

Electronic Thesis and Dissertation Repository

8-25-2014 12:00 AM

Peat as an Archive of Remote Mercury Deposition in the Hudson Bay Lowlands, Ontario, Canada

William James Goacher, *The University of Western Ontario*

Supervisor: Dr. Brian Branfireun, *The University of Western Ontario*

A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Geology

© William James Goacher 2014

Follow this and additional works at: <https://ir.lib.uwo.ca/etd>



Part of the [Biogeochemistry Commons](#), [Geology Commons](#), [Soil Science Commons](#), and the [Stratigraphy Commons](#)

Recommended Citation

Goacher, William James, "Peat as an Archive of Remote Mercury Deposition in the Hudson Bay Lowlands, Ontario, Canada" (2014). *Electronic Thesis and Dissertation Repository*. 2320.
<https://ir.lib.uwo.ca/etd/2320>

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlsadmin@uwo.ca.

PEAT AS AN ARCHIVE OF REMOTE MERCURY DEPOSITION IN THE
HUDSON BAY LOWLANDS, ONTARIO, CANADA

Thesis format: Integrated Article

by

William James Goacher

Graduate Program in Geology

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science - Geology

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

© William James Goacher 2014

Abstract

Peat from the Hudson Bay Lowlands (HBL) in Northern Ontario, Canada was used to reconstruct historical accumulation of mercury (Hg) over more than 7000 years before present. Nine cores, many with previously published paleoclimate studies, were analyzed for Hg and accumulation rates were calculated. Anthropogenic Hg enrichment factors were calculated based on accumulation rates. A more exclusive calculation of the anthropogenic enrichment factor corroborates modelling efforts that have suggested recycling legacy Hg is a much greater contributor to present day deposition than previously thought due to early mining sources. An older pre-industrial record provides a better background accumulation rate than short cores.

Enrichment factors were then compared across a latitudinal gradient. Enrichment factors decreased with latitude as well as distance from the James Bay. These spatial trends are attributed to differing halogen chemistry above the bay as well as distance from point sources of Hg.

Keywords

Mercury, peat, Hudson Bay Lowlands, chronology, paleoarchives, deposition, accumulation, anthropogenic enrichment

Co-Authorship Statement

I hereby declare that I am the sole author of this thesis, except where noted (below). I understand that my thesis may be made electronically available to the public.

I conducted all mercury laboratory work, processed and analyzed the data. Original coring was done by Dr. James W. McLaughlin and his team at the Ministry of Natural Resources and subsequent sampling of the cores for mercury was done by me.

Radiocarbon dating and age-depth model reconstructions were done by Dr. Sarah Finkelstein and her students (Dr. Joan Bunbury, Ben O'Reilly, and Maara Packalen).

Depth to water table reconstructions were done by Dr. Joan Bunbury.

Brian Branfireun has provided funding, supervision, guidance and editing for each of the following chapters and he will be listed as a co-author to any publications that result from this data.

This thesis has also made use of paleoclimate research done by Dr. Sarah Finkelstein and her research group at the University of Toronto. Her previous and current students, Dr. Joan Bunbury, Ben O'Reilly, and Maara Packalen have all agreed to allow me the use of their previously published data to supplement my own mercury research and their work has been appropriately cited throughout this thesis.

Chapter 2 and 3 will be submitted to the Journal of Environmental Science and Technology individually, but may need to be combined depending on peer review suggestions.

Acknowledgments

I would like to thank the following people for their support of my graduate work:

Dr. Brian Branfireun for his exemplary dedication to research. My thesis is exponentially better thanks to his keen mind. I greatly appreciate the opportunities he afforded me during my time in his lab group. The field work, lab work, conferences, and even regular lab meetings, were all sources of learning for me. I will take all of the skills that I have acquired and apply them to my future endeavors.

Ashley Warnock for recruiting me to the cult that is graduate life. Thank you for seeing something in me and giving me a chance to succeed. It has been wonderful to know someone with such a diverse set of interests and passions.

Michelle Morris for being exceptionally patient with me as I learned the dos and don'ts of ultra-trace lab work. I will always aspire to have an accent as beautiful as yours.

Tom Ulanowski for being the trailblazer that many of us have followed. You are a natural leader and were always a pleasure to take instruction from.

The whole 'Branfireun Lab Group' for being so helpful at every stage of this process. As a team you run like a well-oiled machine. Keep cranking out top-notch research!

Dr. Sarah Finkelstein for allowing me the use of your lab space and access to a wealth of knowledge to improve my research and hone my ideas. Your bright personality made it a joy to work with you.

Maara Packalen for providing the most organized, regimented, and surprisingly fun field experience I had during my degree. I learned more from you in two weeks than I did from two months of reading.

Pete Whittington and Melanie Columbus for being stellar post-docs. I greatly appreciate your editing advice and thank you for your support.

DeBeers Canada for providing so much support to our research. Every experience I had at their facilities was unforgettable.

My little sister, LG, for always reminding me that I'm a big nerd. She supports me unconditionally but isn't afraid to get sassy when need be. She has always been the person I go to when I need a laugh, whether she does it intentionally or not.

My parents, Mark and Cathy, for turning a curious little terror into a young man with a thirst for knowledge. I may never know for certain how much my mother had to bribe my kindergarten teacher for me to pass, but I do know that she would do anything for me. My father is a man of few words, but those words have always pushed me to be the best. Both of my parents showed me different ways to be successful and set me on a path to do the same. I hope that this thesis brings them as much pride as it has brought me.

My partner, Ben, for being my ~~sugar daddy~~ personal chef, life coach, style assistant, ~~chauffeur~~, best friend, ~~landlord~~, ~~dog walker~~, and mentor in so many ways. Throughout the last 5 years, he has seen me at my best, and my worst, and has always been an unwavering source of support. Thank you for reminding me there are more important things in life than grad school. Thank you for literally and metaphorically planting roses in order for me to stop and smell them.

Table of Contents

Abstract.....	ii
Acknowledgments.....	iv
List of Tables	x
List of Figures.....	xi
List of Appendices	xiv
Chapter 1.....	1
1.1 Introduction.....	1
1.1.1 Natural Occurrence of Mercury	1
1.1.2 Historical Human Uses of Mercury	3
1.1.3 Atmospheric Mercury Chemistry	4
1.1.4 Bioaccumulation and Toxicity.....	7
1.1.5 Anthropogenic Impacts on the Mercury Cycle.....	7
1.1.6 Mercury Paleoarchives.....	8
1.1.7 Peat Paleoarchives	10
1.1.8 Age Depth Modelling in Peat	13
1.1.9 Anthropogenic Enrichment Factors	14
1.1.10 Objectives	15
1.1.11 References.....	16
Chapter 2.....	23
2 Using Pristine Peat Archives to Quantify True Pre-Anthropogenic Mercury Accumulation and Contemporary Enrichment Factors.....	23
2.1 Introduction.....	23
2.2 Site Description and Methods.....	27
2.2.1 Core collection.....	28

2.2.2	Sample Handling and Preparation	30
2.2.3	Mercury analyses	31
2.2.4	Dating techniques.....	31
2.2.5	Depth to Water Table.....	32
2.2.6	Carbon and Mercury Accumulation Rate Calculations	32
2.2.7	Calculation of Enrichment Factor	32
2.3	Results and Discussion	33
2.3.1	General Core Stratigraphy and Age-Models.....	33
2.3.2	Mercury Maxima and Anthropogenic Onset	36
2.3.3	Pre-Anthropogenic Mercury Increases	37
2.3.4	Depth to Water Table Relationship with Mercury.....	38
2.3.5	Enrichment Factors	40
2.3.6	Using Paleoclimate Data to Improve Enrichment Factors.....	41
2.3.7	Comparison to Other Paleomercury Records	42
2.4	Conclusion	43
2.5	References.....	44
Chapter 3	49
3	Spatial Gradients of Atmospheric Mercury Accumulation in Peat Cores from the James Bay Lowland, Canada	49
3.1	Introduction.....	49
3.1.1	Mercury as a Global Pollutant	49
3.1.2	Historical Mercury Accumulation Rates Across Latitudinal Gradients ...	50
3.2	Methods.....	51
3.2.1	Study Site	51
3.2.2	Core Selection.....	54
3.2.3	Core Sampling	55

3.2.4	Core Characteristics and Stratigraphy	55
3.2.5	Mercury Analysis.....	56
3.2.6	Dating of Peat and Estimation of Accumulation Rates	56
3.2.7	Enrichment Factor.....	56
3.3	Results.....	57
3.3.1	Core Characteristics and Stratigraphy	57
3.3.2	Mercury Profiles	57
3.3.3	Enrichment Factors	62
3.3.4	Latitudinal Gradient	63
3.4	Discussion.....	63
3.4.1	Mercury Profiles and Stratigraphy.....	63
3.4.2	Vegetation Succession	63
3.4.3	Onset of Anthropogenic Mercury Contributions to Peat Core Accumulation.....	64
3.4.4	Comparison with Enrichment Factors from other Records	65
3.4.5	Latitudinal Gradient in Mercury Accumulation Across the Hudson Bay Lowlands.....	67
3.4.6	Atmospheric Halogen Chemistry.....	68
3.5	Conclusions.....	69
3.6	References.....	70
Chapter 4	75
4	Conclusions and Future Work.....	75
4.1	Peat as an Archive of Mercury.....	75
4.2	Importance of Remoteness and Temporally Long Records.....	75
4.3	Improving Estimates of the Anthropogenic Enrichment Factor	76
4.3.1	Utility of an Improved Anthropogenic Enrichment Factor.....	77

4.3.2	Depth to Water Table.....	77
4.4	Spatial Gradients in the Hudson Bay Lowlands	79
4.4.1	Comparison to Other Mercury Records.....	79
4.5	Future Work	80
4.6	References.....	82

List of Tables

Table 1 - 1. Relative contributions of natural sources of Hg globally in 2008. Taken from Pirrone <i>et al.</i> 2010.....	2
Table 2 - 1. Summary of core collection local characteristics.....	30
Table 2 - 2. Summary of Hg accumulation (Hg Accum.) and Hg concentration [Hg] enrichment factor calculations using both traditional and adapted methods for 3 bog cores in the HBL. Pre-anthropogenic (P) and Modern (M) accumulation rates are used to calculate the enrichment factor (M/P).....	41
Table 3 - 1. Summary of core collection site local characteristics from vegetation surveys at time of core collection. See Chapter 2: Table 2 - 1 for Victor Mine core collection site local characteristics.....	53
Table 3 - 2. Mean pre-anthropogenic and modern Hg accumulations in micrograms per meter squared per year and [Hg] (Hg concentrations in micrograms per kilogram) with their associated standard deviations as used to calculate the anthropogenic enrichment factor for each peat core.....	58
Table 3 - 3. Summary of Hg accumulation and concentration maxima and minima as well as their associated variance in both the pre-anthropogenic and modern timeframe.	59
Table A - 1. ¹⁴ C-AMS measurement summaries of peat macrofossil ages for 5 sites in the Hudson Bay Lowlands, Canada; listed by increasing latitude.....	A-3
Table B - 1. ¹⁴ C-AMS measurement summaries of peat macrofossil ages for 5 sites in the Hudson Bay Lowlands, Canada; listed by increasing latitude. Red wording indicates bomb pulse curve dates that were assigned a large error do to unlikely rapidity in recent accumulations (see Figure B – 5).....	B-4

List of Figures

Figure 1 - 1. Conceptual diagram of Hg sources, transport, and cycling in the environment. Solid red arrows are inorganic Hg, and open red arrows are methylmercury. Adapted from Kruczynski and Fletcher 2012 p 137. 2

Figure 1 - 2. Conceptual diagram of global mass balance of atmospheric mercury including oxidation and reduction. From Holmes *et al.* 2010. 6

Figure 2 - 1. Study site location (black star; 52.821° N, -83.884° W) in the Hudson Bay Lowlands (darker shading) near the Attawapiskat River in Northern Ontario, Canada. ... 28

Figure 2 - 2. Hg accumulation rates for Bog 1 and Bog 2 through time (calibrated radiocarbon age in years BP). Hg accumulation rates are in micrograms per meter squared per year. Vertical grey lines represent the adapted enrichment factor method's calculation of pre-anthropogenic Hg accumulation rates for each core. 35

Figure 2 - 3. Hg accumulation rates for core Bog 3 and the Fen core through time (calibrated radiocarbon age in years BP). Hg accumulation rates are in micrograms per meter squared per year. Vertical grey lines represent the adapted enrichment factor method's calculation of pre-anthropogenic Hg accumulation rates for each core. 36

Figure 2 - 6. Depth to Water Table (DWT) reconstruction using testate amoeba (adapted from Bunbury *et al.* 2012) versus total Hg concentrations. A trend of increasing Hg concentrations during times of greater DWT (lower water table, dry conditions) has an R² of 0.441 (p < 0.001). 38

Figure 3 - 1. North; Mid; Southwest; and Southeast in the Hudson Bay Lowlands and reference cities are indicated by black circles in Northern Ontario, Canada. 54

Figure 3 - 2. Hg data for Southwest, Southeast 1 and Southeast 2 peat cores (from left to right). Hg accumulation in micrograms per meter squared per year. 60

Figure 3 - 3. Hg data for Mid-HBL cores Bog 1, Bog 2, Bog 3, and Fen core (from left to right). Hg accumulation is in micrograms per meter squared per year. Data is repeated

from Chapter 2 for reader convenience. Note that x-axis units are larger than in Chapter 2 in order to compare all HBL cores equally.	61
Figure 3 - 4. Hg data North 1 and North 2 peat cores (from left to right). Hg accumulation is in micrograms per meter squared per year.	62
Figure A - 1. LiDAR imagery of coring sites for VM43, VM45 and VM33 (green dots) in the HBL of Northern Ontario, Canada.	A-4
Figure A - 2. ^{210}Pb dates for core VM43 from Bunbury <i>et al.</i> 2012.	A-5
Figure A - 4. Bog 2 additional information including Hg concentration, Hg accumulation, carbon to nitrogen ratio (C:N) (provided by Maara Packalen and Dr. Sarah Finkelstein), and bulk density (provided by Maara Packalen and Dr. Sarah Finkelstein).	A-7
Figure A - 5. Bog 3 additional information including Hg concentration, Hg accumulation, carbon to nitrogen ratio (C:N) (provided by Maara Packalen and Dr. Sarah Finkelstein), and bulk density (provided by Maara Packalen and Dr. Sarah Finkelstein).	A-8
Figure A - 6. Fen additional information including Hg concentration, Hg accumulation, and bulk density (provided by Ben O'Reilly and Dr. Sarah Finkelstein).	A-9
Figure B - 1. Latitudinal gradient of mercury enrichment factors in 9 cores from the Hudson Bay Lowland, Ontario, Canada.	B-5
Figure B - 2. Longitudinal gradient of mercury enrichment factors in 3 cores from the Hudson Bay Lowland, Ontario, Canada.	B-5
Figure B - 3. Age-depth model of Southwest core using the <i>clam</i> package in the software program R.	B-6
Figure B - 4. Age-depth model for North 1 using the <i>clam</i> package in the software program R.	B-7
Figure B - 5. Age-depth model for North 2 using the <i>clam</i> package in the software program R.	B-8

Figure B - 6. Age-depth model for Southeast 1 using the *clam* package in the software program R. B-9

Figure B - 7. Age-depth model for Southeast 2 using the *clam* package in the software program R. B-10

List of Appendices

Appendix A Supplemental Information to “Using Remote Archives to Quantify True Pre-Anthropogenic Mercury Accumulation and Contemporary Enrichment Factors” A - 1

Appendix B Supplemental Information to “Spatial Gradients of Atmospheric Mercury Accumulation in Peat Cores from the James Bay Lowland, Canada” B - 1

Chapter 1

1.1 Introduction

Mercury (Hg) has a number of unique properties that have made it a source of fascination for millennia. It is the only metal that is a liquid at standard temperature and pressure (STP). It is also unique in that it evaporates at relatively low temperatures and cycles as a gas. This atmospheric cycling of Hg poses numerous problems as it becomes a global pollutant. Hg undergoes complex chemical reactions in the atmosphere (as well as other environments) that make it a complicated element to study. Due to the complexities of the study of Hg, the relative contributions of Hg through time and from anthropogenic vs. natural sources remain contentious.

1.1.1 Natural Occurrence of Mercury

Natural sources of atmospheric Hg in the form of gas and particles include hydrothermal systems, volcanism, soil erosion, biomass burning, marine vent emissions, and simply evasion of previously deposited Hg back to the atmosphere (Schroeder and Munthe 1998; Figure 1 – 1; Table 1 – 1). Hg can be lost from sources as gaseous Hg at relatively low temperatures ($\sim 30^{\circ}\text{C}$), which is why heating processes are the principal means of atmospheric Hg emissions. Hg occurs naturally in rocks and minerals, typically as sulphides. Cinnabar and marcasite are the most common minerals in which Hg is found, but Hg can also become mutually enriched with other precious metals in hydrothermal fluidized processes. Thus, Hg is commonly found in gold, silver, copper, and sulphide ores. Natural sources of Hg have been contributing to atmospheric Hg concentrations for billions of years, no doubt in variable quantities through time. For the last 670, 000 years, Hg concentrations in glacial snow have been highest during the coldest periods, which also coincides with periods of highest atmospheric dust loads (Jitaru *et al.* 2009).

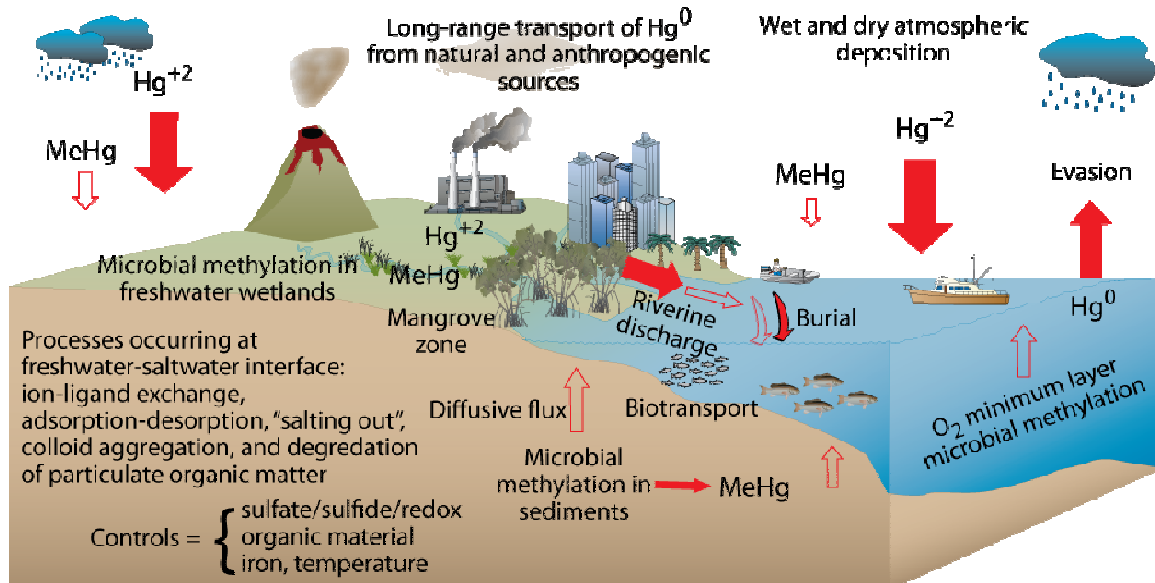


Figure 1 - 1. Conceptual diagram of Hg sources, transport, and cycling in the environment. Solid red arrows are inorganic Hg, and open red arrows are methylmercury. Adapted from Kruczynski and Fletcher 2012 p 137.

Table 1 - 1. Relative contributions of natural sources of Hg globally in 2008. Taken from Pirrone *et al.* 2010.

Source	Mercury (Mg yr ⁻¹)	Contribution (%)
Oceans	2682	52
Lakes	96	2
Forests	342	7
Tundra/Grassland/Savannah/ Prairie/Chaparral	448	9
Desert/Metalliferous/Non-vegetated Zones	546	10
Agricultural areas	128	2
Evasion after mercury depletion events	200	4
Biomass burning	675	13
Volcanoes and geothermal areas	90	2
TOTAL	5207	100

1.1.2 Historical Human Uses of Mercury

Hg derives its chemical symbol from the Latin word *hydrargyrum*, which means liquid silver. With an attractive silvery metallic appearance, it was treated as a valuable metal by ancient cultures. Anthropogenic sources of Hg may have been large, but relatively little is known about these historical sources and research describing and quantifying them is scarce. The earliest reported use of pure Hg was in the ancient Egyptian city of Kurna, where Hg was found in elemental form in a 3500-year-old tomb (Caley 1928). Rich members of society would have often been adorned with Hg trinkets during their burial. Similar to gold and silver, Hg was valued for aesthetic properties and was used in various jewellery such as amulets. Hg was also used in ancient Chinese cultures as early as 2500 years ago to create lavish artefacts gilded with Hg and gold (Bunker 1993). Commonly used by the Greek and Roman alchemists, Hg was a source of fascination and was included in many writings (Caley 1928). In addition to the use of elemental liquid Hg as an alchemical ingredient or decoration, cinnabar (a Hg-bearing mineral) was used as an embalming agent in Spain (Martin-Gil *et al.* 1994). Based on this evidence, it seems that the antimicrobial properties of Hg were at least indirectly known to early civilizations. Later, medical advances led to the discovery of Hg's antimicrobial properties and Hg compounds were used for hundreds of years in the treatment of syphilis until penicillin was invented in the 1940s (Norn *et al.* 2008). Almaden, Spain, which is currently known for geogenic Hg contamination from large cinnabar deposits (Martinez-Cortizas *et al.* 1999), was also a well-documented exporter of cinnabar to ancient Rome (Caley 1928).

More modern uses of Hg have included thermometers, fluorescent lights, and dental amalgams. The ability of Hg to form amalgams with other precious metals is the reason it was, and continues to be, used extensively in mining practises. Beginning in the 1500s, Hg was used as an amalgam to extract silver and gold, most notably in Spain (Nriagu 1993). These artisanal gold mining practises involve concentrating secondary sources of gold (Hinton *et al.* 2003a). This could then be easily concentrated and gravimetrically separated (Hinton *et al.* 2003a). Rocks are crushed, amalgamated with Hg, and then the final product is burned to remove the Hg. Although this type of mining is illegal in most

developed countries, it still exists in the developing world. The International Labour Organization estimates that there are 13 million miners in over 55 countries still practising artisanal mining because it is cheap and environmental protection is not affordable in most third world countries (ILO 2003; Hinton *et al.* 2003b).

Large amounts of Hg were also released in California gold and Hg mining in the 1800s (Alpers *et al.* 2005). Hg was imported to North America, as it was to ancient Rome, from Almaden, Spain, for use in amalgamation extraction of gold in Appalachian gold deposits (Nriagu *et al.* 1994). In the U.S. alone, gold production increased by more than 600 times between 1847-1852 (Nriagu *et al.* 1994). Beginning in the late 1800s to early 1900s in North America, increasingly heavy reliance on fossil fuels, particularly coal, caused atmospheric emissions of Hg to increase drastically (Nriagu and Pacyna 1988). Still, there is a high degree of uncertainty when calculating the exact quantities of Hg emitted prior to 1850 (Streets *et al.* 2011), and it is difficult to distinguish historical anthropogenic sources from natural sources of Hg given that there was no atmospheric monitoring until recently.

1.1.3 Atmospheric Mercury Chemistry

Unlike most metals that are aerosols in the atmosphere, 95% of atmospheric Hg exists as a gas (Schroeder and Munthe 1998). Gaseous and particulate Hg species can enter ecosystems by dry deposition (adsorbance onto dry surfaces) or wet deposition (the introduction of Hg through precipitation). In the atmosphere, Hg participates in a number of complex chemical reactions. While elemental Hg (Hg^0) is relatively inert and participates in few atmospheric reactions, particulate and reactive gaseous Hg (Hg^{2+}) are more easily adsorbed or dissolved in rain, thereby removing them from the atmosphere (Iverfeldt and Lindqvist 1986; Schroeder and Munthe 1998). Divalent Hg (Hg^{2+}), which exists predominantly in the atmosphere as HgCl_2 , is much more water-soluble than other Hg species and it therefore easily removed from the atmosphere by rain (Carpi *et al.* 1997). Due to these various reactions, Hg species can have different transport distances in the atmosphere with particulate matter and Hg^{2+} being deposited close to point sources and Hg^0 being deposited in remote ecosystems. Overall, Hg can travel thousands of kilometers (Schroeder and Munthe 1998) and is therefore considered a global pollutant.

The average atmospheric residence time of Hg is estimated to be 0.75 years, which provides ample time for atmospheric mixing and long-range transport (Lindberg *et al.* 2007), and has resulted in elevated Hg in remote regions (Fitzgerald *et al.* 1998). To track long term changes in Hg, it is important to use a media from a pristine, remote location to avoid Hg from local-regional sources that would obfuscate the signature of well-mixed atmospheric pool of Hg (Fitzgerald *et al.* 1998).

Current estimates of Hg emissions from anthropogenic and natural sources are approximately equal when accounting for re-evasion of previously deposited anthropogenic Hg (Pirrone *et al.* 2010). Models have also been used to estimate the relative contributions and some are as low as only 13% emissions resulting from natural sources due to this large legacy of Hg from historical anthropogenic sources (Amos *et al.* 2013). Still, there is a large discrepancy between estimates using different models and measures of these contributions predominantly because Hg released prior to industrialization from human activity is not well constrained.

1.1.3.1 Atmospheric Mercury Halogen Interactions

Arctic sites have shown the complexity of the atmospheric cycling of Hg and some have posited that the Arctic may be a sink for Hg (Ariya *et al.* 2004). Additionally, it was shown in the subarctic that there was greater deposition of Hg to lake sediments than would be expected based on atmospheric Hg concentrations alone (Lockhart *et al.* 1998). Atmospheric Mercury Depletion Events (AMDE) were discovered by Schroeder *et al.* (1998) in Alert, Nunavut to begin to explain the higher than expected Hg deposition in northern regions. During polar sunrise, free radical oxidation from BrO and BrCl cause enhanced deposition of Hg as Hg⁰ is converted to Hg²⁺ (Figure 1 – 2). These BrO plumes have been traced from Siberia to Hudson Bay and their transport indicates that this may be more than just an arctic phenomenon (Begoïn *et al.* 2010). More than 90% of Hg deposition in areas of the Arctic and Hudson Bay occurs in a timeframe of only 3 months and is subsequently flushed from the snowpack in 2-4 weeks during spring snowmelt (Lu *et al.* 2001). However, subsequent study demonstrated that a significant portion (~90%) of the snowpack deposited Hg was then re-emitted to the atmosphere (Poulain *et al.* 2004). Overall, this results in only a minor net increase in snow surface Hg if any at all.

Even during AMDE where snow surface Hg was measured to be 11 times higher than background levels, Hg concentrations returned to normal within 48 hours after the event (Poulain *et al.* 2004).

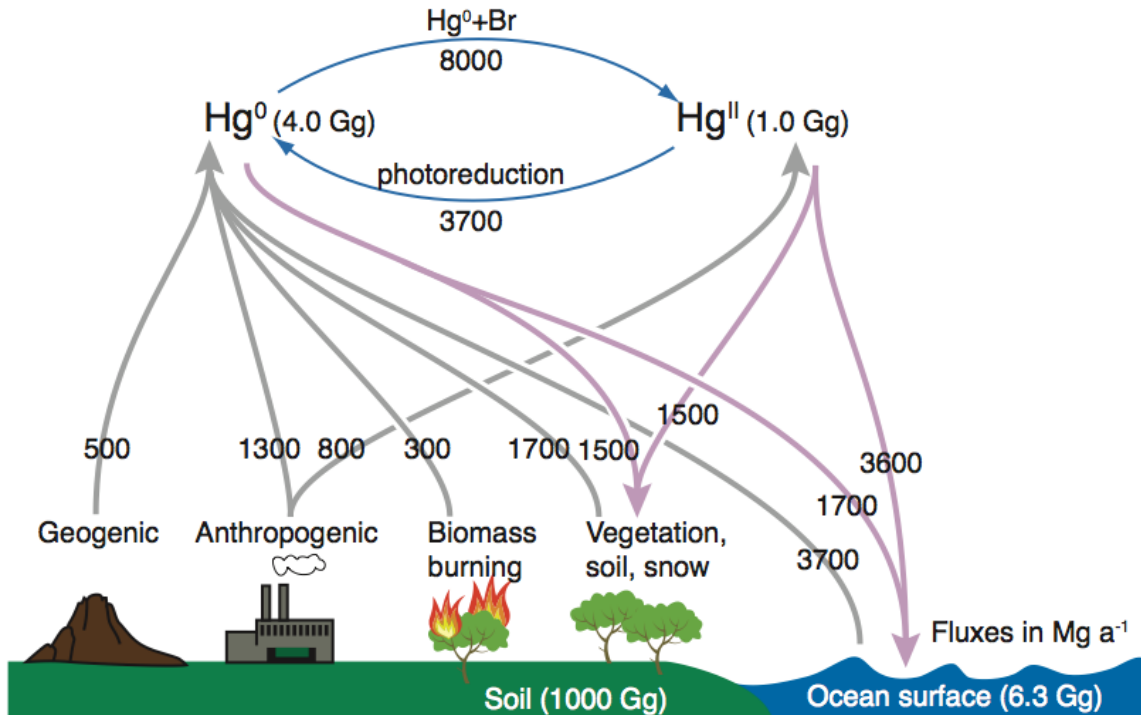


Figure 1 - 2. Conceptual diagram of global mass balance of atmospheric mercury including oxidation and reduction. From Holmes *et al.* 2010.

The Arctic has few local sources of Hg. The dominant source of Hg to remote terrestrial soil is through atmospheric deposition (Fitzgerald *et al.* 1998). Once deposited, Hg can then be re-emitted back to the atmosphere from both terrestrial and aquatic pools with varying efficacy depending on the medium. Lake surfaces can lose ~45% of Hg in the epilimnion (uppermost layer of water) in summer months due to enhanced turbulence and lower association with particulate matter in the water column (Southworth *et al.* 2007). Very little Hg (~10%) is lost from bog surfaces where Hg is more associated with particulate and organic matter or adsorbed to plants (Amyot *et al.* 2004; Xin *et al.* 2007). Hg is often only found in trace amounts (parts per trillion) in natural systems, however,

this can be enough to cause harm to flora, fauna and humans when bioaccumulation occurs.

1.1.4 Bioaccumulation and Toxicity

There is a direct relationship between the amount of inorganic Hg deposited on land and the amount of organic Hg produced there. If atmospherically deposited Hg is not re-emitted, it can become bioavailable as it converts to organic Hg species through microbial activity. Hg first becomes bioavailable (more easily taken up by biota) through methylation of reduced Hg by sulphate reducing bacteria and conversion to methylmercury (MeHg) (Compeau and Bartha 1984). Then, Hg is sorbed (surface adhesion) to low trophic level organisms (phyto/zooplankton; algae) and subsequently ingested by increasingly higher trophic level organisms as it bioaccumulates to much larger quantities in top predator tissues (Morel *et al.* 1998; Bloom 1992).

Bioaccumulation and biomagnification are also the principle mechanisms of human Hg toxicity (Morel *et al.* 1998), which results in a number of symptoms including neurological effects (sensory distortion, lack of coordination), organ damage, and teratogenic effects (fetal deformation) (Clarkson *et al.* 2003). Most Hg uptake in fish is through diet, and most Hg uptake in humans is through consumption of fish (Fitzgerald *et al.* 2007), which illustrates the clear mechanism of biomagnification. Changes in atmospheric Hg concentrations result in proportional changes in fish tissue [Hg] (Harris *et al.* 2007). Thus, atmospheric Hg trends throughout history are important toward the understanding of current factors affecting bioaccumulation.

1.1.5 Anthropogenic Impacts on the Mercury Cycle

The natural cycle of Hg has been drastically altered quite recently in terms of the geological timescale. Some scientists now refer to the current era as the 'Anthropocene' due to the massive human influence on Earth systems (Meybeck and Vorosmarty 2004). Included in the human-caused changes are increased inputs of Hg to the atmosphere. Human fossil fuel combustion, mining, and various industrial practises have caused large increases in atmospheric Hg concentrations. Current global Hg emissions are estimated to be 2000 Mg y⁻¹ (Streets *et al.* 2011). Evidence from a glacier ice core from Wyoming in

the western U.S.A. showed that anthropogenic contributions to total Hg deposition in this area were 52% over the past 270 years and up to 70% in the last 100 years (Schuster *et al.* 2002). More global estimates suggest that the all time anthropogenic Hg emissions total about 350 Gg (Streets *et al.* 2011).

Polluting practices are slowly being halted because of their environmentally damaging effects, which led to measured decreases in local Hg deposition in some areas since the 1990s of North America and Europe (notably Scandinavia) (Iverfeldt *et al.* 1995; Schuster *et al.* 2002; Slemr *et al.* 2003). While coal is still used as a primary energy source in many developing nations (Pirrone *et al.* 2010), reductions in Hg emissions in North America occurred in the late 1980s and continued into 2000 (Engstrom *et al.* 1997; Pacyna and Pacyna 2006). This was largely due to introduction of emissions control technology such as flue gas desulphurization (Pavlish *et al.* 2003). Recently at the Minamata Convention, the Global Treaty on Mercury Pollution was struck and subsequently signed by more than 90 countries around the world to set emission reduction targets “where feasible”, and to increase Hg research. Canada and the United States of America, as well as more than 50 other countries, have ratified the treaty which now becomes legally binding on those parties, but the toothless agreement does not do nearly enough to combat the growing Hg problem.

1.1.6 Mercury Paleoarchives

In order to quantify the anthropogenic impact on the Hg cycle, Hg paleoarchives are often employed. There are several natural archives commonly used to determine historical Hg deposition and accumulation. Peat, ice, and lake sediment have all been consistently verified as reliable media and are chosen based on availability at study sites. However, pre-anthropogenic Hg accumulation rate estimates vary among paleorecord mediums and geographic locations. Peat paleoarchive studies, for example, have found that pre-industrial Hg accumulation rates were about $1 \mu\text{g m}^{-2} \text{y}^{-1}$ in the high Arctic of Canada (Givelet *et al.* 2004b), $1.4 \pm 1.0 \mu\text{g m}^{-2} \text{y}^{-1}$ in southern Ontario, Canada (Givelet *et al.* 2003), $1.7 \pm 1.3 \mu\text{g m}^{-2} \text{y}^{-1}$ in Maine, U.S.A. (Roos-Barracough *et al.* 2006), $0.5\text{-}1 \mu\text{g m}^{-2} \text{y}^{-1}$ in Sweden (Bindler 2003), and $0.3\text{-}3 \mu\text{g m}^{-2} \text{y}^{-1}$ in Greenland and Denmark (Shotyk *et al.* 2003). Other studies using ice cores from the Upper Fremont Glacier in

Wyoming, U.S.A., have found pre-industrial Hg accumulation rates to be $0.78 \mu\text{g m}^{-2} \text{y}^{-1}$ (Shuster *et al.* 2002), which is not significantly different from those of peats.

While the pre-industrial Hg accumulation rates are similar, the environmental processes that affect Hg diagenesis within the records are different, depending on the medium. In ice, Hg dynamics are not well understood. Due to preferential elution (washing away of adsorbed Hg) from melting ice, major ions can be lost from ice cores and this results in lower Hg accumulation than what was initially deposited (Brimblecomb *et al.* 1985). In mid-latitude ice cores, these meltwater processes affect the surface chemistry and therefore sequestration of Hg in the ice (Davies *et al.* 1982), but these changes in Hg accumulation have not been exactly quantified. While this phenomenon is not a problem if the rate of loss is constant through time, more needs to be known about this process to ensure Hg archives in ice are accurate.

In general, lake sediment records show higher pre-industrial accumulation rates than other archives ($\sim 6.9 \mu\text{g m}^{-2} \text{y}^{-1}$) (Biester *et al.* 2007). Higher pre-industrial accumulation estimates in lake sediment cores are not surprising because, in addition to that which is received directly to the lake surface, Hg can be mobilized from the surrounding watershed and subsequently deposited in the lake basin (Swain *et al.* 1992). For this reason, complicated concentration, or ‘basin focusing’ factors must be applied to lake sediment archives to account for the amount of Hg derives from the entire watershed, which is variable. The amount of runoff, organic matter, and mobility of sediment all contribute to variable Hg accumulation rates in lake sediment archives. Furthermore, algal scavenging of Hg has been shown to enhance deposition of Hg to lake sediment and there is not yet a clear method to account for this (Outridge *et al.* 2007; Brazeau *et al.* 2013). Although redox conditions at the sediment surface can affect iron (Fe) and manganese (Mn) bonding, thereby causing upward movement of Hg in sediment cores, these conditions are generally accepted to be negligible in the anaerobic zone (Biester *et al.* 2007). Given the various complexities of lake sediment archives, peat cores are often used as a more simple approach to historical estimation of Hg accumulation.

1.1.7 Peat Paleoarchives

Given that paleorecords derived from peat are thought to be climate sensitive, it is important to understand the geography and hydrology of the landscape these records are taken from. In Canada, a vast expanse of land exists in the boreal region and the Arctic, which are remote ecosystems that are globally recognized as valuable and sensitive to climate change. Wetlands are defined as areas that are saturated with water for at least a majority of the year, causing anaerobic, reducing conditions and a specific ecology that allows for only a unique set of aquatic plants and microbial organisms to survive (Mitsch and Gosselink 2007). Anoxic conditions provided by the regular inundation of peatlands provides reducing conditions that preserve organic matter by slowing decomposition, which has allowed the peatlands to sequester ~30 Pg of carbon (Packalen *et al.* 2014). Organic binding of Hg limits its mobility in the soil, hence why peat provides such a good Hg record.

Within wetlands, there are patterned peatland topographic features called bogs and fens. Bogs are typically raised features that are characterised by mosses such as *Sphagnum spp.*, lichens, short ericaceous shrubs, and sparse black spruce (*Picea mariana*) (NWWG, 1997). Fens can often be characterised by plant species such as sedges (*Cyperaceae spp.*), and tamarack trees (*Larix laricina*), but can support many more various species than bogs (Shotyk 1988). Fens may receive hydrological inputs from surface flow and lateral movement of water, which makes them less likely to be good indicators of past atmospheric Hg deposition.

The boreal ecozone has experienced some of the fastest warming of any region on earth and this is predicted to continue (Meehl *et al.* 2005). Changes in Hg accumulation can occur when shifts in vegetation result from climate changes because some vegetation species accumulate Hg faster or slower than others (i.e. the difference between fens and bogs). The largest peatland in Canada is within this boreal ecozone and happens to be the second largest contiguous peatland in the world: the Hudson Bay Lowlands (HBL). The HBL stretches across 320, 000 square kilometres, 83% of which is in Ontario (Roulet *et al.* 1994). Compared to peatland complexes globally, the peatlands of the HBL are relatively early in their stages of development.

After the retreat of the Laurentide Ice Sheet, proglacial lakes formed within the confines of the crustal depression left by the massive glacier until about 7800 cal yrs BP (Dyke and Prest 1987). After the last glaciation, extremely fine deposits from glacial runoff left glaciomarine and glaciolacustrine sediments, which act as an almost impervious layer on top of which poor drainage conditions supported the formation of a wetland (Glooschenko *et al.* 1994). The timing of glacial rebound limited initiation of peat in the southern HBL to produce a young peatland of ~7000 years in age (Halsey *et al.* 1998). The average current rate of isostatic rebound is ~1.5m per century, which will drive what is likely the most important force in the wetland; hydrology (Glooschenko *et al.* 1994). The body of water in the Hudson Bay is salty and mixes with coastal freshwaters to form marshes in close proximity to the bay, which transitions into fen and bog peatlands further inland (Glooschenko *et al.* 1994). However, all but marshes nearest to the bay in the HBL grow in isolation of the salty bay water.

The HBL is remote from any significant human-related influences, which is important for the study of the global atmospheric pool of Hg. Here, Hg is derived predominantly from long-range atmospheric transport of Hg^0 . Incorporation of particulate or short range Hg^{2+} would artificially enhance recent accumulation in the top layers of the soil. It is more important to know how much the global atmospheric pool has been enriched in Hg. Other than the previous lake sediment study from the Hudson Bay itself (Lockhart *et al.* 1995), no peat paleo-Hg records have been created in the HBL, which represents a large gap in current data. The vast expanse of land and relative homogeneity of land type allows for good comparison across the landscape, which is useful when looking at latitudinal and longitudinal gradients as well as climate gradients. Lake sediment archives in North America suggest that there is a latitudinal gradient of Hg deposition (Muir *et al.* 2009), but this has not been replicated in peat cores or in the HBL.

Ombrotrophic peat has been consistently verified as a medium for measuring historical Hg accumulation rates from atmospheric deposition. Bogs are acidic and have low dissolved mineral content (Shotyk 1988). Bogs can have hydrology that is exclusively rain-fed, in which case they are described as ombrotrophic (Damman 1978). As peat accumulates, the uppermost layer grows in isolation of the underlying groundwater

(Ingram 1982), which is why they preserve records of atmospheric deposition and organisms stratigraphically. This hydrology also allows isolation of atmospheric inputs of these preserved elements, such as Hg. Fens, on the contrary, often have multiple hydrological inputs including groundwater upwelling, surface flow, and precipitation (Siegel and Glaser 2006). Due to the groundwater input, fens are often minerotrophic and have much higher pH and greater dissolved content (Shotyk 1988). Unlike lake sediment, peat archives are not subject to focusing factors or sedimentation rate calculations. Hg is present in high enough concentrations in peat that it does not challenge the detection limits of conventional ultra-trace techniques, as can be the case with ice cores. Redox indicators such as a relationship with Hg and Fe or Mn have not been seen in peats. Peatlands are also geographically widespread, which makes them attractive as a standard global archive.

Certainly caveats exist for the use of peat as an Hg archive as well. Proximity to point source emitters of Hg and variability in annual precipitation rates may also contribute to site-specific variability. Small-scale variability in peatland biogeochemistry (Ulanowski *et al.* 2013), and local hydrology (Branfireun 2004), all have implications for Hg sequestration and methylation potential in peatlands. These features make even intra-site comparisons complicated and help to explain peat archive variability within a site.

Another criticism for peat archives is that they are prone to diagenesis. This is crucial to historical Hg records because it can result in vertical movement of Hg. Thus, peat Hg records would not be reflective of the associated deposition through time. Additionally, this could result in ‘smearing’ where vertical movement causes large Hg accumulations to be distributed through many centimeters of the core. Although there has not been a consensus in the literature about whether or not this is a significant concern, many authors have attributed the lack of correlation between peat humification and peat Hg accumulation rates to an assumed lack of diagenesis (Shotyk *et al.* 2005; Roos-Barraclough *et al.* 2006; Zaccone *et al.* 2009, 2011; Outridge and Sanei 2010). These studies suggest that there is no preferential loss of Hg as peat decomposes. Still, there is not sufficient data to prove unequivocally that there is no diagenesis within the peat column.

Another criticism of peat as an archive of Hg is that ^{210}Pb can be smeared (moved vertically post deposition) when it is used to date the most recent ~200 cal yrs BP (Biester *et al.* 2007). However, there have been many studies with reliable Pb isotope profiles. Even before Hg was studied as a conservative element in peat archives, Pb history was reconstructed from peat cores and the results were supported by lake sediment records and modern Pb deposition monitoring (Bindler 2006). Despite changing redox conditions and depth to water table, ~95% of Pb is still retained by peat (Vile *et al.* 1999). Since other elements with similar properties, like Pb, have shown negligible diagenesis, Hg is often assumed to behave analogously.

Givelet *et al.* (2004a) outlined a clear protocol for processing Hg in peat records to account for common errors associated with peat Hg archives. These methods include clean collection, clean handling procedures, proper storage, suggested sampling interval, as well as other refinements. Beyond this it has been established that multiproxy analysis, combining both biological and geochemical records, is best for paleoarchive analysis (Bindler 2006). For example, a geochemical C:N ratio can provide information about humification (and therefore climate), which can further corroborate testate amoeba inferred climate records. Given the evidence of climate sensitivity of Hg accumulation records in peat (Martinez-Cortizas *et al.* 1999; Shotyk *et al.* 2002), multiproxy analysis is absolutely critical. Millennial changes in ocean currents have been shown to correlate to terrestrial changes in bog surface wetness (Langdon *et al.* 2003), which could change Hg accumulation rates given its suggested sensitivity to climate. As the evidence for climatic influence on Hg accumulation rates strengthens, researchers need to remove this type of natural variability from historical peat archives for more accurate accounts of anthropogenic enrichment factors.

1.1.8 Age Depth Modelling in Peat

Although this is an entire field of study on its own, paleorecords rely on accurate age depth models for their cores. The most common and well-accepted method of peat core dating is using radiocarbon. The basic principles of radiocarbon dating use the three isotopes of carbon (C): ^{12}C , ^{13}C and ^{14}C . During photosynthesis, atmospheric carbon dioxide (CO_2) is incorporated into plant tissue and the $\delta^{14}\text{C}/\text{C}$ increases. ^{14}C has a known

half-life time, thus the $\delta^{14}\text{C}/\text{C}$ ratio will decrease through time once the organism dies – prior to this $\delta^{14}\text{C}/\text{C}$ is in equilibrium with the atmosphere. That ratio can then be used to calculate age of material in the peat including *Sphagnum* stems, twigs, woody debris, and pine needles. However, radiocarbon dates are not absolute dates because atmospheric $\delta^{14}\text{C}/\text{C}$ has not been perfectly linear through time (Stuiver *et al.* 1998), and time and/or financial constraints require researchers to interpolate between radiocarbon ages (Blaauw *et al.* 2003; Blaauw and Christen 2005).

Although sampling error is avoidable using standard methods of radiocarbon sample collection (Appendix B), radiocarbon dates must still be calibrated to account for the non-linear changes in atmospheric ^{14}C . The internationally accepted calibration curve for peat core work in the northern hemisphere is INTCAL09 (Reimer *et al.* 2009). This curve is available for free online and through packages in the open source statistical software, R (R Development Core Team 2010). Individual radiocarbon dates must be interpolated to create a full age-depth model, which can be done using the *clam* package for R, which was developed by Blaauw (2010) to simplify and standardize the process of classical age-depth modelling.

1.1.9 Anthropogenic Enrichment Factors

It is scientifically accepted that there is a large anthropogenic contribution of Hg to the atmosphere in addition to the sources that comprise to the natural background contribution (Lindberg *et al.* 2007). The degree of increase is where less consensus lies, given that different archives and geographic locations present a range of estimates (Biester *et al.* 2007). Using paleoarchives, the pre-anthropogenic accumulation rate of Hg can be calculated and compared to the modern anthropogenic contribution of Hg. The ratio of these two is the ‘anthropogenic enrichment factor’ for Hg, which is currently estimated to be 3-5 times natural background levels (Biester *et al.* 2007).

Many published reconstructions of past atmospheric deposition have studied peat cores that are relatively short, and as a consequence, relatively young. However, when the oldest peat dates back only a few hundred years (*i.e.* Shuster *et al.* 2002), there is potential for early (*i.e.* non-industrial) anthropogenic activity to be incorporated into the

'pre-industrial' signature and as such, underestimate the enrichment factor of the much larger recent emissions relative to true background. In order to accurately quantify the contributions of anthropogenically-derived Hg to the atmosphere and subsequent deposition, and more clearly contextualize modern industrial Hg emissions relative to a natural background, studies need to look at records that date back thousands of years.

1.1.10 Objectives

The objective of my research presented in this thesis is to use peat cores from the remote and pristine peatlands of the Hudson Bay Lowlands, Ontario to contribute to our understanding of historical and contemporary anthropogenic contributions to Hg deposition.

In Chapter 2, my objectives are to build replicated, robust Hg records using fully age-constrained cores. Using these as well as supporting paleoclimate data, I will constrain the anthropogenic enrichment factor by comparing post-industrial Hg accumulation rates to true background rates (~3000 yrs BP) that certainly pre-date anthropogenic contributions. Then, I will compare these results to a recent Hg deposition model (Amos *et al.* 2013) to test whether or not actual data supports the model's predictions.

In Chapter 3, I will analyze long-term spatial gradients within the HBL to provide a representative enrichment factor of the entire region. I will look for latitudinal and longitudinal trends that may result from heterogeneous deposition of Hg due to southerly and westerly point source Hg emitters as well as other atmospheric chemistry changes that may affect northerly Hg deposition. These results will then be compared to Muir *et al.* (2009) to determine whether bog cores in the HBL show similar spatial trends given that they are uncomplicated by focusing factors and sedimentation rates.

In Chapter 4, I will conclude with a summary of the findings within this thesis and suggest future work that could be done to further these results.

1.1.11 References

- Alpers, C.N.; Hunerlach, M.P.; May, J.T.; Hothem, R.L. Mercury contamination from historical gold mining in California. **2005**.
- Amos, H. M.; Jacob, D. J.; Streets, D. G.; Sunderland, E. M., Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. *Global Biogeochem. Cy.* **2013**, 27, (2), 410-421.
- Amyot, M.; Southworth, G.; Lindberg, S.; Hintelmann, H.; Lalonde, J.; Ogrinc, N.; Poulain, A.; Sandilands, K., Formation and evasion of dissolved gaseous mercury in large enclosures amended with $^{200}\text{HgCl}_2$. *Atmos. Environ.* **2004**, 38, (26), 4279-4289.
- Ariya, P. A.; Dastoor, A. P.; Amyot, M.; Schroeder, W. H.; Barrie, L.; Anlauf, K.; Raofie, F.; Ryzhkov, A.; Davignon, D.; Lalonde, J., The Arctic: a sink for mercury. *Tellus B* **2004**, 56, (5), 397-403.
- Begoin, M.; Richter, A.; Weber, M.; Kaleschke, L.; Tian-Kunze, X.; Stohl, A.; Theys, N.; Burrows, J. P., Satellite observations of long range transport of a large BrO plume in the Arctic. *Atmos. Chem. Phys.* **2010**, 10, (14), 6515-6526.
- Benoit, J.; Fitzgerald, W.; Damman, A. The biogeochemistry of an ombrotrophic bog: Evaluation of use as an archive of atmospheric mercury deposition. *Environ. Res.* **1998**, 78 (2), 118-133.
- Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D.R. Modelling the past atmospheric deposition of mercury using natural archives. *Environ. Sci. Technol.* **2007**, 41 (14), 4851-4860.
- Bindler, R. Mired in the past—looking to the future: geochemistry of peat and the analysis of past environmental changes. *Global Planet. Change* **2006**, 53 (4), 209-221.
- Bindler, R. Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in southern Sweden. *Environ. Sci. Technol.* **2003**, 37 (1), 40-46.
- Blaauw, M. Methods and code for ‘classical’ age-modelling of radiocarbon sequences. *Quat. Geochronol.* **2010**, 5 (5), 512-518.
- Blaauw, M.; Christen, J. A., Radiocarbon peat chronologies and environmental change. *J. Roy. Stat. Soc. C-App.* **2005**, 54, (4), 805-816.
- Blaauw, M.; Heuvelink, G.; Mauquoy, D.; van der Plicht, J.; van Geel, B., A numerical approach to ^{14}C wiggle-match dating of organic deposits: best fits and confidence intervals. *Quaternary Sci. Rev.* **2003**, 22, (14), 1485-1500.
- Bloom, N. On the Chemical Form of Mercury in Edible Fish and Marine Invertebrate Tissue. *Can. J. Fish. Aquat. Sci.* **1992**, 49 (5), 1010-1017.
- Branfireun, B. Does microtopography influence subsurface pore-water chemistry? Implications for the study of methylmercury in peatlands. *Wetlands* **2004**, 24 (1), 207-211.

- Brazeau, M.L.; Poulain, A.J.; Paterson, A.M.; Keller, W.B.; Sanei, H.; Blais, J.M. Recent changes in mercury deposition and primary productivity inferred from sediments of lakes from the Hudson Bay Lowlands, Ontario, Canada. *Environ. Pollut.* **2013**, *173*, 52-60.
- Brimblecombe, P.; Tranter, M.; Abrahams, P.; Blackwood, I.; Davies, T.; Vincent, C. Relocation and preferential elution of acidic solute through the snowpack of a small, remote, high-altitude Scottish catchment. *Ann. Glaciol* **1985**, *7*, 141-147.
- Bunker, E.C. Gold in the ancient Chinese world: A cultural puzzle. *Artibus Asiae* **1993**, 27-50.
- Caley, E.R. Mercury and its compounds in ancient times. *J. Chem. Educ.* **1928**, *5* (4), 419.
- Carpi, A. Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. *Water Air Soil Pollut.* **1997**, *98* (3-4), 241-254.
- Clarkson, T. W.; Magos, L.; Myers, G. J., The toxicology of mercury—current exposures and clinical manifestations. *N. Engl. J. Med.* **2003**, *349*, (18), 1731-1737.
- Compeau, G. and Bartha, R. Methylation and Demethylation of Mercury Under Controlled Redox, Ph, and Salinity Conditions. *Appl. Environ. Microbiol.* **1984**, *48* (6), 1203-1207.
- Damman, A. Distribution and Movement of Elements in Ombrotrophic Peat Bogs. *Oikos* **1978**, *30* (3), 480-495; 10.2307/3543344.
- Davies, T.; Vincent, C.; Brimblecombe, P. Preferential elution of strong acids from a Norwegian ice cap. *Nature* **1982**.
- Dyke, A. S.; Prest, V. K., Late Wisconsinan and Holocene history of the Laurentide ice sheet. *Géographie physique et Quaternaire* **1987**, *41*, (2), 237-263.
- Engstrom, D. R.; Swain, E. B., Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* **1997**, *31*, (4).
- Fitzgerald, W.F.; Lamborg, C.H.; Hammerschmidt, C.R. Marine biogeochemical cycling of mercury. *Chem. Rev.* **2007**, *107* (2), 641-662.
- Fitzgerald, W.; Engstrom, D.; Mason, R.; Nater, E. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32* (1), 1-7.
- Givelet, N.; Le Roux, G.; Cheburkin, A.; Chen, B.; Frank, J.; Goodsite, M. E.; Kempter, H.; Krachler, M.; Noernberg, T.; Rausch, N.; Rheinberger, S.; Roos-Barraclough, F.; Sapkota, A.; Scholz, C.; Shotyk, W., Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses RID E-7026-2010. *J. Environ. Monit.* **2004a**, *6*, (5), 481-492.
- Givelet, N.; Roos-Barraclough, F.; Goodsite, M.; Cheburkin, A.; Shotyk, W. Atmospheric mercury accumulation rates between 5900 and 800 calibrated years

- BP in the high Arctic of Canada recorded by peat hummocks RID E-7026-2010. *Environ. Sci. Technol.* **2004b**, 38 (19), 4964-4972.
- Givelet, N.; Roos-Barraclough, F.; Shoty, W., Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years) RID E-7026-2010. *J. Environ. Monit.* **2003**, 5, (6), 935-949.
- Glooschenko, W.; Roulet, N.; Barrie, L.; Schiff, H.; Mcadie, H. The Northern Wetlands Study (NOWES) - an Overview. *J. Geophys. Res. -Atmos.* **1994**, 99 (D1), 1423-1428.
- Halsey, L.; Vitt, D.; Bauer, I. Peatland initiation during the Holocene in continental western Canada. *Clim. Change* **1998**, 40 (2), 315-342.
- Harris, R. C.; Rudd, J. W. M.; Amyot, M.; Babiarz, C. L.; Beaty, K. G.; Blanchfield, P. J.; Bodaly, R. A.; Branfireun, B. A.; Gilmour, C. C.; Graydon, J. A.; Heyes, A.; Hintelmann, H.; Hurley, J. P.; Kelly, C. A.; Krabbenhoft, D. P.; Lindberg, S. E.; Mason, R. P.; Paterson, M. J.; Podemski, C. L.; Robinson, A.; Sandilands, K. A.; Southworth, G. R.; Louis, V. L. S.; Tate, M. T., Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *P. Natl. Acad. Sci. U. S. A.* **2007**, 104, (42), 16586-16591.
- Hinton, J.J.; Veiga, M.M.; Veiga, A.T.C. Clean artisanal gold mining: a utopian approach? *J. Clean. Prod.* **2003a**, 11 (2), 99-115.
- Hinton, J.; Veiga, M.; Beinhoff, C. Women, mercury and artisanal gold mining: risk communication and mitigation. **2003b**, 107, 617-620.
- Holmes, C. D.; Jacob, D. J.; Corbitt, E. S.; Mao, J.; Yang, X.; Talbot, R.; Slemr, F., Global atmospheric model for mercury including oxidation by bromine atoms. *Atmos. Chem. Phys.* **2010**, 10, (24), 12037-12057.
- ILO*; Facts on Small-Scale Mining; International Labour Office: Geneva, Switzerland, 2003; http://www.ilo.org/wcmsp5/groups/public/---dgreports/---dcomm/documents/publication/wcms_067582.pdf.
- Ingram, H. Size and shape in raised mire ecosystems: a geophysical model. *Nature* **1982**.
- Iverfeldt, Å.; Lindqvist, O., Atmospheric oxidation of elemental mercury by ozone in the aqueous phase. *Atmos. Environ. (1967)* **1986**, 20, (8), 1567-1573.
- Iverfeldt, Å.; Munthe, J.; Brosset, C.; Pacyna, J., Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia. *Water Air Soil Pollut.* **1995**, 80, (1-4), 227-233.
- Jitaru, P.; Gabrielli, P.; Marteel, A.; Plane, J.M.; Planchon, F.A.; Gauchard, P.; Ferrari, C.P.; Boutron, C.F.; Adams, F.C.; Hong, S. Atmospheric depletion of mercury over Antarctica during glacial periods. *Nat. Geosci.* **2009**, 2 (7), 505-508.
- Kruczynski, W. L.; Fletcher, P. J., *Tropical Connections: South Florida's Marine Environment*. IAN Press, University of Maryland Center for Environmental Science: 2012, 492 pp.

- Langdon, P.; Barber, K.; Hughes, P. A 7500-year peat-based palaeoclimatic reconstruction and evidence for an 1100-year cyclicity in bog surface wetness from Temple Hill Moss, Pentland Hills, southeast Scotland. *Quaternary Sci. Rev.* **2003**, *22* (2), 259-274.
- Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C., A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36*, (1), 19-32.
- Lockhart, W.; Wilkinson, P.; Billeck, B.; Danell, R.; Hunt, R.; Brunskill, G.; Delaronde, J.; Louis, V.S. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry* **1998**, *40* (2-3), 163-173.
- Lockhart, W. L.; Wilkinson, P.; Billeck, B. N.; Hunt, R. V.; Wagemann, R.; Brunskill, G. J., Current and historical inputs of mercury to high-latitude lakes in Canada and to Hudson Bay. *Water Air Soil Pollut.* **1995**, *80*, (1-4), 603-610.
- Lu, J.Y.; Schroeder, W.H.; Barrie, L.A.; Steffen, A.; Welch, H.E.; Martin, K.; Lockhart, L.; Hunt, R.V.; Boila, G.; Richter, A. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28* (17), 3219-3222.
- Martinez-Cortizas, A.; Pontevedra-Pombal, X.; Garcia-Rodeja, E.; Novoa-Munoz, J.; Shotyk, W. Mercury in a Spanish peat bog: Archive of climate change and atmospheric metal deposition. *Science* **1999**, *284* (5416), 939-942.
- Martin-Gil, J.; Martin-Gil, F.; Delibes de Castro, G.; Zapatero-Magdaleno, P.; Sarabia-Herrero, F. Preserving the ancients with vermilion. *Lancet* **1994**, *344* (8939), 1776-1777.
- Meehl, G.; Washington, W.; Collins, W.; Arblaster, J.; Hu, A.; Buja, L.; Strand, W.; Teng, H. How much more global warming and sea level rise? RID C-1342-2010. *Science* **2005**, *307*(5716), 1769-1772.
- Meybeck, M.; Vörösmarty, C. J.; Schulze, R. E.; Becker, A., Conclusions: Scaling relative responses of terrestrial aquatic systems to global changes. In *Vegetation, water, humans and the climate*, Springer: 2004; pp 455-464.
- Mitsch, W.J. and Gosselink, J.G. *Wetlands*. Hoboken. **2007**.
- Morel, F.M.; Kraepiel, A.M.; Amyot, M. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* **1998**, *29* (1), 543-566.
- Muir, D. C. G.; Wang, X.; Yang, F.; Nguyen, N.; Jackson, T. A.; Evans, M. S.; Douglas, M.; Koeck, G.; Lamoureux, S.; Pienitz, R.; Smol, J. P.; Vincent, W. F.; Dastoor, A., Spatial Trends and Historical Deposition of Mercury in Eastern and Northern Canada Inferred from Lake Sediment Cores. *Environ. Sci. Technol.* **2009**, *43*, (13), 4802-4809.
- National Wetlands Working Group (NWWG). *The Canadian Wetland Classification System - Second Edition*. University of Waterloo, Waterloo, Ontario, 2003.

- Norn, S.; Permin, H.; Kruse, E.; Kruse, P.R. Mercury--a major agent in the history of medicine and alchemy. *Dan. Medicinhist Arbog* **2008**, *36*, 21-40.
- Nriagu, J.O. Mercury pollution from the past mining of gold and silver in the Americas. *Sci. Total Environ.* **1994**, *149* (3), 167-181.
- Nriagu, J.O. Legacy of Mercury Pollution. *Nature* **1993**, *363* (6430), 589-589.
- Nriagu, J.O. and Pacyna, J.M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **1988**, *333* (6169), 134-139.
- Outridge, P.; Sanei, H.; Stern, G.; Hamilton, P.; Goodarzi, F. Evidence for control of mercury accumulation rates in Canadian High Arctic lake sediments by variations of aquatic primary productivity. *Environ. Sci. Technol.* **2007**, *41* (15), 5259-5265.
- Outridge, P.; Sanei, H., Does organic matter degradation affect the reconstruction of pre-industrial atmospheric mercury deposition rates from peat cores? A test of the hypothesis using a permafrost peat deposit in northern Canada. *Int. J. Coal Geol.* **2010**, *83*, (1), 73-81.
- Packalen, M. S.; Finkelstein, S. A.; McLaughlin, J. W., Carbon storage and potential methane production in the Hudson Bay Lowlands since mid-Holocene peat initiation. *Nat. Commun.* **2014**, *5*.
- Pacyna, E. G.; Pacyna, J. M.; Steenhuisen, F.; Wilson, S., Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* **2006**, *40*, (22), 4048-4063.
- Pavlish, J. H.; Sondreal, E. A.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A., Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **2003**, *82*, (2), 89-165.
- Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason, R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G., Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10*, (13), 5951-5964.
- Poulain, A. J.; Lalonde, J. D.; Amyot, M.; Shead, J. A.; Raofie, F.; Ariya, P. A., Redox transformations of mercury in an Arctic snowpack at springtime. *Atmos. Environ.* **2004**, *38*, (39), 6763-6774.
- R Development Core Team *R: a language and environment for statistical computing*, R Foundation for Statistical Computing: Vienna, Austria, 2011.
- Reimer, P.J.; Baillie, M.G.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Burr, G.S.; Edwards, R.L. IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. **2009**, .
- Roos-Barraclough, F.; Givelet, N.; Cheburkin, A.; Shotyk, W.; Norton, S. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: A 10000-year record from Caribou Bog, Maine. *Environ. Sci. Technol.* **2006**, *40* (10), 3188-3194.

- Roulet, N.; Jano, A.; Kelly, C.; Klinger, L.; Moore, T.; Protz, R.; Ritter, J.; Rouse, W. Role of the Hudson-Bay Lowlands as a Source of Atmospheric Methane. *J. Geophys. Res. -Atmos.* **1994**, *99* (D1), 1439-1454.
- Schroeder, W.H. and Munthe, J. Atmospheric mercury—an overview. *Atmos. Environ.* **1998**, *32* (5), 809-822.
- Schroeder, W.H.; Anlauf, K.G.; Barrie, L.A.; Lu, J.Y.; Steffen, A.; Schneeberger, D.R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394* (6691), 331-332.
- Schuster, P.; Krabbenhoft, D.; Naftz, D.; Cecil, L.; Olson, M.; Dewild, J.; Susong, D.; Green, J.; Abbott, M. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **2002**, *36* (11), 2303-2310.
- Shotyk, W. Review of the inorganic geochemistry of peats and peatland waters. *Earth-Sci. Rev.* **1988**, *25* (2), 95-176.
- Shotyk, W.; Goodsite, M. E.; Roos-Barraclough, F.; Givelet, N.; Le Roux, G.; Weiss, D.; Cheburkin, A.; Knudsen, K.; Heinemeier, J.; van Der Knaap, W., Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands. *Geochim. Cosmochim. Acta* **2005**, *69*, (1), 1-17.
- Shotyk, W.; Krachler, M.; Martinez-Cortizas, A.; Cheburkin, A.K.; Emons, H. A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12 370 ¹⁴C yr BP, and their variation with Holocene climate change. *Earth Planet. Sci. Lett.* **2002**, *199* (1), 21-37.
- Shotyk, W.; Goodsite, M.; Roos-Barraclough, F.; Frei, R.; Heinemeier, J.; Asmund, G.; Lohse, C.; Hansen, T. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve" RID E-7026-2010. *Geochim. Cosmochim. Ac.* **2003**, *67* (21), 3991-4011.
- Siegel, D.I. and Glaser, P. The hydrology of peatlands, In *Boreal Peatland Ecosystems*; Springer: 2006; pp. 289-311.
- Slemr, F.; Brunke, E. G.; Ebinghaus, R.; Temme, C.; Munthe, J.; Wängberg, I.; Schroeder, W.; Steffen, A.; Berg, T., Worldwide trend of atmospheric mercury since 1977. *Geophys. Res. Lett.* **2003**, *30*, (10).
- Southworth, G.; Lindberg, S.; Hintelmann, H.; Amyot, M.; Poulain, A.; Bogle, M.; Peterson, M.; Rudd, J.; Harris, R.; Sandilands, K. Evasion of added isotopic mercury from a northern temperate lake. *Environ. Toxicol. Chem.* **2007**, *26* (1), 53-60.
- Streets, D.G.; Devane, M.K.; Lu, Z.; Bond, T.C.; Sunderland, E.M.; Jacob, D.J. All-Time Releases of Mercury to the Atmosphere from Human Activities. *Environ. Sci. Technol.* **2011**, *45*(24), 10485-10491.

- Stuiver, M.; Reimer, P. J.; Bard, E.; Beck, J. W.; Burr, G. S.; Hughen, K. A.; Kromer, B.; McCormac, G.; Van der Plicht, J.; Spurk, M., INTCAL98 radiocarbon age calibration, 24,000-0 cal BP. *Radiocarbon* **1998**, *40*, (3), 1041-1083.
- Swain, E.B.; Engstrom, D.R.; Brigham, M.E.; Henning, T.A.; Brezonik, P.L. Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **1992**, *257*(5071), 784-787.
- Ulanowski, T. A.; Branfireun, B. A., Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay Lowland, Canada. *Sci. Total Environ.* **2013**, *454*, 211-218.
- Vile, M.A.; Wieder, R.K.; Novák, M. Mobility of Pb in *Sphagnum*-derived peat. *Biogeochemistry* **1999**, *45* (1), 35-52.
- Wu, J. Response of peatland development and carbon cycling to climate change: a dynamic system modelling approach. *Environ. Earth Sci.* **2012**, *65* (1), 141-151.
- Xin, M.; Gustin, M.; Johnson, D., Laboratory investigation of the potential for re-emission of atmospherically derived Hg from soils. *Environ. Sci. Technol.* **2007**, *41*, (14), 4946-4951.
- Zaccone, C.; Casiello, G.; Longobardi, F.; Bragazza, L.; Sacco, A.; Miano, T. M., Evaluating the 'conservative' behavior of stable isotopic ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$) in humic acids and their reliability as paleoenvironmental proxies along a peat sequence. *Chem. Geol.* **2011**, *285*, (1-4), 124-132.
- Zaccone, C.; Santoro, A.; Cocozza, C.; Terzano, R.; Shotyk, W.; Miano, T., Comparison of Hg concentrations in ombrotrophic peat and corresponding humic acids, and implications for the use of bogs as archives of atmospheric Hg deposition. *Geoderma* **2009**, *148*, (3), 399-404.

Chapter 2

2 Using Pristine Peat Archives to Quantify True Pre-Anthropogenic Mercury Accumulation and Contemporary Enrichment Factors

2.1 Introduction

Mercury (Hg) is a persistent global pollutant that is toxic even in trace amounts when it bioaccumulates in higher organisms as methylmercury (MeHg) (Lindberg *et al.* 2007). Human health concerns are a result of fish consumption (Clarkson *et al.* 2003) and there is elevated Hg in freshwater and marine fishes far from any point sources (Swain 1992). Natural sources of Hg to the atmosphere include volcanoes, biomass burning, (re)evaporation from soils and surface water, and weathering of Hg-bearing rocks and minerals. Relatively recent anthropogenic inputs from fossil fuel burning, mining, and industrial processes have contributed to the global atmospheric pool of atmospheric Hg and subsequent deposition (Pirrone *et al.* 2010). Despite the obvious importance of this information for emissions regulations and controls on Hg use that seek to reduce the direct anthropogenic contribution to the global cycle, the actual anthropogenic contributions of Hg to the atmosphere and subsequently to aquatic and terrestrial environments remains poorly constrained.

Differentiating industrially-emitted/deposited Hg from that of natural sources in air, soils, water or biota is not possible using standard analytical methods, although new stable isotope approaches show promise (e.g. Gehrke *et al.* 2011). These approaches would likely only be of utility at the local to regional scale due to the complexity of accounting for many different point sources. The use of Hg stable isotope tracers provide insights into Hg fate and transport processes of newly-deposited Hg, however this does not provide any information about the sources of the Hg that is being deposited via natural pathways.

Globally, terrestrial soil receives a disproportionately large quantity of atmospheric Hg deposition with more than 60% depositing on only 30% of the Earth's surface, which

reflects the large impact of point sources (Mason *et al.* 1994). Current estimates of anthropogenic sources to the atmosphere are about 30%, but this does not include re-evasion of previously deposited Hg (Pirrone *et al.* 2010). Comparing anthropogenic to natural emissions estimates, one of the first anthropogenic enrichment factors was calculated as approximately 3 times (Mason *et al.* 1994). After decades of disagreement, recent Hg archives seem to be suggesting that this original enrichment factor of 3 was a good estimate.

Modelling historical Hg emission and deposition is a newer approach to understanding the anthropogenic contribution. These studies, often using an inventory approach, lack data regarding historical anthropogenic contributions from sources such as early mining practices, medical and cultural uses. Due to this lack of data, the confidence interval for estimates of the pre-1850 anthropogenic contributions to the global atmospheric Hg pool is -50% to +300% (Streets *et al.* 2011). Furthermore, historically deposited Hg continues to cycle in the atmosphere, as it can be re-emitted after deposition. Evasion such as this is a large source of atmospheric Hg (Amos *et al.* 2013). Depending on how this historical data has been utilized, anthropogenic enrichment factor calculations can result in drastically different values. Amos *et al.* (2013) calculated a contemporary enrichment factor of 2.6 relative to 1840 levels, but a factor of 7.5 relative to natural levels, which were estimated at ~4000 years BP. Clearly, the dates and corresponding accumulation rates used to calculate the anthropogenic enrichment factor have a significant bearing on the calculated value. There is a clear need to constrain the current estimate of the enrichment factor using long-term, multiproxy studies of historical Hg accumulation data.

Peat paleorecords offer an ideal medium to study the anthropogenic enrichment factor of Hg. However, Hg accumulation rates are variable between paleorecord mediums and geographic locations. Pre-industrial Hg accumulation rates in peat range from 1-3 $\mu\text{g m}^{-2} \text{y}^{-1}$ depending on geographic location (Givelet *et al.* 2004b; Roos-Barraclough *et al.* 2006; Shotyk *et al.* 2003). Pre-industrial Hg accumulation rates in ice are even lower at 0.78 $\mu\text{g m}^{-2} \text{y}^{-1}$ (Shuster *et al.* 2002). Lake sediment records indicate a much higher pre-industrial accumulation rate of ~6.9 $\mu\text{g m}^{-2} \text{y}^{-1}$ (Biester *et al.* 2007). Clearly there is a large amount of variability among Hg paleorecords.

In peatlands, micro-topography (Bindler *et al.* 2004; Coggins *et al.* 2006), and drainage patterns are micro to meso-scale factors that may contribute to variability in accumulation rates of Hg in peat. Peat archives of Hg have long been used as indicators of relative changes to Hg accumulation rates (Benoit *et al.* 1998; Fitzgerald *et al.* 1998; Fitzgerald *et al.* 2005) however, concerns remain about the reliability of peat archives of Hg (see Rasmussen *et al.* 2004; Biester *et al.* 2007), which has made it imperative to use multiproxy analyses in order to best interpret these archives. Such proxies include geochemical and biological measures of decomposition, vegetation, and stable isotope tracers, which can be used to complement the interpretation of the peat Hg accumulation records (Bindler 2006). For example, the effects of vegetation community on Hg accumulation in peatlands are not well documented and these changes could be a source of uncertainty when calculating and interpreting Hg changes in peat.

Another source of uncertainty in paleoarchives is the identification of the time period after which anthropogenic activity made measureable contributions to the global Hg cycle. Although 1850 is a common date that is used to mark the onset of the Industrial Revolution, some have indicated that significant anthropogenic Hg emissions would have occurred well before 1850 (Nriagu 1993). As such, some authors have suggested that paleoarchives should extend back thousands of years to establish a satisfactory pre-anthropogenic atmospheric Hg accumulation rate (Goodsite *et al.* 2013), however it is rarely possible to obtain a pristine core with this kind of temporal extent combined with a reliable age-depth model due to geographic limitations. While some studies use other unique geochemical indicators of anthropogenic emissions to distinguish between natural and anthropogenic periods in peat cores (e.g. Givelet *et al.* 2003), many studies simply use short cores that have basal dates of 200-300 years BP and assume that the older layers are representative of pre-anthropogenic conditions.

Diagenesis of Hg within ombrotrophic bog peat cores is assumed to be small in the absence of conclusive data to suggest otherwise, but it is not well understood and must therefore be cautiously considered (Goodsite *et al.* 2013). Furthermore, the assumption of reliability of peat cores is based heavily on the ombrotrophic nature of the peat so that only atmospheric deposition contributes to Hg found in the cores (Clymo 1987; Shotyk

1996). Other peatland types such as fens can have minerogenic and hydrologic Hg input from sources such as groundwater input. Fen Hg records have been studied in a limited way, and “fen focusing” (concentration of Hg in fens due to lateral hydrological movement of Hg from raised bogs to lower fen features) was identified as a source of Hg from the surrounding peatland, however a clear need to quantify this effect has been acknowledged (Franzen *et al.* 2004). Since there is evidence to suggest that peatlands shift between bog-like and fen-like vegetation throughout their history, studies must consider that what may currently seem like an ombrotrophic bog may very well have been a fen during one or more periods in the chronology (Hughes *et al.* 2000).

In North America, there are few published records of peat Hg archives in northern mid-continental locations where the influence of regional emitters would be expected to be small. Other relatively high latitude records are more marine coastal locations, such as those from Alaska (Fitzgerald *et al.* 2005) and Greenland (Bindler *et al.* 2001; Shotyk *et al.* 2003). A short record (150 years BP) was collected from Manitoba, Canada (Outridge *et al.* 2011), but this cannot be representative of the true pre-anthropogenic accumulation rate as it only dates back to 1890. Recently, Engstrom *et al.* (2014) compiled a number of lake sediment archives to look for pre-industrial Hg accumulations to explain the domination of Hg in recent global Hg inventories. However, these archives still do not extend back to the >3000 yr BP time period mentioned in the global Hg inventories they set out to explain, which could understandably be due to age-depth model limitations.

The peatlands of the Hudson Bay Lowlands (HBL) are prime candidates for historical Hg research because the region is well characterized with basal peat age of ~8200 years in some locations (Packalen *et al.* 2014), and are distant from regional emitters. Unlike lakes, there are no watershed Hg focusing effects (see Biester *et al.* 2007) and, unlike forested locations, there are virtually no canopy effects (see St. Louis *et al.* 2001). The lack of long-term, midcontinental, remote records makes the peatlands of the HBL an area of interest for paleo-Hg research. A long-term record of the historical Hg accumulation from the HBL is a prime candidate for constraining current estimates of the anthropogenic enrichment factor (i.e. the increase in Hg accumulation rates since industrialization) because it is reasonable to assume that the well-mixed pool of longer

residence time atmospheric Hg is the only source. The objectives of this study are to use temporally long peat cores from the central James Bay Lowlands to:

- 1) Build replicated, robust Hg accumulation chronologies using age-constrained cores, and;
- 2) Calculate the anthropogenic enrichment of atmospheric Hg using different temporal windows to test if using true pre-anthropogenic (~3000 yrs BP) accumulation rates produces results that reflect more recently refined deposition model estimates by Amos *et al.* (2013).

2.2 Site Description and Methods

This study site is located in the HBL, approximately 90 km from the west coast of James Bay near the Attawapiskat River (52.821° N, -83.884° W; Figure 2 – 1). The site is accessed through the DeBeers Diamond Mine operation and is also the site of long-term climate and carbon monitoring by both the Ontario Ministry of the Environment and Ontario Ministry of Natural Resources. The HBL is a low-lying, spatially extensive ecoregion dominated by peatland complexes and covering an area of ~372,000 km² (Figure 2 – 1 shaded area, Appendix A). Peatland establishment followed deglaciation and the retreat of the Tyrrell Sea *ca.* 8500 cal yr BP (Dyke and Prest 1987). Peat overlies strata of fine-grained marine and proglacial lacustrine sediments, till and diamicton, which in turn overlie Paleozoic limestone bedrock (Martini 2006; Riley 2003; Riley 2011). Peat thickness varies from < 1 m in the young peatlands of the coastal regions to a maximum of ~4 m inland where the oldest basal radiocarbon dates are recorded (Packalen *et al.* 2014). The gradient in peat depth and basal radiocarbon dates is a result of rapid rates of isostatic rebound since deglaciation estimated to be ~3 m per century immediately post deglaciation (Andrews and Peltier 1989), slowing to no more than 1.5 m per century at present (Glooschenko *et al.* 1994). A nearby inland weather station at Lansdowne House has a mean annual, January and July temperature of -1.3°C, -22.3°C and 17.2°C respectively, and a mean total annual precipitation of 700 mm from 1981-

2010 (Environment Canada 2011). Permafrost occurs sporadically throughout the central HBL, with a band of continuous permafrost only along the north / northeast coast bordering Hudson Bay.



Figure 2 - 1. Study site location (black star; 52.821° N, -83.884° W) in the Hudson Bay Lowlands (darker shading) near the Attawapiskat River in Northern Ontario, Canada.

2.2.1 Core collection

The cores were collected in 2009 using standard methods (Givelet *et al.* 2004a) from four distinct locations. Surface peat (upper ~ 50 cm) was collected using a Jeglum corer (Jeglum *et al.* 1992) with 10 x 10 cm box to eliminate compaction. Lower sections were collected in sections using a Russian chamber peat corer with a 50-cm barrel (Jowsey 1966). Mineral contact at the base of the peat cores was retrieved in all cases. Cores were double wrapped in plastic and aluminum foil, stored in rigid plastic pipe in the dark at +4°C until analysis.

Ontario Forest Ecosystem (FEC) classification was used to identify the vegetation communities of each core collection site (Table 2 – 1). Tree and shrub cover ranged from 1-10% in the bogs, but was 40% in the fen. Surface vegetation was primarily *Sphagnum fuscum*, but there was also *Sphagnum capitulum*, *Cladonia spp.*, and some herbaceous species such as *Eriophorum vaginatum*, *Rubus chamaemorus*, and *Scirpus caspitosus*.

Table 2 - 1. Summary of core collection local characteristics.

Core	Vegetation classification	Vegetation survey
Bog 1	Shrub bog with a hummock and hollow structure	Surface vegetation consisted of <i>Sphagnum fuscum</i> and <i>Cladonia spp.</i> , with occurrences of the herbaceous plants <i>Eriophorum vaginatum</i> , <i>Rubus chamaemorus</i> , <i>Scirpus caespitosus</i> , and <i>Carex spp.</i> in the immediate vicinity. Trees were scarce, shrubs were more abundant, and taxa encountered included <i>Picea mariana</i> , <i>Larix laricina</i> , <i>Chamaedaphne calyculata</i> , and <i>Kalmia angustifolia</i> . The core was taken in a hollow.
Bog 2	Shrub bog with a hummock and hollow structure	1% cover in trees/shrubs 2-10m in height including <i>Picea mariana</i> , 10% cover in shrubs 0.5-2m in height including <i>Picea mariana</i> and <i>Larix laricina</i> , 50% cover of shrubs less than 0.5m in height including <i>Chamaedaphne calyculata</i> , <i>Picea mariana</i> , and <i>Vaccinium spp.</i> , 25% herbaceous cover including <i>Carex spp.</i> , <i>Rubus chamaemorus</i> , <i>Eriophorum vaginatum</i> , and <i>Menyanthes trifoliata</i> , 95% moss and lichen cover including <i>Sphagnum fuscum</i> , <i>Cladonia spp.</i> , and <i>Sphagnum capitulum</i> . The core was taken half in hollow and half in hummock soil.
Bog 3	Domed Bog	10% cover in shrubs 0.5-2m in height including <i>Picea mariana</i> , 55% cover of shrubs less than 0.5m in height including <i>Chamaedaphne calyculata</i> , and <i>Picea mariana</i> , 25% herbaceous cover including <i>Carex spp.</i> , <i>Rubus chamaemorus</i> , <i>Eriophorum vaginatum</i> , and <i>Menyanthes trifoliata</i> , 95% moss and lichen cover including <i>Sphagnum fuscum</i> , <i>Cladonia spp.</i> , and <i>Sphagnum capitulum</i> . The core was taken half in hollow and half in hummock soil.
Fen	Treed low-shrub fen	40% cover in trees and shrubs 2-10 m in height including <i>Larix laricina</i> and 50% cover of <i>Betula pumila</i> <0.5 m in height. Herbaceous cover was 75-100%, dominated by <i>Cyperaceae spp.</i> , with <i>Menyanthes trifoliata</i> and bryophytes. There was no coverage of trees taller than 10 m.

2.2.2 Sample Handling and Preparation

Clean procedures for sample handling was followed in accordance with ultra trace metal protocols (EPA 2007a). Samples for Hg analyses were taken at one-centimeter intervals using a stainless steel blade (Givelet *et al.* 2004a). The outside edge of each sample was removed to avoid using any sample that had possibly been contaminated by smearing in the coring device (Givelet *et al.* 2004a). Each sample was squeezed of excess water, double bagged in 50 ml zip-closure plastic bags, and frozen at -25°C. For freeze-drying,

sample bags were opened and carefully placed on shelves within the large-chamber freeze-drier. Samples were freeze-dried for approximately twenty-four hours or until the samples could be crushed manually within their bag to a homogeneous, fine powder consistency.

2.2.3 Mercury analyses

Samples were analyzed on a Milestone DMA-80 direct Hg analyzer in accordance with EPA method 7473, which entails thermal decomposition, amalgamation onto a gold trap, then atomic absorption spectrophotometry (EPA 2007b). Each set of sample analyses included duplicates (within ± 20 relative percent difference) and SRM (NRCC estuarine sediment MESS-3: $91 \pm 9 \mu\text{g g}^{-1}$). All Hg analysis was completed in an ISO 17025 certified laboratory at the Biotron Institute for Experimental Climate Change Research at the University of Western Ontario.

2.2.4 Dating techniques

Samples of wood, *Sphagnum* stems, conifer needles, twigs, and herbaceous remains were collected and cleaned for radiocarbon analysis (summarized in Appendix A). The core chronology in Bog 1 was created using ^{210}Pb and accelerator mass spectrometry (AMS) radiocarbon dating (^{14}C) methods (Bunbury *et al.* 2012; therein known as VC04-06). Dried samples for ^{210}Pb dating were analyzed at Flett Research Ltd. (Winnipeg, Manitoba) for analysis by alpha spectrometry and a constant rate of supply (CRS) model was applied to the ^{210}Pb data. Eleven ^{210}Pb dates and six radiocarbon dates were collected and calibrated for 'Bog 1', six radiocarbon dates were collected and calibrated for Fen core by O'Reilly *et al.* (2014) (therein known as VM33), and two-three radiocarbon dates were collected and calibrated for Bog 2 and Bog 3 by Packalen *et al.* (2014) (therein known as VM45 and VM13). Radiocarbon data was measured at Beta Analytics (Miami, Florida) and were calibrated in the program CALIB (ver 6.0.1) using the INTCAL09 calibration curve (Reimer *et al.* 2009; Stuiver *et al.* 1998). ^{210}Pb was attempted for the Fen core but they were abnormal (vertical profile) and therefore not used (O'Reilly 2011). The program *clam* for R (Blaauw 2010; R Development Core Team 2011) was used to develop all age-depth models, using linear interpolation between data points.

Chronologies were constructed from AMS radiocarbon dates on terrestrial macrofossils and details are presented elsewhere (Bunbury *et al.* 2012; O'Reilly *et al.* 2014; Packalen *et al.* 2014).

2.2.5 Depth to Water Table

Reconstructions of Depth to Water Table (DWT) over time were done on Bog 1 by tallying testate amoeba species abundance by Bunbury *et al.* 2012. They used a weighted-averaging transfer function and plotted these in the software package C2 (Juggins 2003). For this analysis, *Cyclopyxis arcelloides*, *Phryganella acropodia* and *Diffflugia globulosa* were grouped. Standard error and model performance statistics were calculated using bootstrap simulations (1000 iterations; Bunbury *et al.* 2012 for further details).

2.2.6 Carbon and Mercury Accumulation Rate Calculations

For the bog cores, 1 cm³ of peat was sub-sampled every ~2.5 cm and dried to constant mass at 105°C to measure bulk density, %C and %N. Specifically for Bog 1 and the fen core, 1 cm³ of peat was sub-sampled approximately every 3 cm and dried to constant mass at 60°C (to prevent Pb volatilization as ²¹⁰Pb was used in this core for recent carbon accumulation modelling) to measure bulk density, %C and %N. The Hg accumulation rate was determined as:

$$\text{Accumulation Rate} = \text{HgT} * \text{BD} / \text{time}$$

HgT is the total Hg concentration (µg g⁻¹), BD is the bulk density (g cm⁻³) and time is the difference between interpolated radiocarbon and/or ²¹⁰Pb dates. After unit conversions, this is a measure of the average Hg mass that accumulated per square meter area each year.

2.2.7 Calculation of Enrichment Factor

The Hg enrichment factor is calculated using the Hg accumulation rates from one time period and dividing them by another time period. The traditional enrichment factor was calculated using 1850 as the onset of industrial anthropogenic activity:

$$\text{EF} = \text{Average Hg Accumulation 1850 to Present} / \text{Average Hg Accumulation 1850 to Basal}$$

The specific timeframe used for the anthropogenic enrichment factor calculations was chosen using the paleoclimate studies previously published from the cores presented here. Using this data, it was possible to eliminate suspected and well-established periods of climate instability from the enrichment factor calculation. For example, several major (relative to the rest of Holocene) climate shifts have occurred in the last ~1000 years. Thus, the uppermost layers of peat were used to calculate a modern average. Only recent Hg accumulations that are known to be predominantly anthropogenic, therefore only recent Hg accumulations are used in the calculation. The adapted enrichment factor also uses a much older pre-anthropogenic timeframe of 2700-3800 cal yrs BP. This is within the time window suggested by Amos *et al.* (2013) and also a period that Packalen *et al.* (2014) suggest had a climate most similar to modern time. Due to oversampling of some areas of individual cores, Hg samples could not be taken and small data gaps exist in the profiles. The timeframe of 2700-3800 was the only period that an average could be retrieved from all cores. The following equation summarizes the adapted method of calculating the enrichment factor:

$$EF = \frac{\text{Average Hg Accumulation 1940 to Present}}{\text{Average Hg Accumulation 2700 to 3800 cal years BP}}$$

2.3 Results and Discussion

2.3.1 General Core Stratigraphy and Age-Models

Bulk density in the bog cores ranged from 0.03 to 0.18 g cm⁻³ with an average of 0.08 ± 0.02 g cm⁻³ (Appendix A). Total Hg concentrations ranged from 5.31-213.52 µg kg⁻¹ with a standard deviation of 30.16 µg kg⁻¹ and all standards and duplicates were within 20 relative percent difference in compliance with EPA method 7473 (Figure 2 – 2; Figure 2 – 3; Appendix A). All three of the bog cores were similar in their average total Hg concentrations (40.6-43.6 ± 23.6-27.0 µg kg⁻¹) (Figure 2 – 2; Figure 2 – 3; Appendix A). Hg concentration maxima were 197.8, 180.8, 160.0 µg kg⁻¹ in the bog cores and 213.5 µg kg⁻¹ in the fen core (Figure 2 – 2; Figure 2 – 3; Appendix A). These occurred at depths of 12cm, 17cm, and 9cm in the bogs and 24cm in the fen. The overall similarities between the bog cores suggest that all three cores were good records of atmospheric Hg

accumulation throughout history. Bog 1 alone was used for enrichment factor calculations because periods of fen characteristics could be excluded and this core had the best chronology using both radiocarbon and ^{210}Pb dating. Bog 2 displayed similar values and further support the calculations from Bog 1. Bog 3 and the fen provided excellent examples of landscape shift that can affect the calculation of the enrichment factor and were therefore confidently excluded from enrichment factor calculations.

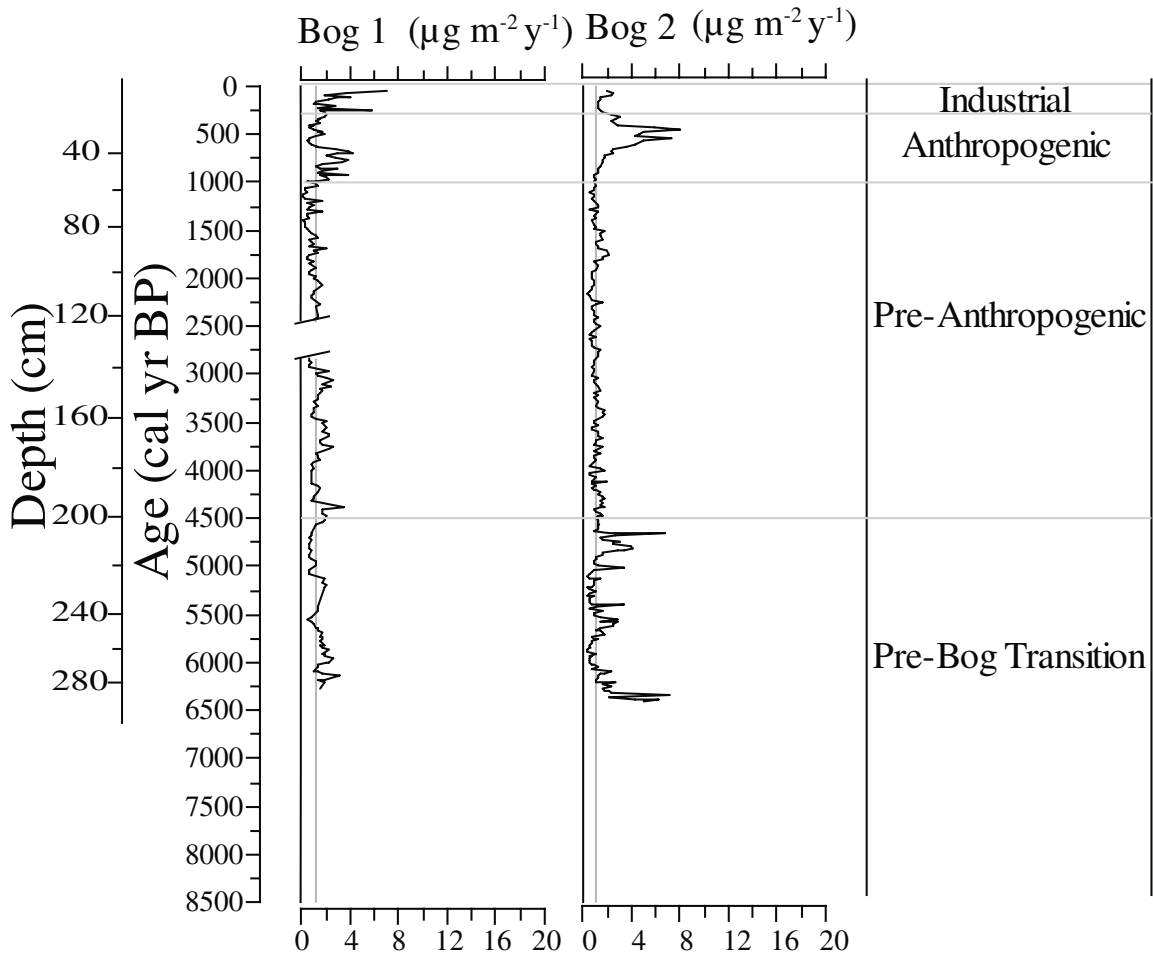


Figure 2 - 2. Hg accumulation rates for Bog 1 and Bog 2 through time (calibrated radiocarbon age in years BP). Hg accumulation rates are in micrograms per meter squared per year. Vertical grey lines represent the adapted enrichment factor method's calculation of pre-anthropogenic Hg accumulation rates for each core.

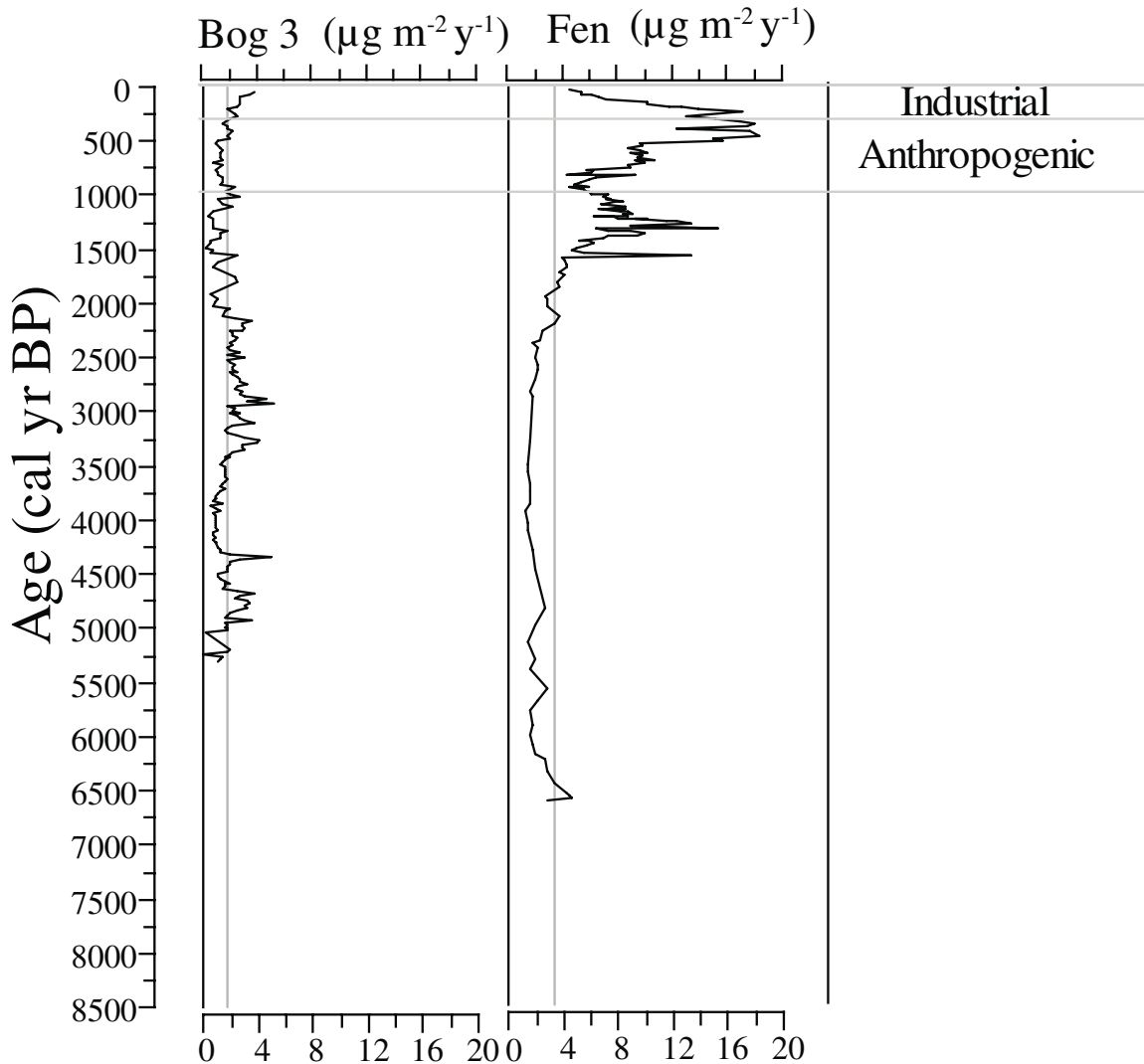


Figure 2 - 3. Hg accumulation rates for core Bog 3 and the Fen core through time (calibrated radiocarbon age in years BP). Hg accumulation rates are in micrograms per meter squared per year. Vertical grey lines represent the adapted enrichment factor method's calculation of pre-anthropogenic Hg accumulation rates for each core.

2.3.2 Mercury Maxima and Anthropogenic Onset

Maximum Hg concentrations and accumulation rates were seen at ~200 cal yrs BP (1800s), which is within ~50 years of the modeled peak Hg emissions in North America (Streets *et al.* 2011). However, earlier increases in Hg concentrations and accumulation were also noteworthy. These are most visible in VM43 and VM45 at ~500 cal yrs BP. This result (earlier than anticipated increases in Hg accumulation rates) is ubiquitous in Hg records and has been linked to early Spanish mining (Nriagu 1994; Martinez-Cortizas

et al. 1999; Alpers *et al.* 2005). In the Hg accumulation rate profiles, this period may seem overly inflated due to a confounding period of low C:N and high DWT (see Appendix A for further analysis), but this could not account for all of the Hg increase since previous periods of low C:N do not have the same Hg concentrations.

Greater than expected Hg deposition prior to the 1800s was also a prediction of the Streets *et al.* (2011) model, which estimated 137 Gg of Hg emissions prior to 1850 based on model inputs. Although the model is thought to overestimate the pre-1850 Hg emissions (Engstrom *et al.* 2014), the occurrence of enhanced Hg accumulation 500 cal years BP is strongly suggested by many other Hg archives, including a lake sediment archive from the northern HBL (Lockhart *et al.* 1995). While the Hg emissions prior to 1850 may have been overestimated by Streets *et al.* (2011), the combination of uncertainty and well documented medieval warm period (MWP) at the time necessitate the use of much earlier accumulation rate data from paleoarchives to get a true average pre-anthropogenic accumulation rate.

2.3.3 Pre-Anthropogenic Mercury Increases

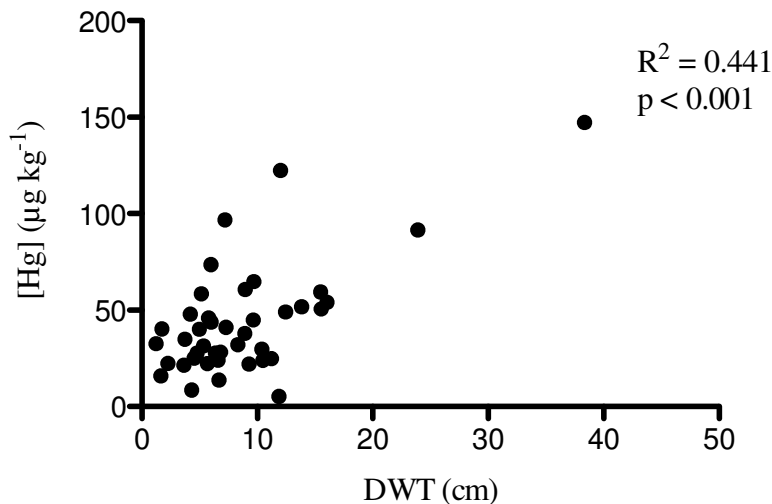
Relatively steady pre-anthropogenic (2700-3800 cal yrs BP) accumulation of Hg was seen in the bog cores. Consistent spikes in Hg accumulation occurred at 150, 600, 2150, and 4650 cal yrs BP in at least two of the cores. More generally, the core Hg accumulation patterns seem to diverge prior to 900 cal yr BP among all three cores. The cores then seem to plateau around ~2700 cal yr BP and intra-core variability is lower until ~3800 cal yr BP.

VM13 displayed enhanced accumulation between 1900-3400 cal yr BP, while VM43 and VM45 displayed average pre-anthropogenic accumulation. Here, the carbon:nitrogen (C:N) ratio drops, which indicates greater nutrient input (N) and less productivity (C) (Appendix A). The C:N quotient can be used as an indicator of humification (how much carbon remains), which is primarily driven by wetness and reinforced by temperature in a peatland (Charman *et al.* 2009). The C and N indicators suggest that the site became more nutrient rich and potentially fen-like, which resulted in an accumulation rate that was 1.7 times higher here than in the rest of the pre-anthropogenic period of the core.

VM43 and VM13 showed low Hg accumulation at ~1400 cal yrs BP, but this is not as clear in VM45. Increases in Hg accumulation on the centennial scale such as those seen in VM43 prior to 3500 cal yrs BP are due to both changes in Hg concentration as well as bulk density (Figure 2 – 1). Some natural climate cycles may explain this periodicity (Appendix A).

2.3.4 Depth to Water Table Relationship with Mercury

Since the cores had been used for previously published paleoclimate reconstructions (Bunbury *et al.* 2012; O'Reilly *et al.* 2014; Packalen *et al.* 2014), qualitative comparisons were made between the inferred climate changes and the variability seen in the core Hg profiles. DWT was one such paleoclimate measure from Bunbury *et al.* (2012) that showed a significant trend when plotted against Hg concentrations in VM43 (Figure 2 – 6). Spearman's non-parametric test was used to compare Hg to DWT reconstructions from VM43, which revealed that wet conditions typically corresponded to times of decreased Hg concentrations ($R^2=0.441$, $p < 0.001$).



changed in peatlands of the Northern Hemisphere (Langdon *et al.* 2003). Hg profiles may have been affected by some of these climate shifts and in a more substantial way than in previous study sites (Givelet *et al.* 2003), which may be due the sensitivity of the study region. Periods of high DWT, associated with dry conditions, occurred most prominently at 3100-3400, 2400, 1400-1600, 600 and present-200 cal yrs BP. These points corresponded to times of increased Hg concentrations.

The reason for the relationship between THg and DWT could have been that wet conditions promoted re-evasion of Hg since this has been demonstrated to promote Hg⁰ emissions from soil similar to the high rates of evasion from lake surfaces (Scholtz *et al.* 2003; Bahlmann *et al.* 2004; Gustin and Stamenkovic 2005; Southworth *et al.* 2007). These studies demonstrated the importance of soil chemistry toward adsorption of Hg onto the soil surface, which is important for retention of Hg. With changing redox and pH characteristics from a raised water table, this could also affect the adsorption of Hg and therefore Hg accumulation. The converse would also be true in that dry peat might have increased adsorption of Hg, which could also be an indicator that these periods had decreased vertical smearing of deposited Hg.

There was no relationship between modeled temperature and Hg, but this is likely due to the use of an old, unrepresentative data set from a geographically distant lake sediment record in the HBL (i.e. not enough was known to complete a temperature using the cores used to study Hg here) (McAndrews *et al.* 1982). Although temperature may have had an effect, very little of the atmospherically deposited Hg would have been re-emitted as a result of change in temperature directly (Amyot *et al.* 2004; Xin and Gustin 2007). Future work should perform paleoclimate analysis directly on the cores being studied for Hg rather than relying on other records for this information.

The relatively small pre-historic variations seen in Hg accumulations, which were originally identified as millennial climate oscillations but did not have enough supporting evidence, could have been the result of changing drainage patterns as the Lowlands rebounded from the previous glaciation (Glaser *et al.* 2004). As drainage patterns changed, the vegetation response to altered water table levels could have been enough to

cause the observed oscillations in Hg concentrations, as well as the inter-core variability. However, further paleohydrology work will need to be done for this process to be completely elucidated. Future work should focus on the relationship between DWT and Hg accumulation in peat so that climate change scenario models can be more accurately incorporated into peatland Hg reservoir models.

2.3.5 Enrichment Factors

Table 2 – 2 shows the increases in enrichment factor using the adapted method over the traditional method of calculation. However, a t-test comparing the enrichment factors of the traditional versus the adapted method shows that the difference is not statistically significant. Although ^{210}Pb dating was not available for VM45, if it had a more similar age-depth model to VM43, VM45 would have had an enrichment factor of 2.88, which is within 4% of the calculated value of VM43. These enrichment factor results are summarized for all three bog cores in Table 1.

Table 2 - 2. Summary of Hg accumulation (Hg Accum.) and Hg concentration [Hg] enrichment factor calculations using both traditional and adapted methods for 3 bog cores in the HBL. Pre-anthropogenic (P) and Modern (M) accumulation rates are used to calculate the enrichment factor (M/P).

	<u>Traditional Method</u>				<u>Adapted Method</u>			
	Hg Accum.	[Hg]	Dates Used	Standard Deviation	Hg Accum.	[Hg]	Dates Used	Standard Deviation
VM43								
P	1.46	38.65	Pre-1850	0.81	1.51	45.30	2700-3800BP	0.56
M	2.85	91.34	Post-1850	1.78	4.20	130.51	Present-1940	2.08
M/P	1.96	2.36			2.78	2.88		
VM45								
P	1.38	38.87	Pre-1850	1.01	1.08	35.07	2700-3800BP	0.29
M	1.72	75.73	Post-1850	0.56	2.07	85.48	Present-1940	0.47
M/P	1.24	1.95			1.92	2.44		
VM13								
P	1.74	43.45	Pre-1850	0.78	1.95	36.00	2700-3800BP	0.78
M	2.88	114.93	Post-1850	0.48	2.96	63.73	Present-1940	0.30
M/P	1.66	2.65			1.52	1.77		
VM33								
P	0.89	52.78	Pre-1850	0.07	1.95	36.00	2700-3800BP	0.78
M	1.61	86.39	Post-1850	0.86	2.38	63.73	Present-1940	0.22
M/P	1.81	1.64			1.22	1.77		

2.3.6 Using Paleoclimate Data to Improve Enrichment Factors

Slightly greater Hg concentrations were seen at the bottom of each core during peat initiation. There were major climate events that caused the initiation of peat in the HBL ~7000 cal yrs BP, so the lowermost sections of the cores were also avoided in the anthropogenic enrichment factor calculation. Particularly near the point of mineral contact there could have been enhanced Hg binding and the underlying clays could have been a source of Hg. Furthermore, in the earliest stages of the coring site VM43 began as a marsh (transition between aquatic and terrestrial vegetation) and subsequently transitioned from a fen to a bog at about 4400 cal yr BP (Bunbury *et al.* 2012). During

those pre-bog periods of marsh and fen characteristics, the increased total Hg concentrations likely came from lateral hydrological and even diagenetic inputs rather than exclusively from the atmosphere. This is likely the case for the fen core of this study, which had an average Hg concentration of $72.8 \pm 42.0 \mu\text{g kg}^{-1}$.

Testate amoeba from VM43 showed a dominance of bog species from ~4400-2400 cal yrs BP, which began to narrow the timeframe used for calculation of pre-anthropogenic Hg accumulation rates. Due to lack of samples from one section of core VM43, further narrowing of the timeframe resulted in the selection of 2700-3800 cal yrs BP for the pre-anthropogenic natural Hg accumulation rates. Not only was the climate relatively consistent during the period of 2700-3800 years BP, this was also during a time where the rate of isostatic rebound began to slow and remained relatively constant (Andrews and Peltier 1989). Ideally, drastic climate and drainage shifts should be avoided in the calculation of the anthropogenic enrichment factor since these can cause Hg accumulation in the peat to become variable.

2.3.7 Comparison to Other Paleomercury Records

Several lake sediment archives from Arctic Alaska, Greenland, New Zealand, Wisconsin and Minnesota show a 3-fold increase in atmospheric Hg concentrations since pre-industrial time (Fitzgerald *et al.* 2005; Bindler *et al.* 2001; Lamborg *et al.* 2002; Swain *et al.* 1992), while others in Minnesota and Nova Scotia have been higher than the values presented here, between 3 and 6-fold increases (Engstrom and Swain 1997; Lamborg *et al.* 2002). However, unlike previous studies, this study shows a difference between enrichment factor results depending on the timeframe used to calculate them. These findings substantiate some of the modelling efforts of Amos *et al.* (2013), who found an atmospheric Hg reservoir mass enrichment factor of 2.6 relative to 1840, but a factor of 7.5 relative to natural (oceanic, terrestrial, and geogenic emissions). While the results here have a large standard deviation, the differences between the two methods of enrichment factor calculation presented in this study are important because they represent an approximate doubling of the anthropogenic enrichment factor when using a more selective timeframe.

Recent criticisms from lake sediment Hg records have suggested that peat archives overestimate Hg accumulations (Engstrom *et al.* 2014; Biester *et al.* 2007). Lake sediment Hg records have reported an average pre-industrial accumulation rate of 3-3.5 $\mu\text{g m}^{-2} \text{y}^{-1}$, and post-industrial of 10-20 $\mu\text{g m}^{-2} \text{y}^{-1}$. In this study of peat from the HBL, the bog cores displayed a lower pre-industrial ($1.51 \pm 0.56 \mu\text{g m}^{-2} \text{y}^{-1}$) and industrial accumulation rate ($4.20 \pm 2.08 \mu\text{g m}^{-2} \text{y}^{-1}$), but a similar relative enrichment factor. These results seem to refute some concern that peat consistently overestimates the enrichment factor and suggest that the enrichment factor in previous paleorecords may actually underestimate the anthropogenic enrichment factor.

2.4 Conclusion

It is clear from this study that paleo-Hg records must extend thousands of years into the past in order to adequately quantify pre-anthropogenic Hg accumulation rates. Using a comparison of more recent and much older Hg accumulation rates as suggested by Amos *et al.* (2013) produces higher anthropogenic enrichment factors in bog cores. The results also suggest that large-scale climate variations, small changes in local factors such as micro-topography and drainage can have large effects on the amount of Hg that accumulates in peat. Further investigation of Hg dynamics using both paleoclimate and paleohydrology may better explain these trends.

2.5 References

- Alpers, C. N.; Hunerlach, M. P.; May, J. T.; Hothem, R. L., Mercury contamination from historical gold mining in California. **2005**.
- Amos, H.M.; Jacob, D.J.; Streets, D.G.; Sunderland, E.M. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. *Global Biogeochem. Cy.* **2013**, 27 (2), 410-421.
- Amyot, M.; Southworth, G.; Lindberg, S.; Hintelmann, H.; Lalonde, J.; Ogrinc, N.; Poulain, A.; Sandilands, K., Formation and evasion of dissolved gaseous mercury in large enclosures amended with $^{200}\text{HgCl}_2$. *Atmos. Environ.* **2004**, 38, (26), 4279-4289.
- Andrews, J. and Peltier, W. Quaternary geodynamics in Canada. *Quaternary geology of Canada and Greenland* **1989**, 1, 541-572.
- Bahlmann, E.; Ebinghaus, R.; Ruck, W., The effect of soil moisture on the emission of mercury from soils. *Materials and Geoenvironment* **2004**, 51, (2), 791-794.
- Benoit, J.; Fitzgerald, W.; Damman, A. The biogeochemistry of an ombrotrophic bog: Evaluation of use as an archive of atmospheric mercury deposition. *Environ. Res.* **1998**, 78 (2), 118-133.
- Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D.R. Modeling the past atmospheric deposition of mercury using natural archives. *Environ. Sci. Technol.* **2007**, 41 (14), 4851-4860.
- Bindler, R. Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in southern Sweden. *Environ. Sci. Technol.* **2003**, 37 (1), 40-46.
- Bindler, R., Mired in the past—looking to the future: geochemistry of peat and the analysis of past environmental changes. *Global Planet. Change* **2006**, 53, (4), 209-221.
- Bindler, R.; Klarqvist, M.; Klaminder, J.; Förster, J., Does within-bog spatial variability of mercury and lead constrain reconstructions of absolute deposition rates from single peat records? The example of Store Mosse, Sweden. *Global Biogeochem. Cy.* **2004**, 18, (3).
- Bindler, R.; Renberg, I.; Appleby, P.G.; Anderson, N.J.; Rose, N.L. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: A coast to ice margin transect. *Environ. Sci. Technol.* **2001**, 35 (9).
- Blaauw, M. Methods and code for 'classical' age-modelling of radiocarbon sequences. *Quat. Geochronol.* **2010**, 5 (5), 512-518.
- Bunbury, J.; Finkelstein, S.A.; Bollmann, J. Holocene hydro-climatic change and effects on carbon accumulation inferred from a peat bog in the Attawapiskat River watershed, Hudson Bay Lowlands, Canada. *Quatern. Res.* **2012**, 78 (2), 275-284.

- Clarkson, T.W.; Magos, L.; Myers, G.J. The toxicology of mercury—current exposures and clinical manifestations. *N. Engl. J. Med.* **2003**, *349* (18), 1731-1737.
- Clymo, R. Interactions of Sphagnum with water and air. *Effects of Atmospheric Pollutants on Forests, Wetlands, and Agricultural Ecosystems*. Springer-Verlag New York. 1987. p 513-529, 4 fig, 35 ref. **1987**.
- Charman, D. J.; Barber, K. E.; Blaauw, M.; Langdon, P. G.; Mauquoy, D.; Daley, T. J.; Hughes, P. D.; Karofeld, E., Climate drivers for peatland palaeoclimate records. *Quaternary Sci. Rev.* **2009**, *28*, (19), 1811-1819.
- Coggins, A. M.; Jennings, S. G.; Ebinghaus, R., Accumulation rates of the heavy metals lead, mercury and cadmium in ombrotrophic peatlands in the west of Ireland. *Atmos. Environ.* **2006**, *40*, (2), 260-278.
- Dyke, A. S.; Prest, V. K., Late Wisconsinan and Holocene history of the Laurentide ice sheet. *Géographie physique et Quaternaire* **1987**, *41*, (2), 237-263.
- Engstrom, D. R.; Fitzgerald, W. F.; Cooke, C. A.; Lamborg, C. H.; Drevnick, P. E.; Swain, E. B.; Balogh, S. J.; Balcom, P. H., Atmospheric Hg emissions from preindustrial gold and silver extraction in the americas: a reevaluation from lake-sediment archives. *Environ. Sci. Technol.* **2014**, *48*, (12), 6533-43.
- Engstrom, D. R.; Swain, E. B., Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* **1997**, *31*, (4).
- Environment Canada, 2011. Canadian climate normals. Environment Canada, Ottawa. Available at http://www.climate.weatheroffice.gc.ca/climate_normals/.
- E.P.A. (2007a) Chapter 3 – Inorganic Analytes. Revision 4. Retrieved from <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap3.pdf>
- E.P.A. (2007b) Method 7473 – Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry, Revision 0. Retrieved from <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7473.pdf>
- Fitzgerald, W.F.; Engstrom, D.R.; Lamborg, C.H.; Tseng, C.; Balcom, P.H.; Hammerschmidt, C.R. Modern and historic atmospheric mercury fluxes in northern Alaska: global sources and Arctic depletion. *Environ. Sci. Technol.* **2005**, *39* (2), 557-568.
- Fitzgerald, W.; Engstrom, D.; Mason, R.; Nater, E. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32* (1), 1-7.
- Franzen, C.; Kilian, R.; Biester, H. Natural mercury enrichment in a minerogenic fen—evaluation of sources and processes. *J. Environ. Monit.* **2004**, *6* (5), 466-472.
- Gehrke, G. E.; Blum, J. D.; Slotton, D. G.; Greenfield, B. K., Mercury isotopes link mercury in San Francisco Bay forage fish to surface sediments. *Environ. Sci. Technol.* **2011**, *45*, (4), 1264-1270.
- Givelet, N.; Le Roux, G.; Cheburkin, A.; Chen, B.; Frank, J.; Goodsite, M. E.; Kempter, H.; Krachler, M.; Noernberg, T.; Rausch, N.; Rheinberger, S.; Roos-Barraclough,

- F.; Sapkota, A.; Scholz, C.; Shotyk, W., Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses RID E-7026-2010. *J. Environ. Monit.* **2004a**, 6, (5), 481-492.
- Givelet, N.; Roos-Barraclough, F.; Goodsite, M.; Cheburkin, A.; Shotyk, W. Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the high Arctic of Canada recorded by peat hummocks. *Environ. Sci. Technol.* **2004b**, 38 (19), 4964-4972.
- Givelet, N.; Roos-Barraclough, F.; Shotyk, W. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years). *J. Environ. Monit.* **2003**, 5 (6), 935-949.
- Glaser, P.H.; Hansen, B.; Siegel, D.I.; Reeve, A.S.; Morin, P.J. Rates, pathways and drivers for peatland development in the Hudson Bay Lowlands, northern Ontario, Canada. *J. Ecol.* **2004**, 92 (6), 1036-1053.
- Glooschenko, W. A.; Roulet, N. T.; Barrie, L. A.; Schiff, H. I.; McAdie, H. G., The Northern Wetlands Study (Nowes) - an Overview. *J. Geophys. Res.-Atmos.* **1994**, 99, (D1), 1423-1428.
- Goodsite, M.E.; Outridge, P.; Christensen, J.H.; Dastoor, A.; Muir, D.; Travnikov, O.; Wilson, S. How well do environmental archives of atmospheric mercury deposition in the Arctic reproduce rates and trends depicted by atmospheric models and measurements? *Sci. Total Environ.* **2013**, 452, 196-207.
- Gustin, M. S.; Stamenkovic, J., Effect of watering and soil moisture on mercury emissions from soils. *Biogeochemistry* **2005**, 76, (2), 215-232.
- Hughes, P.; Mauquoy, D.; Barber, K.; Langdon, P. Mire-development pathways and palaeoclimatic records from a full Holocene peat archive at Walton Moss, Cumbria, England. *Holocene* **2000**, 10 (4), 465-479.
- Jeglum, J.; Rothwell, R.; Berry, G.; Smith, G. A peat sampler for rapid survey. *Frontline Technical Note, Can. For. Serv., Sault Ste.Marie, Ont, Canada* **1992**, .
- Jowsey, P. An improved peat sampler. *New Phytol.* **1966**, 65 (2), 245-248.
- Juggins, S., C2 User guide. *Software for ecological and palaeoecological data analysis and visualisation. University of Newcastle, Newcastle upon Tyne, UK* **2003**, 69.
- Lamborg, C. H.; Fitzgerald, W. F.; Damman, A. W. H.; Benoit, J. M.; Balcom, P. H.; Engstrom, D. R., Modern and historic atmospheric mercury fluxes in both hemispheres: Global and regional mercury cycling implications. *Global Biogeochem. Cy.* **2002**, 16, (4), 11.
- Langdon, P. G.; Barber, K. E.; Hughes, P. D. M., A 7500-year peat-based palaeoclimatic reconstruction and evidence for an 1100-year cyclicality in bog surface wetness from Temple Hill Moss, Pentland Hills, southeast Scotland. *Quatern. Sci. Rev.* **2003**, 22, (2), 259-274.

- Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C., A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36*, (1), 19-32.
- Lockhart, W.; Wilkinson, P.; Billeck, B.; Hunt, R.; Wagemann, R.; Brunskill, G. Current and historical inputs of mercury to high-latitude lakes in Canada and to Hudson Bay. *Water Air Soil Pollut.* **1995**, *80* (1-4), 603-610.
- Martinez-Cortizas, A.; Pontevedra-Pombal, X.; Garcia-Rodeja, E.; Novoa-Munoz, J. C.; Shotyk, W., Mercury in a Spanish peat bog: Archive of climate change and atmospheric metal deposition. *Science* **1999**, *284*, (5416), 939-942.
- Martini, I.; Martini, I.; Cortizas, A.; Chesworth, W., The cold-climate peatlands of the Hudson Bay Lowland, Canada: brief overview of recent work. *Peatlands: Evolution and Records of Environmental and Climate Changes* **2006**, 53-84.
- Mason, R. P.; Fitzgerald, W. F. a.; Morel, F. M. M., The biogeochemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Ac.* **1994**, *58*, (15), 3191-3198.
- McAndrews, J. H.; Riley, J. L.; Davis, A. M., Vegetation history of the Hudson Bay Lowland: a postglacial pollen diagram from the Sutton Ridge. *Le Naturaliste Canadien* **1982**.
- Nriagu, J. O., Legacy of Mercury Pollution. *Nature* **1993**, *363*, (6430), 589-589.
- Nriagu, J. O., Mercury pollution from the past mining of gold and silver in the Americas. *Sci. Total Environ.* **1994**, *149*, (3), 167-181.
- O'Reilly, B.C.; Finkelstein, S.A.; Bunbury, J. Pollen-Derived Paleovegetation Reconstruction and Long-Term Carbon Accumulation at a Fen Site in the Attawapiskat River Watershed, Hudson Bay Lowlands, Canada. *Arct. Antarct. Alp. Res.* **2014**, *46* (1), 6-18.
- Outridge, P.; Rausch, N.; Percival, J.; Shotyk, W.; McNeely, R. Comparison of mercury and zinc profiles in peat and lake sediment archives with historical changes in emissions from the Flin Flon metal smelter, Manitoba, Canada. *Sci. Total Environ.* **2011**, *409* (3), 548-563.
- Packalen, M. S.; Finkelstein, S. A.; McLaughlin, J. W., Carbon storage and potential methane production in the Hudson Bay Lowlands since mid-Holocene peat initiation. *Nat. Commun.* **2014**, *5*.
- Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R. B.; Friedli, H. R.; Leaner, J.; Mason, R.; Mukherjee, A. B.; Stracher, G. B.; Streets, D. G., Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10*, (13), 5951-5964.
- R Development Core Team *R: a language and environment for statistical computing*, R Foundation for Statistical Computing: Vienna, Austria, 2011.
- Rasmussen, P.E. Current methods of estimating atmospheric mercury fluxes in remote areas. *Environ. Sci. Technol.* **1994**, *28* (13), 2233-2241.

- Reimer, P. J.; Baillie, M. G. L.; Bard, E.; Bayliss, A.; Beck, J. W.; Blackwell, P. G.; Ramsey, C. B.; Buck, C. E.; Burr, G. S.; Edwards, R. L., IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. **2009**.
- Riley, J. L., *Flora of the Hudson Bay Lowland and its postglacial origins*. NRC Research Press: 2003.
- Riley, J. L., Wetlands of the Ontario Hudson Bay lowland: a regional overview. *Nature Conservancy of Canada: Toronto, Ontario, Canada* **2011**, 156.
- Roos-Barraclough, F.; Givelet, N.; Cheburkin, A.; Shotyk, W.; Norton, S. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: A 10000-year record from Caribou Bog, Maine. *Environ. Sci. Technol.* **2006**, 40 (10), 3188-3194.
- Scholtz, M.; Van Heyst, B.; Schroeder, W., Modelling of mercury emissions from background soils. *Sci. Total Environ.* **2003**, 304, (1), 185-207.
- Schuster, P.; Krabbenhoft, D.; Naftz, D.; Cecil, L.; Olson, M.; Dewild, J.; Susong, D.; Green, J.; Abbott, M. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **2002**, 36 (11), 2303-2310.
- Shotyk, W. Natural and anthropogenic enrichments of As, Cu, Pb, Sb, and Zn in ombrotrophic versus minerotrophic peat bog profiles, Jura Mountains, Switzerland. *Water Air Soil Poll.* **1996**, 90 (3-4), 375-405.
- Shotyk, W.; Goodsite, M.; Roos-Barraclough, F.; Frei, R.; Heinemeier, J.; Asmund, G.; Lohse, C.; Hansen, T. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the ^{14}C "bomb pulse curve". *Geochim. Cosmochim. Ac.* **2003**, 67 (21), 3991-4011.
- St. Louis, V.L.; Rudd, J.W.; Kelly, C.A.; Hall, B.D.; Rolfhus, K.R.; Scott, K.J.; Lindberg, S.E.; Dong, W. Importance of the forest canopy to fluxes of methyl mercury and total mercury to boreal ecosystems. *Environ. Sci. Technol.* **2001**, 35 (15), 3089-3098.
- Streets, D.G.; Devane, M.K.; Lu, Z.; Bond, T.C.; Sunderland, E.M.; Jacob, D.J. All-Time Releases of Mercury to the Atmosphere from Human Activities. *Environ. Sci. Technol.* **2011**, 45(24), 10485-10491.
- Stuiver, M.; Reimer, P.; Bard, E.; Beck, J.; Burr, G.; Hughen, K.; Kromer, B.; McCormac, G.; Van der Plicht, J.; Spurk, M. INTCAL98 radiocarbon age calibration, 24,000-0 cal BP. *Radiocarbon* **1998**, 40 (3), 1041-1083.
- Swain, E.B.; Engstrom, D.R.; Brigham, M.E.; Henning, T.A.; Brezonik, P.L. Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* **1992**, 257(5071), 784-787.
- Xin, M.; Gustin, M.; Johnson, D., Laboratory investigation of the potential for re-emission of atmospherically derived Hg from soils. *Environ. Sci. Technol.* **2007**, 41, (14), 4946-4951.

Chapter 3

3 Spatial Gradients of Atmospheric Mercury Accumulation in Peat Cores from the James Bay Lowland, Canada

3.1 Introduction

3.1.1 Mercury as a Global Pollutant

Mercury (Hg) is a global, persistent pollutant that is toxic and ubiquitous in the environment. Sources of Hg to the atmosphere today are predominantly anthropogenic: fossil fuel burning; mining; and manufacturing (Pirrone *et al.* 2010). Still, natural sources such as volcanoes, geothermal, and re-evaporation/erosion of Hg from the landscape are contributors to atmospheric Hg concentrations (Pirrone *et al.* 2001). Once emitted, elemental Hg has an atmospheric residence time of ~0.75 years (Lindberg *et al.* 2007), which allows sufficient time for Hg to be transported to remote locations. The dominant source of Hg to remote ecosystems is atmospheric deposition of elemental Hg (Fitzgerald *et al.* 1998; Schroeder and Munthe 1998, Lindberg *et al.* 2007).

In northern high latitudes, complex atmospheric interactions can occur to cause heterogeneous deposition of Hg. Polar regions of Canada are sites of phenomena called Atmospheric Mercury Depletion Events (AMDE), which occur during polar sunrise in the spring (Schroeder *et al.*, 1998; Lindberg *et al.*, 2002). These depletion events cause periodic reductions of gaseous elemental Hg concentrations in the atmosphere due to rapid deposition. Photo-chemically reactive free radical halogens such as chloride (Cl) and bromide (Br⁻) species, in addition to ultraviolet (UV) radiation, cause oxidation of Hg⁰ to Hg²⁺ in the atmosphere and therefore speed the rate of Hg deposition from the atmosphere (Schroeder and Munthe 1998).

Plumes of reactive bromine monoxide (BrO) have been shown to infiltrate the troposphere around the Hudson Bay Lowlands (HBL) and James Bay Lowland (JBL) (Begoïn *et al.* 2010). Br⁻ species have also been previously correlated with Hg accumulation in peat archives (Roos-Barraclough *et al.* 2002). It has not yet been investigated whether or not regular atmospheric Hg depletions could have a long-term

regional effect on Hg accumulation in the peats of more northern sites in the JBL and HBL. Moreover, since sea spray is likely to be the dominant source of Br⁻ to the peat, proximity to the Hudson and James Bay should also play a role in historical Hg accumulation in the HBL.

More recent local emissions could also cause heterogeneous deposition of Hg in the HBL. Sites near the southern tip of James Bay have been settled and are affected by local anthropogenic activity, whereas more northern sites are less impacted. Outridge *et al.* (2011) suggested that there was significant influence from the Flin Flon smelter in a lake sediment archive from Flin Flon, Manitoba, Canada, where Hg emissions were never monitored. In the largest, most spatially extensive lake sediment archive study in North America, small but significant differences were seen across a latitudinal gradient with lower enrichment factors in the Arctic and higher enrichment in subarctic and mid-latitude lakes (Muir *et al.* 2009). However, within the subarctic range, long-term variability across a latitudinal gradient and effects of proximity to marine environments have not yet been explored in the HBL. Moreover, peat archives from central Canada have not yet been used to examine North American latitudinal or longitudinal trends.

3.1.2 Historical Mercury Accumulation Rates Across Latitudinal Gradients

Various studies have suggested that anthropogenic contributions have increased the global atmospheric Hg pool by 2-5 times (*e.g.* Asmund and Nielson 2000; Bindler *et al.* 2003; Fitzgerald *et al.* 2005; Roos-Barraclough *et al.* 2006; Biester *et al.* 2007; Martinez Cortizas 2012). Paleorecords in lake sediments (*e.g.* Engstrom and Swain 1997; Rydberg *et al.* 2008) and peatlands (*e.g.* Benoit *et al.* 1998; Martinez-Cortizas *et al.* 1999) have shown that these media are reliable proxies for historical Hg accumulation rates, albeit with caveats (see Chapter 1). Peatlands are still commonly used archives to represent deposition of Hg (Steinnes and Sjøbakk 2005; Farmer *et al.* 2009; Allan *et al.* 2013) and other pollutants (Outridge *et al.* 2011) because ombrotrophic peat doming causes vegetation to grow in isolation of Hg sources other than rainwater (Damman 1978). Therefore, at ombrotrophic bog sites, there is only one source of Hg, which acts to reduce variability from other possible sources. It is assumed that Hg is immobile once deposited

in ombrotrophic peat, which allows for reliable radiocarbon dating and for paleo-Hg records to be reconstructed (Benoit *et al.* 1998).

Many reconstructions of past atmospheric deposition have studied peat cores that are relatively short, with the oldest peat dating only a few hundred years BP (*e.g.* Shuster *et al.* 2002; Muir *et al.* 2009) and no long-term records have looked at spatial gradients. In general, these reconstructions have been focused on the onset of the modern industrial revolution (*ca.* 1850). In order to accurately quantify the contributions of anthropogenically-derived Hg to the atmosphere and subsequent deposition, studies need to look at records that date back thousands of years (Chapter 2). Otherwise, the natural variability in Hg accumulation can contribute to an overestimation of pre-anthropogenic accumulation rates and therefore an erroneous estimation of the anthropogenic contribution (see Givelet *et al.* 2004). For similar reasons, it is also important to use a medium from a pristine, remote location to avoid Hg derived from local-regional sources that would obfuscate the well-mixed atmospheric pool of Hg (Fitzgerald *et al.* 1998). The HBL offers such a medium in its pristine, northern peatlands. The objective of this study is to use long cores to:

- 1) Provide a representative anthropogenic enrichment factor of the entire HBL, and;
- 2) Analyze a latitudinal and longitudinal gradient across the HBL to test whether Muir *et al.* (2009) lake sediment records are replicable in the peat Hg record.

3.2 Methods

3.2.1 Study Site

Peat cores were collected from 2009-2012 from many locations in the HBL including: Hawley Lake, Kinoje Lake, Fort Hope, and Victor Mine (Table 3 – 1; Figure 3 – 1). Due to availability, several cores were taken from more fen-like peat structures (ridge/flark pattern and poor fen with raised bog). The cores were taken from the bog-like features within these structures (ridge and raised bog). Although Fort Hope is just outside of the strictly delimited HBL, it was collected from a bog feature that was representative of the western HBL.

A weather station nearby Hawley Lake and Fort Hope, located at Big Trout Lake, has a mean annual, January and July temperature average of -2.7, -23.7, and 16.2 respectively and a mean total annual precipitation of 609.1 based on climate normal data from 1981-2010 (Environment Canada 2011). Further south at Moosonee, the closest weather station to Kinoje, the mean annual, January and July temperature averages -1.1, -20.7, and 15.4 respectively and a mean total annual precipitation of 681.6 based on climate normal data from 1981-2010 (Environment Canada 2011). The HBL is an ecoregion dominated by peatlands covering an area of ~372,000 km² (Figure. 3 – 1, shaded area). See Chapter 1 for a description of peatland initiation and underlying strata.

Table 3 - 1. Summary of core collection site local characteristics from vegetation surveys at time of core collection. See Chapter 2: Table 2 - 1 for Victor Mine core collection site local characteristics.

Core	Vegetation classification	Vegetation survey
Southwest	Bog	No vegetation survey available. Collected 2012.
Southeast 1	Bog	No vegetation survey available. Collected 2009.
Southeast 2	Bog	No vegetation survey available. Collected 2009.
North 1	Poor fen, patterned with ridge/flark (floating) structure	<i>Picea abies</i> and <i>Larix laricina</i> present on bog ridges, with lichen and <i>Ericaceae spp.</i> Floating mat dominated by <i>Cyperaceae</i> , with bryophytes throughout. Collected 2011.
North 2	Treed poor fen, patterned with raised treed bog and floating fen features	<i>Picea abies</i> and <i>Larix laricina</i> present on bog ridges, with lichen and <i>Ericaceae spp.</i> Floating mat dominated by <i>Cyperaceae</i> , with <i>Equisetum</i> present along flark margins and bryophyte spp. throughout. Collected 2011.

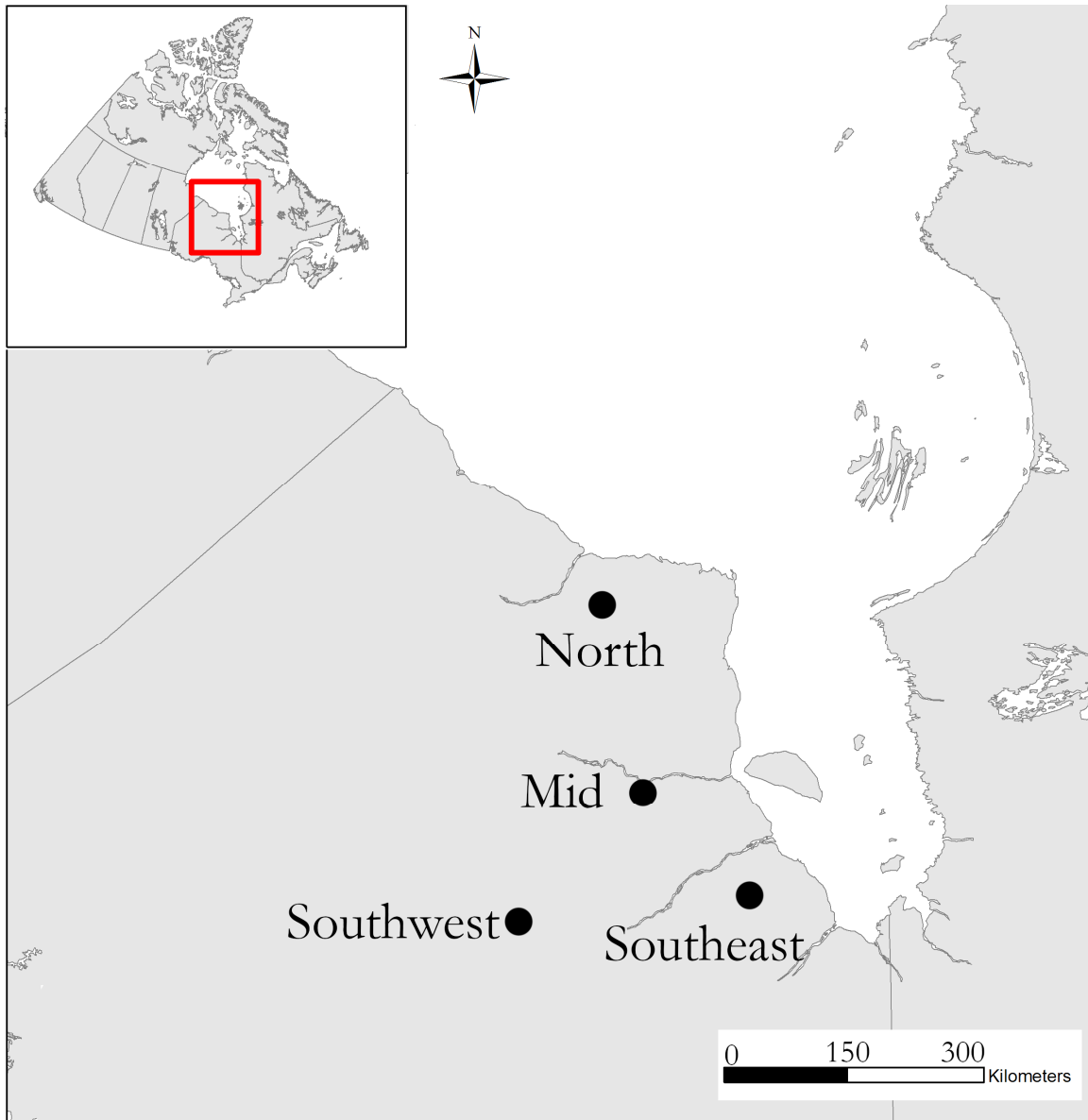


Figure 3 - 1. North; Mid; Southwest; and Southeast in the Hudson Bay Lowlands and reference cities are indicated by black circles in Northern Ontario, Canada.

3.2.2 Core Selection

Cores were selected from an extensive collection taken by the Ministry of Natural Resources (MNR) in 2009 and 2011 as well as a more recent sampling in 2012 by Maara Packalen from the University of Toronto. The collection has a wide spatial distribution,

representing northern, southern, eastern, and western regions of the HBL. The more North core sites were near Hawley Lake, located at 54.68° N, -84.60° W and 54.75° N, -84.53° W. Previously sampled cores from the Mid-HBL at Victor Mine were discussed in Chapter 2.2.1 (approximate coordinates of 53° N, -84° W). At the Southeast core site, cores were sampled near Kinoje Lake, located at 51.59° N, -81.78° W and 51.59° N, -81.79° W. Due to availability, only one core was sampled from the west periphery of the HBL at Southwest core site (51.18° N, -86.78° W). While more cores exist in the MNR collection, only the 9 studied here were chosen for radiocarbon dating, peat type (only bogs features are ideal), completeness of core records, and availability of ancillary data. The exception to the peat type limitation was Hawley Lake, which had to have fen-like cores selected in order to provide a latitudinal gradient.

3.2.3 Core Sampling

Surface peat (upper ~ 50 cm) was collected using a Jeglum corer (Jeglum *et al.* 1992) with a 10 x 10 cm box to eliminate compaction. Lower strata were collected in sections using a Russian chamber peat corer with a 50 cm barrel (Jowsey 1966). Mineral contact at the base of the peat cores was retrieved in all cases except for North core 2, which was assumed to be at the mineral contact even though it was not collected in the corer. Cores were double wrapped in plastic and aluminum foil, stored in rigid plastic pipe in the dark at +4°C until analysis.

3.2.4 Core Characteristics and Stratigraphy

Bulk densities and % carbon (C) were calculated by the Finkelstein lab group at the University of Toronto (Appendix B). Core sub-samples were taken at an interval of 4 cm or less for all cores. A peat sample volume of 1 cm³ was taken from the core with an open topped syringe and transferred to a metal sample dish where it was weighed (wet) and then placed in a drying oven. Samples were dried for more than 24 hours at 100°C, after which the dry weight was measured.

3.2.5 Mercury Analysis

Hg subsamples were taken from the cores from 2012-2013. Analysis was performed as described in 2.2.3.

3.2.6 Dating of Peat and Estimation of Accumulation Rates

Samples of wood, *Sphagnum* stems, conifer needles, twigs, and herbaceous remains were collected from the cores and cleaned using standard methods for radiocarbon analysis (Appendix B). Radiocarbon dates were calibrated in the program CALIB (ver 6.0.1) using the INTCAL09 calibration curve (Reimer *et al.* 2009; Stuiver *et al.* 1998). The package *clam* for the software program R (Blaauw 2010; R Development Core Team 2011) was used to develop all age-depth models, using linear interpolation between data points (Appendix B).

The calculation for accumulation rate is summarized by the following equation:

$$\text{Accumulation Rate} = \text{HgT} * \text{BD} / \text{time}$$

Where HgT is the total Hg concentration ($\mu\text{g kg}^{-1}$), BD is the bulk density (g cm^{-3}), and time is the difference between calibrated radiocarbon dates. After unit conversions, this is a measure of the average Hg mass that accumulated per square meter area each year.

3.2.7 Enrichment Factor

Enrichment factors were calculated using non-standard methods due to the wealth of paleoclimate and stratigraphic information available for the cores. These methods were described in Chapter 2.2.7. Typically, the standard method is to use a single datum (often 1850AD) as a time stamp for the onset of industrial activity. However, this date has been shown to be too recent due to the high uncertainty associated with earlier anthropogenic contributions of Hg to the atmosphere. Additionally, the global pool of atmospheric Hg is thought to be relatively well mixed (Lindqvist and Rodhe 1985), which means that the emissions from other continents can be deposited in Canada. Hg contributions from other continents are known to have begun well before 1850AD.

Although ancient Hg emissions were likely small (Chapter 2, Engstrom *et al.* 2014), there is strong evidence to suggest that mining activity since ~500 cal yrs BP has been a larger than anticipated source of atmospheric Hg (Nriagu 1993; Streets *et al.* 2011). Therefore, enrichment factor calculations should be done using much older peat to avoid biasing the average enrichment with the exclusion of clear anthropogenically derived data points. By taking a Hg accumulation rate average from 2700-3800 cal yr BP, the aforementioned anthropogenic mining periods of Ag, Au, and Hg can be avoided, which reduces the possibility of underestimating the anthropogenic enrichment factor. Correlations of Hg enrichment factors with latitude were done using the software programs Prism and SPSS.

3.3 Results

3.3.1 Core Characteristics and Stratigraphy

Distinct differences in humification and types of decomposing vegetation were observed qualitatively between northern and southern cores (see Appendix B). Northern cores were less decomposed due to the colder temperatures and exhibited characteristics of darker, richer soil. Overall length and age of the cores were different due to varying peat depth. Depth profiles result from timing of emergence of the peatland, which is a function of distance inland, latitude, and elevation (Packalen *et al.* 2014).

3.3.2 Mercury Profiles

The profiles revealed a much earlier than anticipated increase in Hg concentrations and accumulations. Still, most of the cores show Hg concentration maxima more recent than 900 cal yr BP. There was a large discrepancy between timing of each core's Hg maximum. However, for cores such as on Southeast core 1 and one North core 1, this was due to bulk density and age-depth model variation as the Hg concentration maximum occurred much more recently than the Hg accumulation maximum.

Several cores also had higher than normal pre-anthropogenic baseline averages. Both Southeastern cores, and North core 2 had pre-anthropogenic accumulation rates of 1.63 ± 0.46 , 2.32 ± 0.79 , and $1.89 \pm 0.83 \mu\text{g m}^{-2} \text{y}^{-1}$ respectively (Table 3 – 2). Bog 1, Bog 2, and the Southwest core showed an average pre-anthropogenic accumulation rate of 1.32

$\mu\text{g m}^{-2} \text{y}^{-1}$ (Figure 3 – 2; Figure 3 – 3; Chapter 2). The Hg profiles are presented in Figures 3 – 2 through 3 – 4 and timing of Hg accumulation and concentration maxima and minima are summarized in Table 3 – 3.

Table 3 - 2. Mean pre-anthropogenic and modern Hg accumulations in micrograms per meter squared per year and [Hg] (Hg concentrations in micrograms per kilogram) with their associated standard deviations as used to calculate the anthropogenic enrichment factor for each peat core.

	Accumulation	[Hg]	Dates Used	Standard Deviation
Southwest				
Pre-anthropogenic	1.38	34.98	2700-3800 BP	0.56
Modern	2.56	84.14	Present-1940	1.21
Enrichment	1.86	2.41		1.15
Southeast 1				
Pre-anthropogenic	1.63	51.58	2700-3800 BP	0.46
Modern	3.60	76.36	Present-1940	1.17
Enrichment	2.21	1.48		0.96
Southeast 2				
Pre-anthropogenic	2.32	64.96	2700-3800 BP	0.79
Modern	5.68	128.40	Present-1940	2.06
Enrichment	2.45	1.98		1.22
North 1				
Pre-anthropogenic	1.89	75.27	2700-3800 BP	0.83
Modern	4.41	165.73	Present-1940	-
Enrichment	2.33	2.20		-
North 2				
Pre-anthropogenic	1.61	25.66	2700-3800 BP	0.90
Modern	2.06	70.90	Present-1940	0.37
Enrichment	1.28	2.76		0.75

Table 3 - 3. Summary of Hg accumulation and concentration maxima and minima as well as their associated variance in both the pre-anthropogenic and modern timeframe.

	Maximum Hg Accumulation	Maximum Hg Concentration	Minimum Hg Accumulation	Minimum Hg Concentration
Southwest	12.16	218.87	0.34	8.14
Date (cal yr BP)	640	640	3540	3540
Southeast 1	45.07	351.74	0.94	40.39
Date (cal yr BP)	302	302	1456	3405
Southeast 2	15.91	199.98	0.64	26.57
Date (cal yr BP)	216	59	446	193
North 1	7.90	301.84	0.91	43.53
Date (cal yr BP)	70	70	651	2715
North 2	6.62	117.16	0.14	2.09
Date (cal yr BP)	611	381	3298	3298

Southwest shows stable Hg concentrations and accumulation rates until ~900 cal yrs (Figure 3 – 2). This increase also coincides with higher bulk density at nearly the same progression. This gradual increase in Hg concentrations and accumulation rates comes to a maximum at 640 cal yrs BP.

Southeast 1 and Southeast 2 show similar accumulations prior to 900 cal yrs BP (Figure 3 – 2). However, the timing of the Hg maxima are ~100 years apart between these two cores from the same location. These differences are due to the slightly different age-models produced for the cores, the different bulk densities, and even differences in the Hg concentration profile. There is a gap in that data that exists for Southeast 1 because a segment of the core had been overly sampled such that no Hg sub-samples could be taken.

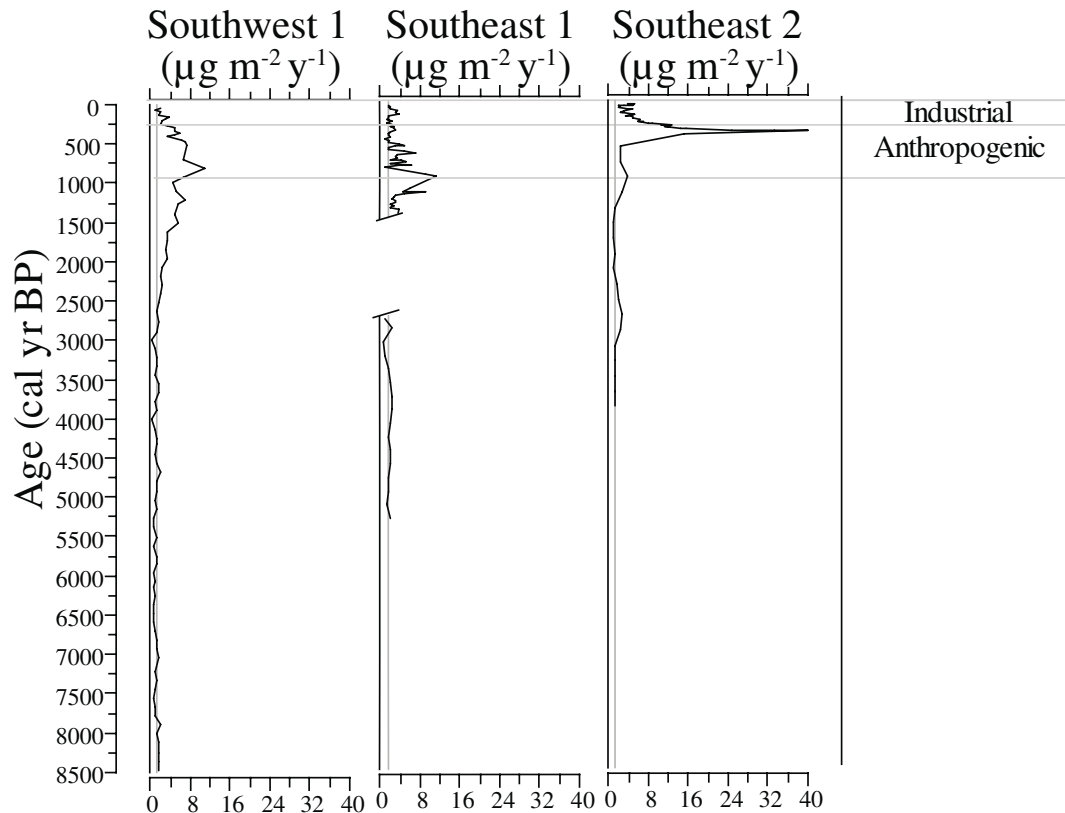


Figure 3 - 2. Hg data for Southwest, Southeast 1 and Southeast 2 peat cores (from left to right). Hg accumulation in micrograms per meter squared per year.

The Fen core was the only core to show large Hg accumulation rates prior to 900 cal yrs BP (Figure 3 – 4). These rates coincided with a period of higher bulk density (likely dry, reduced decomposition, rapid growth rate). The Hg concentration profile is relatively stable except for four points: 1250, 2000, 4750, and 5500 cal yrs BP, where there were increased Hg concentrations. The first point was during the peak long term carbon accumulation rate where peat growth was estimated to be at its fastest. The second and third occurred without any cause indicated by bulk density, C:N, or LORCA (bulk density from O’Reilly *et al.* 2014). Finally, the increased Hg concentration seen at 5500 cal yrs BP occurred during a spike in C:N.

Bog 3 begins to show higher Hg concentrations than any pre-anthropogenic point after 300 cal yrs BP (Figure 3 – 4). There was, however, a period of higher Hg concentrations and accumulations between 2000-3150 cal yrs BP. This period does not correlate to

changes in bulk density of C:N. VM13 had the highest variability of the mid-HBL cores with a standard deviation of $0.78 \mu\text{g m}^{-2} \text{y}^{-1}$.

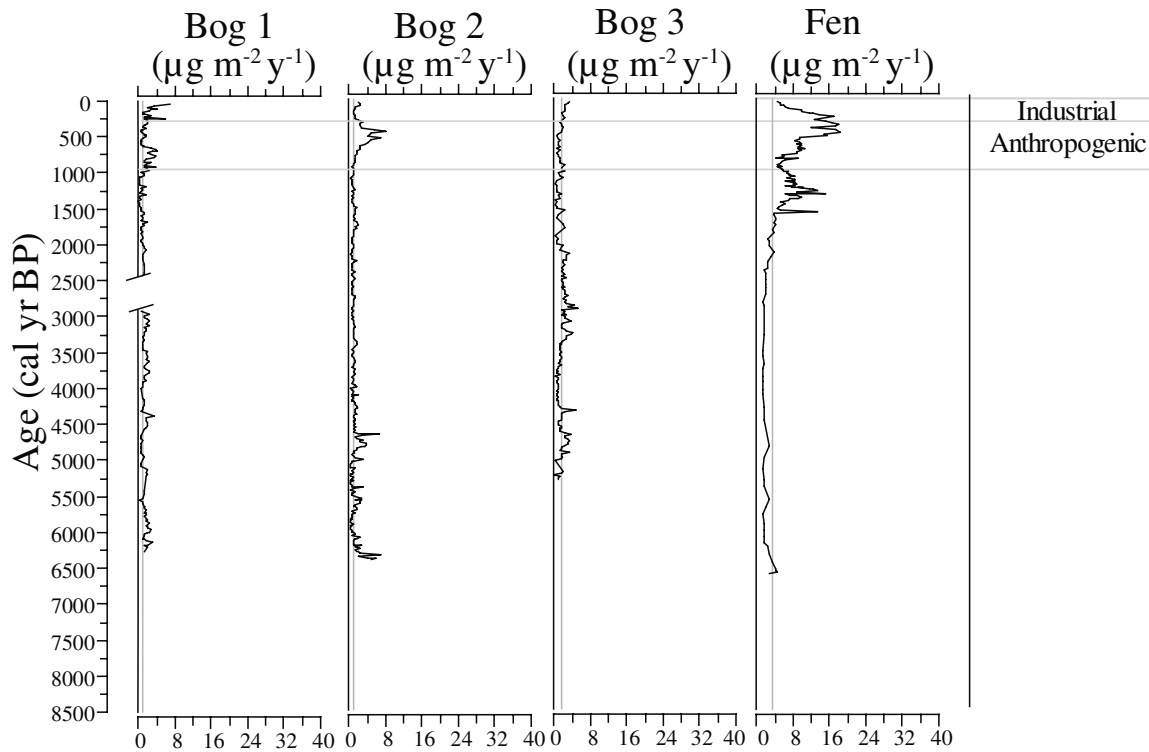


Figure 3 - 3. Hg data for Mid-HBL cores Bog 1, Bog 2, Bog 3, and Fen core (from left to right). Hg accumulation is in micrograms per meter squared per year. Data is repeated from Chapter 2 for reader convenience. Note that x-axis units are larger than in Chapter 2 in order to compare all HBL cores equally.

North 1 shows a very distinct pre-anthropogenic variability (Figure 3 – 4). These oscillations are similar to those seen in Bog 1 (Appendix A), but due to a coarser subsampling interval (4cm) they appear to be pointed. Hg accumulations spike at ~500 cal yrs BP, but due to lower bulk density in the upper layers the accumulation declines to almost pre-anthropogenic levels. The Hg concentration profile shows a continuation of elevated Hg from 500 cal yrs BP to present.

North 2 contrasts to North 1 in that it shows much more stable pre-anthropogenic Hg accumulations and concentrations (Figure 3 – 4). The bulk density profile in this core is the least variable of all 9 peat cores, which could contribute to this stability in the Hg

accumulation profile. While there is a small hump at 1400 cal yrs BP, this doesn't seem to be early anthropogenic activity because there is a similar accumulation rate at 3900 cal yrs BP, well before any major known anthropogenic input. Peak Hg accumulation and concentrations occur within the last 100 cal yrs BP.

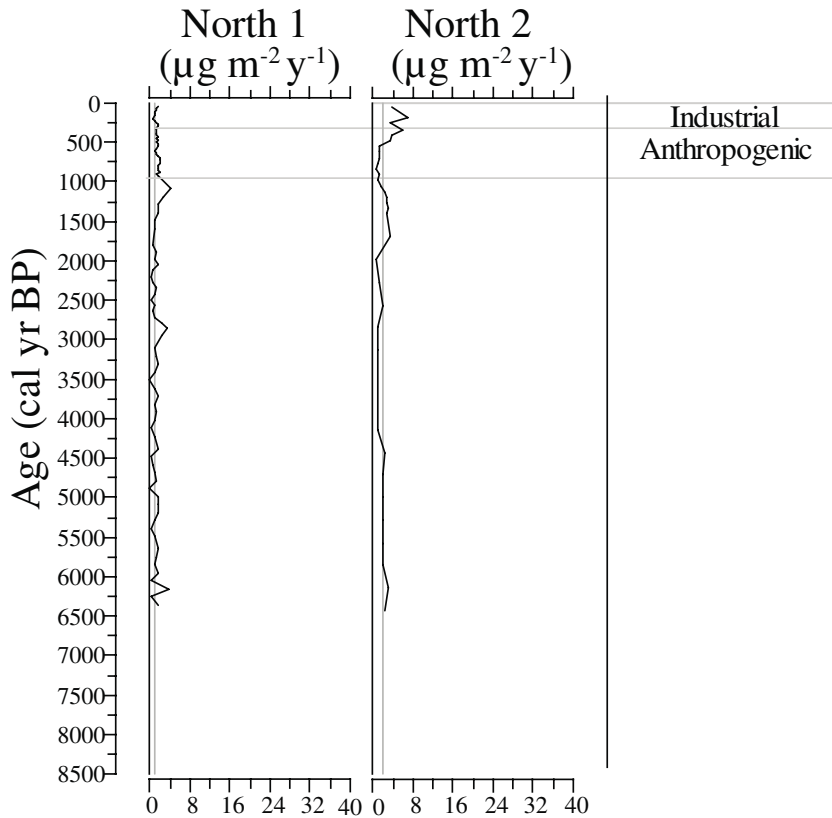


Figure 3 - 4. Hg data North 1 and North 2 peat cores (from left to right). Hg accumulation is in micrograms per meter squared per year.

3.3.3 Enrichment Factors

Anthropogenic enrichment since natural background concentrations were calculated selectively (recall section 2.2.7). The enrichment factors were, on average, 1.86 ± 1.05 , 2.21 ± 1.09 , 2.31 ± 1.14 , and 1.80 ± 0.80 at the southwest, southeast, mid-latitude, and northern latitude sites (Table 3 - 2; Figure 3 - 1).

3.3.4 Latitudinal Gradient

The cores enrichment factor values decrease with increasing latitude, but the correlation was not significant ($R^2 = 0.041$, $p = 0.603$). In addition, there is also a strong increase in inter-site variability with increasing latitude. The cores enrichment factors also decreased with increasing distance from the James Bay (increasing longitude).

3.4 Discussion

3.4.1 Mercury Profiles and Stratigraphy

The varying core lengths are a result of timing of the peatlands' evolution (Glaser *et al.* 2004; Packalen *et al.* 2014; Figure. 3 - 1). Lower latitude cores would have progressed to bog phases earlier than high latitude cores, and their pioneer species may have been different as well. For example, near the northernmost point of Ontario, stratigraphy indicates that the site originated as a mineral wetland (Riley 2011), while more southern sites such as Kinoje Lake are thought to have started as coastal marsh wetlands (Klinger *et al.* 1994). These mineral and nutrient-rich phases have higher Hg concentrations in most of the cores, some with more discrete increases than others. This is to be expected, as Hg has been shown to bind to clay minerals in laboratory studies (Sarkar *et al.* 2000). These mineral rich phases can be seen at the bottoms of the cores where mineral contact also plays a role in Hg sequestration. Hg accumulation rates here have been subject to different geochemical processes than the overlying strata and are therefore not directly comparable.

3.4.2 Vegetation Succession

It is likely that the successional gradient from south to north and east to west in the HBL from more fen-like peats to more *Sphagnum* dominated peats means the transition would have happened earlier in the south and later in the north. However, underlying geomorphological characteristics can cause these transitions to occur at different depths with each column. The palsas common near Hawley Lake, which are karstic remnants of ancient coral reefs, and therefore of significantly different geomorphology, can cause ice expansion and uplift of the peat sometimes by more than a meter (Riley 2011). This is

why peaks in Hg concentrations and accumulations occur more synchronously when the age-depth models are used to correct for differences in growth rates instead of plotting against depth. These characteristics make study of the peat stratigraphy very important toward the overall goal of analyzing historical Hg trends since the timing of anthropogenic Hg accumulation can drastically affect the enrichment factor. There was very little variability in the northern cores' pre-anthropogenic accumulation rates, which suggests that this was not a problem for comparability.

3.4.3 Onset of Anthropogenic Mercury Contributions to Peat Core Accumulation

Many of the cores showed early increases in Hg concentrations prior to the usual description of anthropogenic onset at 150 cal yrs BP. The most common increase was seen at ~500 cal yrs BP. These early Hg increases were also seen in a lake sediment study of the Eastern Hudson Bay, where Hg began to increase as early as ~500 cal yrs BP (Lockhart *et al.* 1995). Other historical peat Hg profiles have presented strong evidence to suggest that early mining practices contributed large amounts of Hg to the global atmospheric pool as well (Martinez-Cortizas *et al.* 1999).

Prehistoric periods of increased Hg accumulation rates are not clearly seen in most cores prior to ~900 cal yr BP, suggesting that significant periods of ancient human use of Hg must not, therefore, have contributed strongly to the global pool of atmospheric Hg as much as some have estimated. This finding helps to reduce the large error associated with pre-historical emissions (Streets *et al.* 2011) for which few records otherwise exist. If there were significant prehistoric emissions and the Amos *et al.* (2013) model of legacy Hg re-evasion were true, then some kind of stepwise increase in Hg concentrations would be evident from the point in time when those emissions began. Instead, a relatively steady accumulation of Hg can be seen until the anthropogenic 'zone' begins at ~900 cal yrs BP. Other historical peat Hg profiles have presented strong evidence to suggest that early mining practices contributed large amounts of Hg to the global atmospheric pool as well (Martinez-Cortizas *et al.* 1999), which has been invoked here to explain early maxima in Hg archives.

Recent declines in Eastern Europe and North American Hg emissions since the 1980s are not evident in most the records due to the relatively poor modern resolution of the cores. In more rapidly accumulating peat at the Southwest coring sites, where the high-resolution sampling interval of 1cm yielded Hg accumulation data points on a decadal scale, recent declines can be seen only in the very top layer of peat. In the other cores, 1cm of peat can represent several decades of accumulation, which makes it difficult to analyze short-term changes. This may also be due to variability in the uppermost surface vegetation, which is known to have impacts on Hg accumulation (Moore *et al.* 1995; Ulanowski *et al.* 2013).

3.4.4 Comparison with Enrichment Factors from other Records

The factor of enrichment is calculated to estimate how much anthropogenic activity has affected the atmospheric pool of Hg. The enrichment factor at the lowest latitude sites, Southeast and Southwest, were 2.33 ± 1.09 and 1.86 ± 1.15 , which is much smaller than the ‘flux ratio’ (enrichment factor) of 3.56 ± 1.00 calculated at mid-latitude lakes in North America (Muir *et al.* 2009). Even in comparison to the 2.50 ± 0.75 calculated ‘flux ratio’ calculated at subarctic lakes (Muir *et al.* 2009), the enrichment factors presented here are still low. Farther north, at the Mid core sites, the enrichment was an average of 2.31 ± 0.83 , which is similar to the Southeast cores and slightly lower than the ‘flux ratio’ of 2.50 ± 0.75 calculated at subarctic lakes in North America (Muir *et al.* 2009). Finally, the enrichment at the North core sites was an average of 1.80 ± 0.80 , which is still lower than the 2.16 ± 0.53 enrichment calculated for the arctic lakes (Muir *et al.* 2009). On average, the enrichment factors presented here are on the lower end of those produced from most lake sediment Hg records, which are typically 2-6.3 (Biester *et al.* 2007). The enrichment factor values presented here are also substantially lower than the average bog enrichment of 32 from other peat Hg records (Biester *et al.* 2007). The differences between lake sediment Hg records and peat Hg records has been discussed in both Chapters 1 and 2. Lake sediment archives must account for the Hg focusing factor, or how much sediment has been derived from the surrounding watershed, which can be quite variable in some cases and would theoretically increase the loading of Hg to the

sediment (Biester *et al.* 2007). Ombrotrophic peat records do not have this type of focusing, which would posit a lower Hg accumulate than lake sediments.

The discrepancy between the average enrichment factors from this study and those of other Hg records could also be due to the remoteness of the study sites used to collect the cores here. Many other records are taken within hundreds of kilometers of point Hg sources. Near point sources, there would be more particulate and reactive Hg deposition since they have a shorter residence time, in addition to gaseous elemental Hg from the well mixed atmospheric pool of Hg. The cores studied here, other than the lowest sites at Southeast and Southwest, are thousands of kilometers from any major industrial point sources of Hg. This reduces the chance of seeing Hg accumulation from particulate and reactive Hg in uppermost layers of the cores, which could bias the enrichment factor values in lower latitude sites to be higher than other geographic locations.

In lake sediment records, several points of high Hg accumulation were related to periods of increased precipitation (Hermanns and Beister 2013). Precipitation was seen as a driver of Hg accumulation in this lake sediment record because the lake is a hydrological end point and precipitation mobilized Hg-OM complexes from the catchment soil. Similar to this catchment process, qualitative analysis showed that there was an increased rate of Hg accumulation in the fen core of during times of high precipitation, particularly near the end of the Holocene. This phenomenon also occurred at times such as immediately after 2000 cal yr BP and 400 cal yr BP when precipitation was greatest (O'Reilly *et al.* 2014). Fens have shown greater mineralization of Hg in the soil due to their raised pH where mineralization seems to occur more efficiently. During times of higher water table and greater hydrological connectivity, a peatland could behave similarly to a watershed where precipitation events could have 'washed' bogs of their mobile Hg and deposited this Hg in the fen where it was mineralized. Similarly, during periods of lower water table, precipitation could have caused Hg-OM complexes to adsorb onto the peat more quickly and avoid any mixing in the upper layers.

3.4.5 Latitudinal Gradient in Mercury Accumulation Across the Hudson Bay Lowlands

In such a remote location as the HBL, one would expect deposition to be solely from atmospheric, long range transport of gaseous elemental Hg. However, it seems that there is a very weak latitudinal gradient with the southern sites having been least enriched in anthropogenically derived Hg at the tops of the cores. Climatic (Gratz *et al.* 2009), vegetation successional, and seasonal differences (Lu *et al.* 2001) across the HBL could have caused the observed gradient. For example, the cores near Hawley Lake were described as more fen-like than the bogs of more southern cores. It was demonstrated in Chapter 2 that fens have higher accumulation rates due to enhanced mineralization of Hg (Franzen *et al.* 2004). However, it has also been shown that the relative factor of increase in fen cores is likely to be similar to bogs (Shotyk *et al.* 2003).

The North cores demonstrated an overall higher Hg accumulation rate in the core rather than just higher accumulation only in the uppermost section of the core. Furthermore, the Flin Flon smelter in Manitoba is at a latitude similar to the North cores (54.77° N), which would suggest a greater recent accumulation of Hg in the northern cores. Although the Flin Flon smelter was estimated to be the largest single source of atmospheric Hg concentrations in Canada, the long-range effects cannot be seen in the peat cores of the HBL despite the fact that they are to the east and would be downwind at least some of the year. Effects from the smelter were seen in lake sediment on the order of 30km from the smelter (Outridge *et al.* 2011), but the cores presented here were taken more than 1000km away. No wind vector analyses were done to consider the likelihood of transport from the Flin Flon smelter to the sites presented here.

Seasonal differences among geographic locations could also be a significant contributor to the observed latitudinal gradient. Strong seasonal climate cycles that become increasingly variable toward the poles can have effects on atmospheric Hg concentrations (Dastoor and Larocque 2004). If the Hg sequestered in the cores were derived from snowmelt, for example, it would certainly have a much different anthropogenic accumulation rate than a core that sequesters most of its Hg from late summer precipitation. Lu *et al.* 2001 have demonstrated that 90% of Hg deposition in the Arctic

occurs in a time span of 3 months (late winter) and is then flushed rapidly from snowmelt in the spring. Future work should use isotopic fractionation of hydrogen, oxygen, and carbon atoms to determine whether or not the sources of rainwater to the peat are isotopically different across the HBL.

The Global/Regional Atmospheric Heavy Metals Model (GRAHM) developed by Dastoor and Larocque (2004) is another tool for corroborating the observed latitudinal gradient as was done by Muir *et al.* (2009). The anthropogenic Hg accumulation rates seen in this study (average 1.61-5.68 $\mu\text{g m}^{-2} \text{y}^{-1}$) are much lower than the deposition rates predicted by the GRAHM model (subarctic estimate of $11 \pm 3.1 \mu\text{g m}^{-2} \text{y}^{-1}$). Although the average GRAHM predicted deposition is 11 ± 3.1 , the model also predicts that autumn and winter deposition is lower, which could account for a large proportion of sequestered Hg in the HBL. Additionally, revolatilization is 18% higher in subarctic snow than in mid-latitude snow (Durnford *et al.* 2012), which could further reduce the amount of Hg sequestered in the more northern peats and helps to explain the observed latitudinal gradient.

3.4.6 Atmospheric Halogen Chemistry

The Hudson and James Bay is a unique source of atmospheric elements that would not otherwise be seen in elevated concentrations across the rest of the HBL. This results in a unique atmospheric chemistry near the bay for Hg interactions. Carignan and Sonke (2010) reported that Hg concentrations in lichens showed strong correlation to halogens Br, Cl, and I. They further demonstrated that this effect diminished with increasing distance from the Hudson Bay because these halogens are derived from sea spray in the Hudson and James Bay. Contrary to these findings, the cores presented in this thesis do not show an increase in Hg concentrations from south-north. However, North, Mid, and Southeast core sites were all approximately equidistant from either the Hudson or James Bay. Fort Hope was the only site that was significantly farther from the Hudson Bay than any of the other cores. Here, there was a gradient between Southwest core and Southeast cores. The farther cores from the bay showed a small decrease in Hg enrichment in the upper layers of peat with 1.86 ± 1.15 at the Southwest site and 2.33 ± 1.09 at the Southeast site, closer to the James Bay.

Cores that were taken from site locations closer to the bay may experience enhanced Hg deposition due to the abundance of halogen elements in the atmosphere. Recall from Chapter 1 that photo-chemically active free radical oxidation from BrO and BrCl chemical species initiate the conversion of Hg⁰ to Hg²⁺, which deposits more readily. Thus, while AMDE may not be significant toward explaining the latitudinal gradient in Hg enrichment factors in the HBL, there does seem to be some effects of proximity to water. To the author's knowledge, no other study has looked at proximity to open ocean and Hg deposition so it is difficult to compare these results to those of other Hg records.

3.5 Conclusions

The results of this Chapter further the results of Chapter 2 to better constrain the anthropogenic enrichment factor using more selective dates by providing a more spatially extensive analysis of enrichment across the HBL. On average, the HBL has been enriched by a factor of 2.13. While this does align well with the currently accepted enrichment factor of 2-5 times (Fitzgerald *et al.* 2005), this Chapter has demonstrated that this enrichment is not homogenous across the HBL. The HBL is heterogeneous with greater enrichment seen in the southern HBL where sites are closer to large point sources of Hg contamination.

The calculated values for Hg enrichment factors are consistently lower than those determined from lake sediment Hg records (Muir *et al.* 2009) and are generally lower than most other paleo-Hg records. Heterogeneous accumulation in the HBL and JBL may occur due to proximity to marine environments as well as latitude of study site. Long term Hg accumulation is sensitive to atmospheric chemistry and modern accumulation varies by latitude and longitude. The HBL is often described as a sensitive ecosystem and the results of this thesis support that statement. This work furthers the conclusions drawn in Chapter 2 that climate is likely to have a large influence on Hg accumulation in the HBL in the future.

3.6 References

- Allan, M.; Le Roux, G.; De Vleeschouwer, F.; Bindler, R.; Blaauw, M.; Piotrowska, N.; Sikorski, J.; Fagel, N., High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium. *Environ. Pollut.* **2013**, *178*, 381-394.
- Amos, H.M.; Jacob, D.J.; Streets, D.G.; Sunderland, E.M. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. *Global Biogeochem. Cy.* **2013**, *27* (2), 410-421; 10.1002/gbc.20040.
- Asmund, G. and Nielsen, S. Mercury in dated Greenland marine sediments. *Sci. Total Environ.* **2000**, *245* (1-3), 61-72; 10.1016/S0048-9697(99)00433-7.
- Begoin, M.; Richter, A.; Weber, M.; Kaleschke, L.; Tian-Kunze, X.; Stohl, A.; Theys, N.; Burrows, J.P. Satellite observations of long range transport of a large BrO plume in the Arctic. *Atmos. Chem. Phys.* **2010**, *10* (14), 6515-6526; 10.5194/acp-10-6515-2010.
- Benoit, J.; Fitzgerald, W.; Damman, A. The biogeochemistry of an ombrotrophic bog: Evaluation of use as an archive of atmospheric mercury deposition. *Environ. Res.* **1998**, *78* (2), 118-133; 10.1006/enrs.1998.3850.
- Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D.R. Modelling the past atmospheric deposition of mercury using natural archives. *Environ. Sci. Technol.* **2007**, *41* (14), 4851-4860; 10.1021/es0704232.
- Bindler, R. Estimating the natural background atmospheric deposition rate of mercury utilizing ombrotrophic bogs in southern Sweden. *Environ. Sci. Technol.* **2003**, *37* (1), 40-46; 10.1021/es020065x.
- Blaauw, M. Methods and code for 'classical' age-modelling of radiocarbon sequences. *Quat. Geochronol.* **2010**, *5* (5), 512-518.
- Carignan, J.; Sonke, J., The effect of atmospheric mercury depletion events on the net deposition flux around Hudson Bay, Canada. *Atmos. Environ.* **2010**, *44*, (35), 4372-4379.
- Damman, A. Distribution and Movement of Elements in Ombrotrophic Peat Bogs. *Oikos* **1978**, *30* (3), 480-495; 10.2307/3543344.
- Dastoor, A.P. and Larocque, Y. Global circulation of atmospheric mercury: a modelling study. *Atmos. Environ.* **2004**, *38* (1), 147-161; 10.1016/j.atmosenv.2003.08.037.
- Durnford, D.; Dastoor, A.; Ryzhkov, A.; Poissant, L.; Pilote, M.; Figueras-Nieto, D., How relevant is the deposition of mercury onto snowpacks?—Part 2: A modeling study. *Atmos. Chem. Phys.* **2012**, *12*, (19), 9251-9274.
- Engstrom, D. R.; Fitzgerald, W. F.; Cooke, C. A.; Lamborg, C. H.; Drevnick, P. E.; Swain, E. B.; Balogh, S. J.; Balcom, P. H., Atmospheric hg emissions from preindustrial gold and silver extraction in the americas: a reevaluation from lake-sediment archives. *Environ. Sci. Technol.* **2014**, *48*, (12), 6533-43.

- Engstrom, D.R. and Swain, E.B. Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* **1997**, *31* (4); 10.1021/es9600892.
- Environment Canada, 2011. Canadian climate normals. Environment Canada, Ottawa. Available at http://www.climate.weatheroffice.gc.ca/climate_normals/.
- Farmer, J.G.; Anderson, P.; Cloy, J.M.; Graham, M.C.; MacKenzie, A.B.; Cook, G.T. Historical accumulation rates of mercury in four Scottish ombrotrophic peat bogs over the past 2000 years. *Sci. Total Environ.* **2009**, *407* (21), 5578-5588; 10.1016/j.scitotenv.2009.06.014.
- Fitzgerald, W.F.; Engstrom, D.R.; Lamborg, C.H.; Tseng, C.; Balcom, P.H.; Hammerschmidt, C.R. Modern and historic atmospheric mercury fluxes in northern Alaska: global sources and Arctic depletion. *Environ. Sci. Technol.* **2005**, *39* (2), 557-568.
- Fitzgerald, W.; Engstrom, D.; Mason, R.; Nater, E. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32* (1), 1-7; 10.1021/es970284w.
- Franzen, C.; Kilian, R.; Biester, H., Natural mercury enrichment in a minerogenic fen—evaluation of sources and processes. *J. Environ. Monit.* **2004**, *6*, (5), 466-472.
- Givelet, N.; Le Roux, G.; Cheburkin, A.; Chen, B.; Frank, J.; Goodsite, M. E.; Kempter, H.; Krachler, M.; Noernberg, T.; Rausch, N.; Rheinberger, S.; Roos-Barraclough, F.; Sapkota, A.; Scholz, C.; Shotyky, W., Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses RID E-7026-2010. *J. Environ. Monit.* **2004**, *6*, (5), 481-492.
- Glaser, P.H.; Hansen, B.; Siegel, D.I.; Reeve, A.S.; Morin, P.J. Rates, pathways and drivers for peatland development in the Hudson Bay Lowlands, northern Ontario, Canada. *J. Ecol.* **2004**, *92* (6), 1036-1053.
- Gratz, L. E.; Keeler, G. J.; Miller, E. K., Long-term relationships between mercury wet deposition and meteorology. *Atmos. Environ.* **2009**, *43*, (39), 6218-6229.
- Jeglum, J.; Rothwell, R.; Berry, G.; Smith, G. A peat sampler for rapid survey. *Frontline Technical Note, Can. For. Serv., Sault Ste. Marie, Ont, Canada* **1992**, .
- Jowsey, P. An improved peat sampler. *New Phytol.* **1966**, *65* (2), 245-248.
- Klinger, L.F.; Zimmerman, P.R.; Greenberg, J.P.; Heidt, L.E.; Guenther, A.B. Carbon Trace Gas Fluxes Along a Successional Gradient in the Hudson-Bay Lowlands. *J. Geophys. Res.-Atmos* **1994**, *99* (D1), 1469-1494; 10.1029/93JD00312.
- Lindberg, S.E.; Brooks, S.; Lin, C.J.; Scott, K.J.; Landis, M.S.; Stevens, R.K.; Goodsite, M.; Richter, A. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **2002**, *36* (6), 1245-1256; 10.1021/es0111941.
- Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36* (1), 19-32.

- Lindqvist, O.; Rodhe, H., Atmospheric Mercury - a Review. *Tellus B* **1985**, *37*, (3), 136-159.
- Lockhart, W.; Wilkinson, P.; Billeck, B.; Hunt, R.; Wagemann, R.; Brunskill, G. Current and historical inputs of mercury to high-latitude lakes in Canada and to Hudson Bay. *Water Air Soil Pollut.* **1995**, *80* (1-4), 603-610.
- Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, A.; Welch, H. E.; Martin, K.; Lockhart, L.; Hunt, R. V.; Boila, G.; Richter, A., Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28*, (17), 3219-3222.
- Martinez Cortizas, A.; Peiteado Varela, E.; Bindler, R.; Biester, H.; Cheburkin, A. Reconstructing historical Pb and Hg pollution in NW Spain using multiple cores from the Chao de Lamoso bog (Xistral Mountains). *Geochim. Cosmochim. Ac.* **2012**, *82*, 68-78; 10.1016/j.gca.2010.12.025.
- Martinez-Cortizas, A.; Pontevedra-Pombal, X.; Garcia-Rodeja, E.; Novoa-Munoz, J.; Shotyk, W. Mercury in a Spanish peat bog: Archive of climate change and atmospheric metal deposition. *Science* **1999**, *284* (5416), 939-942; 10.1126/science.284.5416.939.
- Moore, T.R.; Bubier, J.L.; Heyes, A.; Flett, R.J. Methyl and Total Mercury in Boreal Wetland Plants, Experimental Lakes Area, Northwestern Ontario. *J. Environ. Qual.* **1995**, *24* (5), 845-850.
- Muir, D.C.G.; Wang, X.; Yang, F.; Nguyen, N.; Jackson, T.A.; Evans, M.S.; Douglas, M.; Koeck, G.; Lamoureux, S.; Pienitz, R.; Smol, J.P.; Vincent, W.F.; Dastoor, A. Spatial Trends and Historical Deposition of Mercury in Eastern and Northern Canada Inferred from Lake Sediment Cores. *Environ. Sci. Technol.* **2009**, *43* (13), 4802-4809; 10.1021/es8035412.
- Nriagu, J.O. Legacy of Mercury Pollution. *Nature* **1993**, *363* (6430), 589-589; 10.1038/363589a0.
- O'Reilly, B. C.; Finkelstein, S. A.; Bunbury, J., Pollen-Derived Paleovegetation Reconstruction and Long-Term Carbon Accumulation at a Fen Site in the Attawapiskat River Watershed, Hudson Bay Lowlands, Canada. *Arct. Antarct. Alp. Res.* **2014**, *46*, (1), 6-18.
- Outridge, P.; Rausch, N.; Percival, J.; Shotyk, W.; McNeely, R. Comparison of mercury and zinc profiles in peat and lake sediment archives with historical changes in emissions from the Flin Flon metal smelter, Manitoba, Canada. *Sci. Total Environ.* **2011**, *409* (3), 548-563.
- Packalen, M. S.; Finkelstein, S. A.; McLaughlin, J. W., Carbon storage and potential methane production in the Hudson Bay Lowlands since mid-Holocene peat initiation. *Nat. Commun.* **2014**, *5*.
- Pirrone, N.; Cinnirella, S.; Feng, X.; Finkelman, R.; Friedli, H.; Leaner, J.; Mason, R.; Mukherjee, A.; Stracher, G.; Streets, D. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* **2010**, *10* (13), 5951-5964.

- Pirrone, N.; Costa, P.; Pacyna, J.M.; Ferrara, R. Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmos. Environ.* **2001**, *35*(17), 2997-3006; 10.1016/S1352-2310(01)00103-0.
- R Development Core Team *R: a language and environment for statistical computing*, R Foundation for Statistical Computing: Vienna, Austria, 2011.
- Reimer, P.J.; Baillie, M.G.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Burr, G.S.; Edwards, R.L. IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 years cal BP. **2009**, .
- Riley, J. L., Wetlands of the Ontario Hudson Bay lowland: a regional overview. *Nature Conservancy of Canada: Toronto, Ontario, Canada* **2011**, 156.
- Roos-Barraclough, F.; Givélet, N.; Cheburkin, A.; Shotyk, W.; Norton, S. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: A 10000-year record from Caribou Bog, Maine. *Environ. Sci. Technol.* **2006**, *40* (10), 3188-3194; 10.1021/es051945p.
- Roos-Barraclough, F.; Martinez-Cortizas, A.; Garcia-Rodeja, E.; Shotyk, W. A 14 500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation RID E-7026-2010. *Earth Planet. Sci. Lett.* **2002**, *202* (2), 435-451; 10.1016/S0012-821X(02)00805-1.
- Rydberg, J.; Galman, V.; Renberg, I.; Bindler, R.; Lambertsson, L.; Martinez-Cortizas, A. Assessing the stability of mercury and methylmercury in a varved lake sediment deposit. *Environ. Sci. Technol.* **2008**, *42* (12), 4391-4396; 10.1021/es7031955.
- Sarkar, D.; Essington, M.E.; Misra, K.C. Adsorption of mercury(II) by kaolinite. *Soil Sci. Soc. Am. J.* **2000**, *64* (6), 1968-1975.
- Schroeder, W.H. and Munthe, J. Atmospheric mercury—an overview. *Atmos. Environ.* **1998**, *32* (5), 809-822.
- Schroeder, W.H.; Anlauf, K.G.; Barrie, L.A.; Lu, J.Y.; Steffen, A.; Schneeberger, D.R.; Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394* (6691), 331-332; 10.1038/28530.
- Schuster, P.; Krabbenhoft, D.; Naftz, D.; Cecil, L.; Olson, M.; Dewild, J.; Susong, D.; Green, J.; Abbott, M. Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **2002**, *36* (11), 2303-2310; 10.1021/es0157503.
- Shotyk, W.; Goodsite, M. E.; Roos-Barraclough, F.; Frei, R.; Heinemeier, J.; Asmund, G.; Lohse, C.; Hansen, T. S., Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the ¹⁴C "bomb pulse curve" RID E-7026-2010. *Geochim. Cosmochim. Ac* **2003**, *67*, (21), 3991-4011.

- Steinnes, E. and Sjobakk, T.E. Order-of-magnitude increase of Hg in Norwegian peat profiles since the outset of industrial activity in Europe. *Environ. Pollut.* **2005**, *137* (2), 365-370; 10.1016/j.envpol.2004.10.008.
- Streets, D.G.; Devane, M.K.; Lu, Z.; Bond, T.C.; Sunderland, E.M.; Jacob, D.J. All-Time Releases of Mercury to the Atmosphere from Human Activities. *Environ. Sci. Technol.* **2011**, *45*(24), 10485-10491; 10.1021/es202765m.
- Stuiver, M.; Reimer, P.; Bard, E.; Beck, J.; Burr, G.; Hughen, K.; Kromer, B.; McCormac, G.; Van der Plicht, J.; Spurk, M. INTCAL98 radiocarbon age calibration, 24,000-0 cal BP. *Radiocarbon* **1998**, *40* (3), 1041-1083.
- Ulanowski, T.A. and Branfireun, B.A. Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay Lowlands, Canada. *Sci. Total Environ.* **2013**, *454*, 211-218; 10.1016/j.scitotenv.2013.02.087.

Chapter 4

4 Conclusions and Future Work

4.1 Peat as an Archive of Mercury

Peat archives have been criticized for overestimation of mercury (Hg) accumulation rates in post versus pre-anthropogenic history (Biester *et al.* 2007), however this thesis suggests otherwise. Biester *et al.* (2007) report that the average preindustrial accumulation rate from lake sediment is 3 - 3.5 $\mu\text{g m}^{-2} \text{y}^{-1}$, and post-industrial is closer to 10 – 20 $\mu\text{g m}^{-2} \text{y}^{-1}$. This is a 3 – 5 fold increase, whereas the cores studied here are only a 2.15 fold increase. Biester *et al.* (2007) indicated that, if anything, bog cores should show lower Hg accumulation rates because catchment Hg will focus in lakes from runoff hydrology, but that this phenomenon does not occur in bogs.

The accumulation rates presented in this thesis are consistently lower than most other paleoarchives of Hg. The consistency between cores across the HBL shows that, peat archives are excellent media for studying past environments. Peat offers a ubiquitous, pristine sample that is free from complicated focusing effects, surface elution, or canopy effects. It is often used to reconstruct other types of historical environmental change, which makes multiproxy study much more appropriate. Peatlands also exist in one of the most sensitive ecoregions and will see some of the greatest effects from climate warming. Study of these regions is critical toward prediction of the effects of future environmental change.

4.2 Importance of Remoteness and Temporally Long Records

Many reconstructions of past atmospheric Hg deposition have studied cores that are relatively short, with the oldest date being less than a few hundred years before present (*i.e.* Shuster *et al.* 2002). There is an overly intent focus on the onset of the modern industrial revolution (ca. 1850), which is actually an arbitrary date given the importance

of the overall enrichment since natural Hg levels. In order to accurately quantify the contributions of anthropogenically-derived Hg to the atmosphere and subsequent accumulation in remote ecosystems, studies need to use records that date back thousands of years. For similar reasons, it is also important to use a media from a pristine, remote location to avoid Hg derived from local or regional sources, which can bias what would otherwise be a well-mixed atmospheric pool of Hg (Fitzgerald *et al.* 1998).

Prior to this study, there was an obvious gap in data from subarctic latitudes in the vicinity of the Hudson Bay Lowlands (HBL). This study represents the first, most complete, replicated paleorecord of atmospheric Hg accumulation from ombrotrophic bogs in HBL. The area is much more removed from local and regional Hg emitters and therefore represents a truly pristine site, which many other comparable studies are not.

4.3 Improving Estimates of the Anthropogenic Enrichment Factor

In Chapter 2, the Hg accumulation rates from Victor Mine (mid-HBL) were used to calculate the anthropogenic enrichment factor, or the amount of Hg humans have added to the atmosphere, since pre-anthropogenic time. This was done using an adapted method of calculation that relied on paleoclimate data to narrow the timeframe from which the pre-anthropogenic Hg accumulation average was calculated. A climate stable period that dated back 2700-3800 cal yrs BP was used to calculate the true natural background accumulation of Hg.

Using a more selective approach to the anthropogenic enrichment factor resulted in a higher value, which was predicted by the Amos *et al.* (2013) model. However, the difference between traditional enrichment factor calculations and an adapted method were not as substantial as that which was predicted by Amos *et al.* (2013). Moreover, large increases in Hg accumulation prior to ~900 cal yrs BP were not consistently evident in the cores. These findings add to the results published by Engstrom *et al.* (2014) and further refute the possibility that pre-industrial Hg accumulations could be 300% more

than predicted. While Engstrom *et al.* (2014) did admit that large quantities of 16th century Hg were used in mining practices; the authors did not acknowledge that these emissions would contribute to the atmospheric load of Hg. The results of this thesis suggest that 16th century Hg contributions were significant and this aligns more with the results of Amos *et al.* (2013).

4.3.1 Utility of an Improved Anthropogenic Enrichment Factor

The production of a more accurate anthropogenic enrichment factor allows policy makers to gauge where Hg emissions targets should be. The results presented in this thesis suggest that the anthropogenic enrichment factor is actually underestimated because calculations have been done using erroneous accumulation rates that are much too recent to be truly pre-anthropogenic. Using currently accepted enrichment factors, emissions targets are not aggressive enough. Greater accuracy in the enrichment factor should bolster the argument for more aggressive Canadian emissions targets similar to those currently being made in the United States of America.

Contrary to the conclusions of Amos *et al.* (2013), there is not enough evidence to suggest that there were large anthropogenic Hg contributions prior to ~500 cal yrs BP. Amos *et al.* (2013) argue that potentially large anthropogenic contributions date back thousands of years and that these Hg emissions have resulted in large recycling of legacy Hg. This Hg, similar to the CO₂ reduction concept, would continue recycling even if drastic reductions in Hg emissions were sought. However, the results of this study support the recent findings of Engstrom *et al.* (2014) that large anthropogenic contributions did not occur before ~500 cal yrs BP and therefore legacy Hg should not have such a strong impact on modern Hg accumulation. Similar to other studies that have shown a rapid response to fish Hg concentrations after reduced deposition (Harris *et al.* 2007), the results of this thesis suggest that emissions reductions should have a noticeable effect on Hg accumulation in remote sites.

4.3.2 Depth to Water Table

Although correlation does not indicate causation, the relationship between depth to water table (DWT) and Hg concentrations does suggest that natural climate forces can affect

Hg sequestration in peatlands. These results further the findings of Jitaru *et al.* (2009), who found that throughout the last 670 000 years Hg accumulation has been greatest during periods of intense cold and high atmospheric dust loads. In the core that had DWT measured using abundance and species of testate amoeba (VM43), the greatest Hg concentrations were seen during periods of highest DWT (dry conditions, greater distance between peat surface and water table). No previous study has combined Hg accumulation paleorecords with DWT reconstructions using testate amoeba, which is surprising given the consensus that multiproxy studies must combine geochemical data with biological data for optimal interpretations (see Bindler 2006).

The implications of these findings are that Hg concentrations and accumulations are influenced by climate in the HBL. Specifically, cold temperatures and dry conditions are likely to coincide with times of greatest Hg accumulation. Jitaru *et al.* (2009) suggest that this is due to efficient adsorption of reactive Hg onto mineral dusts. While temperature records in the HBL need improvement, the testate amoeba record is a reliable indicator of past bog surface wetness. If bogs accumulate more Hg in dry periods due to mineral dust particle scavenging, there could also be enhanced adsorption onto the peat surface. Also, dry conditions may reduce evasion from the bog surface or at least reduce the chance of surface flow removing Hg from the bog surface. Future work should continue to build upon the link between climate and Hg accumulation in peatlands.

These findings could also be used to improve recent estimates of Hg accumulation in the uppermost layers of peat. Since it was estimated that DWT is currently high in the bog core that was studied here, it may be that modern accumulation is already being modified by climate. If the relationship between this kind of natural climate variability and Hg accumulation could be quantified, then it could be reliably removed from modern accumulation rates to give a more accurate value. Similar to the usage of bulk density as an indicator of variable decomposition, DWT could be used to account for changes in bog surface wetness to provide more accurate Hg accumulation rates in peat records.

4.4 Spatial Gradients in the Hudson Bay Lowlands

In Chapter 3 the results revealed two spatial gradients in the HBL. The first was the north-south gradient in which more northern peats showed a reduced anthropogenic enrichment factor as compared to their southern counterparts. This was attributed to proximity to point sources in the south, which caused a heterogeneous deposition of recently produced Hg. In pre-historic time, there were no major point sources of Hg in North America (other than several volcanoes that did not erupt during the timeframe discussed here), and so there was no spatial gradient in pre-anthropogenic Hg accumulation rates. The lack of pre-anthropogenic variability in the cores further suggests that the study site was remote from any natural point sources of Hg.

The second spatial gradient was from southwestern to southeastern HBL. Here, there was a weak trend between distance from the James Bay and decreased anthropogenic enrichment factor. The west-east gradient was attributed to changing atmospheric chemistry as a result of distance from the bay. Over the Hudson and James Bay, there is a much higher concentration of common halogen elements such as Br, Cl, and I that results from sea spray of the salty water. These elements cause enhanced deposition of Hg because they readily oxidize Hg^0 to Hg^{2+} . The changed chemistry would show a more pronounced increase in accumulation during times of increased loading to the atmospheric pool of Hg (modern time). The pre-anthropogenic accumulation rates in the southwestern HBL were lower than the southeastern HBL, but the difference in accumulation rate was much more pronounced in modern Hg accumulation rates.

The implications of these findings are that paleorecords must look at multiple cores from a large geographic area in order to accurately estimate the anthropogenic enrichment factor.

4.4.1 Comparison to Other Mercury Records

The results of Chapter 3, similar to Chapter 2, were compared to a specific lake sediment Hg archive study to give context to the results. The latitudinal gradient followed the same weak trend with reduced enrichment in northern sites, but the enrichment factors were consistently lower than Muir *et al.* (2009). Lake focusing effects were not a factor in the

presented peat archives, which is likely the reason for the lower accumulation rates and enrichment factors. Still, there was a positive correlation between Hg enrichment and lower latitude. These results suggest that while specific accumulation rates may not be directly comparable between media, the relative enrichment and spatial trends should be comparable.

4.5 Future Work

Most of the future work that has been suggested in this thesis refers to stable isotope approaches. While stable isotopes have been used extensively for elements such as oxygen, hydrogen, and carbon, Hg isotope research is still novel. Hg has seven isotopes and undergoes many mass independent fractionations in nature with a range of more than 10‰, which allows very distinct differentiation of Hg sources. Hg isotopes have been used to differentiate sources of particulate Hg, which does not fractionate substantially post-emission (Gehrke *et al.* 2011). While these approaches have not been used in ambient air, there would certainly be a utility in using these stable isotopes in peat to differentiate natural from anthropogenic sources of Hg.

Peat has been shown to be a reliable indicator when it comes to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ because these isotopes are strongly correlated to recalcitrant humic substances and are not prone to post-depositional changes (diagenesis) (Zaccone *et al.* 2011). These isotopes can be used to indicate the existence of forest fire ash, which has implications for natural additions of Hg to the soil (Turetsky *et al.* 2006), or to indicate the trophic status of the dominant plant species through time. While the carbon:nitrogen ratio was used in this thesis as an indicator of peat humification, stable isotopes could be used to determine the types of plants that were decomposing at certain periods of time.

Another stable isotope approach could elaborate on paleohydrology of the HBL. Wolfe *et al.* (2001) used $\delta^{18}\text{O}$ from cellulose to create a paleorecord of evaporative enrichment, which was the dominant control on the $\delta^{18}\text{O}$ isotopic fractionation. These values were used to infer relative humidity in summer throughout the late Pleistocene and Holocene.

Since depth to water table was noted as a correlate to Hg concentrations in the peat cores of this thesis, $\delta^{18}\text{O}$ could be used to improve the paleohydrology and paleohumidity profile and further elaborate on bog surface wetness. Wolfe *et al.* (2001) also noted a millennial oscillation in surface wetness, which was linked to changes in summer insolation. These stable isotope approaches could help identify whether or not an ambient moisture oscillation existed in the HBL as well as what could have been the cause of such an oscillation.

Finally, stable isotopes can be used to improve the paleoclimate record in the HBL. Currently, climate records in the HBL rely on an old study that was based on pollen reconstructions (McAndrews *et al.* 1982). Due to the importance of multiproxy research that combines both biological and geochemical data for reconstructing paleorecords, it would be prudent to apply stable isotopes to a peat core to test the accuracy of the pollen paleorecord using a geochemical data. While this has been done using cellulose-inferred pond water $\delta^{18}\text{O}$, the record only dated back a few centuries (Wolf *et al.* 2011). It was demonstrated in this thesis that Hg records must extend much further back in time in order to achieve a true pre-anthropogenic Hg signal and climate records must do the same in order for them to be useful to the Hg record.

4.6 References

- Amos, H.M.; Jacob, D.J.; Streets, D.G.; Sunderland, E.M. Legacy impacts of all-time anthropogenic emissions on the global mercury cycle. *Global Biogeochem. Cy.* **2013**, *27* (2), 410-421; 10.1002/gbc.20040.
- Biester, H.; Bindler, R.; Martinez-Cortizas, A.; Engstrom, D. R., Modelling the past atmospheric deposition of mercury using natural archives. *Environ. Sci. Technol.* **2007**, *41*, (14), 4851-4860.
- Bindler, R., Mired in the past—looking to the future: geochemistry of peat and the analysis of past environmental changes. *Global Planet. Change* **2006**, *53*, (4), 209-221.
- Engstrom, D. R.; Fitzgerald, W. F.; Cooke, C. A.; Lamborg, C. H.; Drevnick, P. E.; Swain, E. B.; Balogh, S. J.; Balcom, P. H., Atmospheric hg emissions from preindustrial gold and silver extraction in the americas: a reevaluation from lake-sediment archives. *Environ. Sci. Technol.* **2014**, *48*, (12), 6533-43.
- Fitzgerald, W. F.; Engstrom, D. R.; Mason, R. P.; Nater, E. A., The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **1998**, *32*, (1), 1-7.
- Gehrke, G. E.; Blum, J. D.; Slotton, D. G.; Greenfield, B. K., Mercury isotopes link mercury in San Francisco Bay forage fish to surface sediments. *Environ. Sci. Technol.* **2011**, *45*, (4), 1264-1270.
- Jitaru, P.; Gabrielli, P.; Marteel, A.; Plane, J. M. C.; Planchon, F. A. M.; Gauchard, P.-A.; Ferrari, C. P.; Boutron, C. F.; Adams, F. C.; Hong, S., Atmospheric depletion of mercury over Antarctica during glacial periods. *Nat. Geosci.* **2009**, *2*, (7), 505-508.
- McAndrews, J. H.; Riley, J. L.; Davis, A. M., Vegetation history of the Hudson Bay Lowlands: a postglacial pollen diagram from the Sutton Ridge. *Le Naturaliste Canadien* **1982**.
- Muir, D. C. G.; Wang, X.; Yang, F.; Nguyen, N.; Jackson, T. A.; Evans, M. S.; Douglas, M.; Koeck, G.; Lamoureux, S.; Pienitz, R.; Smol, J. P.; Vincent, W. F.; Dastoor, A., Spatial Trends and Historical Deposition of Mercury in Eastern and Northern Canada Inferred from Lake Sediment Cores. *Environ. Sci. Technol.* **2009**, *43*, (13), 4802-4809.
- Schuster, P. F.; Krabbenhoft, D. P.; Naftz, D. L.; Cecil, L. D.; Olson, M. L.; Dewild, J. F.; Susong, D. D.; Green, J. R.; Abbott, M. L., Atmospheric mercury deposition during the last 270 years: A glacial ice core record of natural and anthropogenic sources. *Environ. Sci. Technol.* **2002**, *36*, (11), 2303-2310.
- Turetsky, M. R.; Harden, J. W.; Friedli, H. R.; Flannigan, M.; Payne, N.; Crock, J.; Radke, L., Wildfires threaten mercury stocks in northern soils. *Geophys. Res. Lett.* **2006**, *33*, (16), 6.
- Wolfe, B. B.; Aravena, R.; Abbott, M. B.; Seltzer, G. O.; Gibson, J. J., Reconstruction of paleohydrology and paleohumidity from oxygen isotope records in the Bolivian Andes. *Palaeogeog. Palaeocl.* **2001**, *176*, (1-4), 177-192.

- Wolfe, B. B.; Light, E. M.; Macrae, M. L.; Hall, R. I.; Eichel, K.; Jasechko, S.; White, J.; Fishback, L.; Edwards, T. W., Divergent hydrological responses to 20th century climate change in shallow tundra ponds, western Hudson Bay Lowlands. *Geophys. Res. Lett.* **2011**, *38*, (23).
- Zaccone, C.; Casiello, G.; Longobardi, F.; Bragazza, L.; Sacco, A.; Miano, T. M., Evaluating the 'conservative' behavior of stable isotopic ratios ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$) in humic acids and their reliability as paleoenvironmental proxies along a peat sequence. *Chem. Geol.* **2011**, *285*, (1-4), 124-132.

Appendix A

Supplementary Information to “Using Pristine Peat Archives to Quantify True Pre-Anthropogenic Mercury Accumulation and Contemporary Enrichment Factors”

Fen Core

The fen core, VM33, although not useful for calculating a reliable anthropogenic enrichment factor, was useful in determining the effects of changes to paleohydrology on Hg accumulation. VM33 displayed an increase from pre to post-anthropogenic of only 1.5 times. The maximum for this core was 213.52 $\mu\text{g}/\text{kg}$ in 1576 AD. The higher rates of what most would consider to be pre-anthropogenic time were likely the result of diagenesis remobilizing Hg from the upper layers and re-depositing this Hg in deeper layers. It is interesting to compare this likely diagenesis to the other three cores, which were not suspected to have resulted from diagenetic processes.

Millennial Periodicity

Qualitative observation of the cores revealed a periodicity that occurred on a nearly millennial time scale. Since hydrological cycling drives Hg, it was thought that this periodicity could be caused by a millennial climate oscillation, which has been written about extensively in other geochronological studies (Bond *et al.* 1997). While the cause of these climate cycles is still uncertain, it is seen frequently and therefore not likely to be an artefact in the data of this study. The millennial climate oscillation has been found in ice cores (O'Brien *et al.* 1995), marine sediments (Bianchi and McCave 1999; Bond *et al.* 1997; 2001; McManus *et al.* 1994; Oppo *et al.*, 2001), lake sediment (Hu *et al.* 2003; Weber *et al.* 2010; Zhao *et al.* 2010), peat (Yu *et al.* 2003), and pollen records (Viau *et al.* 2002; Willard *et al.* 2005). However, no record of the oscillation has been observed in the HBL. Unfortunately, the dating resolution used to describe long-term trends in Hg accumulation is not good enough to compare to other marine records to determine if this is truly a 'bond cycle'. The future work described in Chapter 4 will help to elucidate the cause of this relatively small pre-anthropogenic variability.

Table A - 1. ^{14}C -AMS measurement summaries of peat macrofossil ages for 5 sites in the Hudson Bay Lowlands, Canada; listed by increasing latitude.

Site	Location (DD)	Peat Type	Peat Depth (cm)	Lab Number	Dated Depth (cm)	Material Dated	$\delta^{13}\text{C}$ (‰ PDB)	^{14}C Age (y BP)	Median Age (cal y BP)*	1 σ Age Range (cal y BP)*	2 σ Age Range (cal y BP)*	Reference
Bog 1	N52.71; W84.18	Bog	63	Beta-281000	62-63	Sphagnum stems	-26	1130 ± 40	1030	970-1070	960-1170	Bunbury <i>et al.</i> 2012
			111	Beta-281001	110-111	Twigs	-28	2140 ± 40	2130	2050-2300	2000-2310	Bunbury <i>et al.</i> 2012
			186	Beta-281002	185-186	Sphagnum stems	-27	3770 ± 40	4140	4090-4230	3990-4280	Bunbury <i>et al.</i> 2012
			238.5	Beta-281032	237-238.5	Wood	-27	4760 ± 40	5510	5470-5580	5330-5590	Bunbury <i>et al.</i> 2012
			304	Beta-281003	303-304	Wood fragments	-26	5820 ± 40	6630	6560-6670	6500-6730	Bunbury <i>et al.</i> 2012
			304	Beta-281004	303-304	conifer needles	-29	5890 ± 40	6710	6670-6750	6570-6840	Bunbury <i>et al.</i> 2012
Bog 2	N52.704; W84.182	Bog	286	UGAMS-11668	53-54	wood	-28.2	1390 ± 20	1302	1290-1310	1290-1340	Packalen <i>et al.</i> , in review
				UGAMS-11267	156-157	wood fragment	-26.7	3670 ± 25	4008	3930-4080	3910-4090	Packalen <i>et al.</i> , in review
				UGAMS-11673	285-286	wood fragment	-26.9	5530 ± 25	6320	6290-6390	6290-6400	Packalen <i>et al.</i> , in review
Bog 3	N52.721; W83.941	Bog	210	UGAMS-11257	72-73	wood	-27.1	2060 ± 25	2028	1960-2100	1950-2110	Packalen <i>et al.</i> , in review
				UGAMS-12715	209-210	herbaceous remains	-25.4	4390 ± 20	4940	4880-5030	4870-5040	Packalen <i>et al.</i> , in review
Fen	N52.712; W84.171	Fen	38.5	Beta-286595	37-38.5	conifer needles imbedded	-29	580 ± 40	600	540-640	530-650	O'Reilly <i>et al.</i> in press
			61	Beta-281774	60-61	twig	-26	1250 ± 40	1200	1140-1270	1080-1280	O'Reilly <i>et al.</i> in press
			121	Beta-281775	120-121	wood conifer	-27	1660 ± 40	1560	1520-1680	1420-1690	O'Reilly <i>et al.</i> in press
			158.5	Beta-286596	157-158.5	needles	-29	2730 ± 40	2820	2780-2860	2760-2920	O'Reilly <i>et al.</i> in press
			195	Beta-281776	194-195	wood conifer	-27	5050 ± 40	5810	5740-5890	5660-5910	O'Reilly <i>et al.</i> in press
			243.5	Beta-281777	241.5-243	needles	-27	5640 ± 40	6420	6350-6480	6320-6490	O'Reilly <i>et al.</i> in press

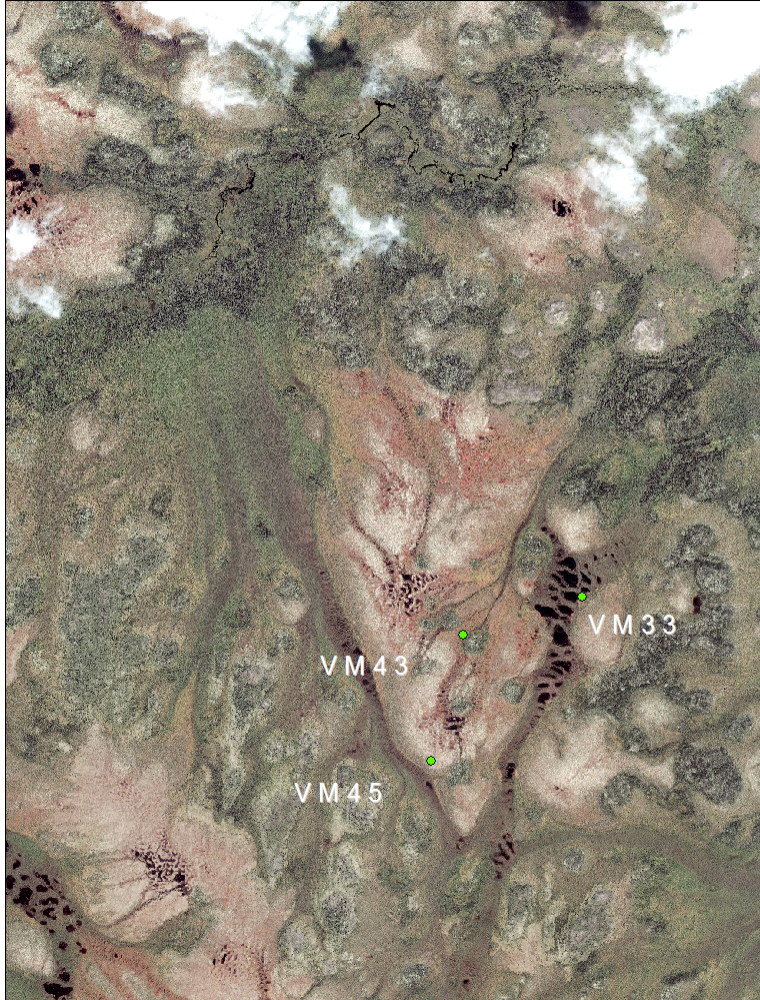


Figure A - 1. LiDAR imagery of coring sites for VM43 (Bog 1), VM45 (Bog 2) and VM33 (Fen core) (green dots) in the HBL of Northern Ontario, Canada.

Interval (cm)	²¹⁰ Pb total activity (DPM/g)	Years before AD 2009
0-1	70.21	18.5
1-2	43.07	36.1
2-3	32.93	59.1
3-4	14.38	75.7
4-5	10.30	92.9
5-6	5.09	104.4
6-7	3.50	
7-8	2.22	
10-11	2.80	
12-13	2.37	
15-16	1.67	

Figure A - 2. ²¹⁰Pb dates for core VM43 from Bunbury *et al.* 2012.

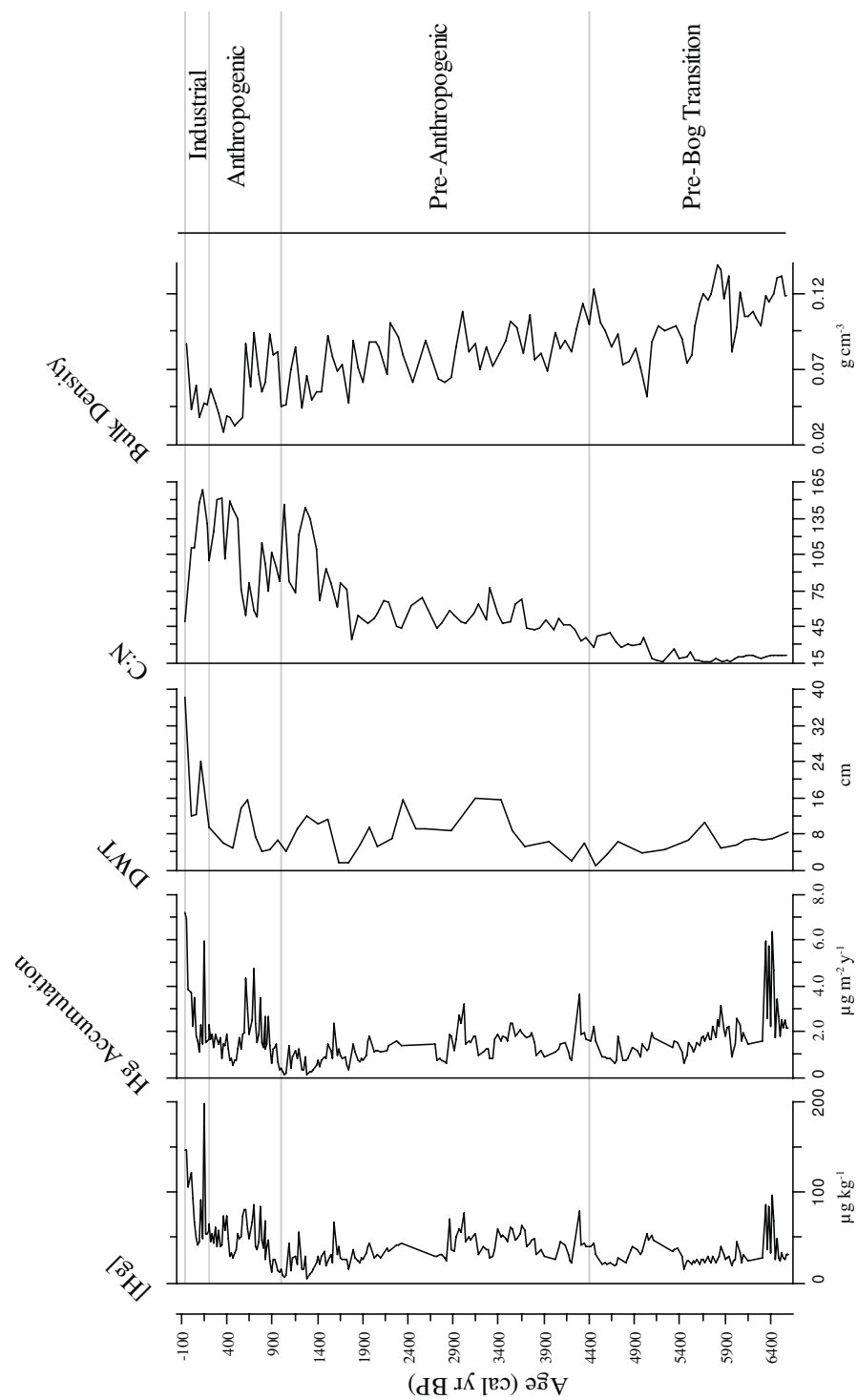


Figure A - 3. Bog 1 additional information including Hg concentration and Hg accumulation. Depth to Water Table (DWT), carbon to nitrogen ratio (C:N), and bulk density were provided by Dr. Joan Bunbury.

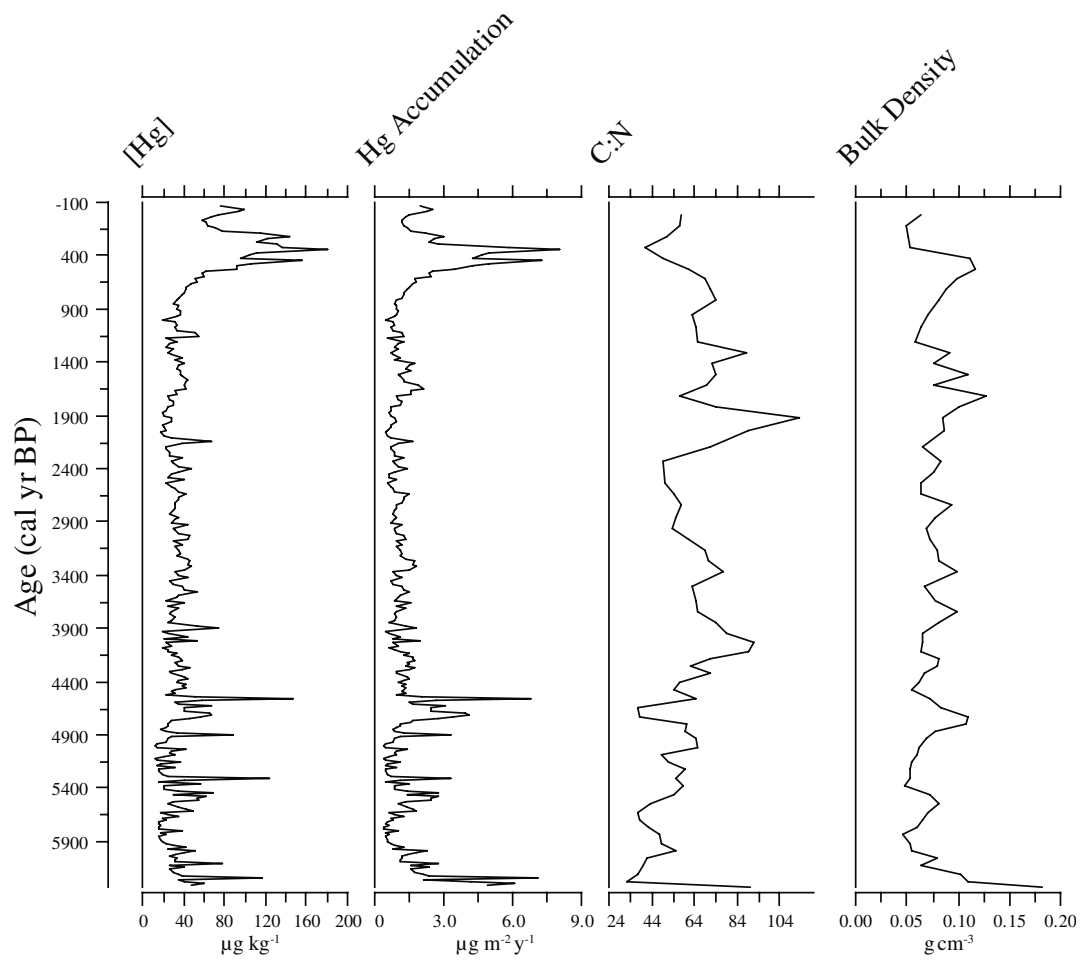


Figure A - 4. Bog 2 additional information including Hg concentration, Hg accumulation, carbon to nitrogen ratio (C:N) (provided by Maara Packalen and Dr. Sarah Finkelstein), and bulk density (provided by Maara Packalen and Dr. Sarah Finkelstein).

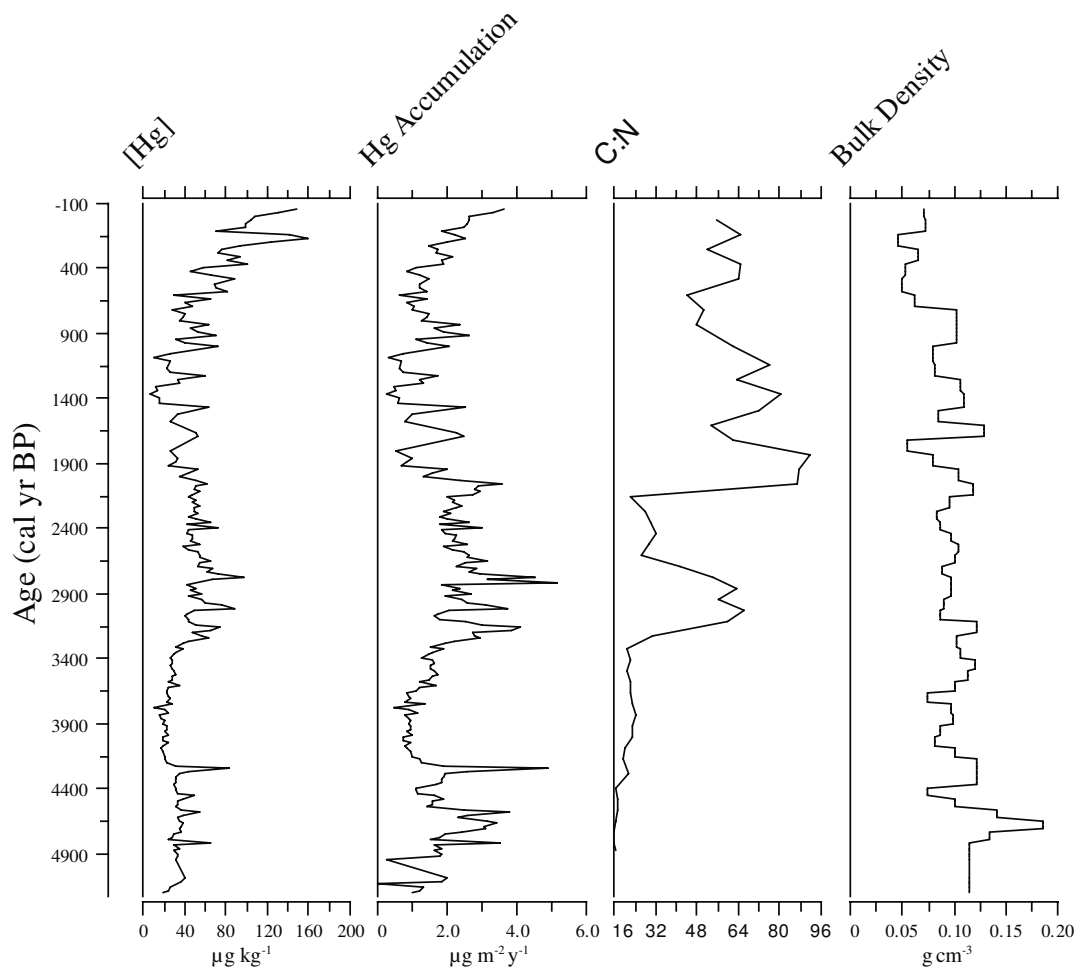


Figure A - 5. Bog 3 additional information including Hg concentration, Hg accumulation, carbon to nitrogen ratio (C:N) (provided by Maara Packalen and Dr. Sarah Finkelstein), and bulk density (provided by Maara Packalen and Dr. Sarah Finkelstein).

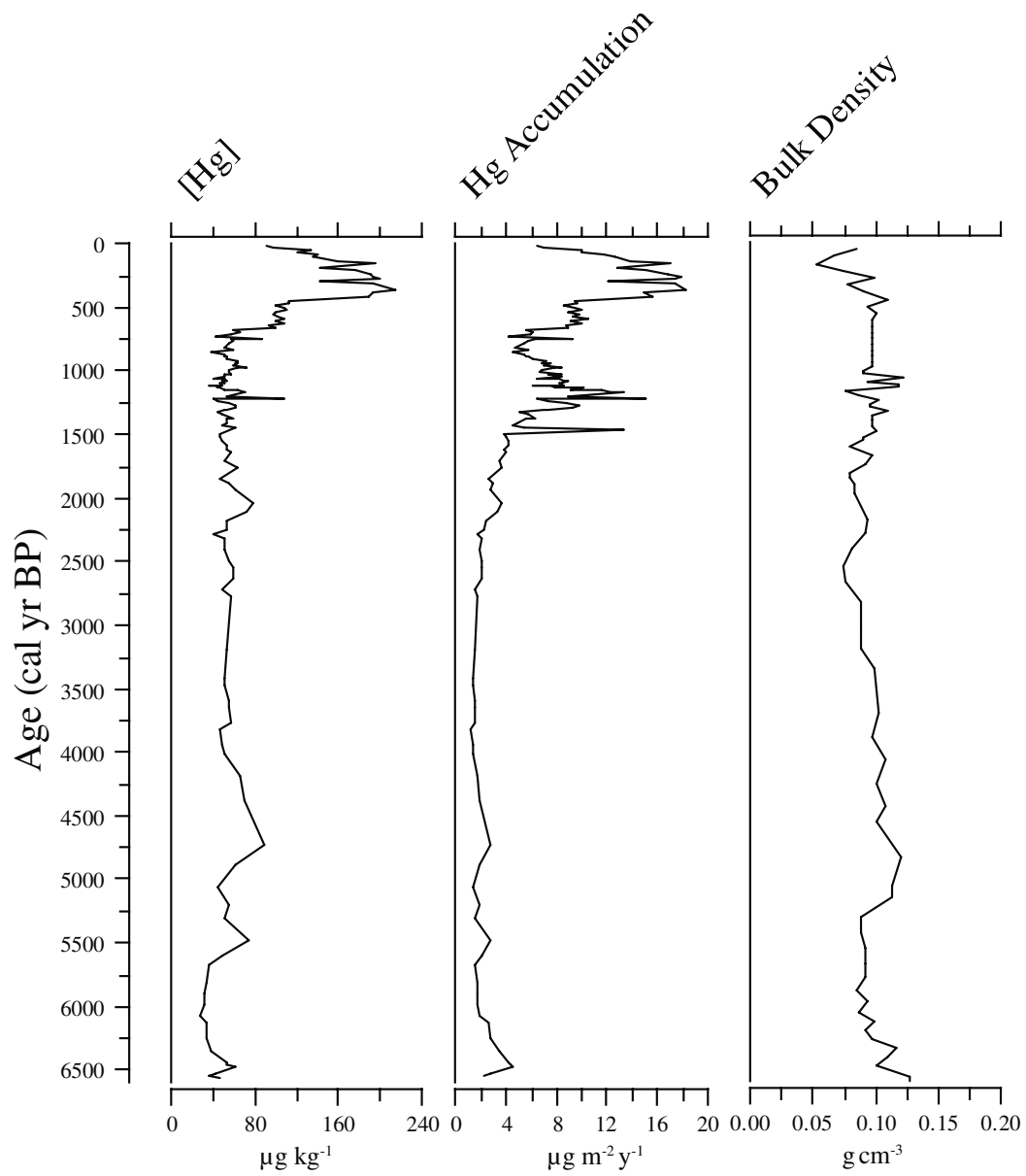


Figure A - 6. Fen additional information including Hg concentration, Hg accumulation, and bulk density (provided by Ben O'Reilly and Dr. Sarah Finkelstein).

References

- Bianchi, G. G.; McCave, I. N., Holocene periodicity in North Atlantic climate and deep-ocean flow south of Iceland. *Nature* **1999**, *397*, (6719), 515-517.
- Bond, G.; Showers, W.; Cheseby, M.; Lotti, R.; Almasi, P.; deMenocal, P.; Priore, P.; Cullen, H.; Hajdas, I.; Bonani, G., A pervasive millennial-scale cycle in North Atlantic Holocene and glacial climates. *Science* **1997**, *278*, (5341), 1257-1266.
- Broecker, W. S., Massive iceberg discharges as triggers for global climate change. *Nature* **1994**, *372*, 421-424.
- Bunbury, J.; Finkelstein, S. A.; Bollmann, J., Holocene hydro-climatic change and effects on carbon accumulation inferred from a peat bog in the Attawapiskat River watershed, Hudson Bay Lowlands, Canada. *Quatern. Res.* **2012**, *78*, (2), 275-284.
- Hermanns, Y.-M.; Biester, H., Anthropogenic mercury signals in lake sediments from southernmost Patagonia, Chile. *Sci. Total Environ.* **2013**, *445*, 126-135.
- Hu, F. S.; Kaufman, D.; Yoneji, S.; Nelson, D.; Shemesh, A.; Huang, Y.; Tian, J.; Bond, G.; Clegg, B.; Brown, T., Cyclic variation and solar forcing of Holocene climate in the Alaskan subarctic. *Science* **2003**, *301*, (5641), 1890-1893.
- McManus, J. F.; Bond, G. C.; Broecker, W. S.; Johnsen, S.; Labeyrie, L.; Higgins, S., High-resolution climate records from the North Atlantic during the last interglacial. *Nature* **1994**, *371*, (6495), 326-329.
- O'Brien, S. R.; Mayewski, P. A.; Meeker, L. D.; Meese, D. A.; Twickler, M. S.; Whitlow, S. I., Complexity of Holocene Climate as Reconstructed from a Greenland Ice Core. *Science* **1995**, *270*, (5244), 1962-1964.
- Oppo, D. W.; Keigwin, L. D.; McManus, J. F.; Cullen, J. L., Persistent suborbital climate variability in marine isotope stage 5 and Termination II. *Paleoceanography* **2001**, *16*, (3), 280-292.
- O'Reilly, B. C.; Finkelstein, S. A.; Bunbury, J., Pollen-Derived Paleovegetation Reconstruction and Long-Term Carbon Accumulation at a Fen Site in the Attawapiskat River Watershed, Hudson Bay Lowlands, Canada. *Arct. Antarct. Alp. Res.* **2014**, *46*, (1), 6-18.
- Packalen, M. S.; Finkelstein, S. A.; McLaughlin, J. W., Carbon storage and potential methane production in the Hudson Bay Lowlands since mid-Holocene peat initiation. *Nat. Commun.* **2014**, *5*.
- Ulanowski, T. A.; Branfireun, B. A., Small-scale variability in peatland pore-water biogeochemistry, Hudson Bay Lowland, Canada. *Sci. Total Environ.* **2013**, *454*, 211-218.
- Viau, A. E.; Gajewski, K.; Fines, P.; Atkinson, D. E.; Sawada, M. C., Widespread evidence of 1500 yr climate variability in North America during the past 14 000 yr. *Geology* **2002**, *30*, (5).
- Weber, M. E.; Tougiannidis, N.; Kleineder, M.; Bertram, N.; Ricken, W.; Rolf, C.; Reinsch, T.; Antoniadis, P., Lacustrine sediments document millennial-scale

- climate variability in northern Greece prior to the onset of the northern hemisphere glaciation. *Palaeogeog. Palaeocl.* **2010**, *291*, (3-4), 360-370.
- Willard, D. A.; Bernhardt, C. E.; Korejwo, D. A.; Meyers, S. R., Impact of millennial-scale Holocene climate variability on eastern North American terrestrial ecosystems: pollen-based climatic reconstruction. *Global Planet. Change* **2005**, *47*, (1), 17-35.
- Yu, Z.; Campbell, I. D.; Campbell, C.; Vitt, D. H.; Bond, G. C.; Apps, M. J., Carbon sequestration in western Canadian peat highly sensitive to Holocene wet-dry climate cycles at millennial timescales. *Holocene* **2003**, *13*, (6), 801-808.
- Zhao, C.; Yu, Z.; Zhao, Y.; Ito, E.; Kodama, K. P.; Chen, F., Holocene millennial-scale climate variations documented by multiple lake-level proxies in sediment cores from Hurleg Lake, Northwest China. *J. Paleolimnol.* **2010**, *44*, (4), 995-1008.

Appendix B

Supplemental Information to “Spatial Gradients of
Atmospheric Mercury Accumulation in Peat Cores from
the James Bay Lowland, Canada”

Radiocarbon Dating Standard Methods for Sampling

Students in Dr. Finkelstein's laboratory at the University of Toronto completed the following procedure. A 1 cm slice of the peat core was taken (avoiding the outermost material to avoid contamination) and put into a 250 ml beaker. To this beaker, 100 ml of 5% KOH was added to disaggregate the peat and the beaker was brought to a light boil on a hot plate for 10 minutes. Next, the sample was sieved through 90- μ m nylon mesh and washed until the solution was clear, thereby removing all KOH. The sample was then transferred to a 50 ml centrifuge tube, shaken well and then a small amount was poured into an unused, rinsed, disposable Petri dish. Using the stereomicroscope, each sample was scanned at 10x magnification and forceps were used to pick out larger pieces of wood, moss, leaves, or other organic remains and fractions of different materials were placed into separate 1.5 ml clear plastic vials. The entire centrifuge tube was picked through, to obtain as much organic material as possible for radiocarbon dating. Material taken for dating included *Sphagnum* stems, conifer needles, twigs and wood debris. Samples were sent to Beta Analytic Inc. for AMS dating.

Humification Sampling and Analysis Technique

Wet samples were taken directly from the core for peat humification analysis, for which a protocol modified from Blackford and Chambers (1993) was used. Samples of 1 cm width were taken at 3 cm intervals (except at edges of core drives), with the outermost material left intact to avoid contamination. These samples were placed in a metal container and dried to a constant weight at 60°C for ~24 hours. Fully dried samples were ground to a fine powder using a mortar and pestle and 0.2 g of powdered peat was transferred to a 150 ml beaker. 50 ml of 8% NaOH was added to each beaker, and samples were kept well mixed with glass stir rods. Each solution was then warmed on a hot plate until it boiled, then heat was reduced and the samples were left to simmer for 45 minutes.

At the end of 45 minutes of heating, the volume of each solution was topped up to 120 ml using distilled water. Samples were stirred, and 50 ml of each solution was added to large centrifuge tubes. The samples were centrifuged at 2500 RPM for four minutes, and then

filtered through Whatman No. 1 (150 mm) qualitative filter paper. A reference blank of 5 ml of 8% NaOH and 12 ml of distilled water was prepared to ensure the spectrophotometer was not drifting during analysis. For each sample, 3 ml was transferred via pipette into a glass cuvette and the absorbance was measured at a wavelength of 540 nm.

Table B - 1. ¹⁴C-AMS measurement summaries of peat macrofossil ages for 5 sites in the Hudson Bay Lowlands, Canada; listed by increasing latitude. Red wording indicates bomb pulse curve dates that were assigned a large error do to unlikely rapidity in recent accumulation (see Figure B-5).

Site	Location (DD)	Peatland Type	Peat Depth (cm)	Lab Number	Dated Depth (cm)	Material Dated	$\delta^{13}C$ (‰ PDB)	¹⁴ C Age (y BP)	Median Age (cal y BP)*	1 σ Age Range (cal y BP)*	2 σ Age Range (cal y BP)*	Reference
FH201	N51.179; W86.71	Bog	298	UGAMS-11671	297-298	wood fragment	-26.6	6740 ± 30	7600	7570-7620	7570-7660	Packalen <i>et al.</i> , in review
KJ43	N51.587; W81.78	Bog	131	UGAMS-11256	45-46	wood fragments	-26.4	130 ± 30	128	(-2) - 268	(-3) - 280	Packalen <i>et al.</i> , in review
				UGAMS-11255	80-81	wood fragments	-25.7	1560 ± 20	1468	1410-1510	1400-1520	Packalen <i>et al.</i> , in review
				UGAMS-12717	129-131	wood fragments	-27.4	3630 ± 25	3940	3910-3980	3870-4070	Packalen <i>et al.</i> , in review
				UGAMS-11663	40-41	<i>Sphagnum</i> remains	-27.0	F ¹⁴ C=1.024 ± 0.003	-5.50	(-4.9) - (-6.1)	(-4.4) - (-6.6)	Packalen <i>et al.</i> , in review
HL04 _{west}	N54.676; W84.60	Poor Fen	269	UCIAMS-97825	175-176	wood + herb stems	--	4170 ± 20	4720	4650-4820	4620-4830	Packalen <i>et al.</i> , in review
				UGAMS-12720	70-71	<i>Sphagnum</i> remains	-27.5	1880 ± 25	1832	1750-1880	1740-1880	Packalen <i>et al.</i> , in review
				UGAMS-12721	127-128	<i>Sphagnum</i> remains	-27.8	2560 ± 25	2723	2620-2740	2520-2750	Packalen <i>et al.</i> , in review
				UGAMS-12722	190-191	<i>Sphagnum</i> remains	-28.7	2920 ± 25	3067	3000-3140	2970-3200	Packalen <i>et al.</i> , in review
				UGAMS-11423	268-269	<i>Sphagnum</i> remains	-26.5	2700 ± 25	3550	extrapolated age	3290-3880	Packalen <i>et al.</i> , in review
				UGAMS-11424	90-91	wood fragments	-29.1	4960 ± 30	5685	5650-5720	5610-5740	Packalen <i>et al.</i> , in review

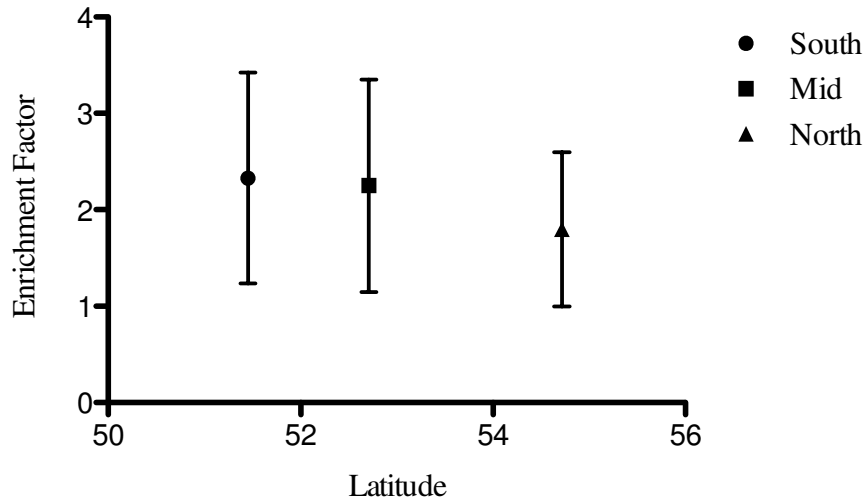


Figure B - 1. Latitudinal gradient of mercury enrichment factors in 9 cores from the Hudson Bay Lowland, Ontario, Canada.

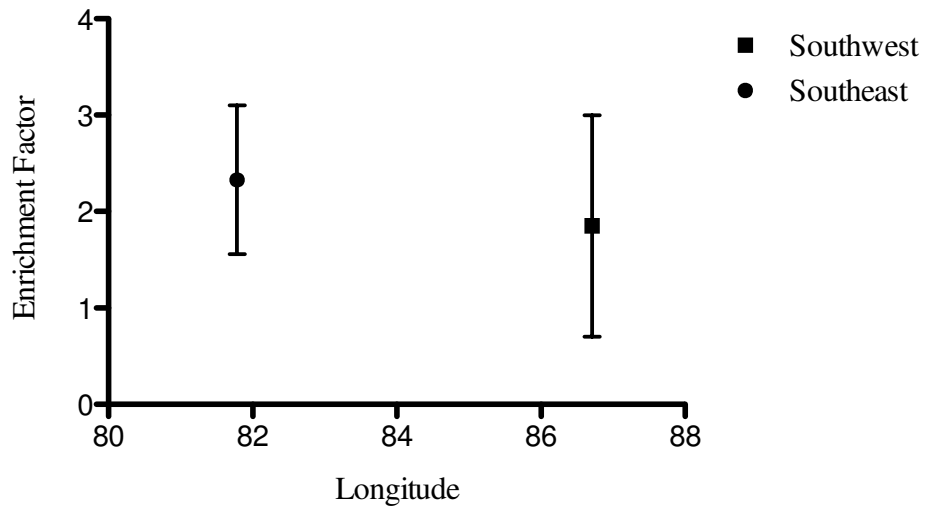


Figure B - 2. Longitudinal gradient of mercury enrichment factors in 3 cores from the Hudson Bay Lowland, Ontario, Canada.

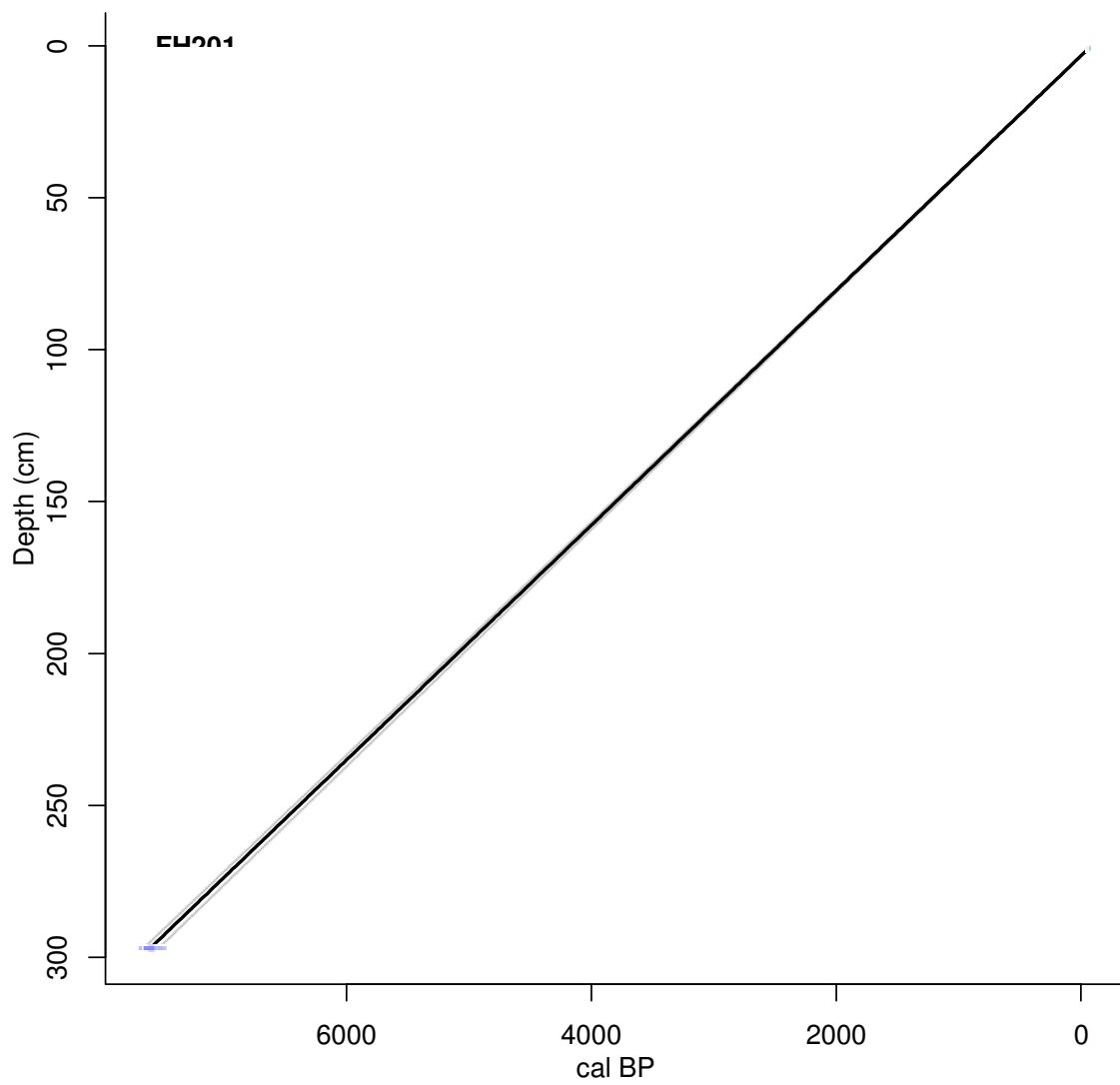


Figure B - 3. Age-depth model of Southwest core using the *clam* package in the software program R.

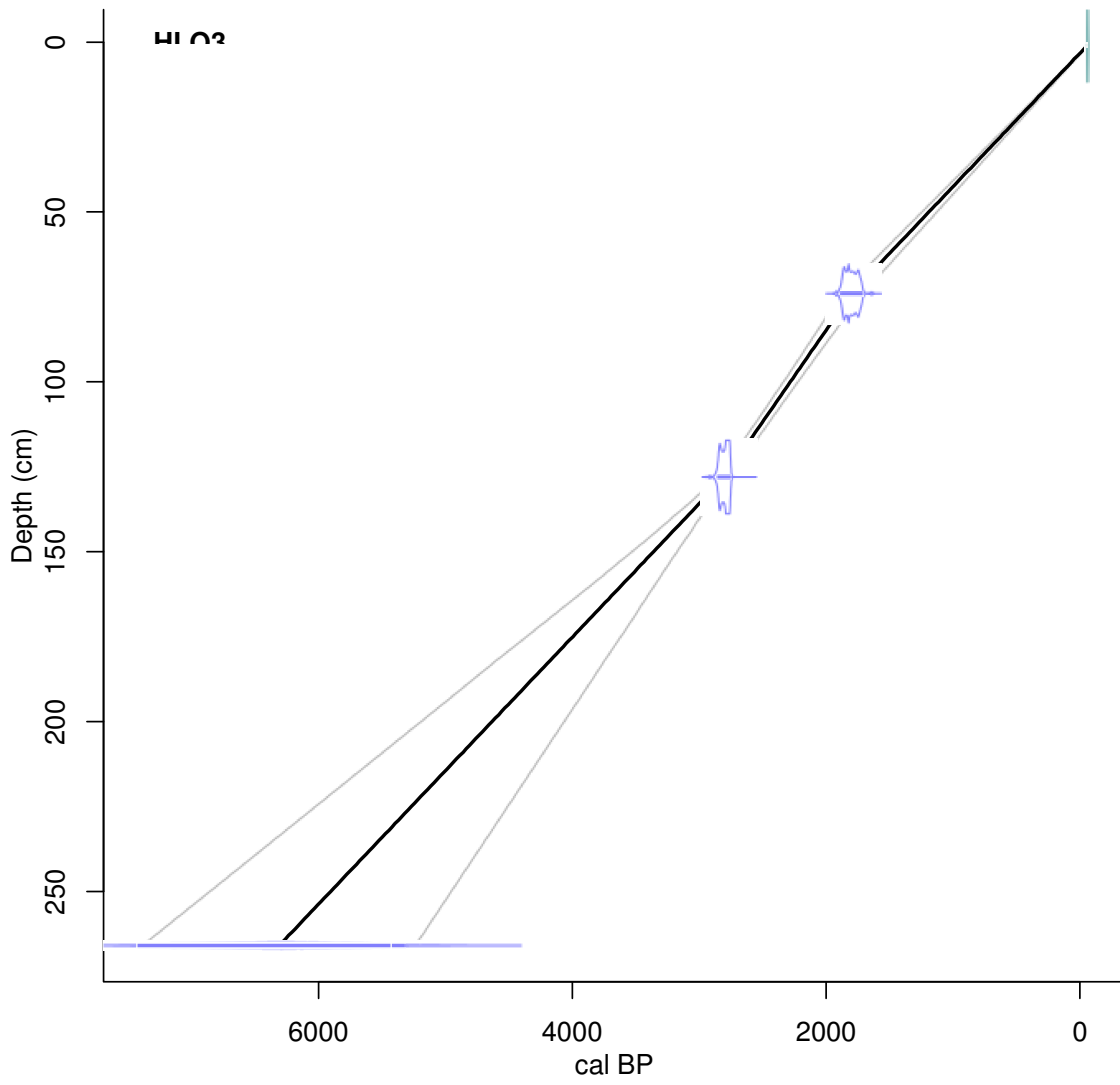


Figure B - 4. Age-depth model for North 1 using the *clam* package in the software program R.

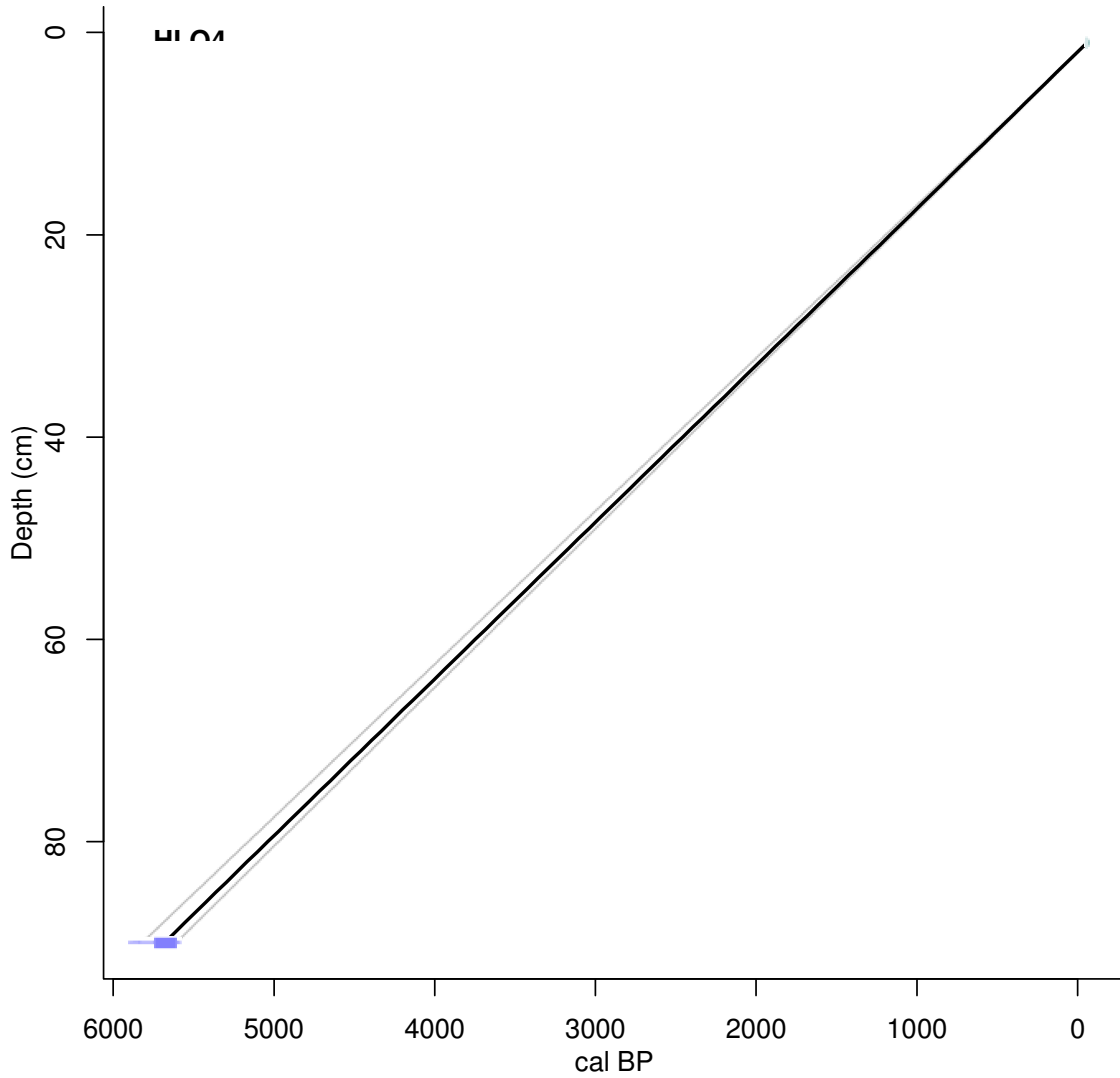


Figure B - 5. Age-depth model for North 2 using the *clam* package in the software program R.

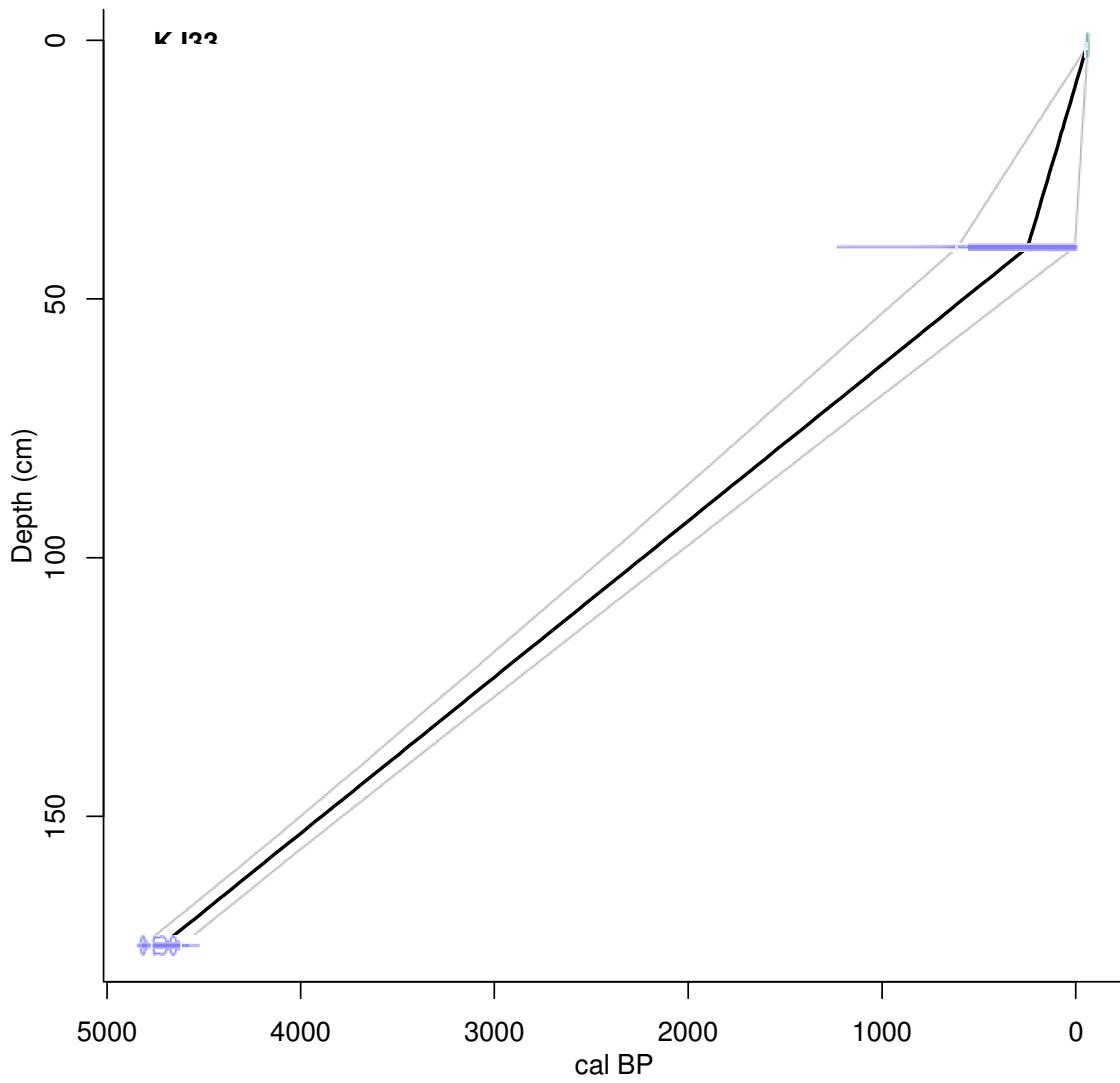


Figure B - 6. Age-depth model for Southeast 1 using the *clam* package in the software program R.

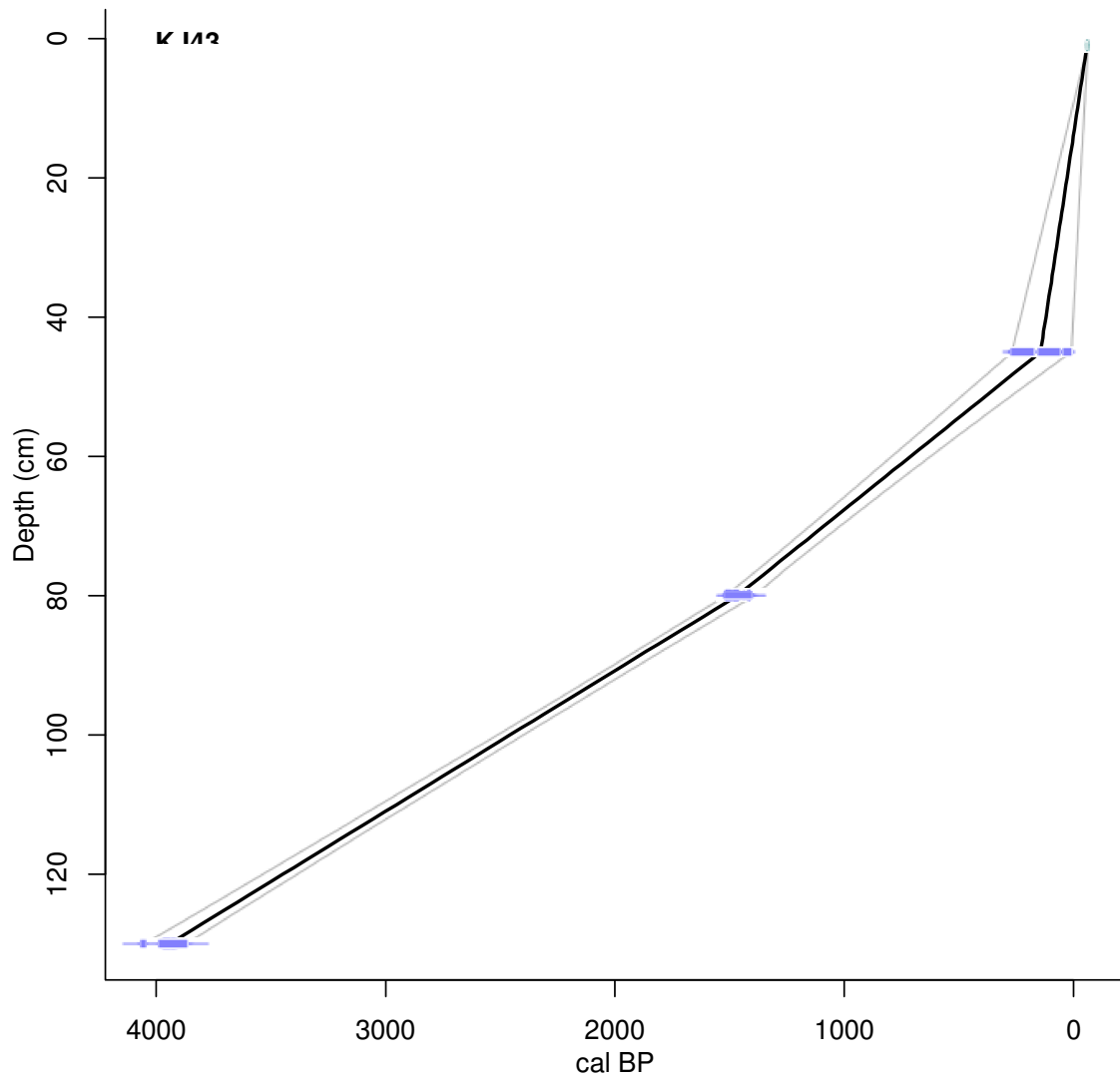


Figure B - 7. Age-depth model for Southeast 2 using the *clam* package in the software program R.

References

- Blackford, J.; Chambers, F., Determining the degree of peat decomposition for peat-based palaeoclimatic studies. *International peat journal* **1993**, *5*, (7.24).
- Bunbury, J.; Finkelstein, S. A.; Bollmann, J., Holocene hydro-climatic change and effects on carbon accumulation inferred from a peat bog in the Attawapiskat River watershed, Hudson Bay Lowlands, Canada. *Quatern. Res.* **2012**, *78*, (2), 275-284.
- O'Reilly, B. C.; Finkelstein, S. A.; Bunbury, J., Pollen-Derived Paleovegetation Reconstruction and Long-Term Carbon Accumulation at a Fen Site in the Attawapiskat River Watershed, Hudson Bay Lowlands, Canada. *Arct. Antarct. Alp. Res.* **2014**, *46*, (1), 6-18.
- Packalen, M. S.; Finkelstein, S. A.; McLaughlin, J. W., Carbon storage and potential methane production in the Hudson Bay Lowlands since mid-Holocene peat initiation. *Nat. Commun.* **2014**, *5*.

Curriculum Vitae

Name: Goacher, William James

Post-secondary Education and Degrees: University of Western Ontario
London, Ontario, Canada
2008-2012 H.BSc.
2012-2014 MSc. Candidate
2014-2017 J.D. Candidate

Honours and Awards: Best Thesis Talk – Undergraduate
2012

Northern Scientific Training Program
2012-2013

Best Student Presentation – International Conference on Mercury as a Global Pollutant, Edinburgh, Scotland
2013

Related Work Experience Research Assistant
The University of Western Ontario
2011-2012

Undergraduate Thesis Project
The University of Western Ontario
2011-2012

Undergraduate Thesis Presentation
The University of Western Ontario
2011-2012

Presentation of “Evidence of Millennial Trends in Pristine Peat Cores from the Hudson Bay Lowlands” – International Conference on Mercury as a Global Pollutant, Edinburgh, Scotland
2013

Teaching Assistant
The University of Western Ontario
2012-2014

VP Academic
Society of Graduate Students
2012-2014