

Impact of lake expansion on mercury concentrations in lake sediments, Mackenzie  
Bison Sanctuary, Northwest Territories, Canada.

by

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## **ABSTRACT**

Spatial and temporal variations in total mercury (Hg), organic matter and lake surface area were assessed to determine if flooding in the Mackenzie Bison Sanctuary (MBS) was influencing Hg inputs to lake sediments. Mercury concentrations in the sediment of all lakes examined are below established guidelines. All lakes demonstrated increased Hg concentration and flux over the past century. Two expanding lakes exhibited maximum total Hg values in surface sediments which correlated with peaks in water surface area and changes in source of organic matter. Reference lakes demonstrated declining total Hg values in recent sediments and no correlation with organic matter or water surface area. This study presents land users and managers with a preliminary assessment of Hg concentrations within MBS lakes. Recommended future work should focus on methyl mercury concentrations and methylation rates in sediments, which often increase after landscapes are flooded, and can pose risks to wildlife species relying on the ecosystem.

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## **ABBREVIATIONS / ACRONYMS**

ACIA	Arctic Climate Impact Assessment
AMAP	Arctic Monitoring and Assessment Programme
AMDE	atmospheric mercury depletion event
ARI	Aurora Research Institute
CCME	Canadian Council of Ministers for the Environment
C:N	carbon : nitrogen ratio
EF	enrichment factor
ELA	Experimental Lakes Area
ENR	Department of Environment and Natural Resources, Government of Northwest Territories
FR	flux ratio
GEM	gaseous elemental mercury
Hg(0)	elemental mercury
Hg(II)	divalent mercury (includes forms of PHg and RGM, see below)
IPCC	Intergovernmental Panel on Climate Change
MBS	Mackenzie Bison Sanctuary
MeHg	methyl mercury
OM	organic matter
PHg	particulate mercury
RGM	reactive gaseous mercury
THg	total mercury
[THg]	total mercury concentration
TOC	total organic carbon
UNEP	United Nations Environment Programme



# 1 INTRODUCTION

Arctic regions are particularly sensitive to climate warming. Notable changes detected in the past 40 years include higher average surface air temperatures, less ice cover, greater precipitation, and warming and degradation of permafrost and ground ice (Overpeck et al. 1997, Serreze et al. 2000, ACIA 2004, Macdonald et al. 2005, Smith et al. 2005b, Romanovsky et al. 2007, Burn & Kokelj 2009, AMAP 2011). These impacts can lead to rapid alteration of northern landscapes, including thermokarst development leading to the catastrophic draining of lakes and, conversely, lake expansion where low-lying terrain and a high water table occur (Hinzman et al. 2005, Smith et al. 2005a, White et al. 2007, Rowland et al. 2010).

The shift in physical processes and pathways can have consequences for the organic carbon cycle and other mechanisms (biotic and abiotic), which can in turn influence the movement of contaminants into (and out of) northern environments (Vorosmarty et al. 2001, Macdonald et al. 2005, AMAP 2011). Reports from the Arctic Monitoring and Assessment Programme (AMAP) and other field investigations have identified several mechanisms which could induce accelerated release of contaminants to the Arctic, including permafrost thaw and subsequent release of organic carbon and nutrients. Mercury (Hg), a potent neurotoxin, is among the pollutants of greatest concern.

Elevated Hg concentrations in environmental systems are hazardous, especially when present as the bio-available form, methyl mercury (MeHg).

Methyl mercury can bio-accumulate in the tissues of organisms over time. Furthermore MeHg can also be biomagnified within food webs, meaning that concentrations are greatest in organisms at higher trophic levels. Mercury concentrations can be found at toxic levels in some northern environments, despite being distant from point sources (Hermanson 1998, Carrie et al. 2010, AMAP 2011). Mercury contamination in the Arctic is of particular concern for Aboriginal Peoples who continue to rely on subsistence hunting and fishing as a major component of their daily dietary nutritional needs, and as an important part of their social and cultural well-being (Lockhart et al. 1995, Hermanson 1998, AMAP 2011).

We have few unequivocally reliable long-term records of Hg deposition and accumulation, particularly in northern environments. Consequently, our understanding of the environmental cycling and fate of Hg is inadequate in many areas. Therefore, there is a need to develop longer records of Hg accumulation in northern regions.

Paleolimnology, the science of inferring past environments using the material preserved in lake and river sediments, provides a useful set of tools that can be used to track longer-term changes in Hg concentrations in the environment (Smol 2008). From these natural sediment archives it is possible to determine historic trends in contaminant accumulation and how these differ from modern fluxes. Understanding Hg accumulation in northern lakes is critical, particularly as climatic and environmental change may be altering previously

existing pathways, sources and sinks (Hinzman et al, 2005, Macdonald et al. 2005, Rowland et al. 2010, Rydberg et al. 2010, AMAP 2011).

An opportunity to examine Hg trends in a region of rapidly changing lake area has recently developed in the western Canadian sub-arctic where lakes have been expanding during the past few decades.

The Mackenzie Bison Sanctuary (MBS) is a 10 000 km<sup>2</sup> wildlife reserve, located on the west side of Great Slave Lake, near Fort Providence, Northwest Territories (NT), and is home to approximately 700 wood bison (*Bison bison athabascae*). The MBS lies within the Great Slave Lowland ecoregion, an area of relatively flat, poorly drained terrain, characterized by thousands of small ponds and several large, shallow lakes surrounded by shrub and sedge meadows and boreal forests.

Recent observational evidence, including satellite images and resident accounts, suggests that the extent of many lakes in the MBS have increased in recent decades, leading to the flooding of large tracts of forested land (ARI 2011, deMontigny 2014). Flooded soils and vegetation can lead to increased Hg in lake environments, and this has been detected previously following the artificial impoundment of water (Hall & St Louis 2004, St Louis et al. 2004; Hall et al. 2005). These studies tend to focus on methylation rates and uptake of MeHg in fish (e.g. Bodaly et al. 1984, Jackson 1988, Jackson 1991, Mucci et al. 1995, St Louis et al. 2004, Hall et al. 2005). Very little work exists on the effects of natural flooding of the landscape, such as is occurring in the MBS, and fewer papers look

at contaminant dynamics resulting from such flooding (Roy et al. 2009). Furthermore, a lack of data focused on Hg accumulation in sub-arctic lake sediments has been identified as a key knowledge gap (Landers et al. 1998, Muir et al. 2009).

While not all lakes in the MBS are increasing in size, historical shorelines are visible around some of the lakes that are expanding; an indication that lakes have been larger in the past and that changes in lake surface area may be driven by climate or atmospheric cycles. Lake surface extent of expanding lakes has varied since the onset of flooding, with periods of expansion and retraction, which could lead to greater inputs of Hg to these aquatic systems.

Increased loading and speciation of Hg in lakes as a result of flooding is particularly worrisome, as this region provides essential habitat for a variety of waterfowl, animals and fish. Furthermore, the Government of the Northwest Territories (GNWT) has developed a 10-year Wood Bison Management Strategy, which highlights the importance of maintaining wood bison habitat quality, and refers to high water levels in the MBS as an impediment to that goal (ENR, 2009).

In light of these circumstances, this research was undertaken to answer the following research questions: (1) Has lake expansion (sustained overland flooding) in the MBS resulted in an increased load of mercury to lake sediments?; and (2) Can the timing of recent lake expansion be inferred by sedimentary proxies of autochthonous and allochthonous production and the relative importance of these carbon sources to the lakes?

The primary objective of this research is to obtain an historical record of Hg accumulation in sediments from five lakes; three that are known to have expanded recently (based on the analysis of remotely sensed images and air photographs), and two that have not. The hypothesis that expansion of these lakes and subsequent flooding of soils and vegetation leads to Hg enrichment in sediments can be evaluated by assessing the variability in Hg concentrations over time from each of these lake environments. Sediment records from lakes that have not expanded will provide a reference against which sediments from expanding lakes can be compared, to determine if flooding influences Hg accumulation. This paleolimnological approach also allows for comparison of records of Hg concentrations and accumulation between the study lakes and those from other high-latitude regions.

This research will contribute to the developing understanding of how and why Hg accumulation and concentrations vary across lakes in the Canadian sub-arctic. In particular, it will contribute to the identified knowledge gap regarding Hg trends in sub-arctic aquatic ecosystems. Finally, the results of this research will provide local land users and managers with preliminary information about the Hg content in lakes from this ecologically sensitive and rapidly changing region.

The organization of this thesis is as follows: Chapter 1 has provided a brief introduction to the research topic. Chapter 2 reviews the current literature pertaining to the topic including the reliability of lake sediments as archives of Hg accumulation, Hg in Arctic lakes and various controls on Hg accumulation in sediments, and increases in Hg in flooded environments. Chapter 3 presents a

description of the study sites and the field, laboratory, and statistical methods employed. Chapter 4 presents the results of the study, while Chapter 5 discusses these findings and their implications in the context of previous studies on this topic. Finally, Chapter 6 summarizes the findings and conclusions of the study and suggests avenues for future research.

## **2 REVIEW OF LITERATURE**

### **2.0 Reliability of Lake Sediments as Records of Mercury**

#### **Accumulation**

Paleolimnological studies are guided by the law of superposition, which holds that sediments are deposited in chronological order with deeper sediments being the oldest and sediments near the top of a profile or exposure representing the youngest material (Smol 2008). This depositional sequence allows sedimentary profiles to be accurately dated in most cases. The assumption is that sediments, and the indicators being investigated, have not undergone significant post-depositional disturbance. However, lake characteristics, environmental conditions, and the behaviour of certain substances can cause post-burial remobilization or mixing within the sediments. Paleolimnological studies examining Hg concentrations are primarily concerned with the loss or mixing of Hg through diagenetic processes, such as by wind or waves, compaction, bioturbation, and migration from solid to liquid at the sediment-water interface, particularly in low sedimentation environments (Poissant et al. 2008).

The use of lake sediments as reliable historical archives of Hg deposition has been widely examined, with particular focus on the mobility of Hg within the sediment (Fitzgerald et al. 1998, Landers et al. 1998, Lockhart et al. 2000, Biester et al. 2007, Rydberg et al. 2008, Feyte et al. 2012). These investigations conclude that once deposited, there is normally little to no mixing of Hg evident.

Lockhart et al. (2000) examined sediment profiles from three different lakes in Canada, with known pollution point sources and dated releases, and found that Hg peaks in the sediment matched with recorded Hg release to the lakes. Furthermore, the peaks (i.e. magnitude) of Hg concentrations did not diminish as they were buried deep in the profile over time (Fig. 2.1; Lockhart et al. 2000). While this study demonstrates that sediments are reliable for larger quantities of Hg ( $\mu\text{g g}^{-1}$ ), many studies focus on remote lakes removed from pollution sources and with much smaller concentrations of Hg ( $\text{ng g}^{-1}$ ).

More recent investigations have examined the reliability of sediments in such a context (Rydberg et al. 2008, Feyte et al. 2012). These studies looked at the loss of carbon during early diagenesis and potential mobilization or loss effects on Hg to which it is closely bonded. Results showed that the sediments did not exhibit any noticeable loss of total Hg (present at parts per billion concentrations) over time (Rydberg et al. 2008, Feyte et al. 2012).

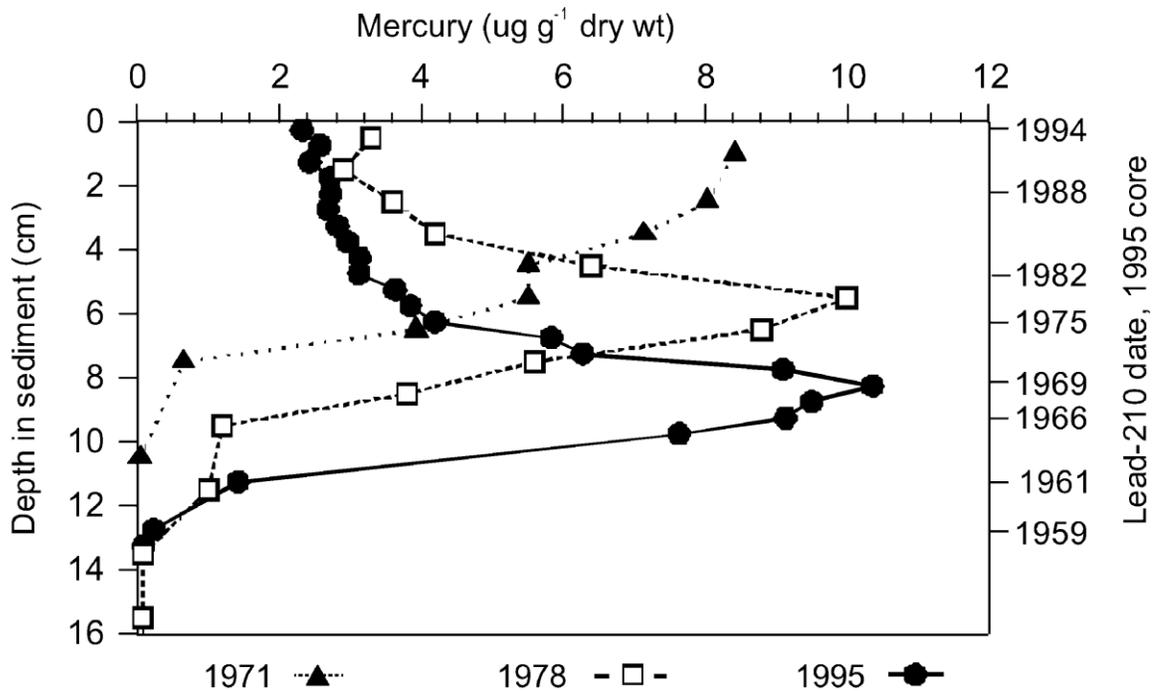


Figure 2.1: Sediment profiles taken in 1971, 1978, & 1995 registering consistent peaks of Hg accumulation over time (from Lockhart et al. 2000)

Lake sediments are not the only natural depositional archives of Hg. Peat bogs are also used to establish historical records of Hg concentration and flux over time (Biester et al. 2007). Recent evaluation of lakes and peat bogs in western and southern Greenland found that modern Hg accumulation rates are higher in peat than in lake sediments, exhibiting increases 300-500 times, and 3-5 times respectively, above background levels (Biester et al. 2007). This extreme difference raises questions about the reliability of these two sedimentological environments to accurately represent atmospheric Hg deposition.

Further examination of each system found that due to the hydrological and biogeochemical characteristics of bogs, such as water table fluctuations and high

macroporosity in the upper layers of peat, trace elements and even pollen can travel vertically within peat. Additionally,  $^{210}\text{Pb}$  which is a radioactive isotope commonly used to date recent sediments, is often mobile in upper layers of peat, allowing it to be washed down deeper into the sediments (Clymo & MacKay 1987, Waddington & Roulet 1997). This 'smearing' of  $^{210}\text{Pb}$  appeared to be the cause of difficulties in establishing an accurate chronology within the peat archive (Biester et al. 2007). Generally, maximum anthropogenic emissions of Hg are dated between 1970 and 1990; however the peat record examined suggested this coincided with intervals dated 1950-1960 (Biester et al. 2007).

Overestimation of Hg concentration and flux in bogs can occur as a result of  $^{210}\text{Pb}$  smearing throughout the sediment column (Biester et al. 2007). While neither archive is perfect, lake sediments can be considered 'closed systems' once they are buried beneath the surface layer, and therefore can offer more reliable and less problematic records. This is supported by the consistency of Hg flux ratios collected from many lakes and cores throughout the northern hemisphere (Landers et al. 1998, Biester et al. 2007).

## **2.1 Mercury in Arctic Lakes**

### *2.1.1 The impact of the global Hg cycle*

Mercury is a naturally occurring element that can be found as deposits in geologic settings and as gaseous emissions from volcanic eruptions and wood burning fires. The weathering of Hg-containing rocks and releases from

volcanoes and fires all contribute to the natural Hg cycle (Fig. 2.2) (Nriagu & Pacyna 1988, AMAP 2011, Swartzendruber & Jaffe 2012, UNEP 2013). Total emissions of Hg from the preindustrial era are believed to have been in steady-state, with total emissions balanced by total deposition to the Earth's surface (Mason et al. 1994, Swartzendruber & Jaffe 2012).

The modern Hg cycle differs from preindustrial times, as Hg from deep reservoirs is mobilized to the atmosphere as a result of anthropogenic activities since the 1800s (Fig. 2.2) (Nriagu & Pacyna 1988, Mason et al. 1994, Hermanson 1996, Landers et al. 1998, Lockhart 1998, Fitzgerald et al. 2005, Pacyna et al. 2006, Lindberg et al. 2007, Pacyna et al. 2010, UNEP 2013). The industries known to contribute the most to anthropogenic emissions of Hg are the combustion of coal and other fossil fuels, mining activities, and artisanal gold smelting (Nriagu & Pacyna 1988, Pacyna et al. 2006, Pacyna et al. 2010, UNEP 2013). It is estimated that human industrial activities have increased the total atmospheric and depositional burden of Hg by a factor of three (Lockhart et al. 1998, Muir et al. 2009, Swartzendruber & Jaffe 2012).

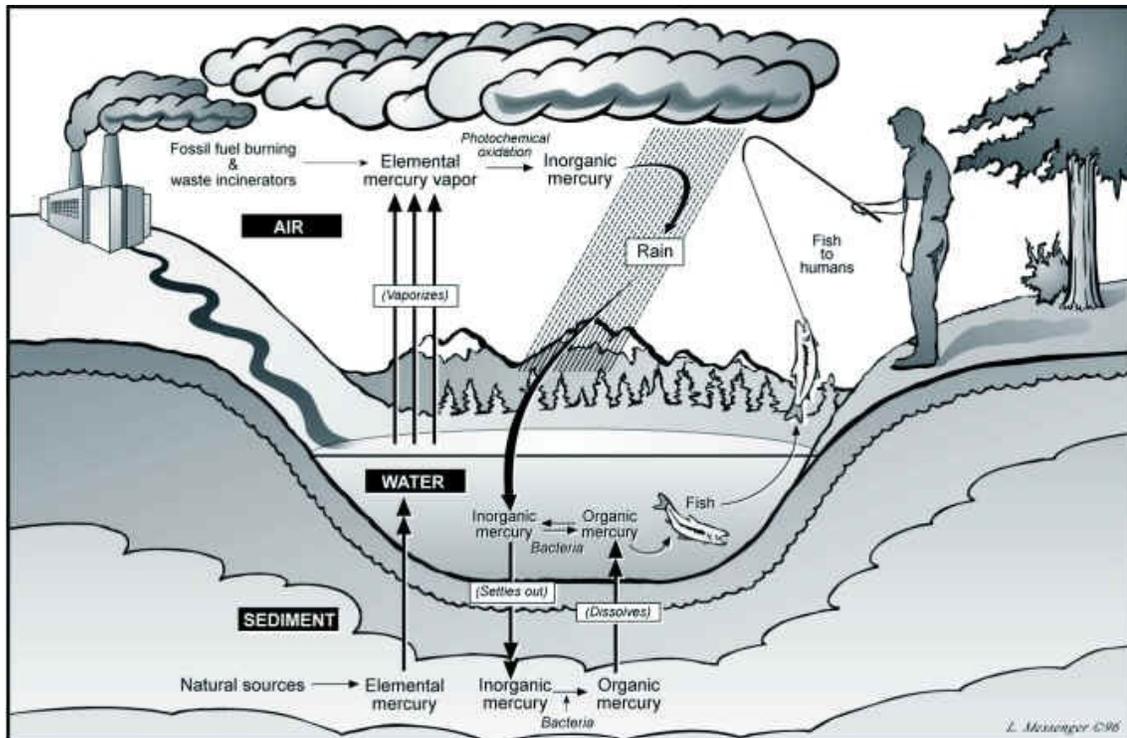


Figure 2.2: Simplified representation of the Hg cycle (Utah Department of Environmental Quality, 2012)

Evaluations of the modern Hg cycle estimate that natural emissions account for 10 % of the global total, anthropogenic emissions make up 30 %, while the remaining 60 % is thought to be re-emission of previously deposited Hg (both natural and anthropogenic) (Pacyna et al. 2010, Swartzendruber & Jaffe 2012, UNEP 2013). It is important to note that natural emissions (including re-emissions) release predominantly gaseous Hg(0), while industrial activities release particulate Hg and reactive gaseous Hg, both forms of Hg(II), as well as gaseous Hg(0) (Swartzendruber & Jaffe 2012). Inorganic Hg forms are removed from the atmosphere within hours/days and contribute to local Hg contamination. Gaseous Hg(0) on the other hand, can be sustained in the atmosphere for approximately one year and is therefore of global concern.

Because Hg can remain in the atmosphere in its gaseous form for approximately one year, it can be transported by global air circulation patterns and deposited at locations distant from its source, including the Arctic (AMAP 2011). Sediment cores from lakes provide evidence of increases in Hg burdens on Earth.

### *2.1.2 Historic and modern inputs of Hg*

Lake sediment studies across the circumpolar north have found that historic inputs of Hg were lower compared to recent additions (Lockhart et al. 1995, Hermanson 1996, Landers et al. 1998, Fitzgerald et al. 2005, Muir et al. 2009). Increases in Hg within lake sediments, above historic background levels, are noticeable late in the nineteenth and early in the twentieth centuries and continue to rise in more recent sediments. The increases through time are associated with additional Hg emissions from intensification of industrial activities in the mid-1800s, and are considered anthropogenic inputs in excess of the natural Hg cycle. Generally, Hg concentrations within the deepest sediments in a core recovered from a lake bottom are averaged to calculate historical (background) fluxes, and concentrations from the top-most sediments of that same core are averaged to calculate modern fluxes (Lockhart et al. 1995, Landers et al. 1998, Lockhart et al. 1998, Muir et al. 2009, Brazeau et al. 2013). The difference between these two values represents the Hg flux derived from anthropogenic sources. Lake sediment records from Alaska indicate marked increases in Hg concentrations at the beginning of the twentieth century

(Fitzgerald et al. 2005), and sediment cores collected from Arctic and sub-arctic lakes across Canada demonstrated significant anthropogenic inputs when compared to their historic levels (Lockhart et al. 1995, Muir et al. 2009), both without nearby Hg emission sources.

While anthropogenic emissions have amplified global atmospheric Hg concentrations, these are not deposited evenly across the planet's surface. This is demonstrated in the differences in the rate and magnitude of Hg accumulation in lake sediments that have been found across the northern hemisphere (Lockhart et al. 1995, Landers et al. 1998, Lockhart et al. 1998, Muir et al. 2009). Often this is related to proximity to emission sources, with lakes closer to pollution sources having higher sediment Hg concentrations (Lockhart et al. 1995, Landers et al. 1998, Lockhart et al. 1998, Muir et al. 2009). While Hg levels generally decline with distance from pollution sources, studies have found that total Hg concentrations have generally increased in lake sediments over time. Some studies have also found that lakes in northeast Canada have higher Hg concentrations compared to those located in the west, which may also be attributed to the proximity of pollution sources as well as the influence of atmospheric circulation patterns (Lockhart et al. 1995, Landers et al. 1998). However other investigations have not found this longitudinal variation (Lockhart et al. 1998, Muir et al. 2009).

Attempts have been made to find regional and continental patterns to Hg deposition. Landers et al. (1998) reviewed Hg flux data from 51 lakes in Arctic and boreal ecosystems from five of the 8 Arctic nations. The study found that

Arctic and sub-arctic lakes have a broad range of pre-industrial Hg fluxes and that the ratios of historical versus modern total Hg flux varied widely; from minimal enrichment in an Alaskan lake to a 9-fold increase in a lake in Finland (Landers et al. 1998). The study also demonstrated that Hg deposition is strongly influenced by regional sources that can overshadow the hemispheric enrichment factor (Landers et al. 1998).

While affirming lake sediments overall as reliable archives of Hg accumulation, some of these studies have highlighted that spatial coverage of data is minimal, which greatly limits the use of the Hg information collected for environmental management, policy development, and future predictions (Landers et al. 1998, Klaminder et al. 2008, Muir et al. 2009, Rydberg et al. 2008, AMAP 2011, Kirk et al. 2011). In particular, information about regional Hg accumulation patterns in sub-arctic lakes is scarce, as are data from neighbouring lakes, which could provide a depositional history of Hg (and other contaminants) and thus an understanding of ecosystem response (Landers et al. 1998, Muir et al. 2009).

## **2.2 Controls on mercury accumulation**

### *2.2.1 Atmospheric deposition*

Overall, global atmospheric emissions have declined throughout the past 20 years in part due to preventative measures applied in North America and Europe (Pacyna et al. 2006, Pacyna et al. 2010, UNEP 2013). However, emissions from Asia continue to increase and contribute approximately one third

of total anthropogenic emissions (Jaffe et al. 2005, Pacyna et al. 2006, Pacyna et al. 2010, UNEP 2013).

Generally, most Arctic lakes have no direct local sources of Hg pollution, but can become contaminated through atmospheric deposition, primarily as inorganic Hg (Hg(II)) (Nriagu & Pacyna 1988, MacDonald et al. 2005, Poissant et al. 2008, AMAP 2011). This is possible owing to the long residence time and transport of elemental Hg (Hg(0)) (Macdonald et al. 1996, Macdonald et al. 2005, St Louis et al. 2004). The gaseous phase of Hg must undergo transformation to one of the many forms of Hg(II) in the atmosphere prior to being deposited on the landscape (MacDonald et al. 2005, AMAP 2011). Removal of Hg from the atmosphere occurs via two processes: wet and dry deposition.

Wet deposition is the removal of Hg from the atmosphere via precipitation and can occur as rain, snow, fog or ice (Sanei et al. 2010). Dominant forms of Hg(II) (including reactive gaseous mercury (RGM) and particulate mercury (PHg)) are scavenged by precipitation because of their high water solubility (Swartzendruber & Jaffe 2012). This occurs when Hg(0) is oxidized in clouds by ozone and taken up by water droplets (Lindberg et al. 2007). Wet deposition of Hg is enhanced when clouds are near pollution sources, as emitted Hg(II) and PHg are taken up by the water droplets (Lindberg et al. 2007).

Dry deposition of Hg occurs when there is no precipitation. There are two possible deposition pathways: (1) direct deposition of gaseous Hg compounds (Hg(0) and RGM), and (2) deposition of atmospheric particles containing Hg,

though the latter occurs less frequently than the former (Lindberg et al. 2007). In mid-latitude regions the occurrence of dry deposition of Hg has been estimated to occur 98 % of the time and subsequently can mean large Hg inputs to aquatic and terrestrial ecosystems (Lindberg et al. 2007). Dry deposition appears to be more significant in forested areas owing to the stomatal uptake of atmospheric Hg via leaves and needles of vegetation (Lindberg et al. 2007, Graydon et al. 2008).

Atmospheric mercury depletion events (AMDEs) are environmental conditions unique to polar regions that enhance Hg removal from the atmosphere. Recognized during the 1990's, AMDEs occur during polar sunrise, during which gaseous Hg(0) is photo-oxidized to various forms of Hg(II) which are readily scavenged from the atmosphere through either wet or dry deposition processes (Schroeder et al. 1998, Lindberg et al. 2007). Recent estimates of Hg deposited in the Arctic due to AMDEs are between 90 and 450 metric tons (Ariya et al. 2004, Skov et al. 2004). Currently, the fate of Hg deposited during AMDEs is contested without data confirming whether it is deposited and then mobilized to downstream aquatic systems during spring snowmelt, or if it is largely re-emitted to the atmosphere (Lindberg et al. 2002, Douglas et al. 2008).

### *2.2.2 Climate change*

Polar regions are particularly vulnerable to environmental change related to global warming. General climate models and observations indicate an increase in temperatures twice that anticipated for temperate areas (ACIA 2005,

AMAP 2011). Temperatures across the Canadian Arctic have increased by 2°C – 3°C in the last 50 years (Burn & Kokelj, 2009). Warmer temperatures have led to erratic and unpredictable weather patterns as well as changes in atmospheric pressure, which bring more southerly winds and potentially greater flux of Hg into (and out of) Arctic regions (AMAP 2011). Much of the change anticipated in the North will occur when temperatures have warmed to the threshold freezing point (-2°C to 0°C), altering hydrologic and carbon cycles (Macdonald et al. 2005, AMAP 2011). Research has shown that many Arctic and sub-arctic aquatic systems have already experienced these changes (Macdonald 1996, Smol et al. 2005, Smol & Douglas 2007). Investigations of lake systems are critical because it is within aquatic systems that most of the risk of Hg exposure to humans and wildlife occurs as a result of methylation and subsequent bioaccumulation, though generally most health risks are associated with marine ecosystem food webs (AMAP 2011).

### *2.2.3 Increased algal scavenging*

Arctic lakes are being exposed to light earlier in the spring and later in the fall, most often attributed to earlier ice break-up and delayed formation at these times of the year (Smol et al 2005). This increase in light exposure has been linked to warming temperatures across the Arctic, which has also caused thinning and / or loss of lake ice during the summer months (where lakes were frozen year-round) (Smol & Douglas 2007). The climate-induced changes in lake ice

cover have resulted in a longer growing season and increased aquatic primary productivity (Outridge et al. 2007, Smol & Douglas 2007, Stern et al. 2009).

Some studies hypothesize that the observed higher rates of autochthonous production may be a contributor of increased accumulation of Hg in sediments of Arctic lakes (Outridge et al. 2005, Outridge et al. 2007, Stern et al. 2009). These studies have shown that the autochthonous organic component of sediments of two high Arctic lakes explained 87-91% of the variance of total Hg flux to sediments, despite overall reductions in global atmospheric emissions (Outridge et al. 2005, Outridge et al. 2007). Proponents of the algal scavenging hypothesis highlight the significant correlation found between S<sub>2</sub> carbon (algal-derived) and Hg concentrations, which accounted for 70-78% of the Hg found in recent sediments in high and sub-arctic lakes studied (Sanei & Goodarzi 2006, Outridge et al 2007, Stern et al 2009).

This hypothesis has implications for current models of Hg transport processes to lakes, since it infers that atmospheric emissions would only account for approximately 30 % of the Hg found in recent sediments, whereas most studies are conducted under the assumption that atmospheric deposition is a major source of Hg to sediments (Lockhart et al. 1995, Hermanson 1996, Landers et al. 1998, Muir et al. 2009, Brazeau et al. 2013). Proponents of the algal scavenging hypothesis have not identified an alternate source for the Hg being scavenged from the water column.

Conversely, other studies of Arctic lakes have not found this link between labile OM and increasing Hg concentrations in sediments. An investigation of 14 lakes across the Canadian Arctic and sub-arctic found that approximately 50 % of lakes studied had positive correlation between the S2 fraction of OM and Hg, while the others did not (Kirk et al. 2011). The authors concluded that while many lakes are experiencing climate-induced changes and increases in Hg deposition, algal scavenging may not be a critical factor in increasing Hg fluxes to sediments in all lakes in all areas of the Arctic (Kirk et al. 2011). Further, an investigation of slump affected lakes in the Mackenzie Delta only found positive correlation between S2 and Hg in five of 8 lakes studied suggesting other mechanisms, besides algal scavenging, are responsible for Hg deposition to sediments (Deison et al. 2012). In addition, analysis of a sediment record from Baffin Island spanning the last 10,000 years found that while early Holocene warming led to increased aquatic primary productivity, no associated increase in Hg was found (Cooke et al. 2012). Furthermore increases in Hg concentrations and fluxes over the past 100 years occurred without increases in primary production (Cooke et al. 2012).

#### *2.2.4 Permafrost degradation*

Permafrost is ground that remains frozen for two or more consecutive years, and underlies almost all of the terrestrial Arctic and large parts of the circumpolar sub-Arctic. Permafrost in Canada is classified according to the percentage estimated to be underlying the landscape and includes classifications

such as continuous (90-100%), discontinuous (50-90%) or sporadic (10-50%) with discontinuous and sporadic found in the more southerly regions (Smith & Riseborough 2002). Permafrost is an important source of carbon and organic-bound Hg (Grigal 2003, Klaminder et al. 2008, Rydberg et al. 2010, AMAP 2011). Climate change models predict that by the mid-21st century permafrost areas will decrease between 13 - 28 % globally (ACIA 2005, IPCC 2007).

Thawing permafrost changes the mobility of carbon and Hg via landscape change and water movement. Investigation of a thawing palsamire affected by thermokarst erosion in Sweden found net Hg storage changes (Klaminder et al. 2008). Submerged or subsided hummocks had lower Hg inventories compared with those that were not inundated ( $< 3.1 \text{ mg m}^{-2}$ ;  $5.5$  and  $8 \text{ mg g}^{-2}$ , respectively), and it was estimated that between 40 - 95 % of the sequestered Hg was released between 1970 and 2000, the equivalent of 34 to 50 g of Hg (Klaminder et al. 2008).

The influence of permafrost and ultimately climate, on the mobilization and sequestration of Hg has also been observed in longer-term historical sediment records. Within the same mire in northern Sweden, three distinct periods of Hg release and sequestration in the past 500 years were inferred through lake sediment and climate proxy data (Rydberg et al. 2010). Between AD 1400 and 1500 the region experienced a warm period and Hg accumulation in sediments increased via export of OM and Hg from the catchment. During the Little Ice Age (AD 1550 - 1850), permafrost was developing and Hg accumulations were variable until ground conditions stabilized and the frozen ground inhibited the

movement of Hg and carbon. Modern warming conditions have encouraged permafrost degradation, increased thermokarst erosion, and led to increasing Hg and OM transport from the mire to the lake (Rydberg et al. 2010).

### 2.2.5 *Organic matter*

Organic matter plays a key role in controlling the distribution of Hg in lake sediments, including in Arctic lakes which are considered Hg sinks (Grigal 2003, AMAP 2011). Organic matter forms strong bonds with Hg compounds, allowing Hg to be sequestered within the sediment. Labile (S1 and S2) components of OM, that degrade more readily, have been associated with the presence of Hg in sediments (Sanei & Goodarzi 2006, Stern et al. 2009). Often there is variation in the distribution of OM in sediments, and subsequently of Hg abundance, with greater concentrations in recent (topmost) sediments and decreasing concentrations down core due to organic matter degradation (Sanei & Goodarzi 2006, Stern et al. 2009). Sequestration of Hg can be achieved by both allochthonous (derived from outside the lake) and autochthonous (within lake) sources of OM, including plants, soil carbon, or algal mats.

While labile OM appears to bond with Hg compounds, it also allows for the transformation of inorganic Hg to MeHg. Methylation commonly occurs under anoxic conditions, which are often found at lake bottoms and within sediments, and where sulfate-reducing bacteria decompose OM (Jackson 1988, Jackson 1991, Hall & St Louis 2004, Hall et al. 2004, Roy et al. 2009). Increased OM and

Hg supply in Arctic lakes from environmental change due to warming could lead to increased production of MeHg.

### **2.3 Inputs from vegetation and soils**

Vegetation and soils are considered sinks for nutrients and contaminants. Leaf stomata are the receptors through which gaseous compounds are taken into and released from plants. Soils, most often organic and humic surface horizons, provide a medium where chemical compounds can be stored. Litterfall, the shedding of vegetative plant material to the soil surface, is the means by which nutrients and energy are (re)cycled within terrestrial systems (Fig 2.3). Understanding how each component has the potential to contribute to Hg accumulation, particularly as it relates to flooded terrain, is therefore critical.

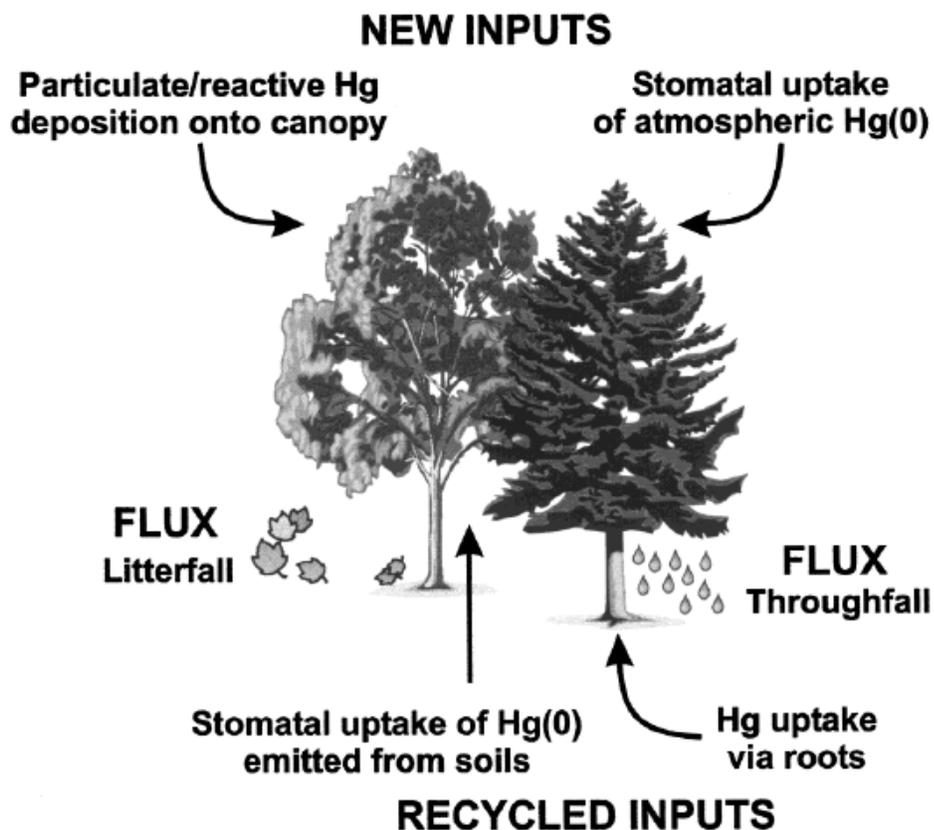


Figure 2.3: Simplified overview of Hg cycling in a forest (from St Louis et al. 2001)

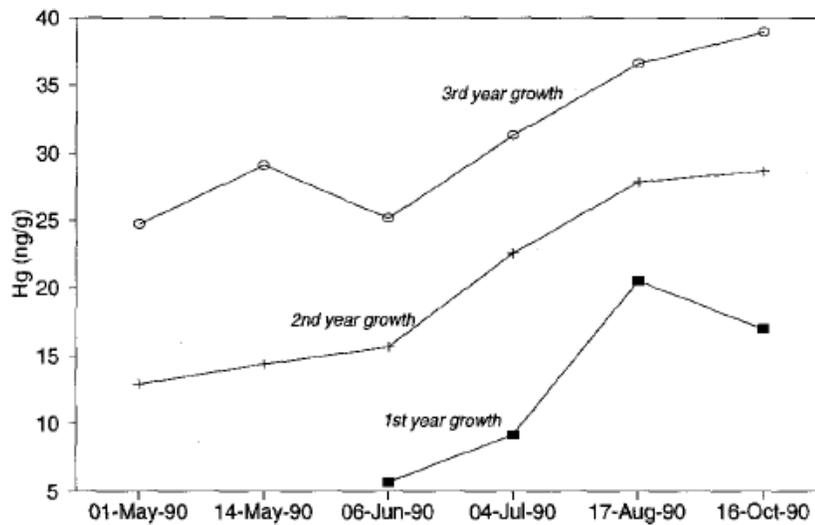
### 2.3.1 Vegetation

Vegetative materials are net sinks of Hg, with concentrations increasing over time (Grigal 2003). Forest canopies, in particular the senesced vegetative material, can significantly increase deposition of Hg to the forest floor, watersheds and lakes downstream (St Louis et al. 2001, Hall & St Louis 2004). Plants accumulate most of their Hg from the atmosphere through dry and wet deposition (Fig. 2.3). They can also accumulate Hg via water contained in the soil, mineral weathering, and throughfall (the removal of elements/nutrients by

precipitation as water washes over the vegetative surface), though these pathways tend to play a more minor role compared with atmospheric sources (Moore et al. 1995, St Louis et al. 2001, Grigal 2002, Hall & St Louis 2004).

Concentrations of Hg increase over the growing season in coniferous and deciduous trees, but also with needle age in conifers (Rasmussen et al. 1991, Rasmussen 1995, Grigal 2003). This is speculated to be a function of residence time as needles are generally retained for longer periods than deciduous leaves and thus, are able to accumulate more Hg (Rasmussen et al. 1991). First year needles demonstrate the greatest rates of increase, doubling over the course of the growing season (Rasmussen 1995). Second and third year needles also double their Hg concentrations during the summer; however it appears that Hg losses can occur over the winter months, evidenced by lower Hg concentrations at the beginning of the growing season in second and third year needles of the spruce tree (Fig 2.4; Rasmussen 1995). Mercury accumulation rates within vegetation can fluctuate from year to year which may reflect variation in factors affecting plant growth rates (temperature, precipitation), and/or the amount of Hg available for uptake (Rasmussen 1995).

### Changes in Hg content through time. Needles collected from one BALSAM tree.



### Changes in Hg content through time. Needles collected from one SPRUCE tree.

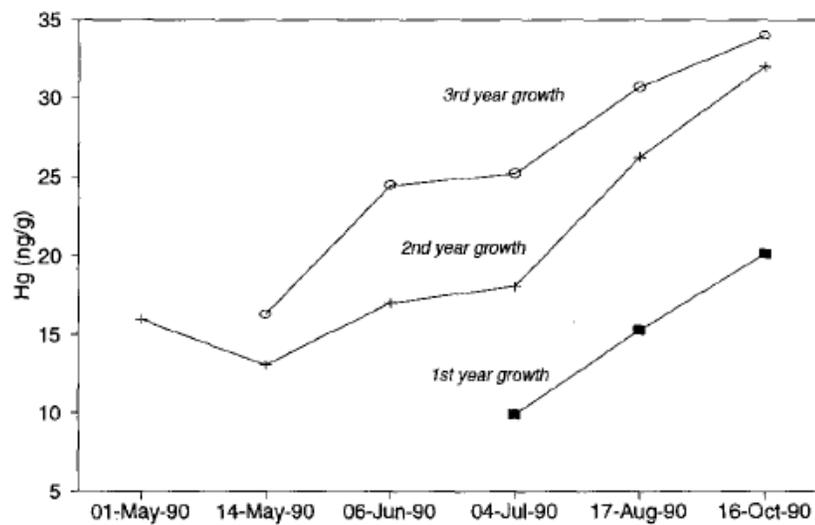


Figure 2.4: Hg concentration in conifer needles of varying age (from Rasmussen 1995)

Regional atmospheric concentrations of Hg affect rates of uptake by plants, with vegetation closer to pollution sources having much higher concentrations (Rasmussen 1995, Grigal 2003). Mercury in non-vascular plants (fungi, lichen, and mosses) have been detected at nearly an order of magnitude greater than those in vascular plants from the same site, and may be evidence of a soil source of Hg (Rasmussen et al. 1991, Moore et al. 1995, St Louis et al. 2001). A study examining various biomass in a wetland at the Experimental Lakes Area (ELA) in northern Ontario found that the lowest concentrations of both total Hg concentrations ([THg]) and MeHg were in leaves and needles of trees and shrubs, while the highest occurred in bryophytes, accounting for 45 % of [THg] and 73 % of MeHg within the biomass examined (Fig. 2.5; Moore et al. 1995).

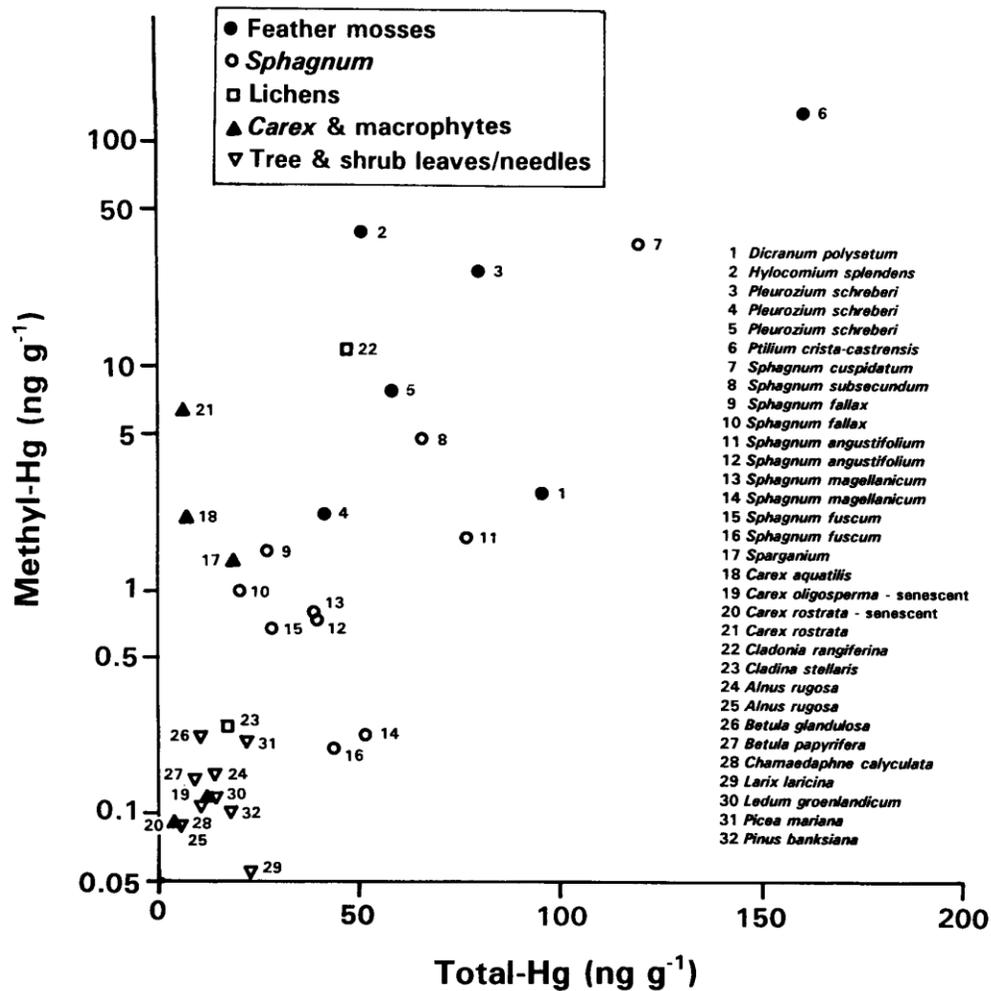


Figure 2.5: Concentrations of THg and MeHg in plant tissues from wetland in ELA, values for tree and shrub vegetation are low represented by upside down white triangles, while values for mosses are high and represented by dark circles (from Moore et al. 1995)

Mercury in vegetation is transferred to soils predominantly via litterfall. In Boreal ecoregions of Canada, litterfall inputs of Hg(II) to watersheds were twice as high as inputs from wet deposition in non-forested regions (St Louis et al. 2001, Hall & St Louis 2004, Graydon et al. 2008). Mercury from litterfall is considered a new input of Hg to the soil because it is atmospherically derived

particulate/reactive Hg, as opposed to a recycled input which occurs when Hg(0) is transferred from soil to leaves via their stomata (St Louis et al. 2001, Hall et al. 2004). When vegetation comes into contact with soil, it becomes an agent for Hg (re)cycling, methylation, or potential mobilisation to downstream aquatic ecosystems should flooding occur (Grigal 2003, Hall et al. 2004).

### 2.3.2 *Soils*

Soils are similarly considered to be Hg sinks, with most of the Hg present in surface humic horizons where OM is most abundant. The most common form of Hg associated with OM is Hg(II) (Grigal 2003). Changes in Hg concentration in soils occur with changes in soil organic matter; the forest floor generally has higher concentrations in comparison to underlying mineral soils (Grigal 2003, Hall & St Louis 2004). Forests with high productivity rates and nutrient cycling tend to have lower soil OM and Hg concentrations (Fleck 1999). While a longer growing season allows for increased uptake of Hg through foliage, simultaneously there is also greater OM decomposition and Hg re-emission from soils to the atmosphere. Consequently in Arctic regions, where growing seasons are short, more Hg can accumulate in soils leading to large reservoirs of Hg potentially available for hydrologic transport to aquatic systems and subsequent methylation (Grigal 2003).

## **2.4 Increases in Hg post-flooding**

Investigations of flooding and its impacts on Hg accumulations have, for the most part, focused on the effects of reservoir impoundment associated with hydro-electric dam establishment (Bodaly et al. 1984, Jackson 1988, Jackson 1991, St Louis et al. 2004, Hall et al. 2005). Flooding of large tracts of land causes the organic carbon in soils and plant materials to decompose, depleting the ecosystem of oxygen and creating anoxic conditions (Jackson 1988, Hall et al. 2004, St Louis et al. 2004). Organic matter decomposition leads to the release of Hg stored within soils and vegetation which can be stored again in sediment, depending on OM content, and/or be methylated by microbial activity (Jackson 1988, Jackson 1991, Rudd 1995, Grigal 2003, Hall & St Louis 2004, Hall et al. 2004).

Following the flooding of reservoirs in northern Manitoba, located in what were forested and muskeg-dominated landscapes, field investigations found increased levels of Hg in fish tissue (Jackson 1991). While different species and sizes of fish had variable accumulation rates, this increase generally occurred within two years of flooding (Bodaly et al. 1984, Jackson 1991). Mercury levels were highest in lakes where water levels were raised the most during impoundment. Researchers speculated that the higher water levels meant a greater proportion of flooded land to pre-flooding lake-bottom which may have resulted in greater concentrations of Hg, which then became available for methylation (Jackson 1991).

Studies examining the effects of reservoir impoundment on Hg concentrations focus on changes in accumulation within the first years post-flooding (Jackson 1988, Jackson 1991, Hall & St Louis 2004, Hall et al. 2004, St Louis et al. 2004, Hall et al. 2005). Research conducted in the ELA, where experimental reservoirs have been created for a number of studies, has been paramount in evaluating the influence of flooding on Hg budgets within forested areas.

Sharp increases in total Hg occur in lake waters and sediments during the first year following inundation, but soon afterwards declines ensue (Jackson 1991, St Louis et al. 2004, Hall et al. 2005). Furthermore flooded reservoirs exported Hg in their water via runoff following flooding, but the exports decreased after one year for THg and after two years for MeHg (Fig. 2.6) (St Louis et al. 2004, Hall et al. 2005). Concentrations of THg in runoff waters can be variable; however it is the total volume of runoff water received by a lake which determines the level of increase in Hg concentrations (St Louis et al. 2004). Thus, even waters with low concentrations can cause large Hg increases if the volume of water is sufficient.

Vegetation type and concentrations of Hg within the biomass can also influence Hg exports in flooded terrain. Initial concentrations of THg in plant material can indicate whether fallen vegetation would be sinks or sources. Plant materials with total Hg concentrations less than  $30 \text{ ng g}^{-1}$  in litterfall were found to be sinks for Hg, while those with concentrations greater than  $30 \text{ ng g}^{-1}$  were sources (Hall & St Louis 2004). One assumption is that the THg concentrations

within decomposing vegetative materials remains in equilibrium with those found in the local environment and can be affected by Hg in precipitation, throughfall, runoff and in organic soils (Hall & St Louis 2004). Higher order plant materials such as leaves, stems, branches from woody shrubs and trees, increased in THg concentrations, while lichens, mosses and bryophytes experienced THg losses in the first year after flooding (Hall & St Louis 2004). Decomposition rates and changes in THg mass of vegetation were found to be faster in flooded terrain compared with non-flooded, which suggested that materials in flooded sites equilibrated faster than did materials in unflooded sites. However, there was no difference in THg concentrations after ~two years in flooded and non-flooded sites (Hall & St Louis 2004).

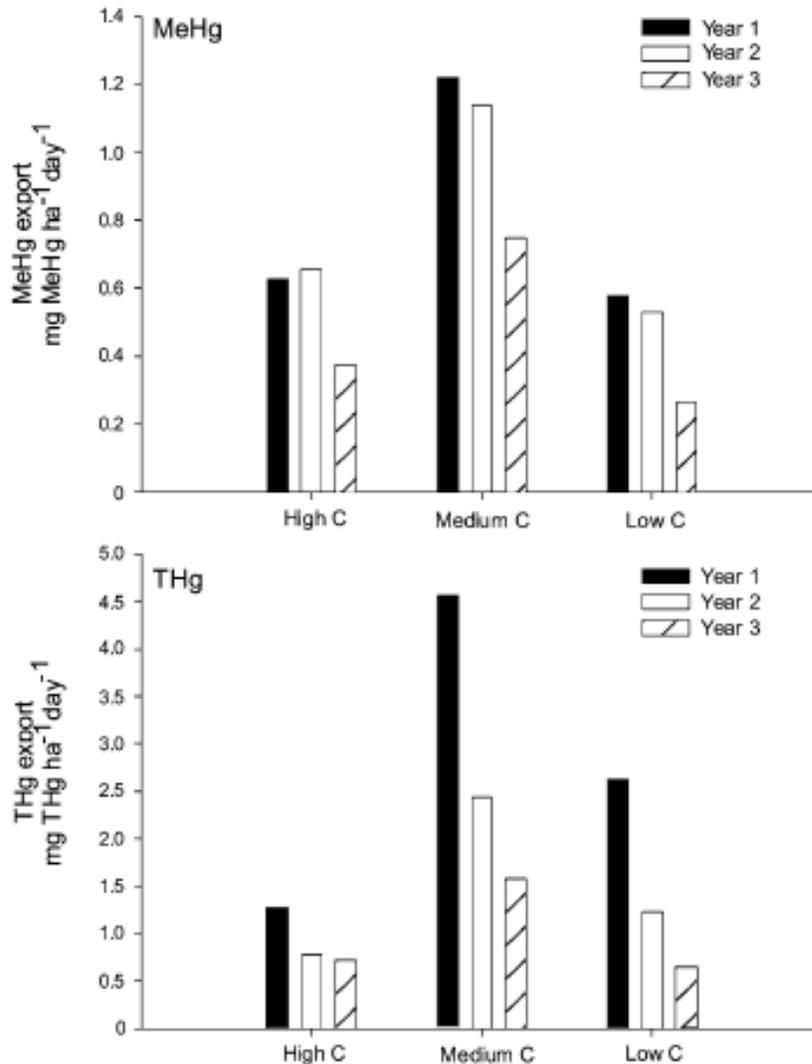


Figure 2.6: Export yields of MeHg (mg ha<sup>-1</sup> day<sup>-1</sup>) and THg (mg ha<sup>-1</sup> day<sup>-1</sup>) from three reservoirs differing in organic carbon content (from Hall et al. 2005)

Few studies are available which investigate natural flooding phenomenon. This may be in part because significant lake expansion leading to inundation of landscapes in northern regions does not occur often, and therefore few opportunities to investigate such events are available. Some studies investigating the complexity of landscape change in the Arctic due to climate change have indicated that lakes could expand resulting from thawing of

previously frozen ground; however few mention specific examples (Hinzman et al. 2005, Rowland et al. 2010).

More commonly, instances of lake disappearance or rapid draining are found related to the degradation of permafrost, but a few examples of lake expansion have been noted. One in particular was found in Siberia, where lakes within a landscape underlain by continuous permafrost were expanding, in contrast to lakes in discontinuous permafrost (Smith et al. 2005). Unfortunately, contaminants were not part of this study. This was also the case for research into lake expansion due to thermokarst conditions in the boreal forest in Alaska (Osterkamp et al. 2000, Jorgensen & Osterkamp 2005).

An investigation into flooding of boreal forests due to beaver dam impoundments in southwestern Quebec, Canada was conducted to evaluate the effects on THg and MeHg concentrations (Roy et al. 2009). Beaver ponds that had been inundated <10 years had higher rates of methylation compared with those in ponds >20 years, possibly due to the relative availability of labile organic matter (Roy et al. 2009).

While similar, the above examples occur in different regions, under different conditions and in some cases at a smaller scale than those being investigated in this project.

Gaps in current knowledge have been identified which the present study addresses. Specifically, the spatial extent of lake sediment studies focused on Hg is currently sparse; particularly in sub-arctic regions where permafrost occurs

at higher temperatures and landscape features include low relief, many lakes, and forests. These conditions have the potential to increase Hg contamination of ecosystems. Investigations of multiple lakes in a region are also few, but are necessary for evaluating the natural variability of contamination pathways. Finally most flooding studies focus on large, rapid inundation of reservoirs for hydroelectric dams or in experimental situations. To date, minimal research has been done investigating changes in Hg concentrations in lakes that are affected by significant expansion in a natural setting, on a decadal timescale. This research addresses these data gaps by examining the total Hg concentration and accumulation as well as sources of organic matter in the sediments of five lakes located in the same region within the Canadian sub-arctic, three of which have been expanding over the past 25 years.



### **3 STUDY SITE AND METHODS**

#### **3.0 Study Region**

The Mackenzie Bison Sanctuary (MBS) is a wildlife reserve that was established in 1963 when a small herd of bison were relocated to this area to protect the species from disease and preserve its genetic diversity. Today there are about 700 bison living within the sanctuary (ENR 2013). The MBS covers an area approximately 10 000 km<sup>2</sup> and lies within the Great Slave Lowlands, a sub-classification of the Taiga Plains Mid-Boreal ecoregion in the NT (ENR 2009; NWT Species at Risk 2012). The Lowlands are bounded by the Mackenzie River to the south, Great Slave Lake to the east and north and the Horn Plateau to the west.

Much of this area was covered by glacial Lake McConnell, which formed in the Great Slave Lake, Great Bear Lake and Athabasca Lake basins during the Laurentide Ice Sheet deglaciation, approximately 11.5 thousand years BP (Day 1972, Smith 1994, Kerr & Wilson 2000). Present-day landscapes are shaped by glacio-lacustrine and till deposits from glacial melt and Lake McConnell water level retreat, that have over time been modified by fluvial and eolian processes (ENR 2009). Discontinuous permafrost can be present beneath the surface, and occurs more frequently west of Great Slave Lake (ENR 2009). The water table throughout this region is generally quite close to the ground surface, and government field investigations have shown that even small increases in water table position can lead to extensive flooding (ENR 2009).

Climate in the Great Slave Lowlands is the mildest across the Taiga Plains Mid-Boreal ecoregion. Mean annual air temperature ranges from -0.3 to -5.1°C. January is generally the coldest month at -22 °C, and July the warmest with temperatures around 16.0°C (averages between 1971 and 2010; Hay River NT station, Environment Canada 2011). Mean annual precipitation is 168-192 mm; 55% of which falls as rain, and the remaining 45% as snow (averages between 1971 and 2010; Hay River, NT station, Environment Canada 2011). The wettest months are between June and September; the driest are between December and April (ENR 2009).

Vegetation in the Great Slave Lowlands includes scattered patches of mixed-wood and jack pine (*Pinus banksiana*) forest, as well as treed, shrubby and sedge-dominated fens. Pure or mixed stands of black spruce (*Picea mariana*), and white spruce (*Picea glauca*), Alaska paper birch (*Betula neoalaskana*), tamarack (*Larix laricina*) trembling aspen (*Populus tremuloides*), and balsam poplar (*Populus balsamifera*), with low-bush cranberry (*Vaccinium vitis-idaea*), prickly rose (*Rosa acicularis*), green alder (*Alnus viridis* ssp. *crispa*) and forbs as understory was the predominant vegetation at the specific study sites (ENR 2009).



Figure 3.1: Map of location of lake study sites within the Mackenzie Bison Sanctuary, NT.

### 3.1 Lake Sites

Five lakes were selected to test whether lake expansion would cause differences in total Hg concentrations in lake sediments. The three expanding lakes are known to have increased in extent recently, while the two reference lakes have not and will be used as control sites. Four of five lakes studied are separated into two distinct pairs of lakes; Jackie and Chan lakes as well as Trio 1 and Trio 3. The two lakes within the pair are in close proximity to each other, but

are exhibiting different behaviours, with one of the lakes expanding while the other is not. Until recently, the sedge meadows surrounding the lakes were preferred wood bison grazing sites, and their inclusion in this study is important in terms of understanding degradation and management of bison habitat (Chowns, 1987). Measurement of lake depths was not captured during the recovery of the cores in spring of 2012, however subsequent core recovery in the spring of 2013 found that the water depth of lakes in the MBS are between 1.5 to 2.0 metres.

Currently there is very little information explaining why some of the lakes within the MBS are expanding. One possible explanation is that the expansion occurring over the past 25 years is in fact part of a cycle during which these lakes expand and contract over long time scales. This is suggested by historic shorelines which do surround some of the expanding lakes, indicating the lakes have been larger in the past. A second possible explanation is modern climate change and its impact on northern regions, either through changing climatic patterns or the thaw of permafrost allowing greater water to be collected at the surface of this low-lying terrain.

### **3.1.1 Expanding Lakes**

#### *Falaise Lake*

Falaise Lake is a large lake located in the eastern portion of the MBS and has been expanding since the mid-1980s, as evidenced by satellite imagery (van der Wielen, 2011; deMontigny, 2014 unpublished data) (Fig. 3.1). The lake has a long, narrow, oval shape and is oriented NE to SW. Lake extent as examined by

LANDSAT images taken in 2011 show the recent water surface area to be ~ 5,600 ha. The satellite images also reveal what appears to be an historic shoreline surrounding the lake, which suggests that the lake has been larger in the past. Analysis of an aerial photograph taken in 1948 confirmed this with water extent estimated at ~ 7,000 ha (van der Wielen, 2011).

### *Trio 1*

Trio 1 is a small irregularly shaped water body also in the eastern portion of the MBS, and situated approximately 18 km north of Falaise Lake (Fig. 3.1). It is one of three water bodies (Trio 1, Trio 2, and Trio 3) grouped closely together. A previously conducted LANDSAT study (van der Wielen, 2011) investigated these three lakes as a single aquatic system; however images, water chemistry, and field observations all point to hydrological separation between the lakes. This study focuses on Trio 1, which has been increasing in extent since the mid to late 1980s. The most recent lake extent based on 2011 imagery was ~ 1 000 ha.

### *Jackie*

Jackie Lake (unofficial name) is located on the west side of Highway 3; approximately 100 km northeast of Fort Providence (Fig. 3.1). It is one of the smallest lakes included in the study. The lake has a narrow, oval shape (similar to Falaise Lake) and is also oriented NE to SW, approximately 2.6 km long.

Based on field observations of recently drowned vegetation, Jackie Lake has been recently expanding. Water surface area, determined from satellite images taken in 2011, was estimated at ~ 151 ha for Jackie Lake.

### **3.1.2 Reference Lakes**

The two lakes used as reference sites for this study are Trio 3 and Chan lakes. Trio 3 is the smallest lake within the Trio Lake system (Fig. 3.1). It is circular in shape and located 5 km south of Trio 1. Chan Lake, the smallest lake included in the study, is the site of a NT Territorial Park, and located on the east side of Highway 3, opposite Jackie Lake (Fig. 3.1). Satellite imagery demonstrates that the water surface area of both lakes has not noticeably changed since 1986. In 2011, lake extent was ~ 300 ha for Trio 3 and 66 ha for Chan Lake.

## **3.2 Methods**

### *3.2.1 Satellite image analysis of lake surface area*

To determine if changes in lake surface area could be associated with THg concentration in sediments, satellite images of the lakes chosen for this study were analyzed. As previously mentioned one such study has been completed, however it did not examine the same lakes selected for this project, or treated them differently (van der Wielen 2011). A study to examine the five lakes used in

this research project was conducted to determine the change in lake surface area and the rate of expansion using remote sensing techniques. This analysis was conducted by using images that were previously collected, corrected and classified by others for a study seeking to determine if climate factors were associated with the increased water surface area in the MBS (deMontigny 2014). All processes described below were completed by deMontigny (2014).

Images were selected based on a number of qualities and attributes. Of the many possible sources of images, LANDSAT 5 Thematic Mapper (TM) images were selected as best to address issues of cost, data storage size, spatial coverage and temporal resolution (deMontigny 2014). Also it was necessary to eliminate seasonal variation in order to make accurate conclusions regarding multi-year environmental changes. To do so images with snow were eliminated as they could affect the image captured by the LANDSAT 5 TM. Images taken during the summer were also avoided as warm temperatures and evaporation rates strongly influence lake levels in the North, as were images with more than 10 % cloud cover which could distort or obstruct the maximum outline of lake shorelines (deMontigny 2014). The average maximum temperature in September of 13.2 °C was selected as optimal to minimize seasonal variation and a date range of August 12<sup>th</sup> and October 13<sup>th</sup> was selected as the window for best image selection based on 30-year climate normal data (1981-2010) (deMontigny 2014).

Images were corrected and classified for the purposes of analysis. This included the correction for Earth curvature and rotation applied by the United States Geologic Survey, from where the images were retrieved. Images were

classified into two broad categories: land and water. The near infrared band was utilized as the filter which could best delineate shoreline boundaries, and pixels were converted to “fuzzy classification” raster data in order to apply more than one attribute to each pixel (deMontigny 2014). A total of 13 images were selected between 1986 and 2011 and assessed for lake surface area (ha).

### *3.2.2 Sample Collection*

Sediment cores measuring 10-50 cm in length, were recovered from the centre of each of the five lakes between March 16 and 18, 2012. An area of frozen lake surface was cleared of 60-75 cm of snow before drilling through the ice with an auger. Sediment was collected using a Glew messenger-operated gravity corer (Glew et al. 2001) and 3” (7.62 cm) clear Lexan core tubes. Cores were retrieved from multiple lakes in a day, and the tubes were capped and secured for transport back to Fort Providence where they were extruded. Coring tubes were cleaned and dried between uses. Cores were sub-sampled at 0.5cm intervals with a vertical extruder (Glew et al. 2001). The sediment was placed into Whirl Pak<sup>®</sup> bags, refrigerated, then shipped in a cooler back to the Carleton University Paleoecological Laboratory (CUPL) where they were stored at 4°C until December 2012 for subsequent analysis.

Table 3-1: Summary of surface core and geographic information for MBS lakes studied.

	Core length (cm)	Water surface area in 2011 (ha)	Coordinates (latitude; longitude)
Falaise	17.0	5,637.6	61°28' 42.47"N; 116°09' 13.29"W
Trio 1	10.0	1,036.4	61°38' 21.58"N; 116°03' 00.08"W
Trio 3	50.5	306.4	61°35' 48.06"N; 116°04' 10.20"W
Jackie	21.0	151.02	61°53' 48.07"N; 116°33' 33.95"W
Chan	26.5	66.2	61°53' 26.64"N; 116°32' 30.56"W

### 3.2.3 Radiometric Dating

Sediment cores were dated using gamma spectrometry. All five cores were analyzed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  following the method outlined by Schelske et al. (1994) and Appleby (2001). Between 8 and 11 discrete intervals were selected from each core to determine sediment age and sediment accumulation rate with a higher density of samples selected from the upper 10 cm. The Constant Rate of Supply (CRS) model was utilised to establish the core chronology and estimate sedimentation rates for horizons selected for analysis, as this model presented the most logical dates of the four models tested. Other horizons were dated by linear extrapolation using the Binford model (Binford 1990).

### 3.2.4 Total Mercury Analysis

Homogenized samples were transferred from Whirl Pak<sup>®</sup> bags to 20 ml glass scintillation vials. Samples were freeze-dried for a period of 72 hours, and homogenized upon removal. Total Hg in sediments was analysed by thermal

decomposition with gold trap amalgamation and cold vapour atomic absorption (CV-AAS) using a Nippon Instruments' Mercury SP-3D Analyzer with detection limits of 0.01 ng per sample size. Sample mass ranged between 17-30 mg sediment (dry weight). Measurement accuracy was estimated by running blanks, and calibrated with MESS-3 ( $91 \pm 9 \text{ ng g}^{-1}$ , NRC of Canada) as reference material every 10 samples.

### *3.2.5 Carbon and nitrogen isotopes*

Elemental and isotopic analyses of all samples were done at the G.G. Hatch Stable Isotope Lab at Ottawa University, Ottawa Ontario. Prior to analysis, dried sediment samples were re-hydrated with de-ionized water and desiccated with hydrochloric acid (HCl) for 48 hours to remove carbonates. Samples were then triple rinsed with de-ionized water, freeze-dried for 72 hours and homogenized prior to sub-sampling.

Sediment samples and a set of standards were weighed into 8 mm x 5 mm tin capsules and submitted to elemental analysis (EA) to determine the quantity of organic carbon and nitrogen. Between 5 to 10 mg of sediment were weighed per sample along with ~20 mg tungsten oxide ( $\text{WO}_3$ ) which was used to bind impurities which might contaminate the sample. From these results, the weights needed for isotopic analysis were determined. Isotopic composition of organic carbon and nitrogen was determined using Isotope Cube isotope ratio mass spectrometer (Elementar, Germany) with a precision of 0.2 %. Results were

reported in delta notation compared to known standards ( $\delta$ ), and the units were in per mil (‰).

### 3.2.6 Flux calculations and statistical analyses

Mercury fluxes, anthropogenic flux, and flux ratios (FR) were calculated using the following equations as outlined in Muir et al. (2009) and used by others (Lockhart et al. 1995, Landers et al. 1998, Lockhart et al. 1998, Brazeau et al. 2013).

$$\text{Mercury flux (ng m}^{-2} \text{ y}^{-1}) = [\text{THg}] (\text{ng g}^{-1}) \times \text{}^{210}\text{Pb-derived sedimentation rate (g m}^{-2} \text{ y}^{-1}) \quad (1)$$

$$\text{Anthropogenic Hg flux (ng m}^{-2} \text{ y}^{-1}) = F_{\text{recent}} - F_{\text{pre-ind}} \quad (2)$$

Where  $F_{\text{recent}}$  is the average of Hg flux in sediment horizons post-1990 and  $F_{\text{pre-ind}}$  is the average of Hg flux in horizons pre-1900 (where possible)

$$\text{Flux ratios (FR)} = F_{\text{recent}} / F_{\text{pre-ind}} \quad (3)$$

Sediment particle focusing factors were also calculated for each sediment core. This was done to correct for any sediment and contaminant focusing towards the deeper part of the lake which may complicate the record of areal inputs of contaminants (Omelchenko et al. 1995). Focusing factors are estimated using predicted rate of radionuclide fallout of  $^{210}\text{Pb}$ . Each core's cumulative unsupported  $^{210}\text{Pb}$  inventory ( $\text{Bq m}^{-2}$ ) was multiplied by the  $^{210}\text{Pb}$  decay constant ( $0.03114 \text{ y}^{-1}$ ) to give an observed  $^{210}\text{Pb}$  flux ( $\text{Bq m}^{-2} \text{ y}^{-1}$ ). This flux rate was

divided by a predicted atmospheric  $^{210}\text{Pb}$  flux of  $80 \text{ Bq m}^{-2} \text{ y}^{-1}$  taken from soil measurements of  $^{210}\text{Pb}$  flux at Lake Laberge, Yukon ( $61.2^\circ\text{N}$ ,  $135^\circ\text{W}$ ) (Omelchenko et al. 1995, Lockhart et al. 1998).

Statistical analyses and correlations were performed using the R statistical environment (x64 v.2.15.3). Data that passed the normality test (Shapiro-Wilk test  $P > 0.05$ ) were analyzed using Pearson's Correlation. Those data that could not be normalized were analyzed using Spearman's Rank Correlation. The confidence interval used for all tests was set at 95 %.

## 4 RESULTS

### 4.0 Lake Surface Area Analysis

#### 4.0.1 *Expanding Lakes*

Analyses of a series of satellite images demonstrated that lakes suspected to be expanding (Falaise, Jackie, Trio 1) have increased in surface area and subsequently flooded the landscape. The three expanding lakes exhibited similar patterns of water surface area fluctuations in the 13 years selected for analysis between 1986 and 2011 (Fig. 4.1 a-c). The lowest water surface area recorded in the remotely sensed images was in 1986. Water levels were variable over the next few images, with increases until the early 1990s, followed by declines in water surface area until the late 1990's (Fig. 4.1 a-c). Steady increases in water surface area began again ~2000 and continued over the next 10 years as all three lakes reached their highest water surface area in 2010-2011 (Fig. 4.1 a-c).

Falaise Lake shows the greatest relative change in water surface area, with a 9-fold increase from 610 ha in 1986 to just over 5,600 ha by 2011 (Fig 4.1 a). Jackie and Trio 1 lakes also exhibited significant change, despite being much smaller lakes, increasing by 400 and 500 %, respectively (Fig 4.1 b-c) (Table 4-1).

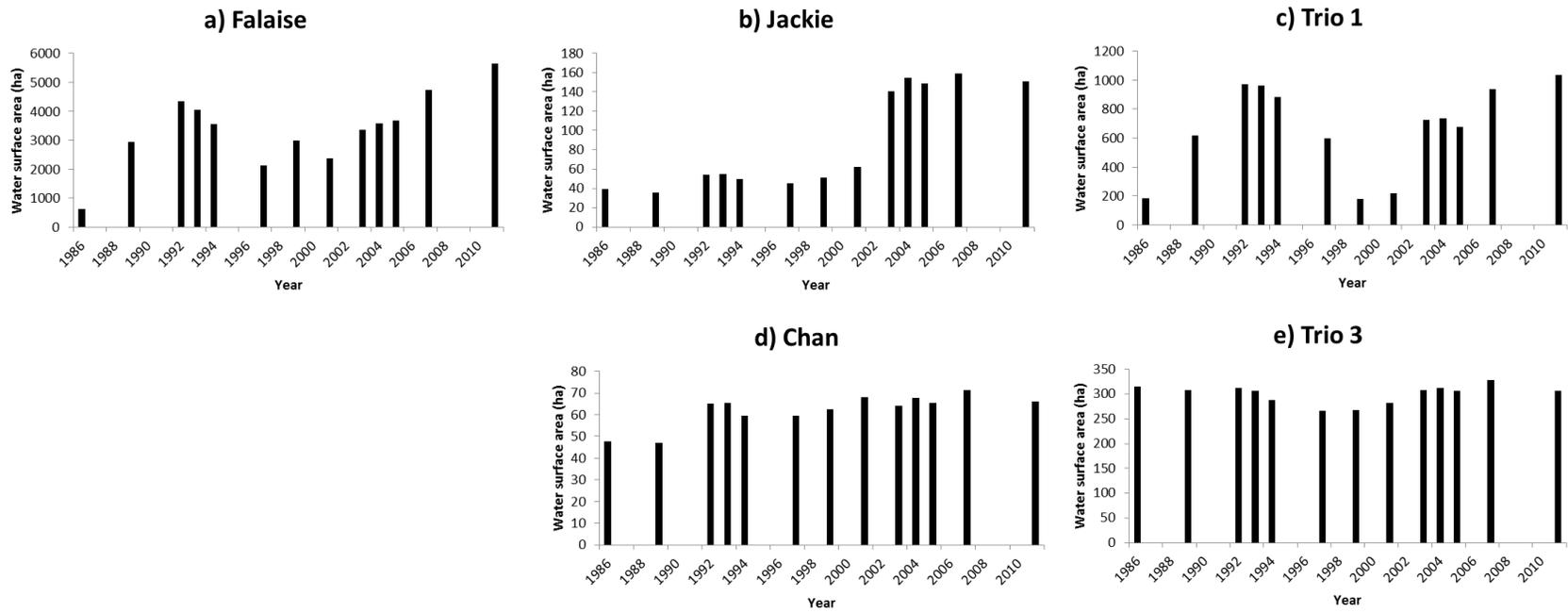


Figure 4.1: Changes in water surface area (ha) over select 13 years between 1986 and 2011 for A) Falaise, B) Jackie, C) Trio 1, D) Chan, and E) Trio 3 lakes.

Table 4-1: Change in water surface area for each year compared to 1986 value, standard deviation (S.D.), and relative standard deviation (R.S.D.) for all years analysed.

	<b>1986</b>	<b>1989</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1997</b>	<b>1999</b>	<b>2001</b>	<b>2003</b>	<b>2004</b>	<b>2005</b>	<b>2007</b>	<b>2011</b>	<b>S.D.</b>	<b>R.S.D.</b>
<b>Falaise</b>	1.0	4.8	7.1	6.6	5.8	3.5	4.9	3.9	5.5	5.9	6.0	7.8	9.2	2.1	37.2
<b>Jackie</b>	1.0	0.9	1.4	1.4	1.3	1.1	1.3	1.6	3.6	3.9	3.8	4.0	3.8	1.3	58.8
<b>Trio 1</b>	1.0	3.3	5.2	5.2	4.8	3.2	1.0	1.2	3.9	3.9	3.6	5.0	5.6	1.6	45.4
<b>Chan</b>	1.0	1.0	1.0	1.0	0.9	0.8	0.9	0.9	1.0	1.0	1.0	1.0	1.0	0.1	6.8
<b>Trio 3</b>	1.0	1.0	1.4	1.4	1.3	1.3	1.3	1.4	1.3	1.4	1.4	1.5	1.4	0.2	11.5

When comparing the pattern of change in water surface area for Trio 1 to Falaise and Jackie Lakes, a minor difference becomes apparent. Both Falaise and Jackie Lakes had higher water levels during the late 1980s and early 1990s, which increased even further between 2004 and 2011 (Fig. 4.1 a-b). Lake Trio 1 also has increased water surface area during both of these time periods, however unlike Falaise and Jackie, the levels attained are similar both in the 1990s and in 2011 (Fig. 4.1 c). Trio 1 is certainly larger than it was in 1986, but it is uncertain how much this change in water level might be related to hydrological connection between the other two lakes in the Trio system. Lake Trio 2, which was not examined in this study, did exhibit modest lake level increases based on observations of the satellite images, and is located between Trio 1 and Trio 3.

Total [Hg] in dated horizons that corresponded to years of lake surface expansion in Falaise lake were significantly correlated ( $r = 0.90$ ,  $p = 0.01$ ). Unfortunately none of the other lake sediment profiles could be statistically analyzed with water surface area as an insufficient number of recent sediment horizons were dated which corresponded with the dates of images analyzed.

#### *4.0.2 Reference Lakes*

During this same time period Trio 3 and Chan lakes, both classified as non-expanding lakes, experienced some fluctuations in water surface area but remained constant with a relative standard deviation of 6.8 for Chan Lake and 11.5 for Trio 3 (Fig. 4.1 d-e) (Table 4-1). The timing of the variability in water

surface area does appear to coincide with changes occurring in the expanding lakes; with slight decreases in water levels in the early 1990s and minimal increases after 2002, though the magnitude of change was far less.

#### *4.0.3 Comparison with previous studies*

These temporal trends are consistent with an investigation of lake surface area for Falaise and the Trio lakes, as well as many other lakes in the MBS, conducted by the Aurora Research Institute (ARI) (van der Wielen 2011). Comparison of water surface area between the satellite images analyzed for Falaise lake in this study, and those utilized in the ARI study are strongly correlated ( $r= 0.75$ ,  $p= 0.007$ ). While water levels differ for some years, the results of the two studies exhibit consistent trends, confirming the expansion over time for Falaise Lake (Table 4-2).

Increase in water surface area for the Trio lakes was not compared statistically between the two studies. This was owing to the different approaches in evaluating the lakes; ARI assessed the Trio Lakes as a single large expanding lake, while this work treated each lake as a separate water body. The water surface area for Jackie and Chan lakes also could not be compared as ARI did not include these lakes in their study, which focused only on the large lakes in the MBS.

Table 4-2: Lake surface area (ha) for Falaise Lake determined through analysis of satellite images, over 13 years between 1986 and 2011 for this study and for ARI.

	This Study	ARI
2011	5638	-
2010	-	5502
2007	4736	4715
2005	3680	4376
2004	3582	4002
2003	3353	3584
2001	2361	3371
1999	2981	3477
1997	2114	3475
1994	3544	3830
1993	4048	4232
1992	4338	3869
1989	2933	4379
1986	610.3	899.2

#### 4.1 Radioisotopic dating

$^{210}\text{Pb}$ -based radioisotopic techniques were used to establish sediment core chronologies for all five lakes.  $^{210}\text{Pb}$  reached background levels in all cores except for Trio 1, the shortest profile at just 10cm (Fig.4.2). The background  $^{210}\text{Pb}$  was reached at variable sediment depths for the remaining four lakes. The unsupported  $^{210}\text{Pb}$  profiles for all lakes exhibited an approximate log-linear decline over time. Average concentrations of  $^{210}\text{Pb}$  in all cores were between 100 and 300 Bq kg<sup>-1</sup>. Estimated sediment ages and sedimentation rates were calculated for the analyzed horizons of all five cores using the constant rate of supply (CRS) model. Table 4-3 lists  $^{210}\text{Pb}$  flux, sediment focus factor, and average sedimentation rates for each core.

#### 4.1.1 Expanding Lakes

The expanding lakes had lower values of  $^{210}\text{Pb}$ ; with average values between 100 and 200  $\text{Bq kg}^{-1}$ .  $^{210}\text{Pb}$  activity in the sediment cores for Falaise and Jackie Lake reached background levels at  $\sim 9.25$  cm. In Lake Trio 1  $^{210}\text{Pb}$  concentrations at 9.25 cm, the deepest horizon analyzed, did not attain background levels and were measured at  $\sim 150 \text{ Bq kg}^{-1}$ .

Focus factors were close to 1.0 for Falaise Lake, with observed  $^{210}\text{Pb}$  nearly matching the predicted flux of  $80 \text{ Bq m}^{-2} \text{ y}^{-1}$  for this latitude. For Jackie Lake, focus factors indicate an underestimation of elemental flux based on observed flux of  $^{210}\text{Pb}$  at  $45.4 \text{ Bq m}^{-2} \text{ y}^{-1}$  and associated focusing factor of 0.6. Corrected average sedimentation rates were higher in the expanding lakes compared with the reference lakes.

#### 4.1.2 Reference Lakes

The sediments of lakes Trio 3 and Chan reach background levels at 19.25 cm and 9.25 cm, respectively. The depth at which background  $^{210}\text{Pb}$  levels are found within Trio 3, indicate sedimentation rates were overall higher within this lake environment. Based on the observed  $^{210}\text{Pb}$  flux for Chan Lake much higher values than expected were found and subsequently this lake has the highest focusing factor value at 2.6 (Table 4-3). Lake Trio 3 had observed  $^{210}\text{Pb}$  flux very similar to the estimated values. Trio 3 and Chan lakes have the lowest average sedimentation rates of the five lakes studied.

Table 4-3:  $^{210}\text{Pb}$  fluxes, focusing factor and corrected average sedimentation rate for each lake.

	Observed $^{210}\text{Pb}$ flux ( $\text{Bq m}^{-2} \text{ yr}^{-1}$ )	Estimated $^{210}\text{Pb}$ flux ( $\text{Bq m}^{-2} \text{ yr}^{-1}$ )	Focusing Factor (FF)	Average sedimentation rate ( $\text{g m}^{-2} \text{ yr}^{-1}$ )
<i>Expanding Lakes</i>				
Falaise	80.8	80	1.01	83.17
Jackie	45.4	80	0.6	76.24
Trio1	72.5	80	0.9	51.67
<i>Reference Lakes</i>				
Trio3	77.0	80	0.9	17.48
Chan	208.5	80	2.6	27.36

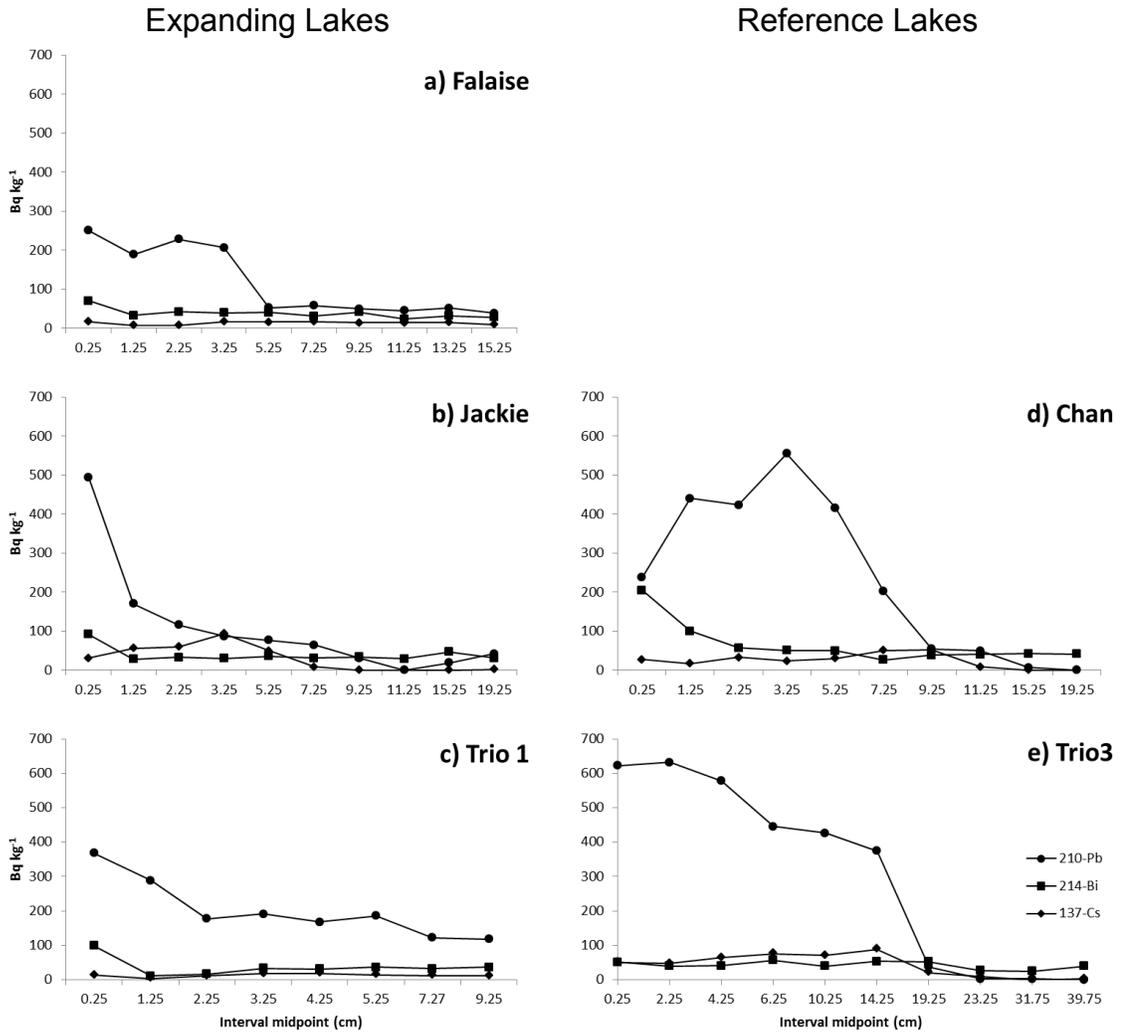


Figure 4.2: Plots of radioactive  $^{210}\text{Pb}$ ,  $^{214}\text{Bi}$  and  $^{137}\text{Cs}$  activity and sediment core depth from (A) Falaise, (B) Jackie, (C) Trio 1, (D) Chan, and (E) Trio 3 lakes.

## 4.2 Total Hg concentrations

Total [Hg] were low in all lakes studied with average values between 25 ng and 43 ng (per gram dry weight) (Table 4-4). The five lakes studied exhibited variable [Hg] trends over time (Fig.4.3, a-e).

Table 4-4: Minimum, maximum THg concentrations and associated depth for each lake, and mean concentrations.

	Min (ng g <sup>-1</sup> )	Depth (cm)	Max (ng g <sup>-1</sup> )	Depth (cm)	Mean (ng g <sup>-1</sup> )
<i>Expanding Lakes</i>					
Falaise	23.1	16.25	33.3	0.25	28.2
Jackie	15.6	17.25	45.2	0.75*	25.7
Trio 1	19.1	0.25	33.6	3.75	27.0
<i>Reference Lakes</i>					
Chan	22.0	21.25	40.7	3.75	30.2
Trio 3	21.5	44.75	62.9	8.75	43.6

\*Most recent sediments analyzed in Jackie Lake for Hg content. All of topmost sediment (first 0.5 cm) in Jackie Lake was used for dating purposes.

### 4.2.1 Expanding Lakes

Jackie Lake was the only expanding lake that demonstrated steady increases in [THg] throughout the sediment core profile. The lowest Hg values were found in the deepest sediments (15.6 ng g<sup>-1</sup> at 17.25 cm) and the highest within the topmost interval analyzed (45.2 ng g<sup>-1</sup> at 0.75 cm), representing an approximate tripling of the concentration in the sediments at this site, with 45 % of the change occurring between 1967 and 2005 (Fig. 4.3, b).

Total Hg in Falaise Lake does increase slightly over time according to values obtained in Hg analysis (core surface 33.3 ng g<sup>-1</sup>; deepest interval 23.1 ng g<sup>-1</sup> at 16.25 cm) (Fig. 4.3, a). Mercury concentrations appear to have remained steady between 1920 and 1976, decreased slightly during the early 1980s and have been slowly increasing since 1986. The magnitude of change over time is unclear from the sedimentary profile presented. When calculated, a 30 % increase in concentrations occurs between the deepest and topmost horizon analyzed.

Lake Trio 1 is the third expanding lake examined in this study and represented by the shortest core recovered of all lakes at only 10 cm deep. The profile for this lake does not display increasing [THg] in the topmost sediments; in fact Hg values have been declining since the late 1980s (Fig. 4.3, c).

#### *4.2.2 Reference Lakes*

Chan Lake has declining [THg] from 2000 to the most recent sediments analyzed (Fig. 4.3, d). While the profile appears to demonstrate increases between 1980 and 2000, there are no values between 1986 and 1932, making it difficult to determine actual changes in concentrations in the past century in this lake.

Lake Trio 3 had the highest [THg] values of all the lakes studied. Concentrations increased from 38.9 ng g<sup>-1</sup> in the mid-1880s to a maximum value

of 62.3 ng g<sup>-1</sup> in 1973 (Fig.4.3, e). Total [Hg] varied over the next 35 years, declining to 35.4 ng g<sup>-1</sup> which was measured in the most recent sediments.

### Expanding Lakes

### Reference lakes

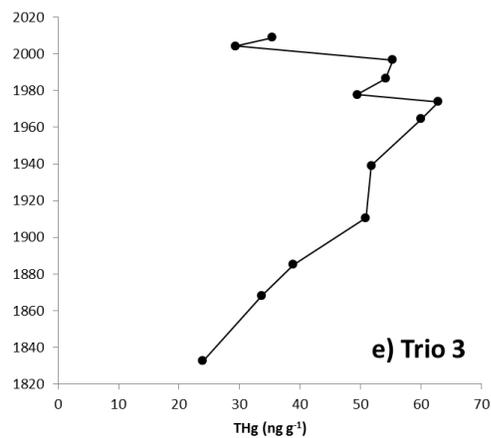
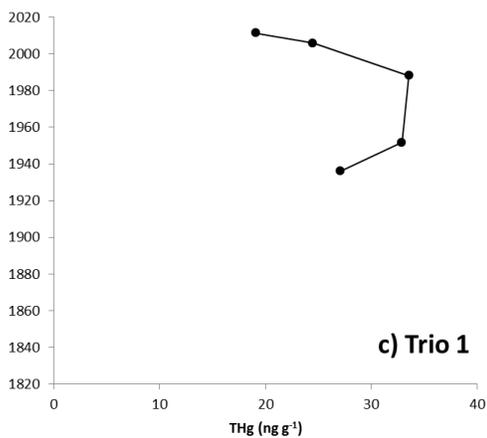
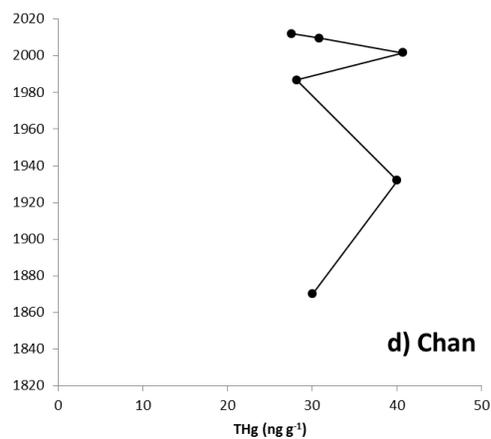
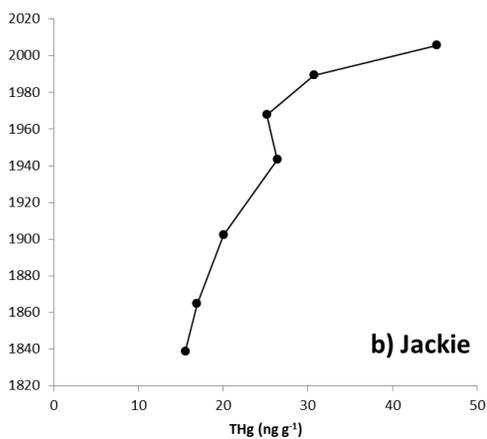
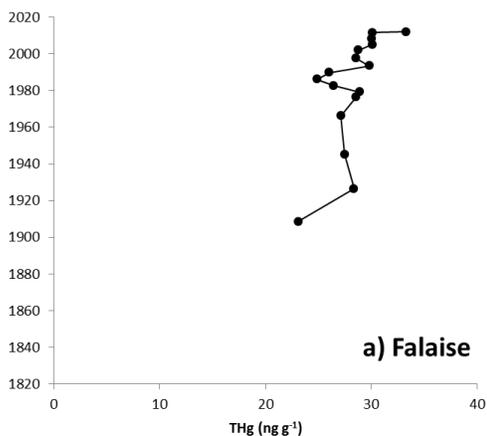


Figure 4.3: Total mercury concentrations (THg) (ng g<sup>-1</sup>) dry weight according to determined dates in sedimentary profiles for A) Falaise, B) Jackie, C) Trio1, D) Chan, and E) Trio 3 lakes.

### **4.3 Sedimentation Rates, Mercury Fluxes and Flux Ratios**

Mercury fluxes were calculated in order to account for differences in sedimentation rates and total Hg accumulation between lakes. In addition, fluxes were evaluated to minimize differences associated with 'background' levels of Hg deposition in lake sediments, which can vary even when lakes are in close proximity due to biological and physical features operating and existing in each lake basin, such as watershed inputs, geologic properties and hydrologic flow (Landers et al. 1998).

Average sedimentation rates were higher in expanding lakes compared with reference lakes; between  $76\text{-}83\text{ g m}^{-2}\text{ y}^{-1}$  and  $17\text{-}27\text{ g m}^{-2}\text{ y}^{-1}$ , respectively (Table 4.3). Overall, Hg fluxes closely tracked changes in modelled sedimentation rates in each of the five sediment cores (Fig. 4.4, a-e). While all lakes, except for Chan Lake (horizons analyzed do not correspond to this period in time), demonstrated increases in both parameters beginning around the 1940s, no other similarities were found within the expanding or reference lakes.

#### *4.3.1 Expanding Lakes*

Changes to sedimentation rates and Hg flux in the expanding lakes occur approximately 50-60 years ago. Both Jackie and Trio 1 show increased sedimentation and associated Hg flux from early 1940 until the late 1990s/early 2000s (Fig. 4.4, b-c). Sedimentation rates have since declined in both lakes; while high Hg flux persists in recent sediments of Jackie Lake and decline in Trio1.

In the largest expanding lake, Falaise, sedimentation rate and Hg flux increased rapidly between 1960 and 1980, the highest of all lakes studied, and subsequently decreased to comparably low rates by ~2000 (Fig.4.4 a). Both sedimentation rate and Hg flux have been slowly increasing since the early 2000s. It is interesting to note that within the profile for Falaise Lake, [THg] are lowest when sedimentation and Hg flux rates are at their highest during the early 1980s. Total organic carbon (TOC) was also minimal at this time (Fig. 4.5 a), indicating that this may be in response to an influx of inorganic sediment which diluted [THg].

#### 4.3.2 *Reference Lakes*

Both sedimentation and Hg flux in Trio 3 have increased since ~1945, and more steadily since 1970. While sedimentation rates increased in the most recent sediments in Trio 3, Hg flux (as with [THg]) has decreased since 1995 (Fig. 4.4 e).

Sedimentation rates in Chan Lake started to rapidly increase ~2000. Mercury flux increased in 1986, while sedimentation rate decreased slightly. Both fluxes continued to increase since 2000, with sedimentation rates falling in the most recent sediments of Chan Lake (Fig. 4.4 d). No samples were analyzed representing the period from 1940 to 1980 for Chan Lake due to time constraints and delays in obtaining sediment dating results which were received six months after the Hg analysis was completed.

Expanding lakes

Reference Lakes

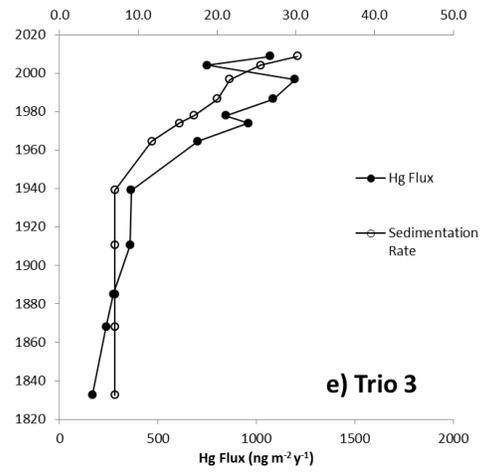
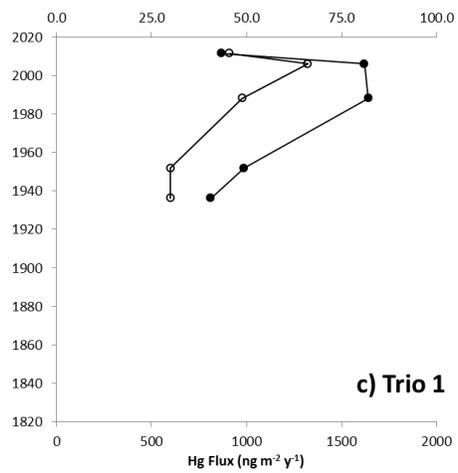
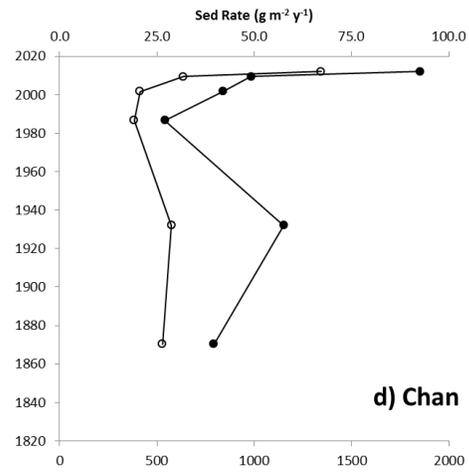
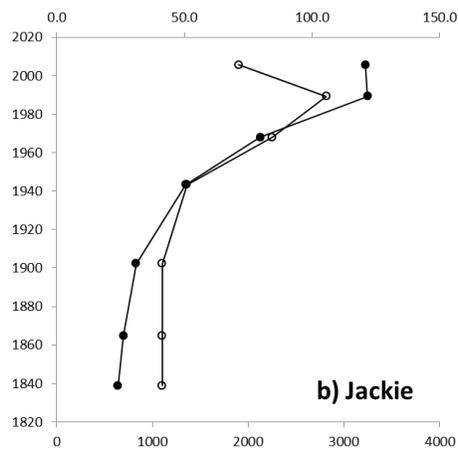
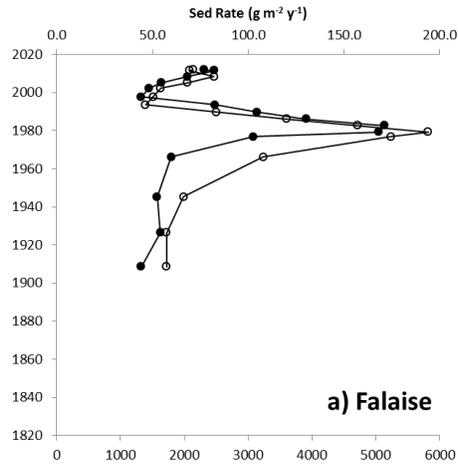


Figure 4.4: Sedimentation rate ( $\text{g m}^{-2} \text{y}^{-1}$ ) and Hg flux ( $\text{ng m}^{-2} \text{y}^{-1}$ ) over time in sedimentary profiles for A) Falaise, B) Jackie, C) Trio1, D) Chan, and E) Trio 3 lakes.

### 4.3.3 Flux Ratios

Flux ratios were calculated for each lake to determine changes in Hg flux between historic (pre-1900) and recent (post-1990) time periods. Anthropogenic flux was also determined in order to estimate the impact anthropogenic emissions have had on Hg flux to lake sediments. Values for each lake can be found in Table 4-5. Jackie Lake had the highest anthropogenic flux at 2,552 ng m<sup>-2</sup> yr<sup>-1</sup>. Both Jackie and Trio 3 had the highest flux ratio at 4.8. Mercury flux ratio values have been previously reported globally across boreal and Arctic ecosystems with values ranging from 0.7 to 8.9, with industrial activity attributed as the main source of Hg to the lakes (Landers et al. 1998).

Table 4-5: Historic, recent and anthropogenic flux, as well as flux ratios, for expanding and reference lakes.

	Historic Hg flux (pre-1900)* (ng m <sup>-2</sup> y <sup>-1</sup> )	Recent Hg flux (post 1990)* (ng m <sup>-2</sup> y <sup>-1</sup> )	Anthropogenic flux* (ng m <sup>-2</sup> y <sup>-1</sup> )	Flux ratio
<i>Expanding Lakes</i>				
Falaise	1327**	1937	610.0	1.5
Jackie	671.6	3224	2552	4.8
Trio 1	755.6**	1244	488.4	1.6
<i>Reference Lakes</i>				
Chan	665.3	1226	560.7	1.8
Trio 3	207.5	1005	797.9	4.8

\*all flux calculations have been corrected for sediment focusing (see table 4-1)

\*\* historic flux is derived from the deepest horizon which was not dated, but the preceding horizon was; 14.25 cm horizon dated to 1908 for Falaise lake (deepest horizon with Hg measurement 16.25 cm), 7.75 cm horizon was dated to 1936 for Trio 1 lake (deepest horizon with Hg measurement 9.75 cm)

#### 4.4 Total Organic Carbon

The percentage of total organic carbon (TOC) was analyzed for each core as this is an important variable which can provide indications of past landscape change, including changes in water surface area. Values in all lakes studied range from 19 to 33 % throughout the sediment profiles.

##### 4.4.1 Expanding Lakes

Total organic carbon remained relatively stable in Falaise Lake between 1926 and 1979. Declines occurred between 1979 and 1986. While TOC has been increasing in Falaise Lake; from 19% in 1986 to 23 % in 2011, these increases are more pronounced between 1986 and 1993 (Fig. 4.5 a). In Jackie Lake, TOC was stable for most of the 20<sup>th</sup> century at ~ 22 % and reached 25 % in 2005 (Fig. 4.5 b). Total organic carbon remained stable in Trio 1, around 20 %, for the entire period represented by this 10 cm sediment core (Fig. 4.5 c).

Total [Hg] and TOC were found to be significantly correlated in Falaise Lake ( $r = 0.7$ ,  $p = 0.002$ ) and Jackie Lake ( $r = 0.7$ ,  $p = 0.05$ ), suggesting that Hg in these lakes is associated with organic material. Correlations were not found between [THg] and TOC of Lake Trio 1.

##### 4.4.2 Reference Lakes

In the non-expanding lakes, TOC increased during the middle of the 20<sup>th</sup> century and reached the highest values in the most recent sediment intervals for

both Trio 3 and Chan lakes at ~ 29 % and 33 %, respectively (Fig. 4.5, d – e). Statistically significant correlations were not found between [THg] and TOC in the non-expanding lakes.

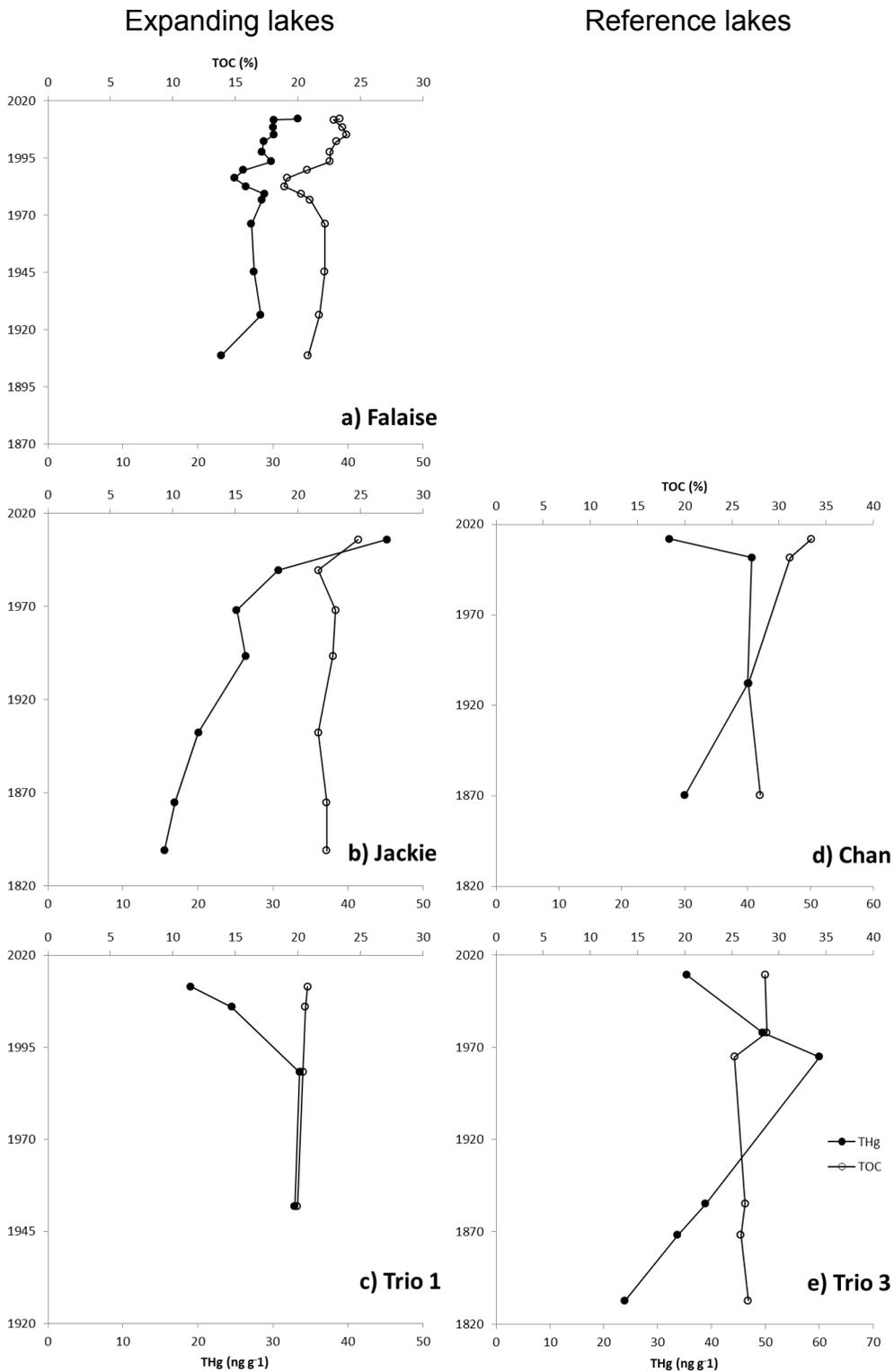


Figure 4.5: Total organic carbon (TOC) percentages and total mercury concentrations (THg) in sedimentary profiles for A) Falaise, B) Jackie, C) Trio1, D) Chan, and E) Trio 3 lakes.

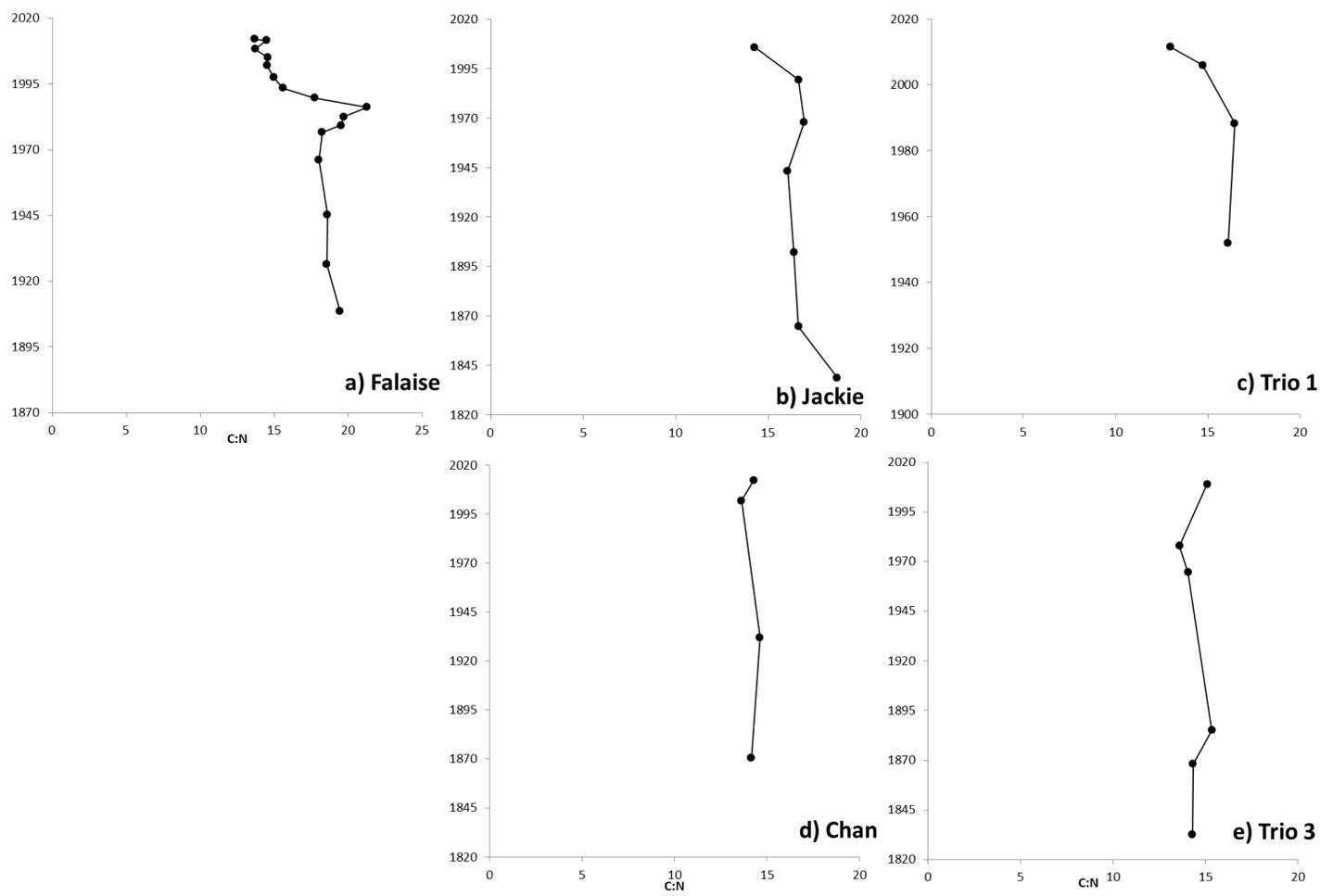
## 4.5 Elemental and Isotopic Analysis

The carbon to nitrogen ratio (C:N) is regularly used to determine the source of organic matter in lake sediments; either autochthonous or allochthonous in origin, as well as whether any changes in source occurred over time. Carbon : nitrogen < 10 suggests organic matter derived from algal sources, while C:N > 10 suggests terrestrial production is the dominant source of organic matter (Leng et al. 2005). Carbon to nitrogen ratios are often accompanied by plots of isotopic composition, most notably  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , which can be used as proxies to infer sources of organic matter as well as temporal changes in the supply of nutrients to aquatic systems (Meyers & Teranes 2001, Talbot 2001, Leng et al. 2005). Carbon to nitrogen ratio plots for all lakes are given in Figure 4.6 and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic composition for each of the cores is presented in Figure 4.7.

### 4.5.1 Expanding lakes

Allochthonous sources dominate the organic matter in the expanding lakes with all values > 10. However C:N declined in recent years from values between 16-20 to 13-14, suggesting a possible shift from terrestrial to greater inputs from algal-derived sources of organic matter (Fig. 4.6 a-c). In Falaise Lake, C:N remained steady at ~ 19 between 1900 and 1980, increased to ~ 23 over the next 10 years, and has declined since 1990 to a value of 13 in 2011. Jackie Lake also had steady C:N between 16 and 17 from 1900 to 1995, and then decreased to 14 by 2011. Carbon to nitrogen ratio also appeared to be steady at 16 in Lake Trio 1 from 1950 until 1988, values declined to 13 by 2011.

Expanding Lakes



Reference Lakes

Figure 4.6: C:N ratio plots over time for: A) Falaise, B) Jackie, C) Trio 1, D) Chan, and E) Trio 3 lakes.

Carbon and nitrogen isotopic composition within the sediments of the expanding lakes show increases in  $\delta^{15}\text{N}$  and decreases in  $\delta^{13}\text{C}$  occurring in the mid-1980s to early 1990s, which correspond with the initiation of increased lake extent. In Falaise Lake, fluctuations begin to occur during the early 1980s, and substantial  $\delta^{15}\text{N}$  increases and  $\delta^{13}\text{C}$  decreases occur from the mid to late 1980's until the most recent sediments (Fig. 4.7 a). Within the record for Jackie Lake, an increase in  $\delta^{15}\text{N}$  and decrease in  $\delta^{13}\text{C}$  occurred between 1900 and 1945 (Fig. 4.7 b). A second episode occurs more recently between 1989 and 2005 in Jackie Lake, as  $\delta^{15}\text{N}$  reaches the highest and  $\delta^{13}\text{C}$  the lowest values in the profile. Also Trio 1 has experienced a slight reduction in  $\delta^{15}\text{N}$  in the most recent sediments (Fig. 4.7 c). Declining  $\delta^{13}\text{C}$  in the profiles of the expanding lakes appears to coincide with the declining C:N ratios in the sedimentary profiles of these lakes.

Significant negative correlations were found between [THg] and  $\delta^{13}\text{C}$  in two of the expanding lakes; Falaise ( $r = -0.6$ ,  $p = 0.01$ ), and Jackie ( $r = -0.8$ ,  $p = 0.04$ ). Also, significant positive correlations were associated with [THg] and  $\delta^{15}\text{N}$  in Falaise ( $r = 0.7$ ,  $p = 0.04$ ), and Jackie ( $r = 0.9$ ,  $p = 0.01$ ) Lakes.

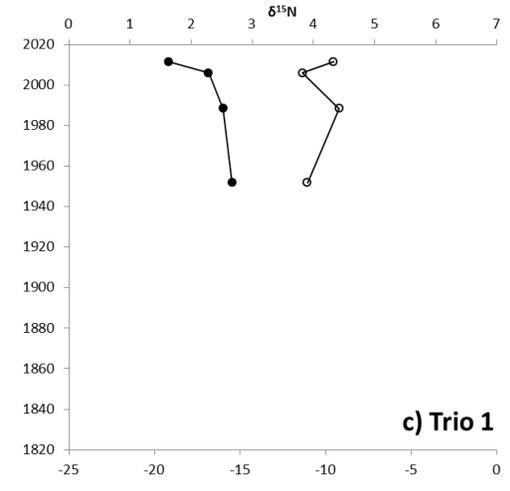
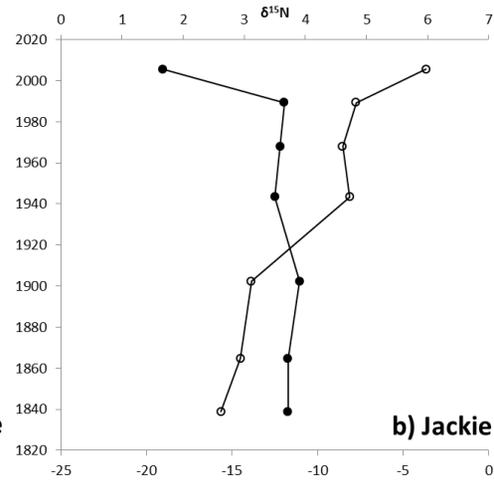
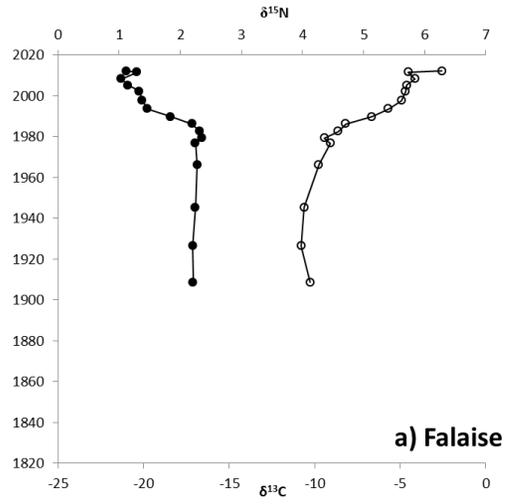
#### 4.5.2 Reference Lakes

In contrast to expanding lakes, both Chan Lake and Lake Trio 3 have relatively stable C:N values of  $\sim 15$  over the past century, suggesting that allochthonous sources have been the greatest input of organic matter to sediments during this time (Fig. 4.6, d-e). Both sediment profiles have minimal to

no data points during the mid-20<sup>th</sup> century (1940 to 1970). The control lakes display variable isotopic composition. Trio 3 has a relatively stable record throughout the 20<sup>th</sup> century followed by slight decreases in  $\delta^{13}\text{C}$  and increases in  $\delta^{15}\text{N}$  in the early 1980s (Fig. 4.7 e) which is similar to that of the expanding lakes. The profile for Chan Lake appears to have declining  $\delta^{13}\text{C}$  throughout the profile, while  $\delta^{15}\text{N}$  increased throughout the 20<sup>th</sup> century (Fig. 4.7 d).

It is difficult to match the isotopic records of the control lakes to characteristics of their C:N ratio profiles. The relative stability of the C:N in both reference lakes and the associated isotopic record does not suggest which source, terrestrial or aquatic, contributes more organic matter to the sediments of this lake. No correlations were found between [THg] and either isotope in the control lakes.

Expanding Lakes



Reference Lakes

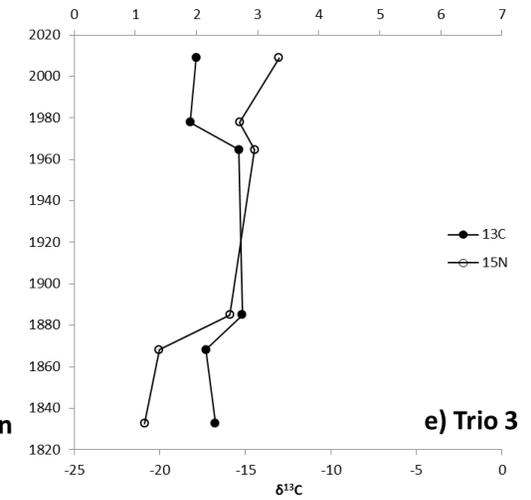
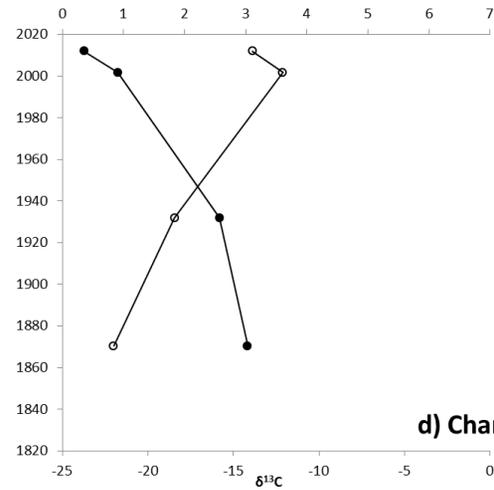


Figure 4.7:  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotope plots over time for: A) Falaise, B) Jackie, C) Trio1, D) Chan, and E) Trio 3 lakes.



## 5 DISCUSSION

### 5.0 Temporal trends in Hg concentrations and fluxes

The levels of [THg] found throughout the profiles of all cores analyzed are well below the sediment quality guidelines for the protection of aquatic life set at  $170 \text{ ng g}^{-1}$  by the Canadian Council of Ministers for the Environment (CCME 1999). All lakes have similar historic concentrations with values between 15 and  $23 \text{ ng g}^{-1}$  while recent maximum concentrations are more variable, with values between 30 and  $62 \text{ ng g}^{-1}$ . The range of values of [THg] for the lakes is similar to those found in other studies of sub-arctic lakes (Lockhart et al. 1995, Lockhart et al. 1998, Muir et al. 2009, Brazeau et al. 2013).

Total [Hg] increased over time in all lakes studied; however patterns of accumulation were dissimilar among the three expanding lakes. Concentrations of Hg in two of the expanding lakes, Falaise and Jackie, reach maximum values in the most recent sediments analyzed. Falaise had relatively stable [THg] throughout the 20<sup>th</sup> century until sudden declines occur in the mid-1980s and then subsequently rise in the uppermost sediments. Jackie Lake, on the other hand, has steady increases in [Hg] throughout the 20<sup>th</sup> century and into the 21<sup>st</sup>. Conversely, Trio 1 Lake did not follow the trend of increasing [THg] of the other two expanding lakes, and displays subsurface maximum concentrations, similar to the reference lakes, Chan and Trio 3. A possible interpretation is that the increase in [THg] to most recent sediments in Falaise and Jackie lakes is due to flooding of the landscape, while [THg] values in the two reference lakes reflect

predominantly atmospheric and watershed inputs. But this does not account for the decline in [THg] in Trio 1.

Despite the brevity of the profile for lake Trio 1, it is curious that the [THg] for this lake appear to be lower and less variable than for the neighbouring reference lake, Trio 3, which has the highest [THg] values of all lakes studied. One possible explanation for this is an as yet unknown hydrologic relationship between the lakes, in which water accumulates in Trio 1 (the northern system), while particulate matter settles out in Trio 3 (the southern system). Based on the horizons analyzed, Trio1 has a higher sedimentation rate than Trio 3, however the profile for Trio 1 is short (only 10 cm) and presents a limited record of temporal change compared with the 45 cm from which subsamples were analyzed for Trio 3. A longer gravity core would need to be recovered from Trio 1 in order to make a more complete assessment.

Sedimentation rates and Hg flux were also variable between expanding and reference lakes. All lakes, except for Chan, show distinct increases in sedimentation rate and Hg flux in the 1940s which is consistent with observations from investigations of other lakes in the Canadian sub-arctic (Landers et al. 1998, Muir et al. 2009, Brazeau et al. 2013). The expanding lakes have increases in both parameters followed by sudden declines. This pattern for Falaise Lake appears to coincide with the onset of flooding in the mid-1980s, with increases occurring when water levels were at their lowest and declines occurring soon after flooding began. This pattern occurs again at a reduced magnitude in Falaise Lake in the early 2000s. Declines in sedimentation rate do occur in

Jackie Lake and in Trio 1, however, unlike Falaise Lake, the declines occur a decade before large expansion in water surface area for Jackie Lake, and a decade after in Trio 1. When we examine the profiles for the reference lakes, for Trio 3, both parameters increased steadily during the 20<sup>th</sup> century until 2011, while increases occurred more recently in Chan, starting in the 1980s.

Many horizons in the top 5 cm of Falaise Lake were analyzed because it was anticipated this profile would provide the best record owing to the size of the lake. If a similar number of horizons had been analyzed in the other cores recovered for this study, this may have provided clearer associations between changes in response parameters (THg, sedimentation rate, Hg flux) and the onset of flooding in the expanding lakes.

Previous studies have evaluated the correlation between Hg and OM in lake sediments, often demonstrating that Hg adsorbs onto organic particles (Sanei & Goodarzi 2006, Bouffard & Amyot 2009, Stern et al. 2009, Deison et al. 2012). Lake sediments can contain OM from numerous sources, but predominantly they occur from terrestrial plants, soil humic substances and aquatic plants and algae (Talbot 2001). Organic matter originating principally from terrestrial plants have a mean C:N of ~ 160 because of their cellulose and lignin content which have minimal nitrogen (Talbot 2001, Wetzel 2001, Leng et al. 2005). Lake sediment OM dominated by phytoplankton inputs have a C:N value of <10 because of the N-rich protein and lipids they contain (Talbot 2001, Wetzel 2001, Leng et al. 2005).

In this study, only the Hg in expanding lakes was found to be significantly correlated to organic matter. In particular the [THg] was positively linked to  $\delta^{15}\text{N}$  and negatively to  $\delta^{13}\text{C}$ , and supported by declining C:N ratios. Carbon: nitrogen values, while they remained above 10 throughout the sediment profiles of the lakes studied, declined in the expanding lakes in the past three decades. This decline suggests that increased lake surface area may be encouraging phytoplankton community growth, leading to increased primary production in expanding lakes.

Primary production is sustained by high nutrient load in the water column of lakes (Talbot 2001, Wetzel 2001). In the MBS, flooding of the landscape would have released nutrients stored within the submerged vegetative materials and organic soils, allowing it to be released to the water body (Talbot 2001, Vorosmarty et al. 2001, Wetzel 2001). These nutrients, coupled with greater water surface area, could have fueled and sustained greater rates of primary productivity. As phytoplankton preferentially use  $^{14}\text{N}$ , this would lead to increased  $^{15}\text{N}$  in sediments (Meyers & Teranes 2001, Talbot 2001, Wetzel 2001).

It should be noted that other factors could also play a role in increased  $^{15}\text{N}$  budgets of OM, including the reduction of nitrate ( $\text{NO}_3^-$ ) to gaseous  $\text{N}_2$  under anoxic lake conditions. During this reaction  $^{14}\text{N}$  is selectively lost to the atmosphere and lake sediment OM can become enriched with  $^{15}\text{N}$  (Meyers & Teranes 2001, Talbot 2001, Leng et al. 2005).

Submerged vegetative materials and soils not only release nutrients but also contaminants they may be storing, including Hg. The relationship between watershed inputs of Hg to lakes has been the subject of many studies, particularly as pertains to experimentally flooded boreal forest sites and litterfall and have shown large increases in Hg released during the first year following flooding (St Louis et al. 2001, Hall & St. Louis 2004, St Louis et al. 2004).

Generally, fallen vegetation in flooded forested areas provide significant THg inputs to lake systems as compared to direct deposition; in some cases twice as much (St Louis et al. 2001, Hall & St Louis 2004). Additionally for the first year following flooding, submerged vegetation becomes a net source of THg which can be transferred via runoff to lakes downstream (St Louis et al. 2004). As water levels of the MBS expanding lakes have been variable, with periods of increase and decrease over the last 25 years, it is possible that more than one instance of 'first year' flooding has occurred. It is likely that the positive correlation found between  $\delta^{15}\text{N}$  and [THg] in the expanding lakes of the MBS is a result of the positive feedback between larger water surface area, availability of nutrients, OM and Hg from flooded vegetation and soils, as well as increased primary productivity over time.

## **5.1 Lake expansion and impact on Hg and other response parameters**

GIS analysis of satellite images confirms that the extent of the three lakes selected as 'expanding' in this study, have greater water surface area than that of the original lake extent determined in 1986. Expansion did not occur simultaneously or similarly in the three lakes. Falaise Lake and Trio 1 increased by 700 % and 500 % respectively between 1986 and 1992, while comparable change in Jackie Lake occurs between 1999 and 2003. The two reference lakes have maintained comparatively constant water levels during the same time period.

Recent lake expansion of the study lakes began in the mid to late 1980s, and continued from the late 1990s to 2011, following a brief period of declining water levels during the early to mid-1990s. Increased [THg] occurred at the precise timing of this increase in water level in Falaise Lake in the mid-1980s and again in the early 2000s. Furthermore water surface area and [THg] were significantly correlated in Falaise Lake. In Jackie, [THg] also rise considerably at the same time as water levels in the late 1990s. This provides strong evidence that lake expansion resulting in overland flooding is related to increasing sedimentary Hg concentrations in Falaise Lake, and possibly other expanding lakes within the MBS.

In both Falaise and Jackie lakes, the highest levels of [THg] occurred in the most recent sediments which also coincided with the greatest extent of water surface area. Peaks in [THg] occur at the same time as the highest water levels

in Falaise Lake which first occurred in the late 1980s, and again in the most recent dated sediments (Fig. 5.1). Two horizons with dates that correspond with increased lake surface area (1986, 2005) were identified for Jackie Lake (Fig. 5.2). If more horizons had been analyzed for Jackie Lake, this may have helped make a stronger case, nevertheless these two points also appear to corroborate the relationship between highest [THg] and high water levels. Lake Trio 1 did not present the same pattern, and while three [THg] points were identified during the flood period, they are declining as water levels increase (Fig. 5.3).

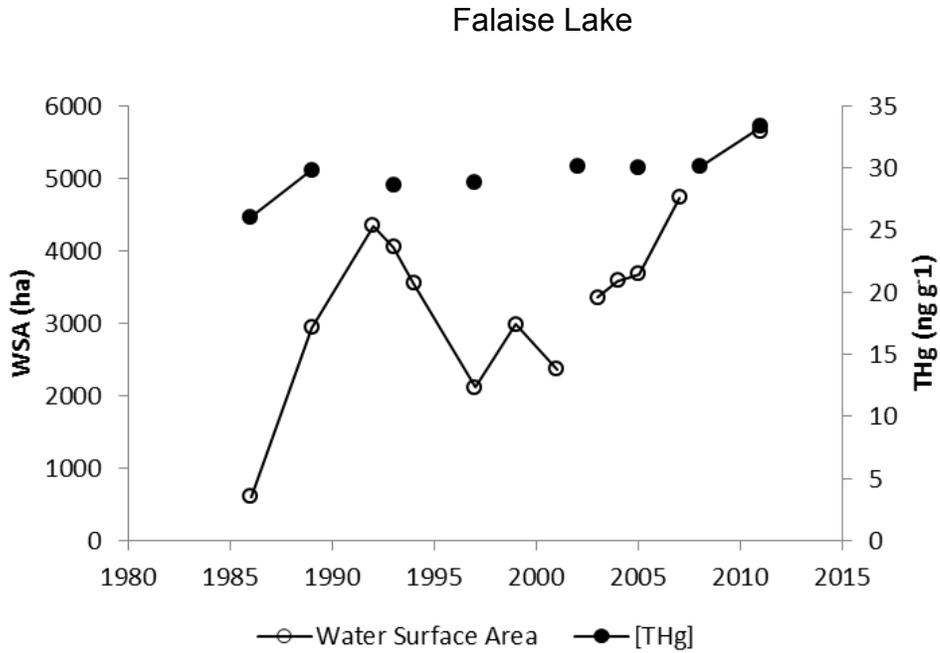


Figure 5.1: Plot showing water surface area (WSA) (ha) and [THg] (ng g<sup>-1</sup>) between 1986 and 2011 for Falaise Lake.

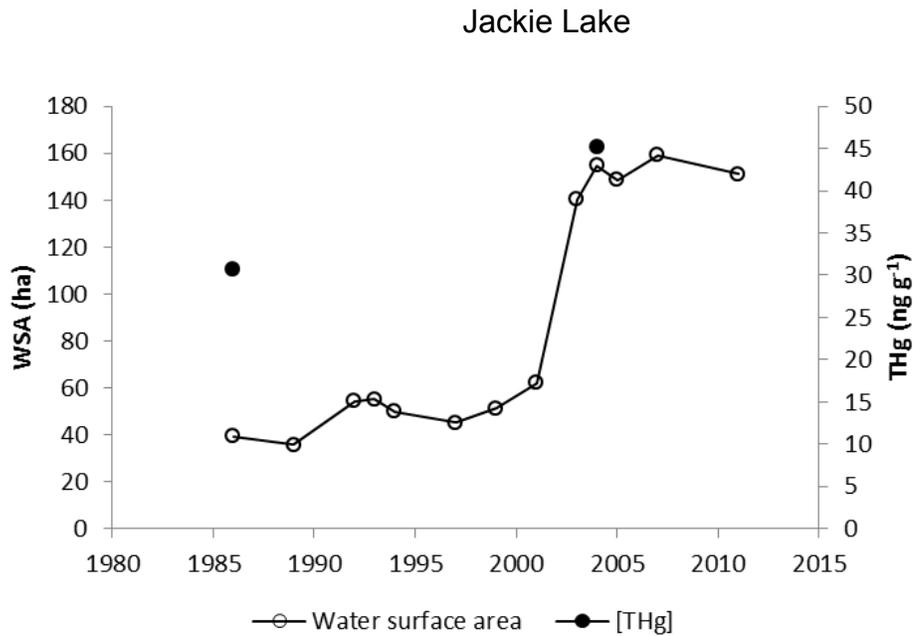


Figure 5.2: Plot showing water surface area (WSA) (ha) and [THg] (ng g<sup>-1</sup>) between 1986 and 2011 for Jackie Lake.

### Lake Trio 1

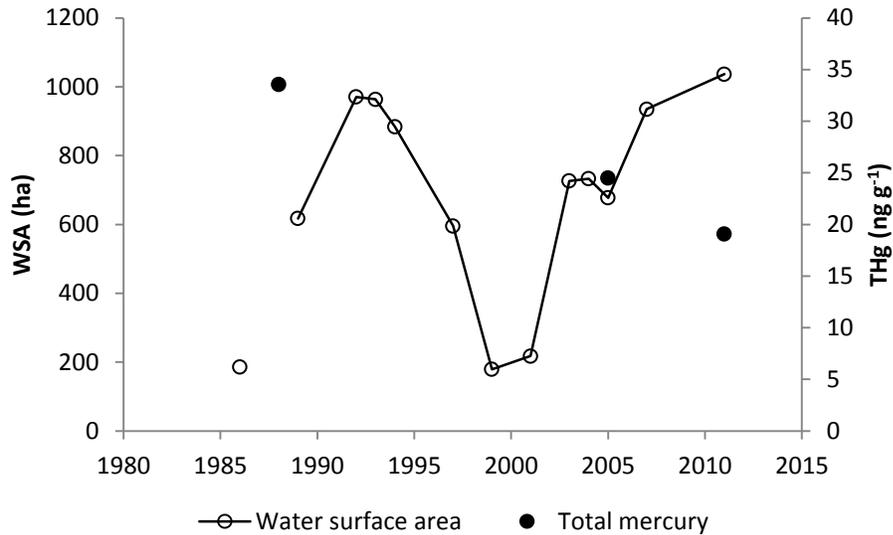


Figure 5.3: plot showing water surface area (WSA) (ha) and [THg] (ng g<sup>-1</sup>) between 1986 and 2011 for Lake Trio 1.

Falaise Lake provides the strongest evidence that flooding has had an influence on [THg], as well as sedimentation rates, Hg flux and C and N content of the lake sediments. The lake was small in 1986, ~ 600 ha. In the early 1980s prior to lake expansion, [THg] and TOC decreased to minimal values, while sedimentation rates and Hg flux increase to the highest rates measured in all lakes studied. The increase in sedimentation may be the result of greater deposition of particles from the large historic shoreline which surrounded the lake when water extent was reduced. The C:N also increased at this time concurrently with a rise in  $\delta^{13}\text{C}$ , which may have resulted from the seven-fold increase in water surface area between 1986 and 1992 which would have submerged much of the surrounding soil and vegetation. Following this initial

flooding event, [THg] increased and sedimentation rates and Hg flux decreased to previous levels. Carbon : nitrogen declined, and was accompanied by decreasing  $\delta^{13}\text{C}$  and increasing  $\delta^{15}\text{N}$ . A similar pattern, though reduced in magnitude, can be seen between the mid to late 1990s in the response parameters for Falaise Lake when water levels were declining and the early 2000s when water surface area was expanding once again.

An equivalent response was not found in the other two expanding lakes. In Jackie Lake, [THg] appear to be rising steadily since the mid-20<sup>th</sup> century. Sedimentation rates and Hg flux however seem to display similar response characteristics as for Falaise Lake, with both increasing while surface area was at a minimum until 1989 and sedimentation rate declining as water surface area increased, while Hg flux remained steady. The sedimentation rate and Hg flux of Lake Trio 1 demonstrated similar responses coinciding with the second flooding event in the late 1990s/early 2000s. A similar response was not found in these same parameters measured during the initial water surface area expansion in the mid-1980s for Trio 1.

The relationship between flooding and increasing THg has been similarly found in lakes that have been impounded by the construction of hydroelectric dams, at test sites at the ELA, or by beaver dams. Elevated levels of THg lasted only up to a maximum of two years post-flooding before returning to pre-flood levels. (Jackson 1991, Hall et al. 2004, St Louis et al. 2004, Kainz & Lucotte 2006, Roy et al. 2009). However these studies indicated that Hg flux also

increases post-flooding, which was not the case in our expanding study lakes, especially Falaise and Jackie lakes.

The situation in the MBS is quite different from dam or experimental impoundment, in that flooding/lake extent is not static, but has been variable over the past 25 years. Water levels have submerged certain areas for a period of time and then receded, as is identified by the lake surface area analysis (Fig.4.1). This could allow Hg reservoirs (soils, vegetation), which may have been fully/partially depleted during initial increases in water level, to be replenished via atmospheric deposition and watershed runoff and create new sources of Hg which could be released during subsequent flooding events. Additionally the lakes in the MBS are shallow, and their entire basins are considered littoral zones, which presents greater area within which available Hg(II) could be methylated.

Based on the data from this analysis it is not possible to determine the relative importance of sources of Hg to the expanding lakes. Much of the Hg contained in sediments was probably released from soils and terrestrial plants as the water inundates the land surface. In a 1981 field study, Falaise Lake is characterized as having minimal water levels, and most of the basin was classified as sedge-grass prairie with willows (*Salix spp.*) on the perimeter, bordered by white spruce (Chowns, 1987). Much of the sedge-grass and willows are now submerged by water. Also, Arctic soils have the potential to store higher concentrations of Hg, compared to soils in more temperate regions, due to lower decomposition rates and reduced Hg re-emission to the atmosphere (Grigal

2003). Therefore, it is possible that Hg stored in vegetation and soils surrounding the lakes could have been released post-flooding and incorporated into lake sediments as has been previously examined and reported (St Louis et al. 2001, Hall & St. Louis 2004, St Louis et al. 2004).

However the cause of the lake expansion in the MBS, which may also be contributing Hg to lake sediments, is not currently known. A recent investigation using dendrochronological techniques found that the timing of lake expansion, both past and present, was not directly related to climate variables, specifically increased precipitation was not the source of increased water levels (deMontigny, 2014 (unpublished data)). The MBS is located within the Canadian sub-arctic, an area with discontinuous permafrost which has experienced increased ground temperatures in the recent past (Smith et al. 2005b, Romanovsky et al. 2007). Thawing permafrost could be contributing to increasing lake extent and simultaneously releasing Hg that was stored, as has been reported in previous studies (Klaminder et al. 2008, Rydberg et al. 2010).

## **5.2 Use of sedimentary proxies of autochthonous / allochthonous production to infer timing of recent expansion events**

Evidence of recent lake expansion in the MBS has been documented with satellite images and recorded since the mid-1980s. While the reason for lake expansion is not clear, the historical records preserved in lake sediment profiles have the potential to provide other means of confirming these hydrologic changes, and extending them further in time beyond the period represented by

remotely-sensed data. Organic matter and the source of this material offer a technique through which the timing of changes in lake extent may be inferred.

The TOC of Falaise and Jackie lakes has increased since the mid-1980s, and the C:N ratio of all three expanding lakes has declined: since the mid-1980s in Falaise Lake, mid 1990s in Jackie Lake and late 1980s in Trio 1 (Fig. 4.5, a-c). The decline in C:N ratios and the increase in water surface area for the three expanding lakes also corresponds to declining  $\delta^{13}\text{C}$  and simultaneous increasing  $\delta^{15}\text{N}$  bulk content (Fig.4.6, a-c). It should be noted that while the C:N for both reference lakes remains relatively stable throughout their profiles, Chan Lake does exhibit increasing  $\delta^{15}\text{N}$  and decreasing  $\delta^{13}\text{C}$  during the 20<sup>th</sup> century (Fig.4.6, d), indicating that reference lakes are experiencing changes to the quality of their organic content.

The changes in Falaise Lake, first increases in C:N with minor increases in  $\delta^{13}\text{C}$  leading up to an expansion event, followed by rapid declines in C:N and  $\delta^{13}\text{C}$  and increases in  $\delta^{15}\text{N}$ , correspond to the timing of significant expansion of water surface area, initially from the mid to late 1908s and again in the early 2000s. These patterns were also occurring at the same time as changes to TOC, [THg] and sedimentation rate and Hg flux in Falaise Lake. This suggests that the bulk isotopic composition of the sedimentary records of expanding lakes and their corresponding C:N values could be used as proxies to infer the timing of expansion events, but should be used with other proxy evidence.

Isotopic analysis has been used previously to determine historic flooding events. A paleolimnological study of African Lake Victoria (located between Uganda, Kenya and Tanzania) examined the bulk content of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  over 16,000 years. Late in the Pleistocene, the sediment record showed increasing  $\delta^{15}\text{N}$  (and corresponding decline in  $\delta^{13}\text{C}$ ) which the authors hypothesized to be a response to the first flooding and filling of the lake; as water washed over terrestrial plant material, nutrients were released to the water and encouraged high rates of primary productivity (Fig. 5.4) (Talbot & Laerdal, 2000, Talbot 2001).

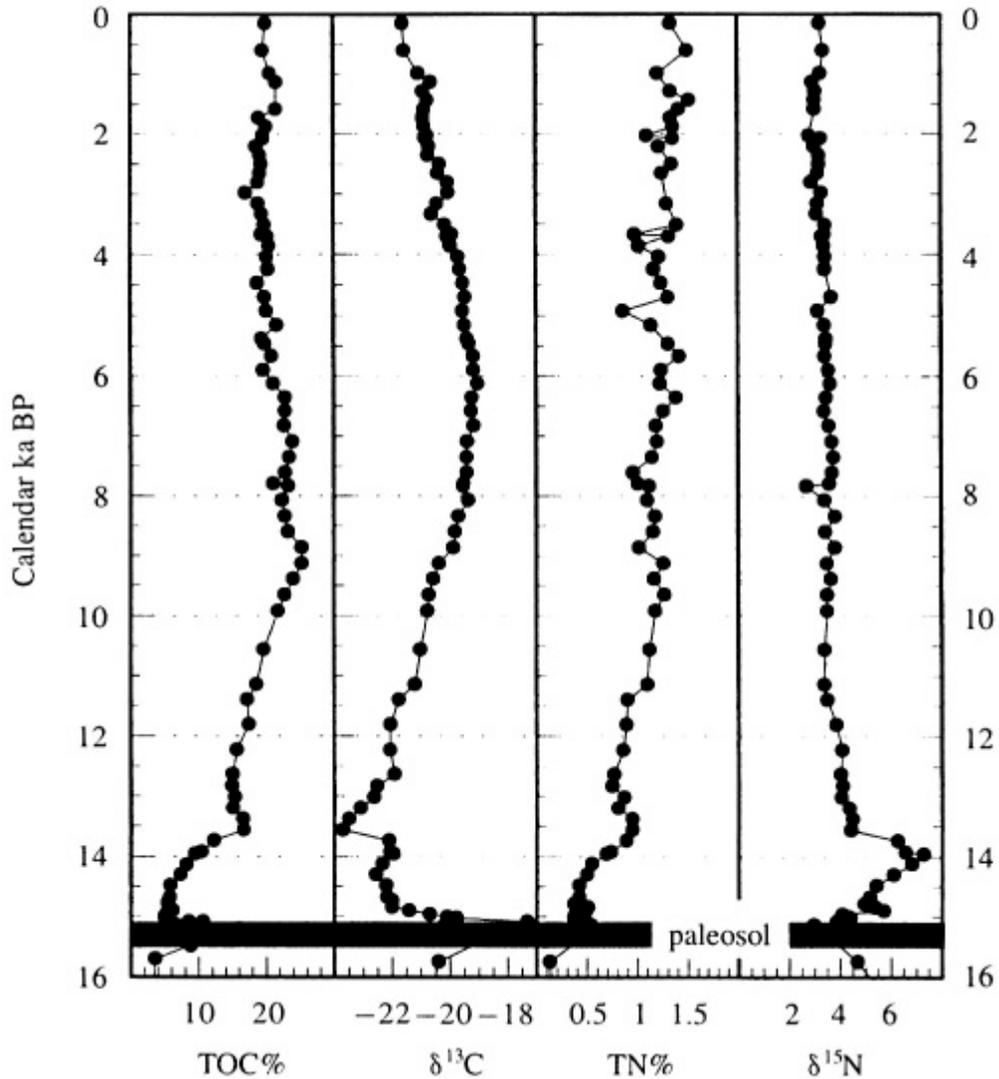


Figure 5.4: Elemental and isotopic profiles from Lake Victoria. The main period of basin filling is represented by the sharply rising trend in  $\delta^{15}N$  between 15 and 14 ka (Talbot and Lærdal 2000).

The example of Lake Victoria, demonstrates that the C:N ratio and bulk organic isotope composition of sediments within the expanding lakes of the MBS can offer proxy evidence of current expanding lake surface area. However, the same profiles are more difficult to analyze regarding past hydrological changes due to their limited length and sampling density. Time constraints and the sub-

sampling strategy employed limited the number of samples that could be taken for OM studies from each of the five lake profiles. Some horizons could not be included for isotopic content as the entire sub-sample was required for  $^{210}\text{Pb}$  dating or biological sedimentary investigations. Further analysis of deeper sub-samples for isotopic and organic composition may elucidate previous changes in OM source inputs to lake sediments and ultimately, previous lake expansions or retractions.

## 6 CONCLUSIONS AND FUTURE RESEARCH

The expansion of lakes and subsequent flooding of large areas of vegetated landscape was investigated to determine the impact these hydrologic changes might be having on [THg], sedimentation rates, Hg flux and organic composition of sediment within lakes of the MBS. This study sought to collect data regarding Hg in sub-arctic aquatic ecosystems, where there exists an identified geographic data gap. This is one of few studies to conduct an examination of the effects of natural overland flooding and its influence on [THg] in lake sediments over time.

Paleolimnological techniques were used to recover sediment cores from five lakes in the MBS; three from expanding lakes and two from control lakes. These sedimentary profiles were analyzed to obtain historic Hg and isotopic records to identify trends in Hg contamination and changes in sources of organic matter over the past ~ 150 years. Satellite images were also analyzed to quantify changes in water surface area since the mid-1980s and to determine if the timing of the expansion events were linked to increases in Hg in sediments and changes in organic content.

Lake expansion has influenced [THg] in the sediments of two of the affected lakes. Increases in [THg], as well as changes to sedimentation rate and Hg flux, corresponded with the timing of increases in water surface area during the mid-1980s and 2000s for Falaise Lake and were positively and significantly correlated. In Jackie Lake, which had the highest [THg] in the most recent sediments when water levels were highest, did not demonstrate changes to sedimentation rate and Hg flux that correlated to changing water surface area.

The highest levels of [THg] in sediments coincided with years of greatest water expansion in both Falaise and Jackie Lakes is similar to the relationship found in lakes that are technologically impounded. Conversely the final expanding lake, Trio1, did not have similar [THg] patterns and in fact had decreasing Hg levels over the past decade. It is currently unknown why the Hg profile for Trio 1 differs from the other two expanding lakes. It is possible this could be attributed to an unidentified hydrologic relationship between the three lakes that make up the Trio system.

Total [Hg] in Falaise and Jackie lakes were also linked to changes in the source of OM to those lakes. Total organic carbon increased since the mid-1980s, with corresponding declines in C:N. Also [THg] in Falaise and Jackie lakes was positively correlated with  $\delta^{15}\text{N}$  and negatively with  $\delta^{13}\text{C}$ . The increasing  $\delta^{15}\text{N}$  content in lake sediments of the expanding lakes in the MBS suggests that aquatic primary productivity is on the rise, which may be the result of nutrient release from flooded vegetation and soils and is occurring concurrently with release of Hg which is being deposited to sediments.

Further work is recommended to better understand Hg in lake sediments arising from the changing hydrologic conditions within the MBS. Retrieving gravity cores from more lakes impacted by flooding in the MBS would contribute to a more complete assessment of how flooding is impacting these lake systems, particularly where Hg accumulation is concerned. In addition, sub-sampling designs for future Hg and organic parameter analysis should be heavily focused on the recent horizons to obtain a more detailed understanding of changes

occurring in the past few decades. Also, the collection of longer sediment cores would allow for examination of more extensive historical records and analysis to determine periods of past hydrologic changes and whether they were accompanied by similar shifts in organic matter. Gravity cores, while useful for modern sediment profile studies, provide limited historical data regarding past lake characteristics regarding sedimentation, OM cycles and landscape change. Longer profiles could help with the creation of longer term historical inferences of hydrologic change occurring within the MBS.

While the [THg] were well below limits established by the CCME, it is important to note that bulk [THg] cannot be used to determine rates of MeHg production or concentration. Therefore, it would be useful in the future to determine the levels of MeHg in these lake sediments. Collection of cores from past littoral zones or lake shore edges could reveal if greater [THg] exist in areas where water has recently flooded vegetation. Examination of littoral sediment would also be useful for analysis of MeHg as its production is higher in these shallow zones. This could be coupled with additional MeHg studies of food webs surrounding the lakes of the MBS as they provide important habitat for water fowl, bison and other wildlife.

This study has provided an initial overview of historic and modern [THg] and Hg accumulation and given some indication of how these have changed over time and possibly due to recent flooding events. It would be beneficial for resource and land use managers if Hg mass balance and source studies to be completed. This would help determine the major sources of Hg to the lakes of

the MBS. Work should include investigations into atmospheric, watershed, and potential permafrost inputs. Work should also determine if algal scavenging plays any substantial role in [THg] and fluxes to these lakes.

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