ARCTIC CHAR OTOLITH RECORDS OF RECENT LIMNOLOGICAL CHANGE IN HIGH ARCTIC LAKES

by

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Abstract

Arctic lakes have been undergoing significant physical and chemical changes in recent years due to climate warming and permafrost thaw. These changes have the potential to impact organisms residing in these environments such as Arctic Char (Salvelinus alpinus) which represent the top predatory fish in Arctic lakes. Otoliths, the inner ear bones of fish, offer a method to monitor these impacts through chemical analysis of their annual rings. However, not only are long-term limnological records in the Arctic limited, but the impacts of climate-driven change on Arctic aquatic ecosystems are not well known. This research investigates a long-term record (2003-16) of the physiochemical properties of two High Arctic lakes at the Cape Bounty Arctic Watershed Observatory on Melville Island, Nunavut. Additionally, 2013 and 2015 otoliths were analyzed to investigate elemental changes associated with limnological and catchment change.

Results indicate that both lakes underwent significant chemical change following a catchment permafrost disturbance episode in 2007 that caused widespread slope disturbances and a deep seasonal active layer thaw. Both lakes have seen increased solute loads, most notably a 500% and 300% increase in water column SO$_4^{2-}$ in the West and East Lakes, respectively. Ionic ratios indicate that the source for the SO$_4^{2-}$ is compositionally similar to disturbed catchment streams. In addition, the West Lake has seen substantial and sustained increases in turbidity associated with internal subaqueous slumps and similar effects are absent from the East Lake. Hence, the synchronous change in solute loading to the lakes reflects increased contributions from the catchment due to deep active layer development.

Otolith analysis reveals an abrupt increase in Mg and a decrease in Ba in fish from both lakes. Results further show that not only is the otolith chemistry statistically different within each individual fish from beginning to end of life, but also between the two lakes. These chemical changes are thought to reflect differential responses to multiple environmental stressors including the chemical and physical changes in
the lakes. Collectively, these studies demonstrate the rapid threshold responses of Arctic lakes and highlights the fact that these physiochemical changes have implications for the whole aquatic ecosystem.
Co-Authorship


Chapter 3 “Arctic char otolith microchemistry records of recent environmental change in High Arctic lakes” was co-authored by K.E. Roberts, S.F. Lamoureux, T.K. Kyser, D.C.G. Muir, and D. Iqaluk.

I am the primary author responsible for analysis and writing of all manuscripts and data collection in the 2015 field season. S.F. Lamoureux and T.K. Kyser provided project guidance and edits on all chapters and comments on Chapter 2 and 3 were provided by all other authors. S.F Lamoureux and M.J Lafrenière provided Cape Bounty meteorological data as well as physical and chemical data records prior to 2015, however, I was responsible for compiling and analyzing all records (Chapter 2). D.C.G. Muir and D. Iqaluk were responsible for providing 2013 fish otoliths and facilitated in the collection of 2015 otoliths. D.C.G. Muir has also provided the fish condition factor data and D. Iqaluk has provided valuable insight into the health of the fish in these systems (Chapter 2,3). All otoliths were analyzed at the Queen’s Facility for Isotope Research (QFIR), which is run and overseen by T.K Kyser. I was responsible for the processing and analysis of all otoliths with support from E. Leduc, the ICP-MS technician (Chapter 2,3). A. Normandeau has provided bathometric lake data and acoustic sedimentary data to evaluate alternative explanations (Chapter 2), and A. Pieńkowski provided 2014 diatom data and contributed to diatom interpretation (Chapter 2). Chapter 2 has been formatted for, and submitted to, Proceedings of the National Academy of Science.
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<th>Description</th>
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<tr>
<td>ALD</td>
<td>Active layer detachments</td>
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<tr>
<td>CBAWO</td>
<td>Cape Bounty Arctic Watershed Observatory</td>
</tr>
<tr>
<td>CTD</td>
<td>Conductivity, temperature, depth instrument used in limnology and oceanography</td>
</tr>
<tr>
<td>DFO</td>
<td>Department of Fisheries and Oceans</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser ablation inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric turbidity units</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component analysis</td>
</tr>
<tr>
<td>ULT</td>
<td>Ultimate lethal temperature</td>
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<td>ULT</td>
<td>Upper incipient lethal temperature</td>
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Chapter 1

Introduction

Arctic regions are undergoing rapid climatic change, including air temperature warming rates that are greater than the global average (ACIA 2004, Kattsov et al., 2005, SWIPA 2011). Temperatures recorded in the last decade have been an average of 4°C warmer than the mean temperatures documented from 1951-2000 (SWIPA 2011) and these record high temperatures appear to be unprecedented in the last two millennia (Kaufman et al., 2009). In addition to this, climate models have predicted annual precipitation increases in both frequency and intensity across the northern regions of North America and Eurasia (Kattsov et al., 2005) which challenges the fact that many Arctic regions, and High Arctic regions in particular, have been historically classified as polar deserts (<160 mm precipitation annually) (Maxwell 1981, Environment Canada Records 2016).

Increasingly warm summer and autumn temperatures will cause this precipitation to fall as rain as opposed to snow which in turn will increase river discharge, soil moisture, catchment connectivity and runoff, and flush near-surface solutes into rivers and downstream lake systems (Lewis et al., 2012). This is particularly important because warm temperatures and increased precipitation have been linked to changes to the thickness, structure, and extent of permafrost (ACIA 2004, Jorgenson et al., 2001, Lawrence and Slater 2005).

Permafrost is defined as ground that remains frozen for two or more consecutive years (Woo 2012) and any degradation has the potential to significantly alter hydrological
regimes of Arctic landscapes including downstream lake aquatic ecosystems (AMAP 2016). The physical and chemical properties of Arctic lakes are highly controlled by the presence of permafrost and ice cover (Vincent and Laybourn-Parry 2008) and these factors cause cold lakes to be highly sensitive to slight changes in climatic conditions. Arctic lakes are typically oligotrophic and dilute but permafrost disturbance events have the potential to increase sediment and solute loading to a lake system (Lyons and Finlay 2008, Bowden et al., 2008). Modeling suggests that there will be a significant reduction in near surface permafrost (the upper 3m) during the next century (Lawrence and Slater 2005) and this will likely have strong effects on the chemical composition of freshwater lakes by allowing pools of previously contained soluble ions to be rapidly transported to rivers and lakes (Kokelj et al., 2005). Physical and chemical properties of these lakes bodies can be rapidly altered by disturbances, and in some cases, may not return to their pre-disturbed state. The primary method of solute loading to lake systems will be through increased soil and groundwater interaction with river and lake waters through increased catchment runoff. Recent surface studies in discontinuous and degrading permafrost by Walvoord and Striegl (2007) and Paytan (2015) have shown that groundwater interaction with rivers is increasing as result of climate warming and is not only increasing baseflow, but the concentrations of nutrients and ions in the river flow as well. Concentrations of major ions in lake systems have been reported to substantially increase with permafrost thaw related slumping around lake systems (Kokelj et al., 2009). However, most of this research is limited to low Arctic environments and less literature exists regarding High Arctic lakes in regions of continuous permafrost.
Historically, Arctic freshwaters have been under-represented in the limnological literature. While numerous baseline studies of small Arctic lakes and ponds now exist (Antoniades et al., 2003, Lim et al., 2001, Hamilton et al., 2001), there is still a lack of long term or multi-year High Arctic limnological studies that span the period of most recent change. In addition, rapid chemical alteration related to climate warming has been well documented for small Arctic ponds, especially related to evaporative enrichment of solutes (Smol et al., 2005, Smol et al., 2007, Douglas et al., 1994) but not for larger lake systems. For these reasons, it is important to understand the geochemical processes that occur in these lakes to predict how they might respond to a rapidly changing climate. This becomes especially important when considering how biota of these aquatic systems may be impacted over time and modelling future environmental change (Williamson et al., 2008). To investigate these knowledge gaps, this study presents a long term record of the physical and chemical properties of two high Arctic lakes and seeks to understand the impact that climate warming and resulting permafrost thaw has on lake aquatic ecosystems including Arctic char and diatom populations.

Arctic aquatic ecosystems are typically simple with food webs that contain only 1-3 tropic levels. Other than algae and plankton, the species that most often dominates High Arctic lakes is Arctic char (Salvelinus alpinus). Climate change has the ability to directly impact Arctic aquatic ecosystems through warming lake temperatures and a reduction in seasonal ice cover (Reist et al., 2006, AMAP 2016). Gradually warming lake temperatures and increased exposure to solar insolation will cause an increase to overall lake productivity (Ruhland et al., 2015) and this may result in more rapid fish growth.
rates (Prouse et al., 2006). The consequences may appear positive for fish populations and health but threshold temperatures for survival exist. Fish are ectotherms, meaning their body temperature is in large part governed by the temperature of their environment and different species will have different preferred temperatures for optimal growth (Beitinger and Fitzpatrick 1979). Fish in northern regions may have significantly narrower optimal thermal ranges than their southern relatives because there is less of a difference between summer and winter lake temperatures (Reist et al., 2006). Mortensen et al. (2007) found that the preferred summer-winter temperature difference for Arctic Char hovered around 3°C. Temperature ranges are species specific, but a large increase in water temperature, even gradual increases, will eventually lead to stress or even mortality in fish populations (Lyytikäinen et al., 1997, Reist et al., 2006). For example, the upper incipient lethal temperature (UILT) is the temperature at which 50% of individuals acclimatized to a certain temperature can survive for a long period of time (Jobling 1981) and the ultimate lethal temperature (ULT) is the temperature at which 50% of individuals can survive for 10 minutes (Baroudy and Elliot 1994). While the UILT and ULT of Arctic char have been found to be upwards of 23°C (Lyytikäinen 1997), it has also been reported that char egg production stops after approximately 11°C (Gillet 1991) and growth rate significantly declines after 7°C (Reist et al., 2006). Regardless, any temperature shifts in the aquatic environment outside of the optimal thermal preferences can place stress on the fish (Kalish 1992).

Arctic char are an important species for northern communities as a country food source and the environmental stresses that they undergo due to climate and permafrost change
can be potentially recorded in their otoliths (Kalish 1992, Friedrich and Halden 2008). Otoliths are the inner ear bones of teleost fish and are composed of annually layered aragonite \((\text{CaCO}_3)\) and proteins (Gauldie and Nelson, 1988). Otoliths are used for a variety of different purposes, and the most common is to age fish individuals. Annually accumulated layers allow for consistent and predictable aging of fish with methods similar to that of tree rings (Campana 2001). While fish can be aged in a variety of ways, such as observing lengths/weights or using scale annuli, counting otolith rings is the most reliable and accurate way to obtain an age (Maceina et al., 2007). Fish morphological features such as length or age of sexual maturity can vary greatly with changing environmental variables and scales have the potential to reabsorb (McFarlane and Beamish 1987, Khan and Khan 2009). Otoliths, on the other hand, do not reabsorb and hence, have the ability to reliably record the chemistry of their environment.

As an otolith grows, it will incorporate elements from the surrounding aquatic environment. For freshwater fish, the main method of element incorporation into the blood stream is through brachial uptake, or water passing over the gills as opposed to marine fish, where the main method is intestinal, as a result of continual drinking (Olsson et al., 1998). The elements in the blood stream will exchange and interact with the endolymph fluid that surrounds the otolith and will as a result, be included in the otolith as it crystalizes on an ongoing basis (Campana 1999). As the calcareous structure is formed, the elemental composition is fixed for that particular year. With recent technological advances in chemical analysis, there is a growing interest in using otoliths as environmental indicators and tracers. Otolith chemistry can reliably serve as an
anadromy route tracer, aid in the reconstruction of historic temperature and salinity conditions of a water body, and have applications in fisheries biology as stock identifiers through stable isotope and trace element analysis (Caampana 1999, Campana and Thorrold 2001, Kennedy et al., 2002, Elsdon and Gillanders 2004). Furthermore, because many fish species can live upwards of 20-25 years, otoliths can be particularly useful in environmental history analysis (Friedrich and Halden 2008). This is important because when environmental stressors recorded as chemical variations in the otolith are coupled with aging techniques, these stresses can be constrained to particular years and events (Kalish 1992). Despite this potential, few studies have recorded the impacts of climate change on otolith growth (Millner et al., 2011), and studied the factors influencing otolith microchemistry (Fowler et al., 1995, Kock et al., 1996, Elsdon and Gillanders 2002, Martin and Thorrold 2005) and none have investigated if observed climate change impacts to Arctic lake systems, whether chemical or physical, can be detected and understood in the otolith.

Recent environmental changes, such as record breaking warm temperatures in 2007, have resulted in significant permafrost disturbance in High Arctic watersheds (Lamoureux and Lafrenière 2009). These localized permafrost disturbance and active-layer detachments can cause sediment and solute loading to rivers and this has implications on downstream lake systems (Dugan et al., 2012). The investigation of the otolith record offers the opportunity to determine how the fish have responded to localized watershed-scale events but also how they respond to rapid physiochemical limnological changes in general.
1.1 Hypothesis and objectives

This research seeks to investigate how climate warming and the resulting permafrost disturbance in the surrounding watershed is impacting downstream lake aquatic ecosystems in the High Arctic. The principal goal of this research is to characterize the temporal chemical and physical variations in High Arctic lake systems related to climate warming and permafrost disturbance and compare that with the chemical variations recorded in the otoliths of Arctic char. This investigation will test the main hypothesis that changes in the physical and chemical aquatic lake environment related to watershed change will be reflected in the trace element composition of Arctic char otoliths.

The objectives of this investigation are as follows:

1. Characterize the physical and chemical changes that have occurred in the water column of two High Arctic lakes that have had catchments subject to notable permafrost change during the past decade;
2. Characterize the micro-chemical variations in Arctic char otoliths collected from both lakes and an upstream headwater control lake; and
3. Relate the changes in the otolith record to that lake water and investigating what particular element shifts can reflect about the changing aquatic and watershed environment.

The study sites of this research are the two main lakes at the Cape Bounty Arctic Watershed Observatory (CBAWO) located on south-central Melville Island, Nunavut (74°50’N, 109°30’W). The two adjacent lakes, East and the West Lake (unofficial
names), have catchments that have been affected by varying degrees of localized permafrost disturbance, representing approximately 1.0% and 2.8% of the total catchments, respectively (Lamoureux and Lafrenière 2009) as a result of record summer warmth and major summer rainfall in 2007. A headwater lake (herein referred to as Headwater Lake) approximately 4 km north of the West lake will also be included in this study and will serve as a control lake as it is unaffected by permafrost disturbance.

To carry out the above objectives, the East and the West lakes were seasonally monitored from 2003-15, which represents the longest detailed limnological record of High Arctic lakes that exists. Monitoring included physical variables such as temperature, turbidity, electrical conductivity and dissolved oxygen in the water column with instruments, and chemical properties such as major ions, metals, and stable isotopes from water samples from the water column. A new water monitoring program was established for the undisturbed Headwater Lake in 2015 as part of this research. In addition to physiochemical sampling, Arctic char have also been sampled from this location since 2008 as part of a larger study investigating mercury cycling in Arctic lakes that have been affected by permafrost disturbance (D.C.G. Muir, Environment and Climate Change Canada).

This thesis presents two chapters as manuscripts. Chapter 2 presents a long term record (2003-15) of the physical and chemical properties of two High Arctic lakes. This study represents the longest continuous limnological record of High Arctic lakes and shows that warming temperatures and increased precipitation have resulted in an abrupt increase of
solute flushing to lake systems. This chapter considers the impact of these changes on aquatic ecosystems through the inclusion of select fish health, diatom and otolith data.

Chapter 3 investigates in more detail the impacts of a changing limnological environment on char otolith microchemistry and seeks to determine if otoliths can be used as indicators of environmental change in lakes where limnological records are limited or absent.

Finally, Chapter 4 summarizes the main conclusions of this research and describes what future work may be done to continue or improve this study. If successful, otoliths may provide a new method for examining the impacts of climate change on aquatic ecosystems that have occurred over the last two decades, which is both the typical lifespan of a char and the period of most climate related change.
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Millner, R. S., et al. "Changes in the timing of otolith zone formation in North Sea cod from otolith records: an early indicator of climate-induced temperature


Chapter 2

Climate and permafrost effects on the chemistry and ecosystems of High Arctic lakes

Abstract

Permafrost exerts an important control over the hydrological regime of Arctic landscapes and lakes, and recent warming and increased precipitation has the potential to alter this regime through thermal perturbation of near surface permafrost and increased mobility of previously frozen solutes to Arctic freshwaters. We present a unique thirteen-year record (2003-16) of the physiochemical properties of two High Arctic lakes and show that the concentration of major ions, especially SO$_4^{2-}$, has rapidly increased up to 500% since 2008. This hydrochemical change has occurred synchronously in both lakes and ionic ratio changes in the lakes indicate that the source for the SO$_4^{2-}$ is compositionally similar to terrestrial sources arising from permafrost thaw. Record summer temperatures during this period (2003-16) following over 100 years of warming and increasing summer precipitation in this polar desert environment provide likely mechanisms for this rapid chemical change. An abrupt limnological change is also reflected in the otolith chemistry and improved relative condition of resident Arctic char (*Salvelinus alpinus*) and diaom community structures point to a positive ecosystem response.

2.1 Significance statement

Arctic warming and permafrost change increases soil water flushing from deep in the seasonal active layer. Increased soil water drainage is sufficient to rapidly alter the
chemistry of downstream lakes and at rates much higher than possible by river inflows alone. These chemical changes constitute abrupt impacts to large and deep Arctic lakes previously observed only in small ponds. Trace element analysis of Arctic char otoliths (ear bones) indicates that permafrost solute transfer also imparts an abrupt elemental change and suggests the potential for a similar rapid response by the aquatic food web. Diatom and fish suggest rapid permafrost solute transfers, in conjunction with lake ice cover reductions, result in amelioration of the aquatic environment in less than a decade.

2.2 Introduction
Freshwater lakes are prominent features of Arctic landscapes and their aquatic ecosystems are highly influenced by the presence of persistent ice cover and permafrost. These factors cause cold lakes to be very sensitive to small changes in climatic conditions. Many studies indicate that Arctic regions are undergoing rapid climatic and permafrost change. Small aquatic systems such as ponds have demonstrated abrupt physiochemical and ecosystem responses, while larger lakes are thought to be more likely to gradually respond due to their larger volume. Climate models consistently project not only warming temperatures in the Arctic, but increased precipitation that can alter hydrological regimes by shifting runoff contribution from early season snowmelt to later season rainfall events. Climate warming has the potential to impact the hydrological regimes of lakes directly by thawing the surrounding permafrost and through degradation and thermokarst in the watershed. Modelling results indicate that a significant increase in near surface permafrost thaw and thermokarst are expected to continue across the Arctic and will have significant effects on the chemical composition.
of freshwater lakes by allowing previously immobile soluble ions in near surface permafrost and transient layer soils to enter rivers and lakes\textsuperscript{12,13}, particularly because the transient layer is often both ice and solute-rich\textsuperscript{14}. Recent studies have documented near surface permafrost degradation leading to altered shallow hydrological pathways\textsuperscript{6}, increased groundwater contribution and solute and nutrient delivery to Arctic river basins\textsuperscript{15,16}, but the impact has not been demonstrated in large lake systems mostly due to their volume and slow water turnover. Moreover, these permafrost thaw effects are usually located in regions with relatively warm permafrost (> -5°C) and are expected to be less pronounced in areas with colder permafrost (< -10°C)\textsuperscript{5}.

In addition to physiochemical changes, significant impacts to aquatic ecosystems have been observed\textsuperscript{7} and are predicted\textsuperscript{17}. Diatom diversity and populations are excellent indicators of environmental change as each species has specific ecological preferences related to physiochemical conditions\textsuperscript{18,19}. With continued climatic warming, a reduction in ice cover may lead to community shifts of benthic species to planktonic species\textsuperscript{19,20}. In addition to this, Arctic char represent the top predator in many Arctic lakes. Warming water temperatures may increase primary productivity, which in turn may lead to increased char body weight and length\textsuperscript{17}, yet there are few studies that demonstrate how rapid limnological change may impact fish species. Fish otoliths, or ear bones, are composed of annual layers of aragonite and proteins that incorporate elements from the surrounding aquatic environment as they grow\textsuperscript{21,22}. These small bone structures provide the opportunity to determine how fish have responded to physiochemical changes of their environment\textsuperscript{22,23}.
This study documents recent rapid chemical change in two similar adjacent High Arctic lakes (Fig. 1) using a long term data set from the Cape Bounty Arctic Watershed Observatory (CBAWO), a limnological and hydrological research site in the Canadian Arctic Archipelago (74°50’N, 109°30’W). The physical and chemical properties of both the unofficially named East and West Lakes have been monitored from 2003 to 2016 and therefore, this study represents the longest seasonal limnological and hydrochemical record in the High Arctic. To further assess the impact of these changes on the ecology of the lakes, the temporal changes in the chemistry of Arctic char otoliths were compared to the temporal changes in lake hydrochemistry. In addition, diatom communities were enumerated in 2004 and 2014 to determine changes in composition during this period of rapid change.
Figure 2.1: Regional Map of Cape Bounty, Melville Island, NU and Mould Bay, Prince Patrick Island, NWT. Regional summer (June, July, August) temperatures since 1948 (Mould Bay), and summer air temperatures and precipitation at CBAWO 2003-15 (WestMet). Lake sampling stations labeled on map.
The paired lakes in this study have similar watersheds, and have maximum depths of 31 and 34 m, respectively (Fig. 1). Record summer air temperatures in 2007 at CBAWO resulted in deep surface thaw of soils and in combination with rainfall that generated over 100 slope failures (active later detachments, ALD) that cover 2.8 and 1.0% of the West and East catchments, respectively\textsuperscript{25}. Subsequent monitoring of runoff from disturbed catchments demonstrated enhanced solute and suspended sediment fluxes\textsuperscript{9} although initial downstream effects in the lakes were limited\textsuperscript{26}. Since 2007, regional warming has resulted in record warm summer (June-August) temperatures. When compared with the nearest long-term monitoring station (Mould Bay 300 km northwest 1948-2015), a clear increase in mean summer temperatures of approximately 2°C is evident in the region (Fig. 1).

Melt season hydrochemical data is initially available from 2003-04 for both lakes and then for 2008-15 and 2006-15 for the East and West Lakes, respectively. Water column properties were measured with repeat vertical instrument (CTD) casts and fixed bottom moorings during the melt seasons and select over-winter moorings (West Lake: 2008-9, 2011-15), along with analysis of water samples for major ion and metal concentrations. Associated measurements of meteorological and hydrological inflows have also been undertaken in this Arctic setting where continuous cold permafrost\textsuperscript{27} likely exceeds 500 m in thickness\textsuperscript{28}. Arctic char have been sampled from this location since 2008 and fish from 2013 and 2015 are included in this study. Physical characteristics of char including length and weight were recorded and otoliths were extracted for aging and chemical analysis. Samples for diatoms included littoral material (rock scrapes, sediment, moss,
plankton) as well as mid-lake sediment traps, at approximately weekly intervals from mid-June to early August in both 2004 and 2014 field seasons.

2.3 Results and Discussion

Both lakes are monomictic and subject to ice cover until late July or early August. The most substantial physical change recorded by the lakes is a considerable rise in turbidity in West Lake from ~4 Nephelometric Turbidity Units (NTU) in 2006, to over 250 NTU in 2015 (SI Fig. 1), while the East Lake turbidity has consistently remained <6 NTU for the entire study period. The increase in turbidity in West Lake is due to three subaqueous slumps that occurred in September 2008, December 2011, and February 2012, unrelated to river inflows or terrestrial permafrost disturbance.

Water column hydrochemistry in both lakes was generally uniform with depth (with slight increases in the bottom 1-2 m) and a gradual overall increase in specific electrical conductivity from 38-102 µS/cm (2004-2016) in West Lake and from 29-136 µS/cm in East Lake. In particular, SO$_4^{2-}$ concentrations increased from approximately 3 to 15 mg L$^{-1}$ (+500%) in West Lake during 2006-2015 and from 5 to 17 mg L$^{-1}$ (+340%) in East Lake during 2008-2015 (Fig. 2). The relationship between SO$_4^{2-}$:Cl$^-$ and SO$_4^{2-}$:Na$^+$ indicates that SO$_4^{2-}$ is increasing largely independently of the other major ions. By contrast, other major ions show a different responses over this period. For instance, the Mg$^{2+}$/Ca$^{2+}$ during 2004-07 in both lakes is constant at ~0.8, but sharply rises to 1.2 at the end of 2009 and returns to 0.8-0.9 by 2012 (Fig. 2). This pattern likely reflects the downstream impact of the 2007 permafrost disturbance episode and is consistent with surface water runoff from disturbed catchments. Conversely, the large increases in the
SO$_4^{2-}$ concentrations following 2009 are not associated with catchment permafrost disturbance. The prominent increase in SO$_4^{2-}$ is accompanied by moderate increases in Cl$^-$, although there is not a matching major cation to balance this increase. In both lakes, there have been a decreases in total Ba, Fe, Mn, and Zn and increases in Ca, Mg, K, Na, and Sr between 2003 and 2015 (SI Fig. 2). Aluminum is the only element that shows an inconsistent response between lakes, with an increase in Al in the West Lake most likely due to the increase in turbidity (SI Fig. 2).

The changes in the chemical compositions of the lakes at CBAWO are directed away from the composition of mean ocean water and coastal hypersaline lakes in the region (Fig. 2) and strongly suggest that the source of the solutes is not marine$^{29,30}$. However, the lakes are shifting towards the composition of disturbed tributaries of the West catchment at CBAWO$^{13}$. Thus, part of the increases in solutes can be attributed to inflows from near-surface permafrost that caused the initial SO$_4^{2-}$ increases to the downstream lake systems. However, river inflows are volumetrically small compared to the lakes, which have a 17-39 year replacement time$^{31}$, so that fluvial inflows are insufficient to generate the necessary SO$_4^{2-}$ flux to the lakes.
Figure 2.2 Left: Concentrations of $\text{SO}_4^{2-}$ (mg/L) and Mg/Ca Ratios (mg/L) over time for East and West Lakes. Right: $\text{SO}_4^{2-}$/Na and $\text{SO}_4^{2-}$/Cl ratios of West and East Lakes compared to marine water, regional hypersaline lakes and West catchment streams (Disturbed = Ptarmigan, 2007-9, Undisturbed = Goose, 2007-09, Lamoureux and Lafrenière 2013, 2012 Unpublished Data).
Each major increase in SO$_4^{2-}$ load occurs in the year following elevated summer air temperatures (2007, 2011, and 2012) and in particular, years with substantial late-season rainfall events (2012). These years represent both the warmest summers since records began in the region in 1949, and likely also for several millennia across the region$^3$. The largest SO$_4^{2-}$ increase occurred between 2012 and 2013, following two consecutive warm years in 2011 and 2012. Continued deep thaw of the transient layer likely provides the mechanism for increased lateral soil water inflows to both lakes. Active layer cores (pre-melt 2012) indicate a substantial increase in soil ion concentrations (especially SO$_4^{2-}$, Cl$^-$, and Ca$^{2+}$) occurs at approximately 70-100 cm depth$^{32}$, below the typical maximum active layer depth of 50-70 cm. Hence, the increase in solutes at depth in the soil suggests the presence of a solute-rich transient layer$^{32}$. Thermally-driven active layer deepening in the lake catchments therefore has the potential to release these ions from the transient layer, and together with increased precipitation, sustain enhanced solute flushing to the lakes. This flushing is likely to be widespread across the landscape compared to the highly localized surface disturbances and hence, holds the potential to deliver large amounts of solutes to the lakes$^{13}$.

To evaluate the ecosystem effect of increased solutes, elemental maps were prepared from laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) scans of Arctic char (Salvelinus alpinus) otoliths from East Lake, West Lake, and Headwater Lake which is a small and shallow (4 m) tributary of West Lake upstream of thermokarst disturbance (Fig. 3). Most elements including Sr, Cu, and Zn showed no consistent variation in concentrations across the maps suggesting no temporal variation in uptake.
However, all otoliths from the East and Headwater Lakes record an abrupt decrease in Ba concentrations and a corresponding increase in Mg concentrations in the outer 100-200 µm of the otolith. This pattern is less consistent in West Lake otoliths where only one of three fish show an increase in Mg around the outer rim and two showed a strong decrease in Ba (Fig. 3). Although the width of this outer rim varies depending on the individual, it represents the last 5-8 years of life, which corresponds to the abrupt change in chemical composition of both lake systems and is consistent with the 80% increase in lake water Mg and 90% decrease in Ba concentrations in both lakes (Supplementary Fig. 2).

Additionally, Ba and Sr are typically preferentially incorporated into the crystal lattice of aragonite due to their ionic size. However, the incorporation of Mg as opposed to Ba into the crystal structure of an aragonite otolith during this period is reflective of the stress that these organisms are undergoing.

These impact of these limnological stresses is also broadly indicated by analysis of inner (early life) and outer (late life) analysis of a larger set of 22 otoliths from all three lakes (10 from West, 10 from East, 2 from Headwater). Principal component analysis indicates that the most important elements driving variance along the positive axis of PC1 are Ba, Sr, and Fe, while PC2 is most strongly influenced by Mg, Zn, and P. Notably, char from the West and East lakes can be separated by the positive and negative axes of PC1 and the early and late life phase of the East Lake are separated by the positive and negative axes of PC2 (Fig. 3). Otoliths from Headwater Lake show a similar elemental response as the West Lake population.
Figure 2.3 Elemental maps (Ba and Mg) of East Lake otolith sampled in 2015. Principal component analysis of inner/outer otolith data 2013-2015 10 from West, 10 from East, 2 from Headwater. Circle = Inner Otolith, X = Outer Otolith
Rapid chemical alteration related to evaporative enrichment of solutes\textsuperscript{7,8,33} during climate warming has been documented for small Arctic ponds, but not for larger lake systems. Given that the SO\textsubscript{4}\textsuperscript{2-} waters at CBAWO are compositionally similar to the disturbed tributary waters, the source is likely increased drainage from both the active layer and the transient layer of the permafrost driven by increased summer temperatures and precipitation. This mechanism would act across the landscape and also deliver solutes via subsurface flow\textsuperscript{13} and has the potential to release sufficient sulfur to rapidly alter the composition of these lakes. Moreover, this mechanism is highly sensitive to small shifts in annual climatic conditions and explains why SO\textsubscript{4}\textsuperscript{2-} concentrations have stabilized in the relatively cool years of 2013-15 (Fig. 1). On average, SO\textsubscript{4}\textsuperscript{2-} concentrations in the West and East Lakes increased by 1.4 and 2.1 mg L\textsuperscript{-1} each year, or approximately 30 and 43 megagrams (Mg) of SO\textsubscript{4}\textsuperscript{2-} added each year to the West and East Lakes, respectively from 2006-15. The ratio of SO\textsubscript{4}\textsuperscript{2-} flux (West:East) of 0.70 is similar to the catchment area ratio (0.69) and is consistent with a landscape-wide contribution to the lakes. The largest increase observed between 2012 and 2014 was approximately 7.5 mg L\textsuperscript{-1} in both lakes, which would have required over 150 Mg of SO\textsubscript{4}\textsuperscript{2-} to be added to each lake during that interval.

The presence of permafrost typically restricts shallow lateral and groundwater inflows to the lakes. This is especially true in regions of thick continuous permafrost, where most small and medium lakes cannot support through taliks (unfrozen ground that extends to the base of the permafrost) that are more common in discontinuous permafrost regions\textsuperscript{34}. As permafrost in this High Arctic region is cold, thick (~500m)\textsuperscript{28} and continuous,
permafrost extent is unlikely to materially change during the next century\textsuperscript{5,17}. Instead, evidence for near-surface permafrost degradation is widespread\textsuperscript{12,25} and permafrost warming has been observed in boreholes\textsuperscript{35}. The input from surface and shallow subsurface flows can be enhanced through active layer deepening and increased summer precipitation. Climate models have predicted Arctic precipitation increases of 7.5-18.1\% mostly in autumn and winter, and less so in summer\textsuperscript{4}. However, increasingly warm summer temperatures may lead to late-summer/early-autumn precipitation falling as rain as opposed to snow, which may shift relative runoff importance from snowmelt to rainfall\textsuperscript{9}. Increased rainfall runoff in the catchment is important because it provides widespread flow connectivity and flow activation of small tributaries.

These results build on observations elsewhere in the Arctic that suggest there could be significant impacts on downstream lake systems with as little as 2\% of catchment area subject to thermokarst activity\textsuperscript{11,36}. In the lower Mackenzie Valley, $\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{Cl}^-$ ratios in thaw slump areas are ten times greater than those of undisturbed runoff waters\textsuperscript{37}. In addition, increased summer rainfall events that occur later in the season can cause disproportionally large biogeochemical responses because the active layer is thickest at this time allowing for maximum flushing of solutes into downstream rivers and lake systems\textsuperscript{9}.

Although the lakes have shown similar chemical responses, the otolith compositions indicate that individual fish have been responding to limnological change differently in each lake (Fig. 4). The declining relative condition of fish from the West Lake is
attributed to decreasing fish mass relative to length over time whereas fish masses in the East Lake are increasing over the same interval. Given the similar hydrochemical changes in both lakes, we attribute the difference in fish condition to turbidity in the West Lake. Char are visual predators and rely on vision to locate prey\textsuperscript{38}. With turbidity >100 times higher than the East Lake, visibility has been substantially limited since September 2008 when the first subaqueous slump occurred. In the East Lake, the fish are not inhibited by water column turbidity and the increase in health status likely reflects warmer water temperatures and reduced ice cover duration during this period. Perhaps more importantly, the increase in catchment soil flushing to the lakes has likely contributed to enhanced growth conditions for the fish through concomitant nutrient delivery\textsuperscript{39,40}. Hence, the rapid physiochemical changes that have occurred in these lakes appear to have contributed to a sustained improvement in fish health in the East Lake, which is consistent with projected outcomes\textsuperscript{17}. 
Figure 2.4: Relative Fish Condition for East and West Lake 2008-15. Note: sample data are not available from 2010 (interpolated with dashed line). Right Top: Changes in diatom diversity 2004-14 in East and West Lakes. Right Bottom: Percent planktonic shifts (Cyclotella pseudostelligera and Cyclotella rossii, grouped as Cyclotella s.l) 2004-14.
These aquatic ecosystem changes are also reflected by diatoms. Littoral assemblages show striking shifts between 2004 and 2014 (Fig. 4). Whereas the 2004 littoral diatoms in both lakes and the 2014 West Lake assemblages are primarily benthics with a minor planktonic component (mostly *Cyclotella rossi*), as much as 50% of the 2014 East Lake littoral assemblages are comprised of small, fast-growing centrics, particularly *Cyclotella pseudostelligera*. This shift, which is consistent with a longer open water season due to earlier ice-off, is driven by physiochemical changes in the lakes influencing vertical mixing, and light availability and nutrients. Hence, the East Lake diatom community response between 2004 and 2014 appears to show compositional shifts consistent with overall ameliorated ecosystem function that is also reflected in fish condition. By contrast, the sustained turbidity in the West Lake appears to have offset improving conditions, resulting in a continuing dominance by benthic diatoms along with deteriorating fish condition.

Long-term climate records indicate warming across the Arctic since ca. 1850. Threshold responses to permafrost change have had major impacts on landscape stability, hydrology, increased groundwater contribution to runoff, and aquatic ecosystems. This study demonstrates a further important dimension of climate-permafrost induced change on Arctic lakes; rapid sustained hydrochemical changes point to increased transient layer and soil water drainage generating a downstream impact in large lakes on a timescale similar to what has been recorded in much smaller Arctic ponds. This work indicates an important mechanism for alteration of Arctic freshwater systems that has been previously undemonstrated in continuous permafrost regions. We further note the
potential role of increased late-summer precipitation as a second element to the rapid threshold response to climate change that appears to be unprecedented in the last 2000 years both locally\textsuperscript{42} and across the Canadian High Arctic\textsuperscript{7,43}. Hence, this threshold response may have been related to this extended period of warming, or alternatively, the exceedance of a key hydrogeological threshold in the permafrost system during the recent decade of record warmth. These dynamics are important to characterize because the rapid shift in lake chemistry affects both water quality and aquatic ecosystems.

2.4 Materials and Methods
Both watersheds are unglacierized and located within 4 km of the coast. The area of the West Lake is 1.4 km\textsuperscript{2} and reaches a maximum depth of 34 m. The East Lake is slightly larger with an area of 1.6 km\textsuperscript{2} and a maximum depth of 31 m. The bedrock geology consists of weathered mid-upper Devonian sandstones, siltstones, and shale, all part of a broad NW-SE trending Parry Islands salt fold belt. The anticlines are genetically associated with salt welts and evaporites and anhydrite deposits that exist at the northern end of the island.\textsuperscript{44} The lakes and catchments are located on the northern limb of the Cape Bounty Anticline, spanning the Hecla and Weatherall formations, with sedimentary units dipping approximately 15° north\textsuperscript{44}. The bedrock is overlain by unconsolidated glacial sediment from the Innuitian ice sheet and early Holocene transgressive marine sediments\textsuperscript{45}. The region became ice-free approximately 11 ka BP with the retreat of the Innuitian ice sheet. Permafrost in the area is continuous and the active layer reaches a depth of approximately 50-70 cm in the summer season.
The climate of the region is amongst the coldest in North America and classified as a High Arctic polar desert. Mean monthly temperatures only rise above freezing in the months of June (0.2°C), July (4.0°C), and August (0.9°C) as measured by the nearest long term monitoring station Mould Bay, NWT. The region is also dry, receiving approximately 160 mm or less of precipitation annually. Meteorological data was recorded at an automated meteorological station (WestMet, 80 m asl) from 2003-15. Temperature was recorded at WestMet with an Onset UA-003 temperature (0.1°C accuracy) rainfall logger equipped with a Davis Industrial tipping bucket gauge (0.2 mm tip) positioned 1.5 m above the ground.

Lake water samples were collected in a 2L Kemmerer water sampler from fixed stations located by GPS coordinates of each respective lake. Samples were recovered at depth intervals of 4-5 meters (year-dependent) to the lake bottom at approximately 32 m in the West and 30 m in the East Lake. Samples were collected in 1 L bottles that were rinsed three times with lake water before filling completely without headspace. Samples were processed within hours of collection and were vacuum filtered through a 0.22 µm polycarbonate membrane filter. The filtrate of each sample was collected in two 25 mL scintillation vials without headspace and was kept cool and dark in the field until returned to the laboratory for analysis. Water samples were shipped to Queen’s University where ion analysis was performed on a Dionex ICS 3000 ion chromatograph. Anions (Cl⁻, SO₄²⁻, NO₃⁻) were separated by gradient elution with 16–40 mM potassium hydroxide, and cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) were measured isocratically with 16 mM methanesulfonic acid eluent. In 2003 and 2004, analysis was conducted at the Analytical Services Unit
(ASU) at Queen’s University using chromatography for ions (Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺). Metals were analyzed at ASU using ICP-MS (Al, Ba, Ca, Fe, Mg, Mn, Ni, K, Na, Sr, Ti, Zn) and ICP-OES (S).³¹

Arctic char were sampled in 2008-15 as part of a study investigating mercury cycling in freshwater ecosystems that have been impacted by permafrost. In 2013, a total of 46 fish were sampled (21 from West Lake, 25 from East Lake) and in 2015 a total of 30 fish were sampled (18 from East Lake, 10 from West Lake, and 2 from Headwater Lake). Ages of fish collected in 2013 and 2015 ranged from 12 to 27 years (East Lake) and 15 to 32 years in West Lake with a mean age of 18. Otoliths were removed on site and transported to Burlington, ON where they were sectioned and aged with low power microscopy.⁴⁷,⁴⁸ Fish relative condition, a measure of health using individual fish weight (W) and the predicted length-specific mean weight (W’), was calculated for all West and East lake fish from 2008-2016 with the exception of 2010.⁴⁹ Sectioned otoliths were then transported to QFIR in Kingston, ON where they were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). A ThermoFinnigan Element 2 XR ICP-MS was couple to an Excimer 193 nm laser to perform chemical analysis. The laser spot size was 50 µm and ablated at a rate of 5 um/s. To create the maps, a series of 12-16 horizontal ablation lines were taken across the width of the otolith and stacked. External standards used include NIST 610, NIST 612, and MACS 3 (certified reference materials). Internal standard used was Ca.
Diatom preparation included digestion of samples (5 ml) overnight in 15 ml sulphuric and nitric acids (50:50 molar ratio), followed by heating in a water bath (2 h at 90°C) and subsequent repeated rinsing with distilled water.

2.5 Supplementary Information Figures

Figure 2.5 Turbidity (NTU) of East and West Lake (depths 10-20m) 2006-15. Stars indicated dates of subaqueous slumps observed in West Lake: September 2008, December 2011, and February 2012.
Figure 2.6 Percent change in metal concentrations in East and West Lakes based on samples from 2003 and 2015.
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Chapter 3

Arctic char otolith microchemistry records of recent environmental change in High Arctic lakes

Abstract
Recent climate change is projected to impact Arctic freshwaters by increasing temperatures, altering chemical and nutrient compositions, and shifting aquatic communities. There is a growing need to improve our understanding of ecosystem interactions in response to these changes. Arctic char represent the top tier of the food web in many of these lake systems and little is known about their response to these recent climate-induced stressors. Otoliths, which are the inner ear bones of fish, have the potential to record environmental stress and change within their growth annuli. To assess the impact of recent environmental changes, Arctic char otoliths were sampled from three High Arctic lakes located at the Cape Bounty Arctic Watershed Observatory (CBAWO) on Melville Island, NU. Otolith microchemistry was analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to examine chemical changes during fish lifespans and compare these changes to the physiochemical changes of the surrounding aquatic and landscape environment. The results of this study demonstrate that not only are abrupt and substantial trace element shifts recorded in the otoliths, but the timing at which these changes occur coincide with chemical and physical changes recorded in the lake systems. This highlights the ability of otoliths to effectively record the stressors of their environment and provides insight into the health of both the fish and the overall ecosystem.
3.1 Introduction

Otoliths are the inner ear bones of teleost fish and are composed of annually layered aragonite (CaCO$_3$) and proteins (Campana 1985). Otoliths are used for a variety of different analytical purposes, including aging fish populations, migration route tracers, and reconstructing historic salinity and temperature conditions. There has been a growing interest in using otoliths as indicators of environmental change because they incorporate elements from the surrounding water body during the lifespan of the individual (Kalish 1989, Kalish 1992, Campana 1999, Friedrich and Halden 2008). The elemental composition is fixed within the otolith structure, and hence studying the chemical composition provides the means to determine changes to the fish’s aquatic environment over time. Arctic char (*Salvelinus alpinus*) are an important fish species for northern communities as a country food source and top predator in many of these lake systems. Environmental stresses that they undergo due to climate and permafrost change can be potentially recorded in their otoliths (Kalish 1992). Furthermore, Arctic char commonly live 15-25 years, which spans the period of most recent climatic change in northern regions where instrumental aquatic records are rare. Climate change is expected to lead to not only a reduction in lake ice duration, but an overall warming and stratification of the water column (Reist et al., 2006), resulting in increased growth and metabolic rates in fish species (Prowse et al., 2006). In addition to this, Arctic lakes are typically oligotrophic and dilute but catchment disturbance events driven by warm temperatures and increased precipitation have the potential to substantially increase sediment and solute loading to a lake system (Lyons and Finlay 2008, Lewis et al., 2012, Chapter 2).
Despite this, it is currently not well known how these climate driven chemical changes may impact Arctic fish species, especially char.

This study presents an investigation of the char otolith record from three lakes located at the Cape Bounty Arctic Watershed Observatory (CBAWO), Melville Island NU (74°50’N, 109°30’W) in the Canadian High Arctic (Figure 3.1). Otoliths were collected from two downstream lakes 2013-2015 (Muir et al., 2015) and a third headwater lake (2015) in order to evaluate the otolith record relative to a known period of substantial lake change, including hydrochemical and ice cover changes, as well as permafrost change and disturbance in the contributing catchments. This objective will test the hypothesis that the physical and chemical limnological changes seen in the East and West Lakes will be reflected in the otolith microchemistry. This work provides approaches for improving our understanding the long term (multi-decadal) impacts that physical and chemical stresses have on Arctic aquatic ecosystems and is part of a larger study investigating contaminant cycling in freshwater ecosystems that have been impacted by permafrost disturbance (Muir et al., 2015)
Figure 3.1 East, West, and Headwater Lakes of the Cape Bounty Arctic Watershed Observatory (CBAWO), Melville Island, NU
3.2 Materials and Methods

3.2.1 Study Site
The study area includes the unofficially named East and West Lakes at the CBAWO. The area of the West Lake is 1.4 km² and reaches a maximum depth of 34 m while the East Lake is slightly larger with an area of 1.6 km² and a maximum depth of 31 m (Normandeau et al., 2016). The lakes are monomictic and are typically subject to ice cover until mid-July to early-August, followed by ice formation during late September or early October. Both have a pH of approximately 7, are dilute in trace metals and major ions (Chapter 2), and are oligotrophic (Stewart and Lamoureux 2012). Additionally, a small headwater lake approximately 3 km north of the West lake is also included in this study to serve as a control as it is unaffected by permafrost disturbance on the surrounding landscape. Arctic char represent the only fish species residing in all three lakes. Char feed on mostly plankton or juvenile char.

The climate of the region is classified as a High Arctic polar desert with mean monthly temperatures only rising above freezing in the months of June (0.2°C), July (4.0°C), and August (0.9°C), and the area receives less than 160 mm of precipitation annually as measured by the nearest long term monitoring station Mould Bay, NWT, 300 km to the west (Environment Canada 2016). The catchments are comprised of low-relief hills and vegetation cover is dominated by low tundra communities (Atkinson and Treitz 2012). The permafrost in the area is continuous and in excess of 500 m thick (Judge 1973), while the seasonal thawed active layer reaches a depth of approximately 60-80 cm in
mid-summer (Rudy et al., 2013). In summer 2007, unusually warm temperatures and high amounts of precipitation resulted in widespread active later detachments (slope disturbances), representing 2.8 and 1.0% of the West and East catchments, respectively (Lamoureux and Lafrenière 2009). These localized disturbances caused notable hydrological, hydrochemical and sediment transport changes (Lewis et al., 2012, Lamoureux et al., 2014) including increased geochemical and nutrient fluxes to the downstream lakes (Dugan et al., 2012).

### 3.2.2 Field sampling

Arctic char were sampled with gill nets that were located perpendicular to the shore and checked hourly for fish for a maximum of 24 hours. In 2015, a total of 18 fish were collected from East Lake, 10 fish from West Lake, and 2 fish from Headwater Lake. In 2013, 21 fish were collected in East Lake and 25 fish from West Lake. Fish sampled were primarily greater than 30 cm in length, 300 g in weight, and older than 15 years of age (determined by subsequent otolith aging). Fish dissections and removal of otoliths occurred on-site for clean and contaminant-free transport. To extract the otolith, an incision was made on either side of the fish’s mouth to allow the jaws to be pulled wide open. A small cut was made to the roof of the mouth allowing the otoliths to float to the top for easy removal using tweezers (Figure 3.2). Where possible both left and right otoliths were collected, however in some cases, only one otolith could be recovered. Otoliths were stored in sealed bottles and kept cool until analysis. In the laboratory, otoliths were cleaned and embedded in epoxy resin, and subsequently sectioned and aged using standard methods by J. Babaluk of the Department of Fisheries and Oceans (DFO) (Campbell and Babaluk 1979, Babaluk et al. 1993). Fish relative condition, a measure of
health using individual fish weight (W) and the predicted length–specific mean weight (W’), was calculated for all West and East lake fish from 2008-2016 with the exception of 2010 (Blackwell et al. 2000).

Figure 3.2 Steps for otolith removal. A) Create a long incision on either side of the fish’s mouth. B) With the mouth open wide, the small bone on roof of mouth is incised and the otoliths removed with tweezers (Photos: Kaitlyn E. Roberts)

Water column samples were collected in a 2L Kemmerer water sampler from fixed stations in both the East and West Lakes. Samples were recovered at depth intervals of 4 meters (year-dependent) to the lake bottom at approximately 32 m in the West and 30 m in the East Lake. Samples were collected in 500 mL bottles and processed within hours of collection by vacuum filtered through a 0.22 µm polycarbonate membrane filter. Water
column metals for East and West Lake were sampled in 2003 and 2015. Analysis was conducted at the Analytical Services Unit (ASU) at Queen’s University using ICP-MS (Al, Ba, Ca, Fe, Mg, Mn, Ni, K, Na, Sr, Ti, Zn) and ICP-OES (S).

The water column was measured using a Richard Brancker Research (RBR) conductivity, temperature, and depth (CTD) instrument also equipped with a Seapoint STM turbidity sensor. Only turbidity measurements from 10-20 m depth in the water column were used to eliminate influence from the lake bottom and ice dilution. Lake ice cover has been documented by field workers at CBAWO since 2003. A metric of ice free days in July is used to examine changes to ice cover duration over time because of the lack of personnel in August prior to 2012. After 2012, a time lapse camera for each of the West and East lakes were used to determine the ice off date. Historical physiochemical and ice cover data are not available for Headwater Lake prior to 2015.

3.2.3 Otolith laboratory analysis

Fish otoliths from 2013 and 2015 were analyzed because those were the most recent samples available at the time of analysis. All otoliths were embedded, sectioned, and aged using growth annuli. The embedded otoliths were sectioned in half and polished to obtain a smooth surface free from scratches and the rings were then counted manually under a low power dissecting microscope (Babaluk et al. 1993).

Geochemical analysis of the otoliths was conducted at the Queen’s University Facility for Isotope Research (QFIR) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).
A ThermoFisher Scientific Element 2 XR ICP-MS was coupled to a New Wave Research Excimer 193 nm laser to perform chemical analysis on all 2015 otoliths and a New Wave Research 266 nm femtosecond laser was used for the 2013 Otoliths. Calibration standards used include NIST 610 and NIST 612 (glass), and check standards of MACS 3 (pressed-powder carbonate, USGS) and were run every 10 samples. All results were calibrated and normalized to Ca concentration to correct for ablation efficiency. This method involves ablating a selected line on both the inner and outer otolith with a 50 µm spot size laser at 5 µm/s. Length of ablation lines varied with each particular otolith, but were in general 750-800 µm in length (ex. 17 measurements per line). During initial analysis, 63 elements were analyzed (Table 1), although most elements were below detection limits (~0.001-0.01 ppm). Results from this analysis were also used to select a reduced set of 10 elements with consistent detection for analysis to improve analytical precision in subsequent analyses (Table 3.1). Relative standard deviations for elements above detection limits were better than 2.6%.

Table 3.1 Elements analyzed with each method. Short listed elements are the elements that showed a significant change between beginning and end of life

<table>
<thead>
<tr>
<th>Method</th>
<th>Elements</th>
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<tbody>
<tr>
<td>Inner/Outer</td>
<td>Mg  S Ca Cr Mg Fe Cu Zn Sr Ba P Th Mo B Be Bi In Na Pb Th U Hg/Ca Al Cd Co Cs Ga Li Ni Rb Sc Si Ti V W Y As Au Ce Dy Er Eu Gd Ge Hf Ho K La Lu Nb Nd Pd Pr Pt Re Sb Se Sm Sn Tb Tm Yb, Zr</td>
</tr>
<tr>
<td>Short listed elements</td>
<td>Mg  S Ca Cr Mg Fe Cu Zn Sr Ba P Th Mo</td>
</tr>
<tr>
<td>Elemental Maps</td>
<td>Mg  S Ca Cr Mg Fe Cu Zn Sr Ba</td>
</tr>
</tbody>
</table>
Two approaches were used to assess otolith geochemistry. First, analysis of transects from the inner and outer otolith is used to determine if there are any major geochemical changes between the beginning and end of an individual life span (Figure 3.3). The inner otolith corresponds to early life and the outer otolith corresponds to the late stages of life, but the absolute ages are not constrained. This method was primarily used for statistical analyses on a large number of individual fish, including cluster analysis and principal component analysis.

Figure 3.3 Ablation methods illustrated for an otolith from the West Lake (2013) A) Inner (beginning of life) and outer (end of life) ablation method. B) 2D elemental map analysis pattern in order to provide a map of geochemical data. Note that sampling is not carried out in the overlapping locations on the otolith as indicated in this schematic example.
Second, 2D spatial elemental maps were sampled for select otoliths – one from 2013 as a method test, and eight of the oldest fish from 2015 (3 West, 3 East, and 2 Headwater Lakes, respectively) (Figure 3). An Excimer 193nm laser was used once again, but with a ThermoFisher Scientici XSeries II quadrupole ICP-MS, which resolves higher spatial resolution (through micro-second data collection) than is possible with the Element 2 instrument. However, this instrument offers a more limited choice of elements for analysis due to interferences and also has higher detection limits. This method involved taking 12-16 ablation lines at 50 µm spacing across the otolith (Figure 3.3) and the geochemical data, portrayed as elemental maps, were able to resolve spatial patterns across the otolith. However, because the top layer of the otolith is ablated, it is not possible to locate the exact positioning of the growth annuli relative to the spatial maps. Despite this, the general growth pattern can be deduced from the overall shape of the otolith. To eliminate chemical data ablated from the adjacent epoxy, a sharp decrease in calcium intensity was used as an indicator to determine where the otolith material ended. Intensity counts were converted to concentrations using geochemical reference materials NIST 610, NIST 612, and MACS 3 and RSD was better than 1.5% for all short-listed elements.

### 3.3 Results

In 2013, a total of 46 fish were sampled including 25 from the East Lake and 21 from the West Lake. Fish from this collection ranged in age from 12-28 years with an average age of 20. In 2015, a total of 30 fish were sampled with 18 from the East Lake, 10 from West Lake, and 2 from Headwater Lake. Fish ages ranged from 8-32 years with an average age of 18. The two fish sampled from Headwater Lake were both 8 years of age, almost 10
years younger than the mean in the other two lakes. These two fish were comparatively
difficult to obtain and required over 24 hours of net fishing. Hence, the population of the
Headwater Lake is assumed to be substantially smaller than either of the East or West
lakes.

After aging, the chemical compositions of otoliths were determined for select fish in the
early (inner) and late (outer) life phase. Initially, 10 otoliths from 2013 were selected for
inner/outer analysis including 5 otoliths from each of the West and East lakes. The 2015
otoliths were only analyzed for the selected element suite (Ba, Cr, Cu, Fe, Mg, Mn, P, Pb,
Sr, Tl, and Zn) determined by detection limits from the 2013 otoliths (Table 3.1). Cluster
analysis (Ward method) of the reduced set of elements from fish from both years revealed
that not only were there differences between individuals from the East and West lakes,
but there were also differences between clustering of the inner and outer otolith in each
lake (Figure 3.4). In most cases, the respective inner and outer composition of individuals
in the West Lake cluster closely together, whereas inner and outer otoliths cluster
separately into distinct groups in the East Lake fish. On the basis of cluster analysis,
individuals from Headwater Lake are most similar to those of West Lake. Two
exceptions include a 2013 West Lake inner otolith sample and a Headwater outer otolith
that cluster with East Lake individuals.
Figure 3.4 Cluster analysis (Ward method) of West Lake (2013 and 2015), East Lake (2013 and 2015), and Headwater Lake (2015). Sample notation indicates lake for each sample and inner (I) and outer (O).
Principal component analysis was performed on the short list of elements to determine patterns of variance in the geochemical data. The first and second principal components (PC1 and PC2) explain 27.0% and 21.7% of the geochemical variance, respectively. The elements with the highest loadings for the positive axis of PC1 are Ba, Sr, and Fe, while Mg, Zn, and P were the elements with the highest loading for PC2. Individual char from the two lakes are clearly separated along the PC1 axis (Figure 3.5). In addition, the early and late life phase for fish from the East Lake are separated by the positive and negative values of PC2. Conversely, the fish of the West Lake show no clear early/late life elemental separation pattern. Similar to the cluster analysis, otoliths from Headwater Lake are most related to West Lake population with the exception of one Headwater outer sample (Figure 5).

Figure 3.5 Principal component analysis of inner/outer otolith data 2013 and 2015. Pink = East Lake 2013-15, Blue = West Lake 2013-15, yellow = Headwater Lake 2015. Inner otoliths are indicated by solid/open symbols.
Select elements that showed a change from beginning to end of life were analyzed as 2D maps to resolve both geochemical pattern and relative timing of these changes across eight otoliths (Figure 3.6). Most elements including Sr, Cu, and Zn showed no discernable temporal variation in concentration (Appendix C). However, several elements appear to have coherent visual patterns consistent with radial otolith growth patterns. In all East and Headwater Lake otoliths (3 and 2 individuals, respectively), an abrupt decrease in Ba concentrations (from 130 to 60 ppm) and an increase in Mg (from 80 to 180 ppm) concentrations were observed in the outer 50-200 µm of all individuals (Figure 3.6). This pattern was less consistent in West Lake otoliths where only one of three fish analyzed showed an increase in Mg around the outer rim and the other two showed a notable decrease in Ba. The width of this outer rim characterized by Mg and Ba changes varies on an individual basis and estimated to represent the last 5-8 years of the life through microscope analysis of polished otolith faces.
Figure 3.6 Top: Percent metal concentration changes from 2003-15 for East and West Lakes. Bottom: 2D elemental maps of an East Lake otolith. Left: Mg, Right: Ba
Analysis revealed that fish from the West Lake have been experiencing declining relative condition due to lowered weights and lengths from 2008-2015 whereas fish from the East Lake have been experiencing increasing weights and lengths. It is important to note that no data exists for either lake in 2010 (Figure 7).

Figure 3.7 Relative arctic char condition (Method: Blackwell et al. 2000) and West and East Lake turbidity (NTU) (10-20m depth). Note that East Lake turbidity data is not available for 2011
Physical and chemical properties of the East and West Lakes have been monitored from 2003-16. Physical and chemical limnological data for Headwater Lake is only available for 2015-16. Notable physical limnological changes include a substantial rise in turbidity in West Lake from an average of ~4 Nephelometric Turbidity Units (NTU) in 2006, to over 250 NTU in 2015 (Figure 3.7). The East Lake turbidity has consistently remained low (<6 NTU) for the entire study period. Headwater Lake shows turbidity levels similar to East Lake. The rise in West Lake turbidity is due to three subaqueous slumping events that occurred in September 2008, December 2011, and February 2012. The ice-off record has revealed that there has been an increase in the number of ice-free days in July for both the East and West Lakes since 2007. East Lake always experiences ice-off up to 12 days before the West Lake, however in the warmest years (2007, 2012, 2015), West Lake has experienced up to 10 ice-free days in July (Table 3.2). Lake metal analysis has revealed that in both lakes, there has been a decrease in total Ba, Fe, Mn, and Zn and an increase in Ca, Mg, K, Na, and Sr between 2003 and 2015 (Figure 3.6). Notably, there is a 90% decrease in Ba and an 80% increase in Mg concentrations which is consistent with otolith chemistry results. The only metal showing an inconsistent response between lakes is Al.
Table 3.2 Number of ice-free days in July on West and East Lakes. Insufficient observations are available to determine August ice-free days.

<table>
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<th>East Lake ice free days July</th>
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</tr>
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<td>2015</td>
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</tr>
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</table>

\(^1\) Dugan et al. (2012)

3.4 Discussion

Projected impacts of climate change on Arctic freshwater fish are largely associated with increasing air temperatures that will lead to not only a seasonal reduction in lake ice duration, but an increased stratification and overall warming of the water column (ACIA 2004). The latter is important for the metabolic rates of fish species and other related ecosystem effects such as primary productivity and food availability (Reist et al., 2006). In the short term, these conditions may lead to increased fish growth and a decrease in age-at-catch or increased weight-at-catch which is beneficial to populations and
communities who may rely on these fish (ACIA 2004, Reist et al., 2006). Additionally, the growth of otoliths is highly dependent on the size and growth rate of the fish itself (Geffen 1982, Tzeng 1990) and as a result, more rapid otolith growth rates have been reported in response to increased temperatures (Mosegaard et al., 1988, Lombart and Lleonart 1993, Otterlei et al., 2002). Related to this, a faster otolith growth rate will also preferentially uptake an element that is both easier to incorporate and highly abundant in the surrounding environment. Otoliths have been experimentally observed to show that trace element composition is highly dependent on the chemistry of the surrounding aquatic environment (Köck et al., 1995, Wells et al., 2000, Elsdon and Gillanders 2004) and as a result, otoliths have been used as proxies for environmental reconstruction (Campana 1999).

The East and West Lakes of CBAWO have been undergoing substantial physical and chemical change over the most recent decade (Dugan et al., 2012, Chapter 2) due to catchment permafrost change/degradation, hydrological changes, and changes in seasonal ice cover. In addition to these climate-related changes, a persistent increase in water column turbidity has been observed in the West Lake since 2012 (Figure 7). Given the occurrence of multiple observed environmental changes during the past decade at CBAWO, it is difficult to determine which changes are causing the most stress to the fish and furthermore which of these stresses may be reflected in the chemical composition of the otoliths. The estimated timing of the chemical changes seen in these otoliths is consistent with recently-observed limnological changes. Major ion and trace metal concentrations have been substantially, and in some cases abruptly, increasing in these
lakes, particularly since 2007 when widespread permafrost disturbance occurred (Lamoureux and Lafrénière 2009). Additionally, water column SO$_4^{2-}$ concentrations have increased between 300-500% in both lakes, particularly since 2012 and represent the one of the largest limnological changes that has occurred (Chapter 2). While this substantial change could potentially represent a high stress event for the fish, analytical limitations did not allow for accurate detection of sulfur in the otoliths, so a direct association between the chemical change in the lakes and otolith geochemical change is difficult to make.

A change that is more clearly detected in the otoliths is the shifts in concentrations of Mg and Ba. In the last few years of the fish’s life, Mg has been substituting for Ba in the otoliths, which is consistent with changes in lake water metal concentration over time (Figure 6). For example, from 2003-15, Mg concentrations have increased approximately 80% and Ba has decreased approximately 90% in both lakes (Figure 6). In the otolith, the concentration shift occurs in the outer 50-200 µm of the otolith which, depending on the otolith, represents an estimated 5-8 years prior to catch based on microscope analysis of growth rings. However, it is important to note that both the exact timing and rate of change in Ba water column concentrations are unknown because samples were only taken in 2003 and 2015 for both lakes. Detailed Mg concentration measurements from 2003-16 reveal sharp increases in 2008 (Chapter 2). However, the timing of chemical change in the otoliths are consistent with the timing of SO$_4^{2-}$ increase in both lakes, which shows that any changes to whole-lake chemistry may be indirectly causing other chemical changes in the otoliths. These chemical changes are evident in otolith elemental maps.
from all lakes, but are most consistent in East and Headwater Lake otoliths. Two otoliths from the West Lake did not show the same chemical trend, which shows that while the elemental shift in the otolith appears to represent the beginning of a period of high stress to the fish population, the nature of the physiological stress is unknown multiple stressors may be contributing to the observed otolith compositional changes. Additionally, the fact that Mg was preferentially incorporated into the aragonite otolith structure during this period is also reflective of the stress that these organisms are undergoing. Typically, smaller ions such as Ba or Sr will be incorporated into the orthorhombic crystal structure of aragonite. However, stress can alter the kinetics of otolith formation, causing different elements to be incorporated (Kalish 1992, Menadakis 2009).

This differential response of otolith chemistry between lakes was also evident in cluster and PCA analyses. Cluster analysis suggests that the fish from the West Lake are responding on an individual basis. The inner and outer chemistries of individual fish cluster together which shows that the fish are responding differently. Whereas the sampled fish from the East Lake have been responding similarly. All outer otoliths cluster together and all inner otoliths cluster together, respectively. This indicates that the otolith chemistries amongst fish in the East Lake have been changing uniformly over time. PCA analysis separates the fish from both the East and West Lakes and suggests that the otolith chemical changes reflect different responses to the same limnological stresses, or different stresses altogether, for example, the difference in turbidity between the lakes. It is notable that the fish from the Headwater Lake show similar PCA and cluster results to those of the West Lake. Given that the Headwater Lake is an undisturbed system, the
chemical changes seen in these otoliths cannot be attributed to specific catchment
disturbance event, but does not rule out the possibility of water column chemical change
entirely caused by a catchment wide solute influx. Increased ion input to both the East
and West Lakes has been attributed to a warming of the upper active and transient layer
permafrost increasing solute mobility (Chapter 2) and has thus had an impact on whole
lake chemical composition.

While the overall water column chemical changes appear to be similar between the West
and East lakes, notable physiochemical differences are evident. First, high turbidity
occurred due to a series of subaqueous slumps in the West Lake in late 2008 and the
winter of 2011-12 and the water column has remained turbid since that time with minimal
decreases to date (August 2016) (Figure 7). Arctic char, like many fish species, are visual
hunters and rely on good vision to locate prey (Utne-Palm 2002). In addition to effects on
predatory success, turbidity as low as 25 NTU has also been noted to have an impact on
gill function and fish growth (Sigler et al., 1984). Water passing over the gills, or brachial
uptake, is the main method in which elements get absorbed into the blood plasma in
freshwater fish (Olsson et al. 1998, Campana 1999). The persistence of turbidity in the
West Lake may have an impact on the chemical composition of the otolith by causing the
fish physiochemical stress (Kalish 1992). By contrast, the East and Headwater Lakes
have not had had an observed change in turbidity since 2003.

Second, increasingly warm summer air temperatures have led to a reduction in summer
lake ice cover duration across northern regions, including CBAWO. An increase in ice-
free days in July of both the West and East Lakes has been observed since 2007, especially on the East Lake (Table 2). This has a number of implications for the aquatic ecosystems: first, a reduction in summer ice cover causes water column temperatures to warm (Rouse et al., 1997, Reist et al., 2006) and the increased availability of insolation and nutrients is expected to cause an increase in littoral diatom populations (Rühl et al. 2015), which represent the majority of primary productivity in cold, oligotrophic lakes. The increase in primary productivity may not only lead to increased char body weight and length, but faster growth rates in general (AMAP 2016). This phenomena is evident in the overall health of the fish populations of fish in the East Lake (Figure 7). It is likely that the sustained turbidity in the West Lake, along with decreased primary productivity due to longer ice cover duration and reduced penetration of photosynthetic radiation into the upper water column compared to the East Lake, has contributed to declining condition factors in the West Lake fish. While physiological effects of turbidity may be the primary stress, we cannot rule out a combination of the other limnological changes. Though increased temperatures have been found to have an impact on otolith chemistries (Fowler et al., 1995, Köck et al., 1996, Elsdon and Gillanders 2002, Martin and Thorrold 2005), the ranges of experimental temperatures used in these studies are broad (e.g. 12-28°C (Elsdon and Gillanders 2002)) and are not focused on cold-water fish species. Moreover, the water column at CBAWO has not been consistently warming and varies each year according to ice cover and overturn-related heat loss in autumn (Bonnaventure and Lamoureux, Submitted). Hence, it is difficult to conclude that the recent otolith chemical changes in these High Arctic freshwaters are related to water column temperature changes. Instead, the differential chemical responses are likely related to
indirect ecosystem/water column changes whether independent or related to climate warming. Because there are multiple limnological events occurring simultaneously, all could be causing a stress-related chemical response in the otolith and particular events/responses cannot be decoupled.

Finally, this study demonstrates new approaches for otolith trace element analysis. Inner and outer analysis was used to characterize broad changes between beginning and end of life and allowed for a broad range of elements to be examined at very low detection limits (0.001 ppm) in a large number of otoliths. In this study, over 60 elements were analyzed although most were below detection limits. All elements found in previous studies were detected along with some uncommon elements including Mo, Tl, and U. Single line transect analysis is a common technique used other studies to examine chemical changes over time in the otolith (Outridge et al., 2002, Friedrich and Halden 2008). However, the resolution of the laser and mass spectrometer coupled with the small size of the otoliths did not produce optimal results with our study. As a result, this sampling method was not used. The high resolution spatial maps generated from select elements proved to be a key means of assessing and differentiating geochemical change in otoliths, particularly abundant elements (Ba, Mg, Sr, and Zn). The elemental maps showed variability in element concentration across the otolith and is the most useful method to obtain a detailed temporal chemical record of the fish.

Furthermore, absolute chronology cannot be constrained using this method because the whole surface of the otolith is ablated to create a map. As a result, chemical changes in the otolith cannot be constrained exactly. However, we can estimate that the chemical
changes shown in the elemental maps occurred approximately within the last 5-8 years of the fish’s life which corresponds to the approximate timing of multiple physiochemical changes in both the East and West Lakes.

3.5 Conclusions

Fish otoliths can serve as useful tools to not only age a particular fish, but to also understand recent chemical changes to the aquatic environment, particularly in the higher trophic levels. The results of this study demonstrate that chemical changes recorded in the otoliths of Arctic char are consistent with timing of major limnological events (e.g., turbidity increases, seasonal ice cover reduction, and $\text{SO}_4^{2-}$ increases (Chapter 2)) but also appear to reflect chemical shifts in the lake environment (Mg, Ba). Otoliths can record both broad chemical changes affecting all downstream lakes while simultaneously recording lake-specific responses by individual fish, which may relate to different ecosystem stresses or a differential behavioral response to environmental change by fish. The records of ecosystem stress that otoliths provide are valuable as a means to determine contemporary and historical environmental change in lakes where records are limited. This is especially important in Arctic aquatic ecosystems, where lakes are undergoing substantial climate-driven limnological change.
References


CliC/AMAP/IASC, 2016. The Arctic Freshwater System in a Changing Climate. WCRP Climate and Cryosphere (CliC) Project, Arctic Monitoring and Assessment Programme (AMAP), International Arctic Science Committee (IASC).


Mosegaard, H., H. Svedäng, and K. Taberman. "Uncoupling of somatic and otolith growth rates in Arctic char (Salvelinus alpinus) as an effect of differences in temperature response." Canadian Journal of Fisheries and Aquatic Sciences 45.9 (1988): 1514-1524.


Chapter 4

Conclusions

This research sought to understand how climate warming and the resulting watershed permafrost disturbance is impacting the physical, chemical and ecological characteristics of High Arctic lake systems. The ultimate goal of this study was to characterize changes in two High Arctic lakes over a period of significant climatological and limnological change and compare those to chemical variations in the otolith microchemistry. The primary conclusions of the three main objectives are as follows:

1. **Characterize the physical and chemical changes that have occurred in the water column of two High Arctic lakes that have had catchments subject to notable permafrost change during the past decade:**

   The East and West lakes at CBAWO have been monitored continuously from 2003. High air temperatures and increased rainfall have caused increased near surface thaw to occur in the active and transient layers of the catchment permafrost resulting in an influx of solutes to the downstream lake systems. This rapid hydrochemical changes has occurred on a time scale similar to what has been recorded in smaller Arctic ponds but not previously in larger lakes. Chemical changes include a 500% and 300% increase in SO$_4^{2-}$ to the West and East Lakes, respectively. Ion ratios strongly suggest that the increases were not the result of marine influence and were of terrestrial origin. Other major ions such as Mg and Ca experienced short term concentration increases following catchment disturbance but were not sustained. The lakes have also been experiencing a reduction in summer ice duration. The East Lake is always ice free prior to West Lake, but bot lakes
have been experiencing more ice free days since 2007. Independent of the chemical changes (and not demonstrably climate related), West Lake has sustained high turbidity (>200 NTU) following the first of three known subaqueous slumping events in 2008. East Lake has not experienced these events and thus the turbidity has remained minimal.

2. *Characterize the micro-chemical variations in Arctic char otoliths collected from both lakes and an upstream headwater control lake:*

Results from Chapter 3 indicate that fish from the East and West Lake have been responding to physiochemical stress in different ways. Inner and outer otolith (corresponding to early and late life) cluster analysis revealed that fish from the West Lake have been responding on an individual basis to chemical change whereas fish from the East Lake have been responding uniformly. The two lakes are also separated by the primary principal components that are related to the elements Ba, Sr, and Fe. Elemental maps of the otoliths showed a marked increase in Mg (~80-180 ppm) and a decrease in Ba (~130-60 ppm) concentrations in the outer rim (50-200 µm) which is consistent with Mg and Ba water column changes since 2003. This pattern was seen in all East and Headwater lake otoliths, but was inconsistent in three West Lake otoliths analysed. The differences been between the otolith Mg and Ba patterns between the two primary lakes can be attributed to differing environmental conditions such as turbidity and lake ice duration despite the water columns showing similar chemistries. Yearly chemical resolution and connections with chronology were not obtained in this particular study but may be resolved with larger otoliths.
3. **Relate the changes in the otolith record to those of the lake water and investigate what particular elemental responses can reflect about the changing aquatic and watershed environment**

The results of this study demonstrate that microchemical changes recorded in the otolith are consistent with the relative timing of major limnological events such as a reduction in seasonal lake ice cover, and major ion increases (e.g., SO$_4^{2-}$) but also directly reflect other chemical changes in the water column (e.g., increase in Mg, decrease in Ba). Otoliths can record both broad chemical changes affecting lakes while simultaneously recording lake-specific events. Otoliths will record stress, whether physical or chemical that the fish undergoes during its lifetime. This highlights the value of otoliths to examine historical environmental change in lakes where conventional limnological records may be absent. It also indicates the sensitivity and connectivity of Arctic aquatic ecosystems to climate and catchment permafrost related change.

In summary, long-term climate records indicate that unprecedented high temperatures have been occurring across the Arctic over the last century. Warming temperatures have a number of indirect consequences to lake systems including catchment permafrost degradation, the release of previously immobile solutes and ions, and more direct impacts on the lake such as ice loss. Changes to the catchment permafrost in particular can have major impacts on landscape stability, hydrology, groundwater runoff, and aquatic ecosystems. This study demonstrates that rapid chemical change in Arctic lakes can occur as a result of climate-permafrost induced change and that it can occur on timescales not previously observed in large lake systems in regions of continuous permafrost. Rapid
limnological shifts are not only observed in the water chemistry, but can be seen in the responses of the ecosystem including diatoms and fish. Fish otoliths can serve as useful tools to not only age a particular individual, but to also understand recent chemical changes to the aquatic environment that have occurred over the most recent two decades.

4.1 Recommendations for future work

1. Currently, the East and West lake limnological record is the longest continuous limnological record in the High Arctic (2003-16). Monitoring of the physical and chemical properties is needed to extend this record. This includes temperature, turbidity, electrical conductivity, and major ion concentration measurements. Similarly, monitoring programs for other lakes such as the Headwater Lake need to be continued to further create substantial records.

2. Related to above, there is a need to monitor lake metal concentrations more frequently. Currently, the record is quite sparse and a more extended record would be of value especially with continued metal work on the fish species of the East and West Lakes.

3. One major knowledge gap is understanding where exactly the $\text{SO}_4^{2-}$ is entering the lake system. The rivers alone are not able to deliver that amount of $\text{SO}_4^{2-}$ to the lake systems so it is inferred that there is also a large input from the catchment soil water. However, the contribution of groundwater, especially groundwater
coming from below the lake system, is poorly understood. Sulfur stable isotope analyses might provide a means of distinguishing different sources to help identify the inflows.

4. Records of fish weight and length should continue annually at CBAWO to monitor overall fish health. Currently, otolith work spans fish collected in two years: 2013 and 2015. Otolith sampling should also continue for purpose of aging the fish populations; there is not an immediate need for an annual chemical otolith record.

5. However, it would be useful to continue to work on the problems currently present with the otolith record. As of current the timing of chemical change in the otolith is unable to be linked with an exact year or event. This is because the otoliths used in this study are quite small (>2 mm) and because the top surface of the otolith is ablated which effectively removes any ring visibility. Better polishing and imaging techniques to increase ring visibility before chemical analysis would be invaluable in linking chronology with lake specific events. It would also be useful to reattempt the transect analysis with larger otoliths to obtain a more detailed record of some low concentration elements that initially showed change, such as redox active Mo, Th, and U.
Appendix A
Meteorological data and lake chemistry

Table A1: Temperature (°C) and Precipitation (mm) at CBAWO 2003-16

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2003-15

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Table A4: West and East Lake SO$_4$ inflows, outflows, and concentrations at beginning and end of season (Megagrams)

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Table A5: Sulfur isotope data East and West Lake

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<th>Sample Type</th>
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<th>δ34S ‰ vs VCDT</th>
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<td>07WL_17_20</td>
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<td>07WL_23_26</td>
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<td>07WL_29_33</td>
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<td>07EL_07_10</td>
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<td>07EL_16_20</td>
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<td>07EL_23_28</td>
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<td>EL 2+10 m</td>
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Appendix B

Laser operating conditions

Table B1: LA-ICPMS Operating Conditions and Data Acquisition

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<tr>
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<tr>
<td>Auxiliary (Ar)</td>
<td>0.75 L/min</td>
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<tr>
<td>Sample (Ar/He)</td>
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| shield electrode used for analysis |

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<tr>
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</tr>
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<td>Pre-ablation warm-up</td>
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<tr>
<td>spot size</td>
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<tr>
<td>power</td>
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<tr>
<td>incident pulse energy</td>
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<tr>
<td>energy density on sample</td>
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<tr>
<td>laser scan speed</td>
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<table>
<thead>
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</tr>
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<td>BScan and EScan</td>
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<tr>
<td>detector mode</td>
<td>analog and counting and faraday</td>
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<td>dwell time (segment duration)</td>
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<td>runs/passes</td>
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Appendix C

Otolith elemental maps
East Lake 1 – Sampled in 2015, 22 years old (concentrations in ppm)
East Lake 9 – Sampled in 2015, 21 years old (Concentrations in ppm)
East Lake 11 – Sampled in 2015, 21 years old (concentrations in ppm)
Headwater Lake 2 – Sampled in 2015, 8 years old (concentrations in ppm)
Headwater Lake 1 – Sampled in 2015, 8 years old (concentrations in ppm)
West Lake 4 – Sampled in 2015, 32 years old (concentrations in ppm)
West Lake 9 – Sampled in 2015, 21 years old (concentrations in ppm)
West Lake 2 – Sampled in 2015, 20 years old (concentrations in ppm)