	0.98 ± 0.12	1804 ± 648	--	--	--

Table A-3 Annual averages and standard deviations of measurements of char Hg concentration from Meretta Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
2006	10	0.33 ± 0.09	47.7 ± 6	1.07 ± 0.14	1248 ± 545	7 ± 2	11.7 ± 0.3	-25 ± 2.2
2010	20	0.2 ± 0.06	40.4 ± 4.4	0.89 ± 0.12	601 ± 236	5 ± 1	11.5 ± 0.2	-22.3 ± 0.6
2011	10	0.17 ± 0.07	38.3 ± 3.8	0.84 ± 0.04	487 ± 132	5 ± 1	10.8 ± 0.3	-22.8 ± 0.9
2012	18	0.12 ± 0.03	42 ± 2.5	0.84 ± 0.09	634 ± 137	6 ± 0	10.8 ± 0.4	-22 ± 0.8
2015	14	0.08 ± 0.04	43.8 ± 3.9	0.84 ± 0.06	721 ± 186	8 ± 1	12 ± 0.5	-21.2 ± 0.7
2016	14	0.08 ± 0.02	42.8 ± 1.8	0.79 ± 0.06	626 ± 93	8 ± 1	12.8 ± 0.3	-20.4 ± 0.4
2017	14	0.09 ± 0.03	45.4 ± 4.1	0.81 ± 0.06	779 ± 196	9 ± 1	12.4 ± 0.3	-20.6 ± 0.7
2018	11	0.08 ± 0.01	43.3 ± 3.2	0.81 ± 0.04	673 ± 160	--	--	--

Table A-4 Annual averages and standard deviations of measurements of char Hg concentration from Small Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
2005	13	0.17 ± 0.12	37.7 ± 5.2	0.88 ± 0.06	506 ± 245	16 ± 4	--	--
2006	7	0.20 ± 0.13	38.5 ± 5.4	0.92 ± 0.09	537 ± 212	16 ± 2	--	--
2007	8	0.08 ± 0.05	41.8 ± 5.8	0.73 ± 0.15	544 ± 255	16 ± 2	--	--
2008	12	0.07 ± 0.02	35.3 ± 2.9	0.72 ± 0.10	314 ± 59	13 ± 3	8.7 ± 0.4	-23.2 ± 0.3
2009	18	0.11 ± 0.12	34.9 ± 5	0.72 ± 0.05	328 ± 175	--	9 ± 0.7	-23.2 ± 0.4
2010	25	0.08 ± 0.03	34.9 ± 3	0.69 ± 0.08	294 ± 64	11 ± 2	9.3 ± 0.5	-23.3 ± 0.6
2011	15	0.09 ± 0.03	35.8 ± 2.6	0.59 ± 0.08	274 ± 59	14 ± 2	9 ± 0.6	-23.2 ± 0.3
2012	30	0.09 ± 0.03	32.8 ± 2.6	0.74 ± 0.09	263 ± 49	--	9.4 ± 0.6	-23.3 ± 0.4
2013	22	0.17 ± 0.09	36.1 ± 7	0.77 ± 0.08	414 ± 413	--	10 ± 0.8	-23.2 ± 0.5
2014	13	0.10 ± 0.04	36.4 ± 2.3	0.62 ± 0.03	304 ± 56	14 ± 2	8.9 ± 0.6	-23.5 ± 0.3
2015	15	0.14 ± 0.05	37.4 ± 2.1	0.59 ± 0.05	309 ± 55	15 ± 2	9.4 ± 0.6	-23.5 ± 0.3
2016	16	0.11 ± 0.04	36.5 ± 3.8	0.61 ± 0.05	307 ± 85	13 ± 2	10 ± 0.4	-23.7 ± 0.7
2017	13	0.13 ± 0.04	35 ± 4.2	0.64 ± 0.07	277 ± 74	14 ± 4	9.7 ± 0.6	-23.7 ± 0.4
2018	12	0.09 ± 0.03	34.7 ± 1.9	0.70 ± 0.04	296 ± 43	--	--	--

Table A-5 Annual averages and standard deviations of measurements of char Hg concentration from North Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
2000	14	0.20 ± 0.11	35.9 ± 6.2	0.77 ± 0.11	382 ± 143	16 ± 6	10.2 ± 1.2	-23.5 ± 1.1
2005	10	0.30 ± 0.16	34.2 ± 3.8	0.85 ± 0.07	357 ± 105	17 ± 3	--	--
2006	7	0.33 ± 0.24	38.3 ± 9.3	1.03 ± 0.10	695 ± 705	17 ± 3	10.6 ± 1.4	-23.8 ± 0.4
2007	6	0.31 ± 0.14	37.5 ± 10.4	0.74 ± 0.09	466 ± 233	16 ± 2	--	--
2008	22	0.21 ± 0.12	38.4 ± 4.9	0.76 ± 0.08	461 ± 261	15 ± 4	10 ± 0.9	-23.3 ± 0.6
2010	17	0.27 ± 0.30	37.2 ± 4.7	0.75 ± 0.11	424 ± 311	13 ± 5	11 ± 1.3	-23.4 ± 0.6
2011	15	0.33 ± 0.16	41.3 ± 3.7	0.69 ± 0.07	499 ± 154	19 ± 5	11.1 ± 0.8	-23.7 ± 0.8
2012	14	0.22 ± 0.18	38.6 ± 6.5	0.72 ± 0.08	463 ± 387	--	11.2 ± 1.1	-23.8 ± 1
2013	13	0.26 ± 0.15	36.7 ± 5.6	0.89 ± 0.08	488 ± 292	14 ± 2	12.8 ± 1.3	-23.1 ± 0.8
2014	7	0.23 ± 0.08	42.1 ± 5	0.75 ± 0.06	594 ± 306	16 ± 1	12.6 ± 0.9	-23.9 ± 1.6
2015	18	0.22 ± 0.07	38.7 ± 3.1	0.74 ± 0.10	429 ± 94	17 ± 3	12.8 ± 0.7	-23.5 ± 0.6
2016	18	0.24 ± 0.15	38.2 ± 8.4	0.69 ± 0.06	445 ± 238	14 ± 4	13.6 ± 1	-24 ± 1
2017	10	0.42 ± 0.15	43.5 ± 4.9	0.74 ± 0.08	649 ± 315	15 ± 3	14.2 ± 1.2	-24.4 ± 0.7
2018	10	0.32 ± 0.18	41.6 ± 4	0.76 ± 0.07	573 ± 209	--	--	--

Table A-6 Annual averages and standard deviations of measurements of char Hg concentration from Resolute Lake and other biological variables for char.

Year	n	Hg (µg/g ww)	Total Length (cm)	Condition Factor	Weight (g)	Age (years)	δ15N (‰)	δ13C (‰)
1993	7	0.20 ± 0.10	39.8 ± 1.5	--	--	--	--	--
1997	10	0.20 ± 0.10	32.8 ± 3.4	0.91 ± 0.37	305 ± 76	21 ± 7	12.2 ± 0.9	-22.5 ± 0.5
1999	10	0.17 ± 0.07	39.6 ± 2.8	0.79 ± 0.09	507 ± 157	19 ± 2	11.5 ± 0.7	-22.1 ± 0.4
2000	18	0.16 ± 0.06	39.1 ± 2.1	0.72 ± 0.07	433 ± 78	21 ± 5	--	--
2001	17	0.16 ± 0.11	39.3 ± 2.9	0.77 ± 0.08	467 ± 83	20 ± 6	11.8 ± 1.2	-21.7 ± 0.7
2002	10	0.14 ± 0.06	37.1 ± 2.9	0.71 ± 0.06	370 ± 101	--	--	--
2003	10	0.18 ± 0.05	40 ± 2.1	0.78 ± 0.09	501 ± 90	22 ± 4	11.7 ± 0.6	-22 ± 0.4
2004	10	0.17 ± 0.07	37.9 ± 4.9	0.83 ± 0.13	490 ± 287	20 ± 7	11.5 ± 1.1	-22 ± 0.4
2005	10	0.28 ± 0.09	38.3 ± 5.2	0.85 ± 0.10	502 ± 221	--	12.6 ± 1	-22.2 ± 0.7
2006	10	0.25 ± 0.08	38.2 ± 5.1	0.87 ± 0.06	515 ± 239	19 ± 3	--	--
2007	14	0.21 ± 0.06	41.2 ± 2.9	0.78 ± 0.05	554 ± 124	20 ± 4	11.7 ± 0.9	-22.6 ± 0.5
2008	11	0.17 ± 0.06	42.9 ± 3.7	0.79 ± 0.07	628 ± 160	20 ± 3	11.3 ± 1	-22.1 ± 0.5
2009	20	0.18 ± 0.09	41.7 ± 5.9	--	--	19 ± 4	12 ± 1.3	-21.9 ± 0.4
2010	10	0.17 ± 0.07	43.5 ± 3.8	0.79 ± 0.07	657 ± 179	19 ± 4	11.5 ± 0.8	-22.7 ± 1.3
2011	20	0.17 ± 0.07	41.4 ± 4.4	0.79 ± 0.06	585 ± 218	17 ± 6	11.3 ± 1.2	-22.2 ± 0.7
2012	18	0.15 ± 0.08	42.5 ± 5.1	0.73 ± 0.08	591 ± 250	17 ± 3	11.8 ± 1.3	-22.3 ± 1
2013	16	0.16 ± 0.09	38.7 ± 5.3	0.85 ± 0.10	535 ± 289	--	11 ± 1.1	-22.1 ± 0.3
2014	14	0.13 ± 0.05	42 ± 3.4	0.67 ± 0.05	508 ± 146	17 ± 2	10.8 ± 0.8	-22.2 ± 0.3
2015	20	0.16 ± 0.07	42.8 ± 4.2	0.74 ± 0.07	601 ± 221	17 ± 2	11.9 ± 1.4	-22.9 ± 0.7
2016	17	0.16 ± 0.09	42.1 ± 4.6	0.74 ± 0.06	576 ± 231	16 ± 3	11.5 ± 1.6	-23.2 ± 0.8
2017	14	0.09 ± 0.03	45.4 ± 4.1	0.81 ± 0.06	779 ± 196	9 ± 1	12.4 ± 0.3	-20.6 ± 0.7
2018	11	0.08 ± 0.01	43.3 ± 3.2	0.81 ± 0.04	673 ± 160	--	--	--

Table A-7 Regression slopes of the annual mean for each characteristic of the six populations of land-locked Arctic char (Cornwallis Island, NU) over time. * indicates statistical significance of the regression slope at $\alpha = 0.05$.

	Amituk	Char	Meretta	North	Resolute	Small
Total length (cm)	0.22	0.58	-0.019	0.29*	0.28*	-0.38*
Weight (g)	7.8	46.6	-26.3	7.4	12.9*	-17.0*
Fulton's condition factor, K	-0.005*	0.0058	-0.018*	-0.0023	-0.0021	-0.0075*
Age (y)	-0.23*	-0.47	0.23	-0.06	-0.22*	-0.11
δ13C (‰)	-0.23*	-0.071	0.40*	-0.029	-0.043*	-0.036
δ15N (‰)	0.051	0.0018	0.11	0.25*	-0.026	0.040

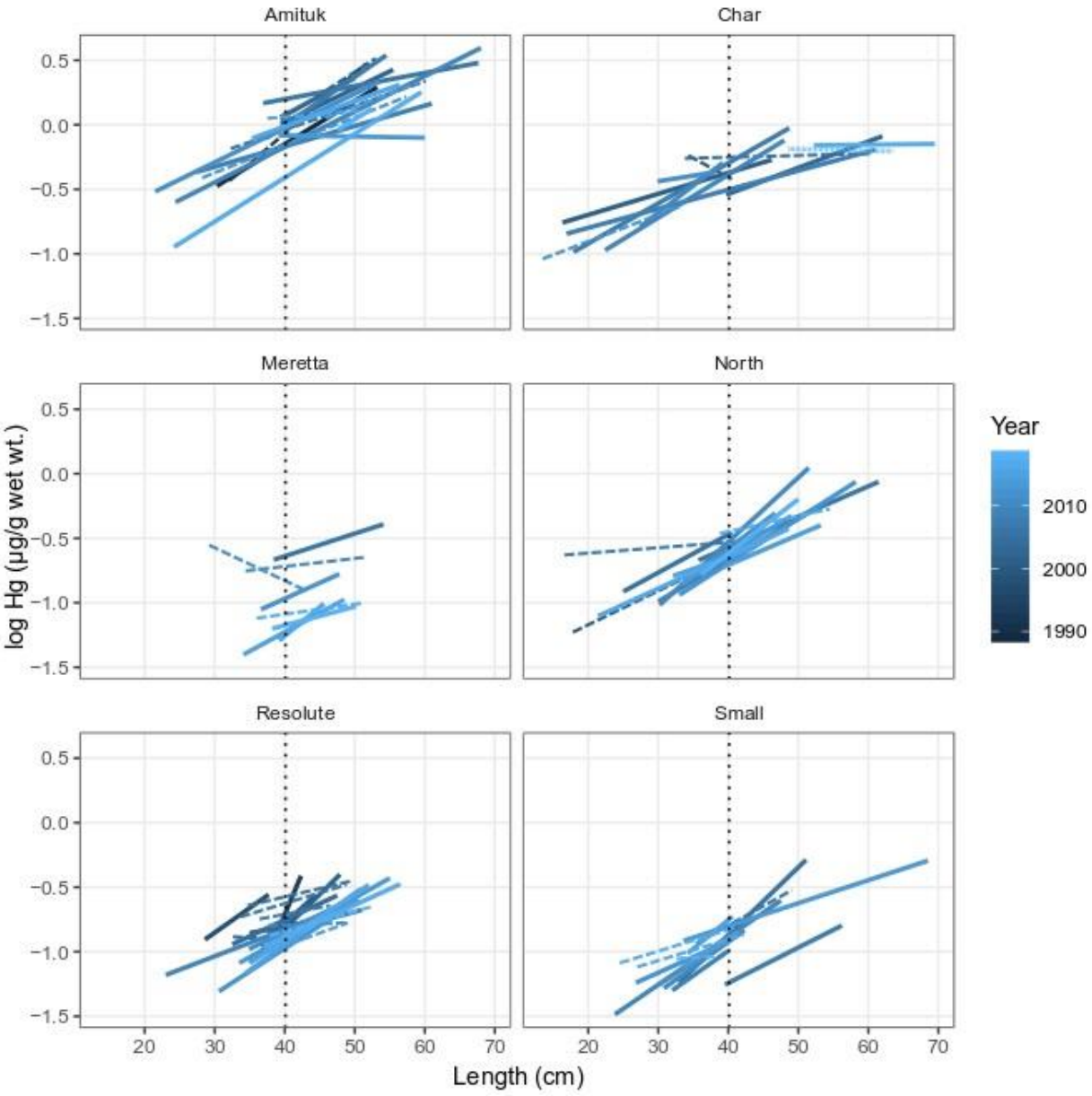

Figure A-1 Regression lines of the log Hg: length relationship for Arctic char for each year of collection in six lakes from Cornwallis Island, NU, Canada.
The mean total length (40.1 cm) of all Arctic char used in this study is indicated by the vertical dashed line. Regression lines are shaded by Year; dashed regression lines indicate non-significant relationship. The point at which each regression line crosses the mean length is presented in Table 2. See Figure A-2 for the log Hg: age relationship.

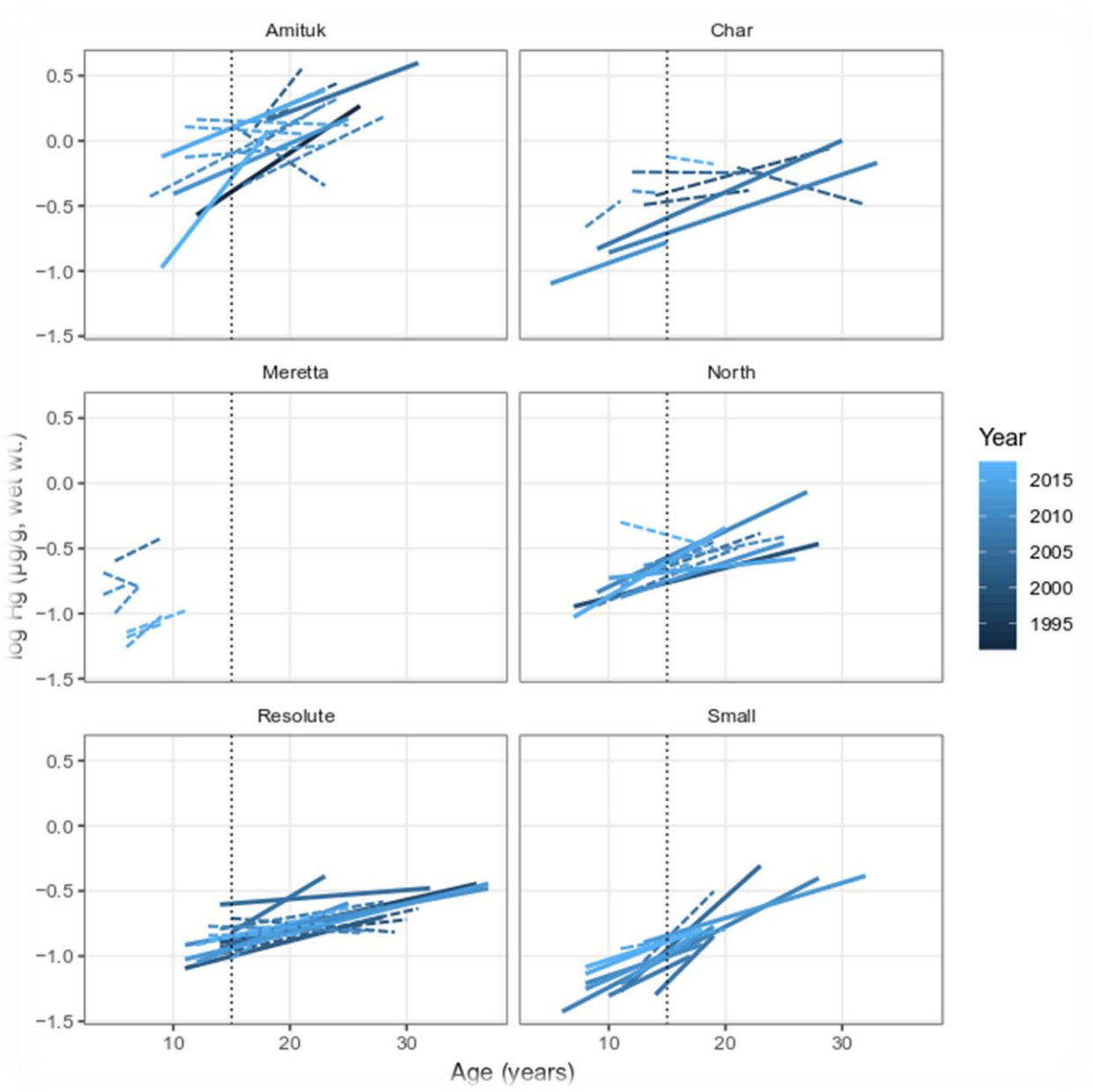

Figure A-2 Regression lines of the log Hg: age relationship for Arctic char for each year of collection in six lakes from Cornwallis Island, NU, Canada.
The mean age of all Arctic char used in this study is indicated by the vertical dashed line. Regression lines are shaded by Year; dashed regression lines indicate non-significant relationship.

Table A-8 Length-adjusted (to 40.1 cm total length) Hg concentration in µg/g wet wt., with sample size in parentheses for Arctic char for each year in the six study lakes from Cornwallis Island, Nunavut, Canada.
Mean ± 1 SD for all years. Concentrations are back-transformed from linear regression relationships for log Hg with length for each lake and year (Figure A-1).

Year	Amituk	Char	Meretta	North	Resolute	Small
1989	0.715[1] (26)	--	--	--	--	--
1990	--	--	--	--	--	--
1991	--	--	--	--	--	--
1992	0.869[1] (14)	--	--	--	--	--
1993	--	--	--	--	0.200 (7)	--
1994	--	--	--	--	--	--
1995	--	--	--	--	--	--
1996	--	--	--	--	--	--
1997	--	--	--	--	0.343 (10)	--
1998	--	--	--	--	--	--
1999	--	--	--	--	0.168 (10)	--
2000	--	0.389 (4)	--	0.228 (14)	0.158 (18)	--
2001	1.155 (4)	0.427 (3)	--	--	0.153 (17)	--
2002	1.057 (4)	--	--	--	0.124 (10)	--
2003	1.201 (5)	0.293 (6)	--	--	0.175 (10)	--
2004	--	--	--	--	0.177 (10)	--
2005	0.917 (6)	0.561 (7)	--	0.341 (10)	0.267 (10)	0.137 (13)
2006	1.586 (7)	--	0.231 (10)	0.271 (7)	0.238 (10)	0.161 (7)
2007	0.998 (10)	0.509 (4)	--	0.295 (6)	0.196 (14)	0.058 (8)
2008	0.683 (2)	0.315 (3)	--	0.216 (22)	0.147 (11)	0.103 (12)
2009	0.679 (13)	0.414 (5)	--	--	0.150 (20)	0.132 (18)
2010	--	0.544 (6)	0.192 (20)	0.301 (17)	0.161 (10)	0.121 (25)
2011	0.952 (10)	0.447 (4)	0.147 (10)	0.266 (15)	0.144 (20)	0.126 (15)
2012	0.702 (10)	0.326 (2)	0.108 (18)	0.203 (14)	0.107 (18)	0.121 (30)
2013	0.829 (8)	--	--	0.236 (13)	0.130 (16)	0.159 (22)
2014	0.866 (11)	--	--	0.198 (7)	0.112 (14)	0.128 (13)
2015	1.152 (20)	--	0.060 (14)	0.229 (18)	0.115 (20)	0.178 (15)
2016	0.976 (15)	--	0.056 (14)	0.230 (18)	0.124 (17)	0.125 (16)
2017	0.393 (5)	0.681 (7)	0.082 (14)	0.357 (10)	0.131 (14)	0.149 (13)
2018	0.502 (3)	0.665 (9)	0.067 (11)	0.243 (10)	0.144 (11)	0.094 (12)
mean	0.90 ± 0.28[a]	0.47 ± 0.13[b]	0.12 ± 0.07[e]	0.26 ± 0.05[c]	0.17 ± 0.06[d]	0.13 ± 0.03[d,e]

1. Values were excluded from some analyses, see section 2.3.2 for details. These points were included in the calculation of the mean.

Table A-9 Area of each feature type of the study lake watersheds on Cornwallis Island Generated by GIS analysis of the Natural Resources Canada Landsat data. This data was used to make the comparisons in Table 3.

Feature	**Amituk**	**Char**	**Meretta**	**North**	**Resolute**	**Small**
% Water	8.62	18.2	10.1	1.39	15.6	21.6
% Barren	83.5	57.3	71.8	49.2	57.5	66.2
% Till / colluvium	6.19	22.0	1.1	29.4	25.0	9.41
% Gramminoid shrub tundra	0	0	0.071	0.027	0	0
% Snow / Ice	1.33	0	0	0.418	0.0946	0
% Bare soil with cryptogram crust	0.181	2.58	0	18.4	1.82	1.46
% Dwarf shrub	0	0	0	0.503	0.0	0
% Tussock tundra	0	0	0	0.480	0.0527	0
% Wet sedge	0	0	0	0.138	0	1.36
% Wetland	0.0954	0	0	0	0	0
% No data	0.0766	0	0	0	0	0

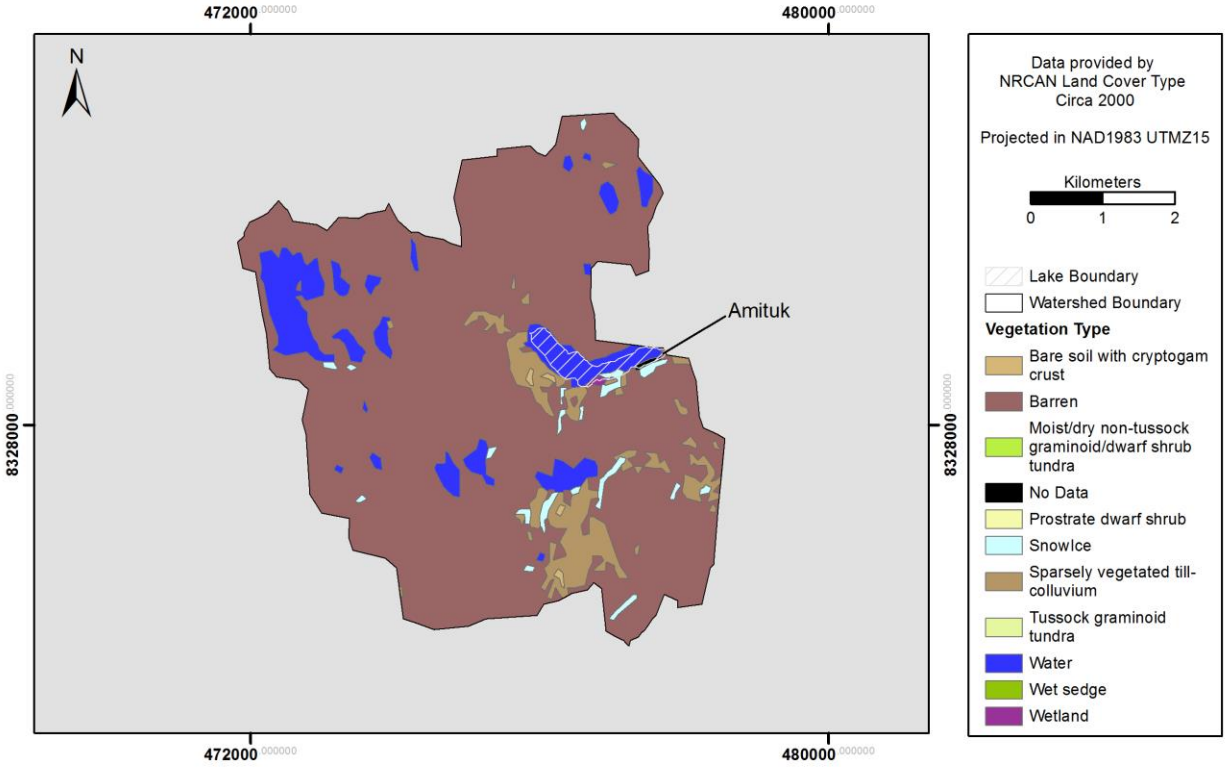

Figure A-3 GIS-derived cover types in the Amituk Lake watershed on Cornwallis Island, NU.

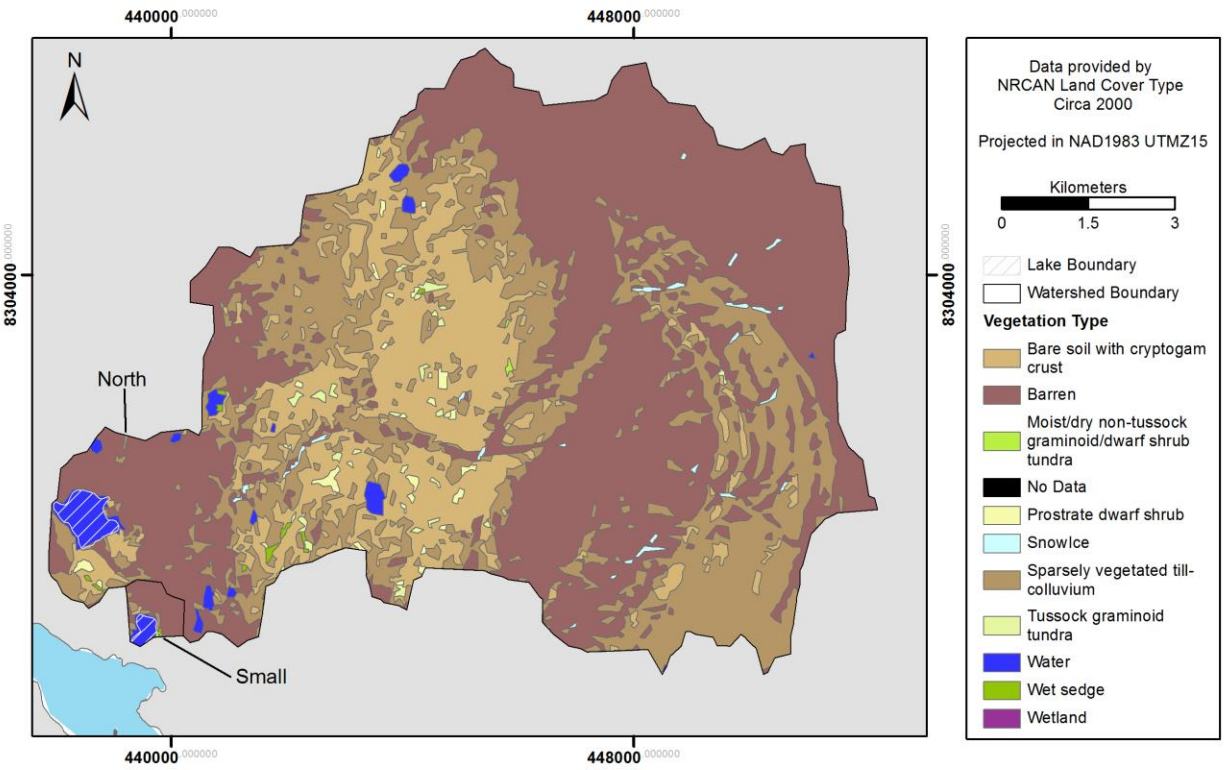

Figure A-4 GIS-derived cover types of North and Small Lakes watersheds on Cornwallis Island, NU.

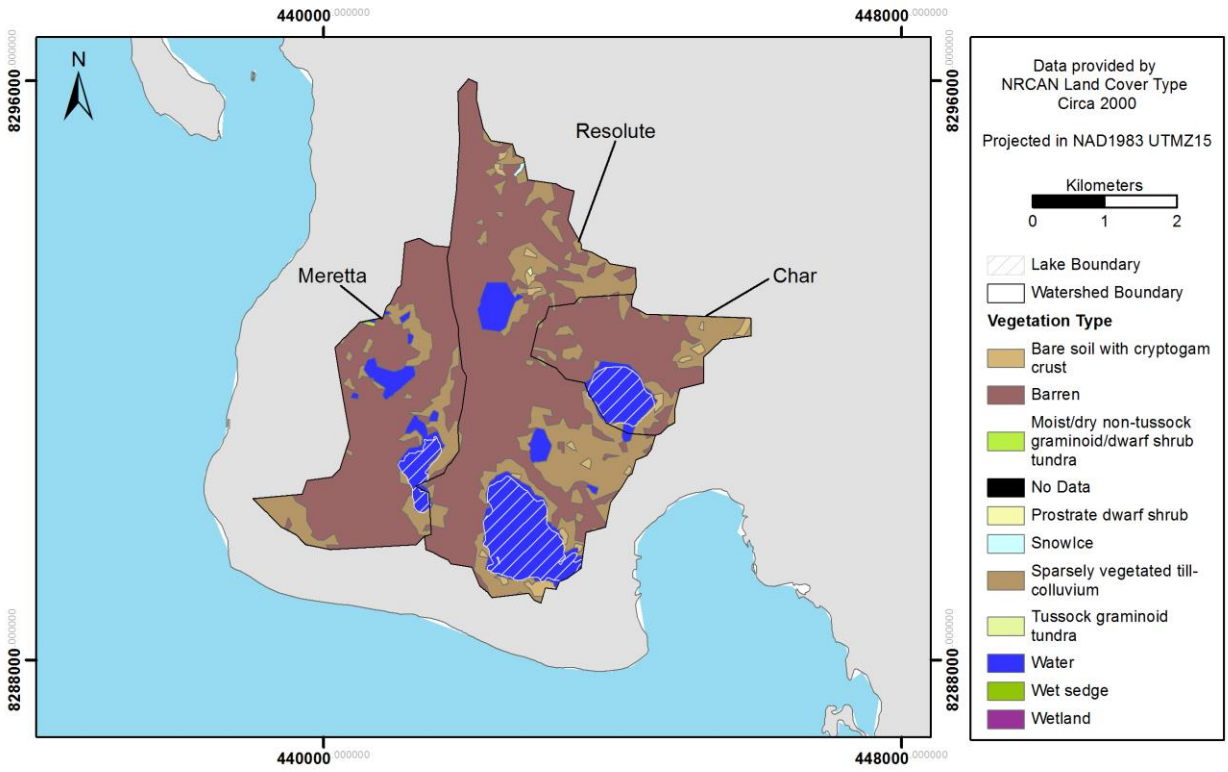

Figure A-5 GIS-derived cover types of Meretta, Resolute, and Char Lakes watersheds on Cornwallis Island, NU.

Table A-10 Water chemistry variables for each lake in both surface (0.5-1 m depth) and deep (1 m from bottom at deepest point) samples. See manuscript 2.3.3.2 for details. This data was used to make the comparisons presented in Table 4.

Lake	**n**	**Chl *a* (µg/L)**	**DOC (mg/L)**	**POC (mg/L)**	**TDP (µg/L)**	**TDN (mg/L)**	**NO_3/NO_2 (µg/L)**
				Surface waters			
Amituk	11	0.75 ± 0.87	0.81 ± 1.03	0.15 ± 0.07	0.85 ± 0.96	0.03 ± 0.05	59.4 ± 29.9
Char	16	0.47 ± 0.52	0.72 ± 0.25	0.17 ± 0.08	1.28 ± 1.35	0.02 ± 0.04	6.7 ± 3.3
Meretta	3	1.38 ± 1.18	1.85 ± 0.22	0.25 ± 0.06	0.25 ± 0.09	[0.002]	13.5 ± 8.2
North	14	1.13 ± 0.85	0.98 ± 0.35	0.19 ± 0.08	0.76 ± 0.63	0.02 ± 0.04	110.2 ± 92.1
Resolute	15	0.53 ± 0.66	1.2 ± 0.26	0.22 ± 0.08	2.78 ± 1.57	0.03 ± 0.06	7.9 ± 5
Small	16	0.75 ± 0.63	2 ± 0.41	0.35 ± 0.16	1.83 ± 1.67	0.02 ± 0.06	11.3 ± 11.1
				Profundal waters			
Amituk	2	[1.60 - 2.40]	[0.30 - 0.30]	[0.098 - 0.10]	[0.40 - 0.40]	[0.002 - 0.002]	[85.0 -81.0]
Char	8	1.16 ± 1.51	0.55 ± 0.11	0.15 ± 0.03	0.49 ± 0.31	1.4e-3 ± 1.4e-3	5.9 ± 1.7
Meretta	2	[2.50 - 0.42]	[1.70 - 2.02]	[0.21 - 0.34]	[0.35 - 0.48]	---	[8.4 -18.0]
North	6	2.05 ± 1.59	0.77 ± 0.12	0.23 ± 0.07	0.82 ± 0.43	0.01 ± 0.01	109.5 ± 90.6
Resolute	2	[1.50 - 0.30]	[0.90 - 1.00]	[0.22 - 0.27]	[2.6 -2.9]	[9e-4 - 9e-4]	[6.0 -5.0]
Small	7	0.97 ± 1	2.03 ± 0.45	0.38 ± 0.11	1.09 ± 0.65	0.01 ± 0.01	10.1 ± 11.5

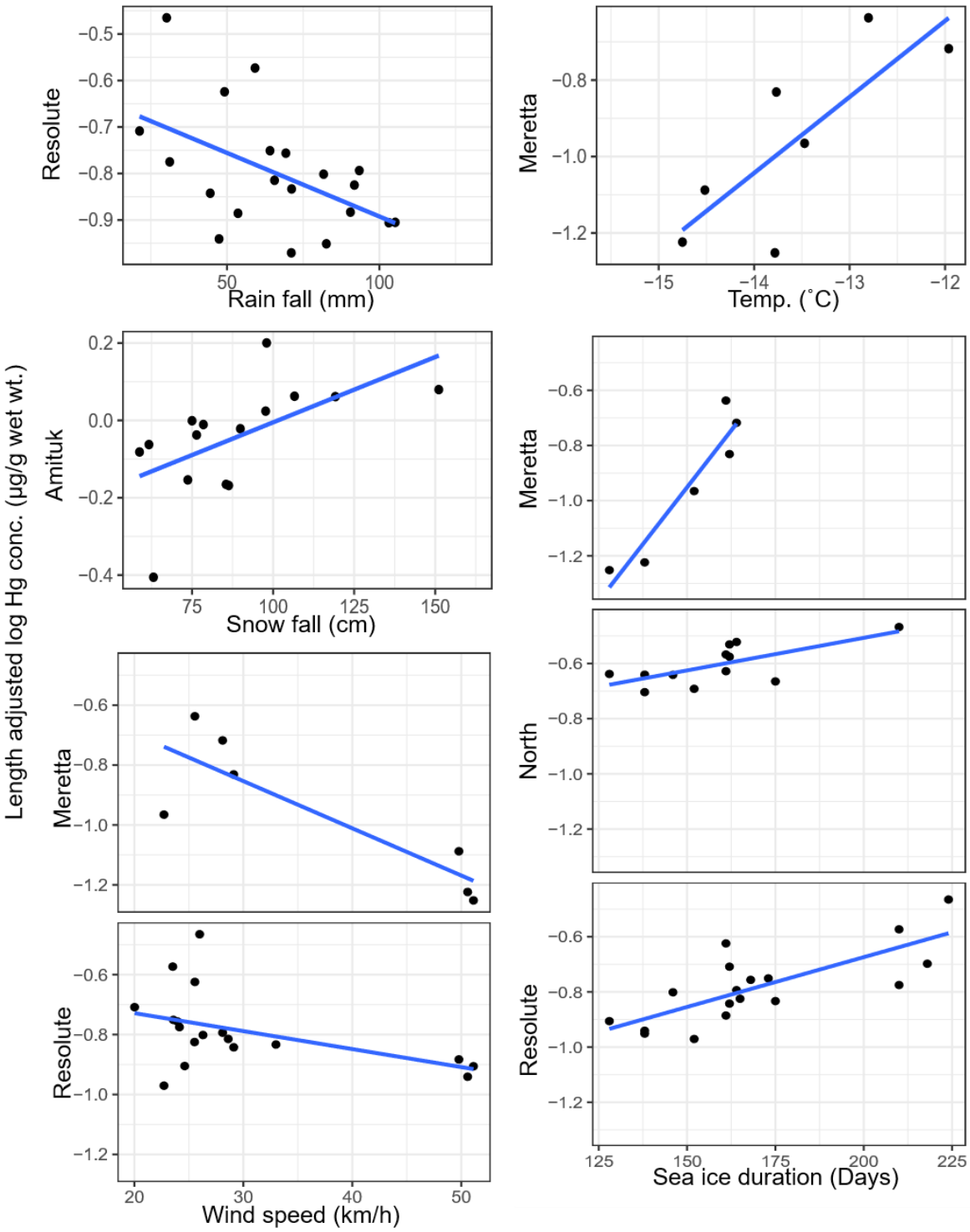

Figure A-6 Significant (at α = 0.05) correlations between length adjusted log Hg concentrations in Arctic char muscle from four populations and climate variables. Lines were included on the plots although the correlation method used allowed for linear and non-linear relationships (Pearson's rho). Plots are included for more detailed understanding of the relationships in Table 5.

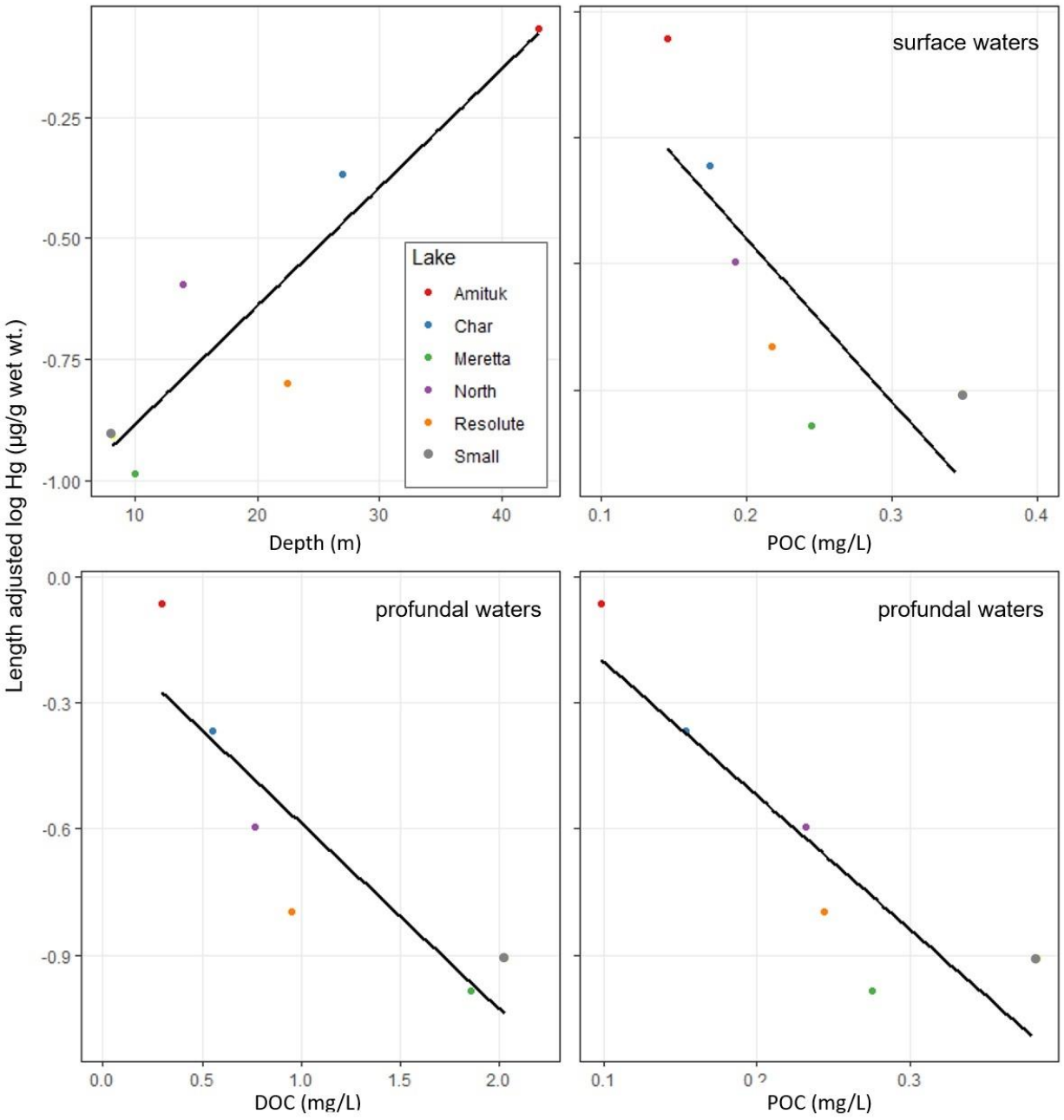

Figure A-7 Regression of mean length-adjusted log Hg concentrations in char vs. lake depth, DOC concentrations in surface water and deep water, and POC in deep water samples for each lake.

Table A-11 Fit statistics, degrees of freedom, and p values of the linear models generated for length-adjusted log Hg concentration from each Arctic char population using the three climate variables (NAO, rain fall and snow fall) selected in the stepwise selection process. The coefficients for these models are presented in A-12.

Trend Type	Population	R^2	R^2 adj.	DF	p value
decreasing	Amituk	0.446	0.295	4	0.079
	Meretta	0.807	0.613	4	0.136
	Resolute	0.477	0.379	4	0.014
non-significant	Char	0.431	0.187	4	0.24
	North	0.081	-0.225	4	0.849
	Small	0.292	0.056	4	0.352

Table A-12 Coefficients and adjusted (Benjamini Hochberg, 1995) p values for linear model applied each of the six study populations of Arctic char length adjusted Hg concentration using the climate variables selected by the stepwise selection process on the decreasing trend populations.
Significant model variable (after p value adjustment) is bolded. Fit statistics for these models are presented in Table 7.

Trend Type	Lake	Variable	Coefficient ± SE	P value
decreasing	Amituk	Intercept	0.008 ± 0.037	0.829
	Amituk	Rain Fall	-0.055 ± 0.037	0.336
	Amituk	NAO Index	-0.043 ± 0.12	0.829
	Amituk	Snow Fall	0.099 ± 0.04	0.125
	Meretta	Intercept	-1.063 ± 0.087	0.005
	Meretta	Rain Fall	-0.277 ± 0.104	0.102
	Meretta	NAO Index	-0.329 ± 0.123	0.102
	Meretta	Snow Fall	-0.208 ± 0.156	0.274
	Resolute	Intercept	-0.789 ± 0.025	<0.001
	Resolute	**Rain Fall**	**-0.085 ± 0.028**	**0.015**
	Resolute	NAO Index	-0.144 ± 0.066	0.059
	Resolute	Snow Fall	0.046 ± 0.028	0.122
non-significant	Char	Intercept	-0.401 ± 0.039	<0.001
	Char	Rain Fall	0.007 ± 0.045	0.888
	Char	NAO Index	0.046 ± 0.085	0.802
	Char	Snow Fall	-0.1 ± 0.043	0.11
	North	Intercept	-0.617 ± 0.044	<0.001
	North	Rain Fall	-0.024 ± 0.034	0.625
	North	NAO Index	-0.032 ± 0.064	0.625
	North	Snow Fall	-0.03 ± 0.052	0.625
	Small	Intercept	-0.834 ± 0.058	<0.001
	Small	Rain Fall	0.074 ± 0.044	0.251
	Small	NAO Index	0.082 ± 0.085	0.361
	Small	Snow Fall	0.084 ± 0.066	0.314

Appendix B Supplemental Material for Chapter 4

Hudelson et al. Influences on bioaccumulation and biota-sediment accumulation factors for methyl-mercury in High Arctic lakes Supplementary Material

Arctic char MeHg bioaccumulation model

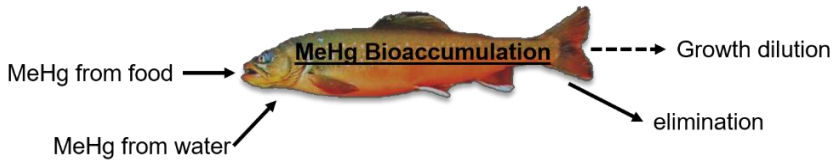

Figure B-1: Illustration of MeHg bioaccumulation model for Arctic char.

To better understand the nature of the relationship between char [Hg] and temperature, we constructed a bioaccumulation model in which rates of Hg uptake and loss vary with temperature. MeHg comprises nearly 100% of the Hg in large predatory fish such as Arctic char and was therefore the only form considered in the model.

$$C_t = \frac{k_{food}C_{food} + k_{water}C_{water}}{k_{elim} + k_{growth}} (1 - e^{-(k_{elim} + k_{growth})t} + C_0 e^{-(k_{elim} + k_{growth})t}$$

Where C_0 is the initial [MeHg] in char, and C_t is the [MeHg] after time *t*; C_{food} and C_{water} are the [MeHg] in food and water, respectively; k_{food} and k_{water} are the rate constants for uptake of MeHg from food and water, respectively; and k_{elim} and k_{growth} are rate constants for loss of MeHg via elimination and growth dilution (note that growth dilution is not a true loss but the model represents it as such), respectively. The model was developed using published rate constants, mathematical functions (Gewurtz et al. 2006; Trudel and Rasmussen 1997; Gobas 1993), and assimilation efficiencies (Hrenchuk 2010).

We used the empirical data from Gantner et al. (Gantner et al. 2010) to determine how this model predicted changes in [MeHg] in Arctic char over several temperatures and varying C_{food}, but keeping *t* and C_0 constant.

In the study lakes, consistent with most unpolluted lakes, [MeHg] in water is very low, so MeHg uptake from water is negligible even at elevated temperatures (Trudel and Rasmussen 2006). For this model, <1% of MeHg in fish was accumulated via uptake from water. Uptake from food thus accounted for >99%. Increased ingestion rate at elevated temperatures exerted a modest effect on [MeHg] in char.

When C_{food} is adjusted, MeHg bioaccumulation in char is highly responsive (Figure 2). Variation of temperature did not generate large differences in char [MeHg], but varying C_{food} resulted in large changes in char [MeHg]. This finding indicates that the primary route of alteration of the MeHg bioaccumulation in Arctic lake food webs under climate change will be due to increased production and food intake. If chironomid biomass increases with increased warming, then it is likely that the overall [MeHg] in chironomids will decrease, resulting in less [MeHg] in Arctic char.

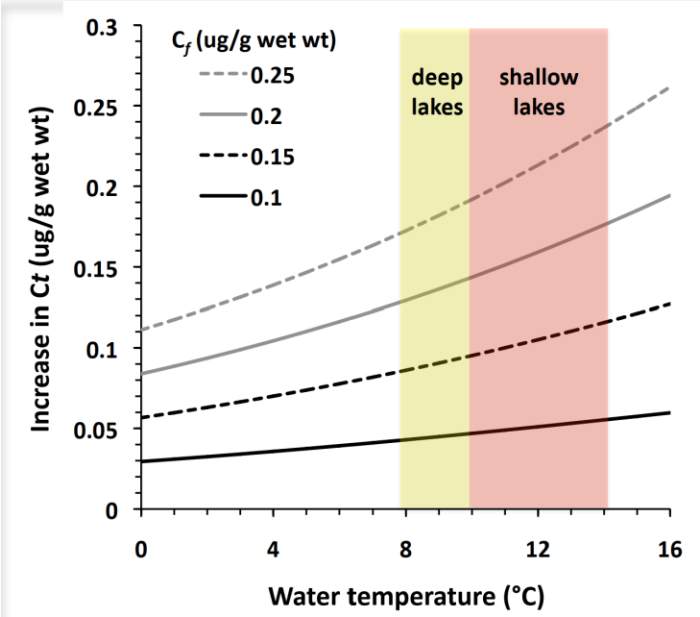

Figure B-2: Estimated change in [MeHg] in Arctic char over a range of temperatures and [MeHg] in food from the bioaccumulation model.

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