Bioaccumulation and Concentration of Mercury in Rivers and Streams of the Hudson Bay Lowland

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Graduate Program in Biology

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

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BIOACCUMULATION AND CONCENTRATION OF MERCURY IN RIVERS AND STREAMS OF THE HUDSON BAY LOWLAND

(Thesis format: Monograph)

by

Ashley L. Warnock

Graduate Program in Biology

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

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Methylmercury (MeHg) is a neurotoxin that biomagnifies in northern aquatic food webs to high enough concentrations to cause concern for human consumption. The Hudson Bay Lowland of Canada is projected to experience climate and land-use impact in the immediate future, and these environmental stressors may affect the exposure to and subsequent bioaccumulation of MeHg in subarctic fish populations. The focus of this research is to evaluate the spatial variability in total and MeHg in water, sediment, and biota within and across a range of subarctic streams and river reaches of the Hudson Bay Lowland. This data was then used to project potential bioaccumulation in subarctic riverine food webs. Across all study sites, MeHg in surface water was low, with a mean concentration of 0.087 ± 0.012 ng/L. Water MeHg was strongly positively correlated to sediment MeHg ($R^2 = 0.80$), and both water and sediment contained a high proportion of total mercury as MeHg. Some individual small-bodied fish mercury concentrations were found to be above Canadian subsistence and commercial sale guidelines. The highest mean concentrations of fish mercury were 361.6 µg/kg and 156.7 µg/kg found at the two sampling sites corresponding to those with the highest water and sediment MeHg concentrations. Furthermore, calculation of MeHg bioaccumulation factors (BAFs) suggests that MeHg transfers predictably and highly efficiently in this subarctic food web. Using BAFs to predict changes to MeHg in fish with potential future changes to MeHg in surface waters demonstrates that small changes in Hg at the bottom of a food web can have large implications for fish tissue Hg.

**Keywords**

Bioaccumulation, ecohydrology, fish, food webs, mercury, subarctic, rivers, streams
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Chapter 1

1 Introduction

1.1 Mercury as a global pollutant

Mercury (Hg) is a toxic heavy metal that has been increasing in aquatic biota since the industrial revolution (Riget et al., 2011). Anthropogenic activities, such as the burning of fossil fuels, are currently the largest sources of Hg to the atmosphere, contributing to a 2-3 fold increase above pre-industrial levels (Lindqvist et al. 1991, Driscoll et al. 2007, Harris et al. 2007, Phillips et al. 2011). There is evidence that levels are still steadily rising in high-latitude regions of the Northern hemisphere, such as the subarctic Hudson Bay Lowland (Riget et al. 2011, Kirk et al. 2012). This is a significant cause for concern because the principle source of exposure of Hg to humans and wildlife is through diet, largely through the consumption of fish (Driscoll et al. 2007, Evers et al. 2011). Most global consumption advisories in food fishes have been implemented in response to elevated levels of Hg in aquatic systems (Evers et al. 2011).

Historical evidence in surficial lake sediments suggest that a significant portion of legacy (historically-deposited) Hg is anthropogenic in nature, as opposed to naturally-derived (Rada et al. 1989); this observation is further supported by recent findings that suggest that most inputs to the Arctic Ocean are from other parts of the world and transported there via long-range atmospheric processes (Kirk et al. 2012). Human activities, coupled with natural inputs of Hg to the environment (e.g., volatilization of Hg from mercuriferous soils and volcanic activity), have correspondingly led to increasing levels of inorganic Hg that include gaseous elemental Hg (Hg(0)) and complexed divalent Hg (Hg(II)), in natural aquatic systems since the industrial revolution (Ullrich et al. 2001, Phillips et al. 2011, Kirk et al. 2012).

The biogeochemical cycle of Hg is complex and relatively little is understood about this cycle in natural waters as compared to other metals (Ullrich et al. 2001) (Figure 1.1). The common dissolved physical states of inorganic Hg (Hg(0) and Hg(II)) readily undergo reactions and transformations to form various mercuriferous compounds, such as
mercuric sulphide (HgS) (Ullrich et al. 2001). Due to the high volatility of Hg(0), it is the dominant form of Hg in the atmosphere (95-100% of all Hg species) (Bloom and Fitzgerald 1988); as such, it can be transported to regions far removed from emission sources (Lindberg et al. 2007, Selin 2009). Atmospheric Hg(0) is oxidized to Hg(II) in the atmosphere and can be precipitated locally either in rain or snow (wet deposition) or associated with dust and aerosols (dry deposition) (Ullrich et al. 2001). If deposited into aquatic systems, this Hg(II) can be reduced back to Hg(0) in the water-atmosphere interface of aquatic systems (Mason et al. 1995). Through volatilization processes, Hg(0) may then be released to the atmosphere as a gas re-entering the atmospheric pool (Denkenberger et al. 2012).

Figure 1.1: A generalized schematic of the Hg cycle that illustrates the cycling and transformations of Hg through both anthropogenic and natural means. Source: State of Utah: http://www.mercury.utah.gov/atmospheric_transport.htm

Atmospheric Hg that is deposited onto the landscape can also be methylated under the right environmental conditions, forming methylmercury (MeHg) (Parks et al. 2013). Methylmercury (chemical nomenclature CH₃Hg⁺) is an organometallic compound, and it
is the most toxic form of Hg to humans and wildlife (Ullrich et al. 2001). This form of Hg is a persistent hepato- and neurotoxin that is readily available for uptake (bioavailable) by aquatic organisms and subsequently bioaccumulates in individuals and biomagnifies in aquatic food webs (Mason et al. 1995, Atwell et al. 1998, Tsui et al. 2009, Ward et al. 2010b). It is the form of Hg of concern and thus the focus of Hg science.

Mercury methylation most commonly occurs in environments that are anaerobic (oxygen-deprived), for instance, non-aerated water zones or the anaerobic sediments of freshwater lakes (Compeau and Bartha 1985, Ravichandran 2004, Lehnerr et al. 2012a, Lehnerr et al. 2012b). The production of MeHg in a system is primarily controlled by the metabolism of methylating microbial bacteria (Sunderland et al. 2006). Microbial methylation is facilitated by the presence of bioavailable inorganic Hg, nutrient-rich organic substrate, and terminal electron acceptors for bacterial metabolism (oxidation of Hg) (Driscoll et al. 2007) and on the anaerobic conditions in which they thrive (Compeau and Bartha 1985). The bioaccumulation of MeHg, and ultimately how much MeHg enters high trophic level organisms, is ultimately a function of how much bioavailable MeHg is at the base of a food web (Chasar et al. 2009, Jardine et al. 2013, Riva-Murray et al. 2013a).

1.2 Bioaccumulation, biomagnification, and depuration of mercury

Through the processes of bioaccumulation and biomagnification, organisms at higher trophic levels of the aquatic food web have tissue concentrations that are orders of magnitudes greater than those at lower trophic levels and the environment in which they live (Zillioux et al. 1993, Wolfe et al. 1998, Driscoll et al. 2007). Definitions of bioaccumulation in the literature are numerous, therefore for clarity, this thesis will operate under the working definition of the International Union of Pure and Applied Chemistry that it is the “progressive increase in the amount of a substance in an organism or part of an organism which occurs because the rate of intake exceeds the organism’s ability to remove the substance from the body” (Holland 1996). Biomagnification, according to Rand and Petrocelli (Rand and Petrocelli 1985), is the “bioaccumulation of a
[contaminant] through an ecological food chain by transfer of residues from the diet into body tissues. The tissue concentration increases at each trophic level in the food web when there is efficient uptake and slow elimination.”

Chemical compounds that undergo bioaccumulation are those that have high lipophilicity (strong affinity for fatty tissues), and/or high persistence (resistant to environmental degradation), and/or low solubility in water (Biddinger and Gloss 1984). Lipophilic (fat-soluble) substances are highly persistent (cannot be broken down) and are not excreted because they are not soluble in water of the body. When MeHg is consumed, it accumulates in fat cells of the gut, persisting until another eats that predator. After being absorbed by the gut, MeHg binds to red blood cells and is transported to muscle tissues. There it is primarily associated with sulphhydryl molecular groups in muscle protein and is highly persistent (Johnston et al. 2001, Hammerschmidt and Fitzgerald 2006, Kutscher et al. 2012). MeHg efficiently bioaccumulates in individuals and biomagnifies in food webs through consumption of lower trophic level organisms by predators (Mason et al. 1995, Tsui et al. 2009). Mercury may also enter a food chain through passive uptake across biological membranes (e.g., gills in fish) (Hall et al. 1997). The specific mechanisms of bioaccumulation, particularly between the water column and the primary producers (algae, microbes, zooplankton, phytoplankton), are not well described (Ullrich et al. 2001, Driscoll et al. 2007). Additionally, the timing and magnitude of bioaccumulation of Hg in fish species is still relatively understudied, considering how central it is to the problem of environmental mercury contamination (Harris et al. 2007, Munthe et al. 2007). As such, uncertainty remains in the understanding of the environmental factors that enhance fish Hg exposure and uptake (Harris et al. 2007).

The internal biological pathway and cellular uptake of MeHg is still poorly characterized, as are the specific sites on the ligands in the proteins where MeHg is believed to bind (Kutscher et al. 2012). There are only a few studies that describe the internal methylation of inorganic Hg to MeHg by bacteria in the gastrointestinal tract of fish and humans (Rudd et al. 1980, Trevors 1986, Boening 2000). Thus, the chemistry of Hg binding and methylating behaviour in living organisms is still not fully understood.
The process of accumulation of MeHg in living organisms is a fundamental physiological component of the global Hg cycle, but depuration (elimination) of MeHg from an organism is also important (Morel et al. 1998). These two processes are essential to the bioaccumulation and biomagnification of MeHg in food webs because they determine how much Hg is available to be transferred through a food web from one compartment to the next.

Two physiological processes govern accumulation in an individual: gross and net trophic transfer (Madenjian et al. 2012). Once ingested via food source or passive uptake, MeHg undergoes high internal (gut) ingestion or uptake and is incorporated into the body. This is referred to as gross trophic transfer (Madenjian et al. 2012). Following gross trophic transfer, an individual may also then retain a portion of the ingested contaminant instead of eliminating it all from the body; this is referred to as net trophic transfer efficiency (Thomann and Connolly 1984). Given high trophic transfer efficiencies (accumulation processes) coupled to strong protein-binding capabilities of MeHg, an organism will not be able to easily depurate MeHg. As a consequence, the subsequent rate of bioaccumulation is generally very high in individuals that are often exposed to MeHg (Madenjian et al. 2012). The rate of elimination of MeHg is slower than inorganic Hg, and in organisms is also negatively correlated to body size (Trudel and Rasmussen 1997), so larger and older organisms who have accumulated a lot of MeHg over their lifespan have even more difficulty ridding their bodies of the compound than their younger, smaller counterparts.

Methylmercury is physiologically eliminated from the body at a rate approximately 2.8 times slower than inorganic Hg (Trudel and Rasmussen 1997). Experiments on depuration rates of MeHg have been performed on a variety of species with similar results: Madenjian et al. (2012) found that MeHg is eliminated very slowly from the bodies of Lake Trout (Salvelinus namaycush) and Lindqvist et al. (1995) found that over 60% of MeHg in a predatory beetle (Pterostichus niger) was retained after a month of no exposure to the compound. These chemo-physiological characteristics of MeHg enable it to effectively bioaccumulate in organisms under constant exposure since they have no opportunity to eliminate it from their systems.
Other persistent organic pollutants, such as polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethanes (DDTs) can also biomagnify in food webs to levels that are hazardous to wildlife and human health (van der Oost et al. 2003, Gewurtz et al. 2010), but humans are more commonly exposed to MeHg through diet. MeHg concentrations in the body tissues of organisms may be orders of magnitudes greater than concentrations in the surrounding water. Hg biomagnifies up a food web relative to water column concentrations. So, if water column concentrations are high, then Hg can biomagnify to high concentrations in biota (Driscoll et al. 2007). Certain environments, such as wetlands, are known to support conditions that enhance the methylation of Hg. As such, biological organisms that inhabit these systems may be eminently exposed to increased background levels of Hg. Not only that, but the concentrations of, and exposure to, MeHg in organisms of a given species are highly variable from one geographical location to the next and among individuals within populations (Eagles-Smith and Ackerman 2009, Rennie et al. 2010, Verdouw et al. 2011), thus adding an additional level of complexity to the study of Hg in natural systems.

The effects of constant exposure to and bioaccumulation of MeHg in human and aquatic biological communities is of particular concern because the toxicity of the contaminant primarily affects the central nervous system (CNS) of the organism (Wolfe et al. 1998). When the CNS is poisoned by MeHg, behavioural and sensory-motor impairment may occur (Wolfe et al. 1998). The toxin also hinders an individual’s reproductive system and may induce developmental abnormalities and fetal death (Johnston et al. 2001). In fish specifically, the larval and early growth stages are particularly sensitive to exposure to contaminants (Boening 2000, Johnston et al. 2001, Driscoll et al. 2007), thus fish in Hg-contaminated environments are exposed to MeHg at all stages of their development and life histories. This exposure increases the potential for and prevalence of debilitating population effects when the health and longevity of individuals in that population are negatively affected.

1.3 Mercury cycling in rivers and streams

The environmental factors that regulate the formation of, and subsequent exposure to, MeHg in lotic systems (flowing water, e.g., rivers) are less well studied than to their
lentic (still water, e.g., lakes) counterparts (Chasar et al. 2009, Ward et al. 2010b, Tsui et al. 2012). Lakes have been the focus of research with respect to fish and Hg because the standing water of lakes provides easier fishing and navigation to fisheries industries. Also, tracing the movement and mixing of contaminants in flowing systems is highly complex (Tsui et al. 2012, Jardine et al. 2013), as is measuring stream inflows and outflows, which limnologists tend not to do. However, when assessing environmental contaminants, it is important to consider spatial variation in distribution of a contaminant. Variability has implications for environmental monitoring and research efforts, as difficulties could arise in assessing baseline conditions or collecting a representative sample of the environment. In order to understand spatial Hg dynamics in a given aquatic system, biogeochemical, ecological, and trophic controls on MeHg bioaccumulation are often considered (Chasar et al. 2009, Ward et al. 2010b).

Empirical studies have identified significant variability in Hg concentrations in fish tissues in spatially-independent small-stream food webs in different regions of the United States of America (Ward et al. 2010a, Ward et al. 2010b, Riva-Murray et al. 2011). In their review paper, Ward et al. (2010b) provide a comprehensive discussion of both abiotic and biotic environmental factors that are identified as potential environmental controls of MeHg accumulation and variability in tissue concentrations in freshwater fish. These controls include species-specific life history characteristics, but also parameters such as hydrology, water chemistry, and wetland characteristics (e.g., carbon storage capacity) (Galloway and Branfireun 2004, Sorensen et al. 2005, Marvin-DiPasquale et al. 2009, Moore et al. 2009). Shanley et al. (2005) identify time of year (seasonality) and hydrological variability as key physical controls to the delivery of Hg to surface water bodies from adjacent wetlands. The relationship between hydrology and transport of bioavailable Hg to aquatic systems has been highlighted in the literature (Branfireun et al. 1996, Heyes et al. 2000), and with climate change and alterations to the global hydrologic cycle, the influence of hydrology on Hg is becoming a prevalent topic. Branfireun et al. (1996) showed that peatland hydrology controls the magnitude and flux of MeHg to downstream ecosystems. Future extreme storm events could result in flushing of MeHg from peatlands to connected streams and rivers.
Lotic systems are often more strongly connected to their drainage basins (catchments) than lentic systems (Marvin-DiPasquale et al. 2009), so alterations to wetland water tables may have a serious affect on river- and stream-dwelling biological communities. For instance, projections for climate change include more frequent cycles of wetting and drying of wetlands, and Sorensen et al. (2005) found that significant variation in mean Hg levels in fish was governed by annual water-level fluctuations. The relationship between this complex suite of variables and Hg concentrations in fish may yield further information about variability in Hg exposure in freshwater systems. Further study, however, is needed to identify the underlying physical processes that govern Hg dynamics in lotic systems, which are both functionally and structurally different than their standing counterparts, e.g., continuous flow in rivers versus stratification in lakes (Ward et al. 2010b, Tsui et al. 2012).

1.4 Mercury in northern environments

The Hudson Bay Lowland of Canada is the second largest continuous peatland (wetland) complex on Earth (Roulet et al. 1994) and approximately 50% of its surface area is covered with lakes, rivers, and streams, collectively known as surface waters. Lotic systems and wetlands, like peatlands, are understood to be particularly sensitive to biogeochemical and physical impact (Driscoll et al. 2007). This is of particular concern in northern Ontario where there are projections for both significant climate and land-use (due to resource extraction) changes in the immediate future. Peatlands are sources of water to rivers and are known sinks (catchments) of Hg and sources of MeHg (Branfireun et al. 1998). However, the peatlands of the Hudson Bay Lowland are located in the north and typically far-removed from point-source anthropogenic pollution (Kirk et al. 2012). Despite this, and generally low ambient (background) Hg concentrations in the water column, MeHg bioaccumulates in biota and biomagnifies in northern food webs to exceptionally high concentrations (Lehnherr et al. 2011, Kirk et al. 2012). For instance, Kirk and St. Louis (2009) found average surface water concentrations of 0.050 ± 0.030 in two major subarctic rivers. These resulting high levels, often above the safe levels for consumption, of MeHg in northern aquatic biota pose a health risk to consumers.
Since the 1960s, efforts have been made to quantify contaminant loads (including Hg) in fish populations in the north. The focus, however, has primarily been on Ontario’s boreal shield/forest lakes and rivers, not the extensive drainage basin of the Hudson Bay Lowland that is dominated by peatlands (Browne 2007). There are a few studies that have assessed Hg concentrations and biogeochemical variability in surface water and wetland ecosystems in northern regions (subarctic and Arctic). Atwell et al. (1998) demonstrated that, in the Arctic, vertebrates are more susceptible to individual tissue variance in Hg concentrations than invertebrates. This variance increases with trophic level. Loseto et al. (2008) and Campbell et al. (2005) have also observed variability and enriched Hg levels in marine vertebrates, ranging from 35 µg/kg in zooplankton to 587 µg/kg d.w. (dry weight) in sculpin. Swanson et al. (2006) documented a similar species-specific trend in variability in northern lakes with measurements of 70 µg/kg in round goby to 860 µg/kg d.w. (dry weight) in sculpin. Recent research conducted in the Arctic...
suggests that northern rivers are a primary source input of Hg to the Arctic Sea (Fisher et al. 2012); this demonstrates the need to quantify an understanding of baseline Hg dynamics in rivers systems of the north. A major knowledge gap exists in understanding these Hg loadings and spatiotemporal variability with respect to lotic systems and in fish populations where, to our knowledge, no published data on the full suite of food web Hg exists.

Spatial variability in lotic food web Hg is poorly understood in high latitude regions. Mercury is known to be spatially variable at both large and small scales (Morel 1998, Ulanowski and Branfireun 2013). This variability may be driven by landscape-level influences, such as differences in climate and watershed hydrology, or by mechanisms that exist at the in-stream microhabitat scale, including local redox conditions and food web complexity. There are a host of environmental conditions and variables that may drive mercury production and mobilization, such as pH, temperature, dissolved organic matter (DOM), nutrient availability and primary productivity, and presence and speciation of Hg-methylating bacteria (Ullrich 2001). The interaction of these variables facilitates differential aquatic Hg exposure, resulting in spatial variability of bioavailable Hg that is available for uptake in food webs (Ward 2010b). Many of these variables are temperature-dependent, so future increases in climatic warming could facilitate changes in environmental Hg exposure.

Environmental conditions, i.e., climate, in northern regions differ from their more southern counterparts. Temperature (climate) is known to be the primary influence on fish ecology and physiology (Ficke et al. 2007), and temperature also influences surface water Hg concentrations and thus the amount of dissolved Hg available to an aquatic food web. Subarctic regions are also characterized by low productivity and short growing seasons as a result of the cold climate, and little is published about the interactions of these climate stressors and species-specific behaviours and habitats on bioaccumulation of Hg. High productivity, specifically, can result in bloom dilution (the partitioning of available Hg into greater amounts of biomass), whereby low productivity increases bioaccumulation through a food web because MeHg is not diluted in biomass (Driscoll et al. 2007, Ward 2010b). Furthermore, in colder, low productivity environments, fish may
expend more energy to forage, thereby effectively increasing their body burden of Hg by not partitioning energy from food intake to growth (Ward 2010b).

1.5 Research objectives

An understanding of the critical environmental drivers of Hg exposure and uptake in these northern systems has not been established. This area of Ontario is far-removed from point sources of Hg contamination, and so Hg in this area is mostly naturally-occurring. Most research that has assessed contaminants in food webs has done so in response to disturbance or in physically stressed systems (Choy et al. 2008, Chasar et al. 2009). The focus of much research in the north, including that presented in this thesis, is to provide baseline environmental data prior to environmental changes.

Understanding northern ecosystems is of particular importance because of the likelihood of environmental impact as a result of extensive resource extraction; of note is the Ring of Fire, an area ~ 120 km northwest of the De Beers Victor mine that is currently undergoing exploration for mining development that is estimated to house billions of dollars worth of chromite deposits. In addition to landscape modifications resulting from resource extraction are the projected impacts from climate change. Climate change will increase the vulnerability of peatlands to changes in chemodynamics. Climate-induced changes in water table fluctuations may influence the cycling and release of carbon in peatland ecosystems (Tarnocai 2006). The carbon cycle is closely linked to that of Hg as dissolved organic matter (DOM) interacts readily with Hg to enhance solubility, mobility, and transport (Ravichandran, 2004), and disturbance of carbon in peatland ecosystems could facilitate this interaction. In peatland-dominated (carbon-rich) systems, mercury may bind to DOM in the wetland and be transported hydrologically to adjacent surface waters. DOM increases the bioavailability of Hg to aquatic organisms, so physical alterations to carbon stores in peatlands may increase the amount of bioavailable Hg that is produced and mobilized for uptake by biota (Ravichandran 2004). This unique and vast region is undergoing significant ecological change and in order to effectively manage freshwater aquatic systems and fish stocks, it is critical to perform science to gain understanding of this environment and how it might be affected by changes in
climatic conditions. As such, the objective of this research is to address the following questions:

1) Is there spatial variability in total and methylmercury in water, sediment, and biota within and across a range of subarctic streams and river reaches of the Hudson Bay Lowland, and if so, what does it look like?

2) Using the data from question 1 combined with mercury data from northern forage fishes, what are the bioaccumulation factors for these northern lotic ecosystems and can they be used to develop an illustration to assess the impact of potential future changes in water MeHg concentrations on trophic transfer and bioaccumulation in these organisms?
Chapter 2

2 Materials and Methods

2.1 Study site

The study area is located approximately 500 km north-northwest of Timmins, Ontario and 90 km west of Attawapiskat, Ontario (52°83’49” N, 83°53’00” W) at the De Beers Canada Victor diamond mine, which has been fully operational since 2008. Samples were collected at eight study locations that comprised a variety of first- through fifth-order (Strahler 1957) rivers and streams which are control and reference sites selected to monitor annual changes in Hg levels in and around the zone of impact at the mine (Whittington and Price 2006). Physical characteristics of the study sites including annual climatic and hydrologic data are presented in Appendix 1. It is important to note that the De Beers mine was used as a base camp and does not produce, use, or discharge Hg as part of any of its processes. That said, the rationale for the multi-stakeholder project that this research is part of was to study this highly sensitive region and examine the impact of land use changes as a result of mining activities on hydrologic patterns and the Hg cycle.

Reference monitoring sites were established prior to operation operation of the mine for an Environmental Effects Monitoring Program, thus presenting the opportunity to do research at these locations. Control sites are located within the geographic zone of mine influence, and reference sites are located outside of the zone of mine influence. Comparison of control and reference sites was outside the scope of this study.

The Attawapiskat River (sites 1-3) (Figure 3.1) is a fifth-order river with a drainage basin of approximately 50,000 km². It is a lotic system extending from the headwaters in the Boreal Shield, through the low-gradient Hudson Bay Lowland Ecozone, and draining into James Bay. Mine effluent discharges into the Attawapiskat River ~100 m upstream of site 2, so for monitoring purposes site 1 was chosen as a control site to sites 2 and 3. The Nayshkootayow River (sites 4 and 5) (Figure 3.1) (basin size ~1,500 km²) is a third- to fourth-order river and major tributary of the Attawapiskat River. Along the
Nayshkootayow River, site 5 is located downstream of the mine, and so site 4 was chosen as its reference site.

**Figure 2.1**: Study sites where samples were collected near the De Beers Canada Victor mine. Insert: map of Ontario, Canada. Hudson Bay Lowlands shaded gray. Star represents study site at the mine. Cross represents location of mine effluent discharge. Scale: 1 cm = 3.2 km. Source: T. Ulanowski, 2013.

The remaining sites are in small, first- and second-order creeks (Figure 3.1). Granny Creek has two sub-watersheds, North (site 6) and South (site 7), and lies within the zone of influence of the mine. Tributary 5A (site 8) is a reference site to North Granny Creek based on similarities in drainage basin characteristics (Appendix 1) but is well outside of the mine influence (Figure 2.1). These latter sites have basin sizes of 30-50 km² and are peatland-dominated streams, although the hydrologic regimes of North and South Granny Creeks have been modified as a result of mining activities. North Granny Creek is supplemented by a pipeline in its lower reaches by water from the Attawapiskat River and South Granny Creek has been physically rerouted around the mine site. For more
information on mining activities, specifically dewatering processes, please refer to

2.2 Sample collection

All samples were collected from the end of August through the beginning of September
in 2011. Each site was only visited once. The units of analysis were the sites, and food
web samples were collected from each site. Sample sizes are listed in Table 3.1. This
time period corresponds with the end of the growing season in this region. Samples
collected included water, sediment, aquatic vegetation (plants), seston (suspended
particulate matter and plankton), algae (periphyton and filamentous algae), benthic
(macro)invertebrates, and fish. There is evidence of small-scale spatial variability in Hg
in temperate streams (Choy et al. 2008, Ward et al. 2010) and in northern peatland
environments (Ulanowski and Branfireun 2013), and so to account for this, samples were
collected at each site along a longitudinal transect spanning 10-50m, depending on the
accessibility and ability to wade in the water. (Refer to Figures 3.6-3.8 for an example of
the transect along which samples were collected.) At sites that were conducive to
wading, samples were collected at three points across the width of the channel, or from
bank to bank. This region of study is highly oligotrophic (low in nutrients) and has low
temperature. Because of the oligotrophic nature of the environment, biological materials
(plants, seston, algae, and benthic invertebrates) were not present in sufficient quantity
(mass) for full chemical analysis (both THg and MeHg) at all sites. MeHg is the Hg
species of interest, and so in the case of insufficient mass only MeHg analysis was
performed.

Water samples were collected using techniques appropriate for ultra-trace metal sampling
(see US EPA 1669, 1996) into sterile 500 mL PETG bottles as either a grab sample or via
peristaltic pump and acid-cleaned Teflon® tubing. Briefly, these techniques involved
having two personnel sampling at all times. Both are gloved (nitrile) when handling
sampling equipment and bottles. One personnel handles the clean sampling equipment
and one only handles the bottle and sample media. All sample bottles were double-
bagged in clean resealable plastic bags. Samples were frozen upon collection and
maintained as such until thawed for Hg analysis. All samples were kept frozen for approximately 4-6 weeks prior to chemical analysis.

Unconsolidated sediment was collected at each site using an Eckman® bucket sampler, sampling approximately the top 10 cm of sediment. Seston was collected at the Attawapiskat River and the Nayshkootayow River by trawling a Nitex® (333 µm) net behind a boat (5-10 minutes, 1 m depth until sufficient sample had been collected). On the creeks (North Granny, South Granny, and Tributary 5A), trawling a boat was not possible, so nets were set up on fixed posts driven into the bed of the stream to allow water to flow through for at least one hour to collect sufficient sample. Sample was then collected from the nets and stored in a plastic bag. Algae and plants were sampled by hand, rinsed in ambient water of debris, and double-bagged in the field. Benthic invertebrates were collected using a Surber sampler, transported to the field laboratory in a plastic bag, and then broadly sorted to order at the field laboratory. Only samples that contained sufficient mass for analysis (>1 g) were preserved for subsequent analyses. All samples were handled following clean procedures (US EPA 1669, 1996) and stored in clean Ziploc® bags or PETG bottles, and frozen immediately after sorting.

Small-bodied fish (trout-perch, *Percopsis omiscomaycus*, and pearl dace, *Margariscus margarita*) were collected for subsequent Hg analysis for the purpose of monitoring physiochemical changes in Hg dynamics that may result from mine dewatering activities. Small-bodied fish were collected from the study sites from the end of August through the beginning of September by employees of AMEC Earth and Environmental. Fish were caught using standard fishing techniques. Electrofishing was primarily used, but gill, seine, and small trap nets were also employed when appropriate and conducive to site conditions. Fish were transported to the laboratory at the mine site, organized, and then frozen. Frozen fish samples were shipped to the University of Western Ontario and were held at -25°C until Hg analysis. Fish samples were not thawed until the day of analysis. Fish were analyzed within 6 hours of being thawed.
2.3 Laboratory analysis

Sediment samples were thawed, subsampled, and lyophilized (freeze-dried) until dry, for approximately 48 hours. Samples were then sieved at 0.861mm, the coarse material reserved for separate analysis. Algae and plants were also subsampled, lyophilized for 48-72 hours or until dry, homogenized, and then stored in a cool and dark location until chemical analysis. Sediment, algae, and plants were all analyzed for both THg and MeHg.

To extract seston from collected water samples, samples were centrifuged at 3000 RPM for 20 minutes in 15mL round-bottom Falcon™ tubes. Following centrifugation, excess water was removed, save for enough water so as to not disturb the cemented sample (~0.5 cm). Samples were then re-frozen, lyophilized for approximately 24 hours, homogenized, and then stored in a cool and dark location until analysis for MeHg. THg analysis was not performed on seston because there was inadequate amount of dry mass for both THg and MeHg.

Prior to THg and MeHg analysis, benthic invertebrates were sorted and then re-frozen and lyophilized for 24 hours, homogenized, and then stored in a cool and dark location until analysis for MeHg. THg analysis was not performed on benthic invertebrates because there was inadequate amount of dry mass for both THg and MeHg. However, benthic invertebrates typically have ~50% of THg as MeHg (%MeHg) (Hildebrand et al. 1975), and MeHg is the Hg species of interest that bioaccumulates and biomagnifies. Decapoda (crayfish), Odonata (dragonfly nymphs), and Veneroida (freshwater mussels) were all analyzed for MeHg as individual samples. However, to obtain an adequate sample mass for analysis, all other benthic invertebrates were analyzed as composite samples for a given sampling location.

Immediately prior to analysis, fish were thawed to room temperature and dorsal muscle tissue was removed using clean techniques (US EPA 1669, 1996). Heads were removed from all trout-perch (n=300) and sent to Northern Bioscience Ecological Consulting in Thunder Bay, Ontario for age analysis of calcified structures. The aging process involves
interpretation and count of circuli (growth rings) on the scales and otolith bones of fish following a crack-and-burn procedure (Casselman 1974).

Mercury in the fish muscle tissue was analyzed for total mercury (THg). In large-bodied fish, 95-99% of the THg is MeHg (Grieb et al. 1990, Bloom 1992). As THg is easier and less expensive to analyze, THg is measured as a proxy for MeHg in large-bodied and small-bodied fish tissue. Tissue, as well as all samples other than water, was analyzed for THg on the Milestone Direct Mercury Analyzer (DMA-80) using a standard method in this field, US EPA Method 7473 (2007). Briefly, this method uses thermal decomposition, catalytic conversion, gold amalgamation, and atomic absorption spectrophotometry. It involves loading a nickel boat on the instrument with 0.5-1 g of sample and running the standard method for fish Hg analysis. This method includes a drying temperature of 300°C and a decomposition temperature of 600°C. The instrument reports results in both concentration (mg/kg) and mass (ng) of Hg. The instrument was calibrated upon each replacement of the catalyst and the gold amalgamator using National Research Council of Canada Certified Reference Materials (CRMs) (TORT-2 0.27 ± 0.06 mg/kg, DORM-2 4.64 ± 0.26 mg/kg). A daily calibration check using the CRMs was included every 10 samples to ensure calibration validity. All check standards, blanks, duplicates, and samples were within the acceptable range of quantification as outlined in US EPA 7473 (2007). The method detection limit (MDL) for the instrument was 0.02 µg/kg d.w. The amount of sample used for THg analysis was typically <0.5g, which corresponds to what is outlined in standard method 7473.

The US EPA offers two standard methods for the analysis of Hg in aqueous matrices, both of which were used to analyze these samples: methods 1630 (for measuring THg), and 1631 (for measuring MeHg). Upon thawing, water samples were split and half the sample was filtered for dissolved-phase Hg analysis using an acid-cleaned Teflon® filtration unit and ashed glass-fibre filters (Whatman® glass microfibre 0.7 µm). All samples were acidified to 1% with ultra-trace grade hydrochloric acid. ~30 mL of filtered (dissolved-phase) and unfiltered (particulate-phase) water samples were analyzed for THg using the Tekran 2600 (EPA 1631, 2002). Briefly, method 1631 includes via oxidation of Hg to Hg(II) with bromine monochloride (BrCl), reduction to Hg(0) with
stannous chloride (SnCl), and followed with purge and trap and cold vapour atomic fluorescence spectrometry (CVAFS). Samples were analyzed for MeHg using the Tekran 2700 (EPA 1630, 1998) which includes via distillation, aqueous ethylation, purge and trap, and CVAFS. The method detection limit (MDL) for the instrument is 0.02 ng/L.

Solid phase MeHg analysis (for sediment, algae, plants, seston, and benthic invertebrates) was achieved by modifying existing USGS methods for MeHg analysis using weak acid digestions (either 25% KOH or 5M HNO₃) (these methods can be found at: http://wi.water.usgs.gov/mercury-lab/analysis-methods.html). The modification included digesting the samples according to their method, but then performing chemical analysis using the standard operating procedures for the Tekran 2700 Hg analyzer, which is located in the Biotron. Following digestion, samples were analyzed for MeHg using the Tekran 2700 Hg analyzer. All laboratory analysis underwent rigorous quality assurance/quality control (QA/QC) measures to ensure validity of results. Acceptable instrument precision is ± 20% of the SRM value.

2.4 Data analysis

All statistical analysis was performed using IBM SPSS v.20.0 statistical software and Graphpad Prism v.5.0a. Statistical significance was set at p<0.05. Analysis of variance (ANOVA) followed by Tukey Kramer’s Honestly Significant Different (HSD) post hoc test was used to examine significance between sites. Figures were created using Graphpad Prism v.5.0a. The coefficient of variation, measured as the ratio of standard deviation to mean, allows for the comparison of variability of data sets regardless of measurement units or magnitude of differences between values (Triola et al., 2002).

All fish tissue concentrations are expressed as wet weight (w.w.) to correspond with most reported values in the literature and the Health Canada consumption guidelines. All other compartments are expressed in dry weight (d.w.).

Trophic relationships and bioaccumulation are known to be log-linear (Cabana and Rasmussen 1994, Atwell et al. 1998, Campbell et al. 2005, Campbell et al. 2008). A bioaccumulation factor (BAF) is the ratio of a chemical concentration in an organism to
the concentration in water (DeForest 1997). Deriving the BAF for each food web compartment allows for comparison of Hg bioaccumulation in biota over space and time. Additionally, BAFs can be used to examine the transfer of Hg between trophic levels in a food web. Bioaccumulation factors (BAF) were determined for MeHg using the following equation:

1) \[ BAF = \log \left( \frac{MeHg_{\text{Biot}}}{MeHg_{\text{Water}}} \right) \]

Assuming that water is the source of Hg, equation 2 was simply used to illustrate a projection of the impact of changes to bioaccumulation (presented in the discussion) with increases in MeHg in water. This shows how increasing water concentrations may affect Hg in higher-level trophic organisms. Concentrations for biota were determined using the following equation:

2) \[ [MeHg] = 10^{BAF *} ([MeHg_{\text{Water}}]^{*}[X]) \]

where \([MeHg] = \) concentration of MeHg in biota, \(BAF = \) bioaccumulation factor determined for a given food web compartment (equation 1), \([MeHg_{\text{Water}}] = \) concentration of MeHg in water, and \(X = \) factor of increase in concentration of MeHg in water. For instance, \(X = 2\) would represent a two-fold increase in water MeHg.

Although fish Hg is commonly reported as THg, MeHg was used to calculate fish bioaccumulation factors because no alternative information was available. THg in fish is assumed to be 95-99% MeHg, so informal sensitivity analysis was performed using 95% of the THg values to calculate BAFs. Because the BAF values only changed by a small amount, \([THg] = \) was used for the calculations in fish. In all other food web biota, \([MeHg] = \) was used to calculate BAFs.
Chapter 3

3 Results

Presented are results of THg and MeHg in the aquatic food web compartments that were sampled: water, sediment, plants, seston, algae, benthic invertebrates, and small-bodied fish (trout-perch and pearl dace). Summary statistics for each compartment by site are presented in Figures 3.1-3.5, Appendix 2a-f, as well as described below. Following the results for each compartment, I present analysis of spatial variability in sediment within sites 6 (North Granny Creek), 7 (South Granny Creek), and 8 (Tributary 5A). Bioaccumulation factors (BAF) are then presented for the subarctic food web under study.

Table 3.1: Summary of the number of samples (n) collected, range of values, and mean (\(\bar{x}\)), for total mercury (THg) and methylmercury (MeHg) concentrations in food web compartments for all sites combined. Mean mercury (Hg) values include ± 1 standard deviation (SD). --- indicates that no data is available.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>n (THg)</th>
<th>n (MeHg)</th>
<th>(\bar{x}) THg ± SD (µg/kg)</th>
<th>(\bar{x}) MeHg ± SD (µg/kg)</th>
<th>%MeHg ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (Filtered 0.45 µm)</td>
<td>85</td>
<td>76</td>
<td>1.61±0.55 (ng/L)</td>
<td>0.087±0.12 (ng/L)</td>
<td>4.98±5.68</td>
</tr>
<tr>
<td>Sediment</td>
<td>68</td>
<td>67</td>
<td>33.64±29.18</td>
<td>0.90±2.43</td>
<td>4.27±9.95</td>
</tr>
<tr>
<td>Plants, Seston(^1), Algae</td>
<td>42</td>
<td>44</td>
<td>28.72±27.38**</td>
<td>4.61±3.08</td>
<td>23.48±24.15**</td>
</tr>
<tr>
<td>Benthic Invertebrates</td>
<td>39</td>
<td>---</td>
<td>---</td>
<td>37.48±26.03</td>
<td>50*</td>
</tr>
<tr>
<td>Trout-Perch (Young-of-Year)</td>
<td>138</td>
<td>---</td>
<td>48.58 ±19.34</td>
<td>---</td>
<td>95-99*</td>
</tr>
<tr>
<td>Trout-Perch (1+)</td>
<td>162</td>
<td>---</td>
<td>79.87±39.32</td>
<td>---</td>
<td>95-99*</td>
</tr>
<tr>
<td>Pearl Dace</td>
<td>262</td>
<td>---</td>
<td>205.41±184.37</td>
<td>---</td>
<td>95-99*</td>
</tr>
</tbody>
</table>

* These estimations are based on values from the literature (Hildebrand et al. 1975, Grieb et al. 1990, Bloom 1992).
** This value does not contain seston. Since seston was not analyzed for THg, %MeHg was calculated using only plant and algae samples.
\(^1\) One seston sample was collected at each site, and due to sample mass limitations was only analyzed for MeHg.
3.1 Water

Box and whisker plots display THg and MeHg (ng/L) in water in Figure 3.1. The water samples from the Attawapiskat River were collected only at one location, located approximately 25 m upstream from site 2 (just below effluent discharge). These samples have therefore have been pooled to represent sites 1-3. Only one value, that being from site 7 (South Granny Creek), fell below the instrument detection limit of 0.02 ng/L. In compliance with EPA QA/G-9S (Data Quality Assessment: Statistical Methods for Practitioners), it was substituted with detection limit/2.

![Box and whisker plots of total mercury (THg) and methylmercury (MeHg) in water.](image)

**Figure 3.1:** Box and whisker plots of total mercury (THg) (white boxes) and methylmercury (MeHg) (gray boxes) in water. The box represents the median and 25th and 75th percentiles, and the whiskers the 5th and 95th percentiles of data. Outlier values are denoted by dots.

3.1.1 THg in water

From Table 3.1, mean (+ one standard deviation) THg in the water column for all sites combined was $1.61 \pm 0.55$ ng/L. Summary data by site for Hg in water is presented in Appendix 2a. The lowest mean sample concentration was $1.39 \pm 0.25$ ng/L at site 5 (Nayshkootayow River) and the highest concentration was $2.04 \pm 0.57$ ng/L at site 6 (North Granny Creek). Site 6 and site 8 (Tributary 5A) had the greatest relative dispersion of values about the mean, with coefficient of variations (CV) of 0.28 and 0.34,
respectively. Site 7 (South Granny Creek) had a wide range of THg values (1.48-1.69 ng/L) but the smallest CV of 0.07 because of a high mean (1.59 ng/L). Analysis of variance by site showed no significant differences in THg among sampling locations (one-way ANOVA, \( F_{5,69} = 2.346, p = 0.0502 \)).

### 3.1.2 MeHg and %MeHg in water

Methylmercury in water at these sites was much lower than THg. Mean (± one standard deviation) MeHg in the water column for all sites combined were 0.087 ± 0.19 ng/L (Table 3.1). Mean MeHg by site was lowest at site 6 (0.13 ± 0.17 ng/L) and highest at site 4 (Nayshkootayow River) (0.086 ± 0.039 ng/L). Site 8 (Tributary 5A) was, like THg, the most variable in MeHg values, with a CV of 6.45. The next largest CV was 1.49 at site 7 (South Granny Creek), which is interesting considering this site was least variable in THg. The smallest CV was 0.35 at site 4 (Nayshkootayow River). Analysis of variance by site showed significant differences among sampling locations (one-way ANOVA, \( F_{5,78} = 5.066, p = 0.0005 \)). Specifically, a Tukey Kramer honest significant difference test revealed that site 6 is significantly different from sites 1, 4, 5, and 8.

In all sites, the average %MeHg in water was 4.98% ± 9.78%. The highest mean %MeHg was found at site 6 at 6.69% ± 9.78%. %MeHg in individual samples at site 6 (North Granny Creek) ranged from 1.71% to 45.49%. The lowest mean %MeHg was found at sites 1-3 (Attawapiskat River) at 3.21% ± 1.09%. These high and low means corresponded to the high and low CVs: 1.46 at site 6 and 0.339 at sites 1-3.

### 3.2 Sediment

Box and whisker plots display THg and MeHg (μg/kg) in sediment in Figure 3.2. Data was collected at all sites (1-8). THg and MeHg found in sediment is roughly 10000x higher than that found in water. Sediment samples exhibited strong heterogeneity both among and within sites.
3.2.1 THg in sediment

From Table 3.1, mean (± one standard deviation) THg in sediment for all sites combined was 33.64 ± 29.18 µg/kg. Summary data by site for Hg in sediment is presented in Appendix 2b. Mean sample concentrations ranged from lowest at site 1 (Attawapiskat River) at 14.97 ± 5.41 µg/kg and highest at site 7 (South Granny Creek) at 69.22 ± 48.81 µg/kg. The range of sediment concentrations was widest at site 7 (21.15-129.02 µg/kg). That said, the largest CV was found at site 5 (Nayshkootayow River) at 0.99. Analysis of variance by site showed significant differences among sampling locations (one-way ANOVA, F7,59 = 4.478, p = 0.0005). Specifically, a Tukey Kramer honest significant difference test revealed that site 7 (South Granny Creek) is significantly different from all other sites.

3.2.2 MeHg and %MeHg in sediment

Methylmercury was determined on the same sediment samples that were analyzed for THg. Sediment MeHg concentrations were the most variable of all ecosystem compartments and exhibited a mean value (± one standard deviation) of 0.90 ± 2.43 µg/kg. Values ranged from trace (method detection limit) (<0.02 µg/kg) to 17.80 µg/kg,
both found at site 7 (South Granny Creek). Mean MeHg was lowest at site 2 (Attawapiskat River) at $0.14 \pm 0.10 \mu g/L$ and highest at site 7 at $3.44 \pm 6.22 \mu g/kg$. The greatest distribution of values around the mean was also found at site 7 ($CV = 1.81$). Analysis of variance by site showed no significant differences among sampling locations (one-way ANOVA, $F_{7,58} = 1.856, p = 0.0938$).

The proportion of MeHg to THg in sediment was determined for all samples and sites. Across all sites, mean ($\pm$ one standard deviation) %MeHg was $3.57\% \pm 4.74\%$ (Appendix 3b). The highest mean %MeHg was found at sites 7 (South Granny Creek) at $12.30\% \pm 24.12\%$ and the lowest at site 2 (Attawapiskat River) at $0.60\% \pm 0.47\%$. In terms of dispersion of values around site means, the largest CV was found at site 7 (1.96) and the lowest at site 3 (Attawapiskat River) (0.15). Also, there is a strong positive correlation between mean MeHg in sediment and water across all sites ($R^2 = 0.80$).

### 3.3 Plants, seston, and algae

The data for plants, seston, and algae were combined due to sample size limitations. Because the 95th percentiles of plant and algae THg data overlapped, the two compartments could be combined for the purpose of analysis and displaying variability in Figure 3.3. Additionally, an analysis of variance showed no significant differences among combined MeHg site data (one-way ANOVA, $F_{2,43} = 1.648, p = 0.2049$). For reference, individual data sets can be found in Appendix 4a-c. One seston sample was collected at each site, and due to sample mass limitations was only analyzed for MeHg.

#### 3.3.1 THg in plants and algae

From Table 3.1, mean ($\pm$ one standard deviation) THg in plants and algae for all sites combined was $28.72 \pm 27.38 \mu g/kg$. THg values in plants ranged from $0.00 \mu g/kg$ at site 4 (Nayshkootayow River) to $109.60 \mu g/kg$ at site 3 (Attawapiskat River). The range of values in algae was $13.31 \mu g/kg$ at site 1 (Attawapiskat River) to $116.86 \mu g/kg$ at site 6 (North Granny Creek). Site 4 exhibited the greatest distribution in values around the mean with a CV of 1.29. Analysis of variance by site showed no significant differences among sampling locations (one-way ANOVA, $F_{5,37} = 1.135, p = 0.3592$). There is no discernible pattern in THg in plants or algae among all sites.
3.3.2 THg in plants and algae

From Table 3.1, mean (± one standard deviation) THg in plants and algae for all sites combined was 28.72 ± 27.38 µg/kg. THg values in plants ranged from 0.00 µg/kg at site 4 (Nayshkootayow River) to 109.60 µg/kg at site 3 (Attawapiskat River). The range of values in algae was 13.31 µg/kg at site 1 (Attawapiskat River) to 116.86 µg/kg at site 6 (North Granny Creek). Site 4 exhibited the greatest distribution in values around the mean with a CV of 1.29. Analysis of variance by site showed no significant differences among sampling locations (one-way ANOVA, $F_{5,37} = 1.135, p = 0.3592$). There is no discernible pattern in THg in plants or algae among all sites.

3.3.3 MeHg and %MeHg in plants, seston, and algae

Methylmercury was determined in plants, seston, and algae. As described above, values from all three compartments were combined at each site in Figure 3.3. Mean MeHg concentration across all sites for combined data was 4.61±3.08 µg/kg. Values in plants ranged from 0.02 µg/kg at site 3 to 8.45 µg/kg at site 8 (Tributary 5A). Algae MeHg values ranged from 0.84 µg/kg at site 5 (Nayshkootayow River) to 12.04 µg/kg at site 3.
Seston ranged from 2.92 µg/kg at site 4 to 12.08 µg/kg at sites 1-3 (Attawapiskat River). Appendix 3c-d shows the %MeHg of THg for plants and algae. Because THg analysis was not performed on seston, %MeHg could not be calculated for that compartment. Overall, mean %MeHg was 23.48% ± 24.15%. The highest mean %MeHg was found at site 4 (Nayshkootayow River) (plants) at 65.99% ± 41.47% and the lowest mean %MeHg was found at sites 3 (Attawapiskat River) (algae) at 4.39% ± 2.88%.

3.4 Benthic invertebrates

Methylmercury concentrations in benthic invertebrate samples by site are presented in Figure 3.4 (numerically in Appendix 2d). Macroscopic benthic invertebrates were rare in grab samples from sites 6 (North Granny Creek) and site 8 (Tributary 5A); only a few Chironomidae (order: Diptera) were present, but they did not provide enough mass to analyze. Benthic invertebrates were very low in abundance at sites 4, 5 (Nayshkootayow River), and 7 (South Granny Creek). Due to insufficient sample mass generally, all benthic invertebrates were pooled by site and only analyzed for MeHg.

3.4.1 MeHg in benthic invertebrates

From Table 3.1, mean (± one standard deviation) MeHg in benthic invertebrates for all sites combined were 37.48 ± 26.03µg/kg. The lowest concentration was in the single sample collected at site 4 (Nayshkootayow River) (7.71 µg/kg) and the highest mean concentration was 50.91 ± 16.78 µg/kg at site 1 (Attawapiskat River). Sites 2 and 3 (Attawapiskat River) showed the greatest dispersion in values about the mean (CV = 0.75 and 0.99, respectively), but this may be a result of the higher sample sizes that were generated at these sites (samples sizes in Appendix 2d). The highest concentrations of benthic invertebrates were in two dragonfly nymphs (order: Odonata) (122.45 µg/kg and 80.89 µg/kg) and a whole-bodied crayfish (order: Decapoda) (77.59 µg/kg), all of which are from sites 1-3 (Attawapiskat River). Analysis of variance was determined for sites 1, 2, and 3, which had sufficient sample size to perform the analysis. No significant difference was determined among sites (one-way ANOVA, F_{2,29} = 1.586, p = 0.2221).
Figure 3.4: Box and whisker plots of methylmercury (MeHg) in benthic invertebrates. The box represents the median and 25th and 75th percentiles, and the whiskers the 5th and 95th percentiles of data.

3.5 Small-bodied fish

Because Hg bioaccumulates over time in fish tissues, fish age is a determining factor of tissue concentration. Trout-perch from the study site were aged as part of the environmental monitoring program, and so I took advantage of this data to look at Hg in fish of different ages. Trout-perch were aged to either young-of-year (less than one year of age) or 1+ (older than one year of age). Pearl dace were not aged. THg concentrations in trout-perch and pearl dace by site are presented in Figure 3.5 (numerically in Appendix 2e-f). YOY trout-perch were only found at from sites 1-3 and 1+ trout-perch from sites 1-5. Pearl Dace were only found in sites 4-8.
Figure 3.5: Box and whisker plots of total mercury (THg) in small-bodied fish. Plot (a) = young-of-year (YOY) trout-perch, (b) = age 1+ trout-perch, and (c) = pearl dace. The box represents the median and 25th and 75th percentiles, and the whiskers the 5th and 95th percentiles of data. Outlier values lie outside of the 95th percentiles and are denoted by dots.
3.5.1 Trout-perch

YOY trout-perch were only found at sites on the Attawapiskat River (sites 1-3). Mean length was 4.77 cm and weight was 1.07 g. Measurements of THg in individual YOY trout-perch ranged from 6.00 µg/kg at site 1 to 112.00 µg/kg at site 3. Mean Hg of all individuals by site was 38.57 ± 16.44 µg/kg, 62.13 ± 14.73 µg/kg, and 40.63 ± 17.01 µg/kg µg/kg at sites 1, 2, and 3, respectively. CV ranged from 0.24 at site 3 to 0.43 at site 1. Analysis of variance by site determined there to be significant differences in mean tissue concentration among sites (one-way ANOVA, F2,297 = 21.78, p = <0.0001). Results of the Tukey Kramer honest significant difference test reveal that site 1 is significantly different than 2 and 3.

Trout-perch 1+ years of age were found at sites 1-5. Mean weight was 7.33 cm and weight was 4.97 g. Measurements of THg in individual 1+ trout-perch ranged from 20.00 µg/kg at site 5 to 291.00 µg/kg at site 1. Mean Hg of all individuals by site ranged from 51.25 ± 16.09 µg/kg at site 5 (Nayshkootayow River) to 97.85 ± 31.82 µg/kg at site 3 (Attawapiskat River). CV ranged from 0.31 at site 5 to 0.33 at site 3. Analysis of variance by site determined there to be significant differences in mean tissue concentration among sites (one-way ANOVA, F4,157 = 9.794, p = <0.0001). Results of the Tukey Kramer honest significant difference test reveal that site 5 is significantly different from sites 1, 3, and 4.

3.5.2 Pearl dace

Mean weight of pearl dace was 6.56 cm and weight was 3.02 g. THg in pearl dace ranged from 31.00 µg/kg at site 4 (Nayshkootayow River) to 1,318 µg/kg at site 6 (North Granny Creek), with lowest mean of 64.21 ± 18.87 µg/kg at site 4 and highest of 361.66 ± 170.36 µg/kg at site 6. CV ranges from 0.29 at site 5 to 1.10 at site 3. Analysis of variance determined there to be significant differences in mean tissue concentration among sites (one-way ANOVA, F4,257 = 69.69, p = <0.0001). Results of the Tukey Kramer honest significant difference test reveal significant differences between many sites, but sites 6 and 7 (South Granny Creek) are different from all other sites.
3.6 Within site variability in Hg

At these study rivers and streams, there is spatial heterogeneity in Hg among sites, but also extreme variability within sites. Figures 3.6 (site 6), 3.7 (site 7), and 3.8 (site 8) are simply meant to illustrate with a picture how variable Hg concentrations are within a site. Sites 6, 7, and 8 are the small creeks that were sampled in this study. Rather than show variability in all 8 sites, these 3 sites were chosen because they are of the same stream order and similar in size. Also, the boxes show where, approximately, samples were collected in each stream. In the figures, 100 (red) represents the highest concentrations of %MeHg in sediment, and all other values are relative to that number. Site 7 (South Granny Creek) exhibited a range of %MeHg of 0% to 71.30% along a 10 m transect.
Figure 3.6: Relative amount of percent methylmercury (MeHg) of total mercury (THg) in sediment samples in site 6 (North Granny Creek) to the sample with the highest amount (red box: 100). 100 represents a sample with 27.95 µg/kg THg and 6.99% MeHg. The numbers are a conceptual representation of where in the stream the samples were collected. Each horizontal transect is 5 m apart. Mean %MeHg in water along the top, middle, and bottom transects is 46%, 22%, and 11% respectively.
Figure 3.7: Relative amount of percent methylmercury (MeHg) of total mercury (THg) in sediment samples in site 7 (South Granny Creek) to the sample with the highest amount (red box: 100). 100% represents a sample with 24.97 µg/kg THg and 70.30% MeHg. The numbers are a conceptual representation of where in the stream the samples were collected. Each horizontal transect is 5 m apart. Mean %MeHg in water along the top, middle, and bottom transects is 4%, 5%, and 0% respectively.
Figure 3.8: Relative amount of percent methylmercury (MeHg) of total mercury (THg) in sediment samples in Tributary 5A (site 8) to the sample with the highest amount (red box: 100). 100% represents a sample with 18.08 µg/kg THg and 6.77% MeHg. The numbers are a conceptual representation of where in the stream the samples were collected. Each horizontal transect is 5 m apart. Mean %MeHg in water along transects from top to bottom is 4%, 3%, 3%, 5%, and 4% respectively.

3.7 Bioaccumulation factors

The previous sections described among and within site variability in Hg in this far north region. These data can be used to calculate bioaccumulation factors to then understand the transfer efficiency of Hg in this food web, which tells us how Hg is moving through
the various compartments. MeHg bioaccumulates and is therefore the Hg species of interest from a health perspective, so bioaccumulation factors were calculated for MeHg. BAF are presented for each food web compartment (Table 3.2) and for each fish species by site (Table 3.3).

**Table 3.2:** Bioaccumulation factors (BAF) of methylmercury (MeHg) in food web compartments in rivers and streams of this far north region. Total mercury (THg) values were used to calculate BAFs in fish. --- indicates that no data is available. BAF presented in this table were calculated using mean MeHg values of all samples from all sites.

<table>
<thead>
<tr>
<th>Food Web Compartment</th>
<th>Mean MeHg (µg/kg)</th>
<th>BAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (Filtered 0.45µm)</td>
<td>1.0×10^(-4) (µg/L)</td>
<td>---</td>
</tr>
<tr>
<td>Aquatic Plants</td>
<td>3.77</td>
<td>4.58</td>
</tr>
<tr>
<td>Seston</td>
<td>5.80</td>
<td>4.76</td>
</tr>
<tr>
<td>Algae</td>
<td>5.20</td>
<td>4.72</td>
</tr>
<tr>
<td>Benthic Invertebrates</td>
<td>37.48</td>
<td>5.57</td>
</tr>
<tr>
<td>Young-of-Year Trout-Perch</td>
<td>48.58</td>
<td>5.69</td>
</tr>
<tr>
<td>1+ Trout Perch</td>
<td>79.87</td>
<td>5.90</td>
</tr>
<tr>
<td>Pearl Dace</td>
<td>205.41</td>
<td>6.31</td>
</tr>
</tbody>
</table>

Mean BAFs were lowest at 4.58 in aquatic plants and highest in small-bodied fish at 6.31. BAFs increased relatively log-linearly across trophic levels. The bioaccumulation of MeHg in fish is of most interest to the general public because of their role as a food product, so BAF in small-bodied fish were calculated to generate a single value for each species (Table 3.2) and then individual values specific to each study site (Table 3.3). BAF in YOY trout-perch were 5.69, 5.90 in 1+ trout-perch, and 6.31 in pearl dace. BAF between study sites ranged from the lowest value of 5.75 in 1+ trout-perch at site 5 (Nayshkootayow River) to the highest value of 6.44 in pearl dace at site 6 (North Granny Creek). The highest BAF in YOY trout-perch (6.09) was identified in fish from site 2 (Attawapiskat River).
**Table 3.3:** Bioaccumulation factors (BAFs) of methylmercury (MeHg) in fish (young-of-year (YOY) and 1+ year-old trout-perch and pearl dace) in rivers and streams of this far north region. Total mercury (THg) values were used to calculate BAFs in fish. --- indicates that no data is available. BAF presented in this table were calculated using mean MeHg values of all samples for individual sites.

<table>
<thead>
<tr>
<th>Water Body</th>
<th>Site No.</th>
<th>Mean Water MeHg (Dissolved) (µg/L)</th>
<th>BAF YOY Trout-Perch</th>
<th>BAF 1+ Trout-Perch</th>
<th>BAF Pearl Dace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attawapiskat River</td>
<td>1</td>
<td>5.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>5.89</td>
<td>6.22</td>
<td>---</td>
</tr>
<tr>
<td>Attawapiskat River</td>
<td>2</td>
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<td>6.09</td>
<td>6.25</td>
<td>---</td>
</tr>
<tr>
<td>Attawapiskat River</td>
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<td>5.91</td>
<td>6.29</td>
<td>---</td>
</tr>
<tr>
<td>Nayshkootayow River</td>
<td>4</td>
<td>6.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>---</td>
<td>6.16</td>
<td>6.03</td>
</tr>
<tr>
<td>Nayshkootayow River</td>
<td>5</td>
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<td>---</td>
<td>5.75</td>
<td>5.89</td>
</tr>
<tr>
<td>North Granny Creek</td>
<td>6</td>
<td>1.3&lt;sup&gt;4&lt;/sup&gt;</td>
<td>---</td>
<td>---</td>
<td>6.44</td>
</tr>
<tr>
<td>South Granny Creek</td>
<td>7</td>
<td>2.0&lt;sup&gt;4&lt;/sup&gt;</td>
<td>---</td>
<td>---</td>
<td>5.89</td>
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<tr>
<td>Tributary 5A</td>
<td>8</td>
<td>5.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>---</td>
<td>---</td>
<td>6.34</td>
</tr>
</tbody>
</table>
Chapter 4

4 Discussion

4.1 Mercury in subarctic aquatic food webs

4.1.1 Water and sediment

Methylmercury was the Hg species of interest because it bioaccumulates in fish tissues and can be hazardous to human health. Measurements of MeHg in a complete suite of food web compartments yield novel information on baseline levels and bioaccumulation in a subarctic river and stream-dominated system. Surface water MeHg among our study sites was on average $0.087 \pm 0.012$ ng/L but as high as $0.13 \pm 0.17$ ng/L at site 6 (North Granny Creek). This is higher than concentrations of MeHg in other subarctic and Arctic freshwater systems. Kirk and St. Louis (2009) found concentrations of $0.050 \pm 0.030$ ng/L in two major subarctic rivers that drain into Hudson Bay, and Kirk (2008) identified concentrations of $0.40 \pm 0.50$ ng/L in Arctic marine waters. MeHg typically comprises $<5\%$ of all Hg species in surface waters (Ullrich et al. 2001). The mean proportion of MeHg in our water data was 4.98%.

At site 6 (North Granny Creek), the mean %MeHg of all water samples was 6.69%, although MeHg accounts for up to 45.49% of Hg species in a single water sample. At site 6, the proportion of MeHg was very high. The proportion of MeHg was similar at site 5 (6.52%). This source of MeHg is likely export from the adjacent peatlands, given that they are known sources of MeHg to downstream systems (Mitchell et al. 2008). Brigham et al. (2009) reported that THg and MeHg water concentrations were positively associated with wetland abundance and, presumably, wetland hydrologic connectivity. These study sites are integrated into a huge wetland complex, which is likely a large source of Hg to these streams and rivers. Those sites that have higher proportions of MeHg in their surface waters are probably more hydrologically-connected to the surrounding peatlands.

The mean sediment MeHg concentration (0.90 µg/kg) was slightly higher than those found in non-urban surface water sites in California (0.25 µg/kg) (Marvin-DiPasquale et
al. 2009) and lower than the mean concentration in streams across the United States (1.65 µg/kg) (Scudder 2010). There is a wide range of values reported in the literature as to what constitutes a ‘high’ %MeHg relative to THg in sediment (Gilmour et al. 1998, Ullrich et al. 2001, Marvin-DiPasquale et al. 2009), but anything >5% has a high potential for MeHg production. In this study, sites 4 and 5 (Nayshkootayow River), and site 6 (North Granny Creek), and site 7 (South Granny Creek) all met this criteria in some samples, with a mean %MeHg of 4.27%, which is close to 5%. Orlova and Branfireun (2014) found that peatland runoff contributed more than half of total streamflow discharge to the Nayshkootayow River. Site 6 and 7 are also cut into the peatland (as opposed to bedrock substrate) and likely receive a large proportion of streamflow from peatland runoff. Since peatlands are known sources of MeHg, this may explain why these sites were higher in Hg.

There was a strong positive between MeHg in water and sediment across all sites. Site 6 (North Granny Creek) and site 7 (South Granny Creek) had the highest mean MeHg concentrations in water (6 = 0.126 ng/L, 7 = 0.203 ng/L) and sediment (6 = 1.06 µg/kg, 7 = 3.44 µg/L). Sites 1-3 (Attawapiskat River) and site 8 (Tributary 5A) had the lowest mean MeHg concentrations in water (1-3 = 0.049 ng/L, 8 = 0.021 ng/L) and sediment (1-3 = 0.16 µg/L, 8 = 0.43 µg/L). In situ production of MeHg in bed sediment may contribute to high levels of MeHg in the surface waters (Gilmour et al. 1998, Ullrich et al. 2001, Lehnherr et al. 2012b), which may explain this association. Sediment at almost all sites showed proportions of MeHg >5%, suggesting that rate of in situ MeHg production in these sediments may be high, or the sediment is being derived from locations where MeHg was produced. This level of MeHg was likely reflected in the water column.

In addition to a high proportion of MeHg in the sediments, there was also variability within each site. This was especially prevalent at sites 6 (North Granny Creek), 7 (South Granny Creek), and 8 (Tributary 5A) (Figures 3.6-3.8). Ulanowski and Branfireun (2013) documented small-scale variability in pore-water biogeochemistry at the peatlands adjacent to this study site, and this level of variability was seen in sediment %MeHg within my relatively small sampling area. Other research on spatial variability of Hg in
sediment shows that MeHg was typically more variable than THg (Marvin-DiPasquale et al., 2009, Morris et al., 2014), likely a result of in situ biogeochemical controls that were outside of the scope of this study. This variability in sediment Hg has implications for future monitoring efforts, as difficulties could arise in collecting a representative sample of the environment. For instance, with an accuracy of ±20% and a significance level of $p = 0.10$, the minimum number of samples needed to achieve a representative sample of sediment MeHg is 1,283 (according to the method outlined in Eckblad 1991). The implications of this variability are that generating an understanding of baseline conditions may be difficult, as would subsequent monitoring of change over time. Recommendations for future research in this area include an intensive survey to identify biogeochemical factors that drive Hg variability.

4.1.2 Fish

Large fish prey on small-bodied fish, and so high levels of Hg in prey fish can cascade up food chains. Mercury in fish tissue is therefore an important point of discussion of this study, especially because people of northern Ontario rely on large-bodied fish as a primary dietary food source. There are no published studies of Hg in tissue of small-bodied or young-of-the-year fish in northern riverine ecosystems. The findings of this study show substantial variation in tissue Hg in small-bodied fish. The concentrations and variability in young-of-the-year trout-perch Hg were especially surprising, given that some of the fish are less than one year of age. The concentrations in young-of-the-year fish in this study ranged from 6.00-4.00 µg/kg w.w., which is above the 200.00 µg/kg w.w. subsistence consumption guideline in Canada (Lockhart et al., 2005).

Comparisons can be made to other studies that use small-bodied fish populations to study aquatic Hg in temperate regions of North America. Choy et al. (2008) found concentrations of Hg in young-of-the-year spottail shiners in southern Ontario to be 30-80 µg/kg, values that are generally lower than those found in this study despite the fact that many of the samples were fish taken from a Hg contaminated location. Data from small-bodied fish collected by Eagles-Smith and Ackerman from the San Francisco Bay Estuary (2009) exhibited mean concentrations of 20-70 µg/kg. These values are more similar to those reported here, but were from an area with high background levels of Hg.
and/or Hg contamination (Hornberger et al. 1999), in contrast with the very low water concentrations found in our pristine environment. Although atmospheric deposition may play a small role in Hg exposure to fish, it is interesting to note that the fish tissue concentrations in my study were very high considering this region is far removed from any point sources of contamination.

The fish tissue concentrations were not only high, but also variable. Variability of fish Hg, even in small-bodied fish, is common (Greenfield et al. 2001, Sorensen et al. 2005, Eagles-Smith and Ackerman 2009, Gabriel et al. 2009, Greenfield and Jahn 2010). As with the data presented here, Eagles-Smith and Ackerman (2009) also found large variability in fish Hg concentrations, which they attributed to changes in MeHg concentration/production, primary production, and fish life histories. Greenfield and Jahn (2010) also explained variation in small fish Hg by a variety of biological factors and noted that these factors vary over space and time. There were so many potential biotic and abiotic factors that affect the variability in exposure of Hg in this environment.

The highest mean fish concentrations, found at sites 6 (North Granny Creek) (361.66 µg/kg) and 7 (South Granny Creek) (156.74 µg/kg) correspond to the sites with the highest water and sediment MeHg concentrations. The substrate of sites 6 and 7 is organic, and in the absence of other food sources, fish ingest organic substrate (or sediment) (Selleslagh et al. 2015). Because most other food web compartments were absent at these sites, it makes sense that fish tissue Hg would reflect Hg in the abiotic food web. However, this association does not hold true across all sites, as site 8 had the lowest water and sediment MeHg concentrations but high mean fish Hg (109.00 µg/kg). There were no obvious associations between water or sediment MeHg and other food web compartments. Comparisons between sites are difficult as all compartments and fish species were not present at all sites, so a regional study may require that data from multiple sites be combined to provide a better understanding of general trophic relationships, bioaccumulation, and fish Hg in this region.
4.2 Bioaccumulation of Hg

The findings of this study show that MeHg transfers to higher levels of aquatic food webs in a log-linear nature, which corresponds to patterns of bioaccumulation in other regions (Watras et al. 1998, Driscoll et al. 2007, Jardine et al. 2013) (Figure 4.1). Generally MeHg bioaccumulates linearly, but the magnitude of difference in MeHg between water-sediment and primary producers was very large (Figure 4.1). The abiotic and biotic factors responsible for Hg transfer in the lower food web is poorly understood in comparison to transfer mechanisms that operate in the upper food web, such as the consumption of prey (Hall et al. 1997). In situ sedimentary production is a primary source of MeHg to seston (Hammerschmidt and Fitzgerald 2006) and this has been found in other regions, including Arctic ponds (Lehnher et al. 2012a). The %MeHg relative to THg in sediment is generally <1% (Ullrich et al. 2001), and 5-10% is considered very high (Gilmour et al. 1998, Ullrich et al. 2001). The %MeHg of THg in sediments in our study was 4.27%, with almost all sites showing proportions of MeHg >5%, suggesting that rate of in situ methylation in these sediments may be high, or the sediment was derived from locations where MeHg was produced. If sedimentary production is also a primary source of MeHg to primary producers in subarctic rivers and streams, and if fish were consuming primary producers as a food source, then identification of the mechanisms that govern methylation and uptake within the abiotic food web (water, sediment, plants) may provide an explanation for why biotic MeHg was high in this region.

It is well documented that MeHg is transferred more efficiently from water to primary producers (e.g., algae) than between subsequent trophic levels (Mason et al. 1995, Driscoll et al. 2007). The range of BAF between MeHg water and seston among the sites of this study were found to be 4.45-5.15. Caution must be taken in interpreting these results because our sample size is very small (n=7). Studies in other freshwater systems have identified BAFs in seston from 3.8-5.2 (Watras and Bloom 1992, Watras et al. 1998), and in marine systems from 3.5-4.2 (Baeyens et al. 2003, Hammerschmidt and Fitzgerald 2006). Hammerschmidt and Fitzgerald (2006) calculated a BAF from water to seston in Long Island Sound, New York of 4.2, a region that has high levels of Hg in top
predator fish. If primary producers are a dietary source of Hg to young-of-the-year and age-1+ fish, seston concentrations (mean BAF 4.76) may contribute to high fish Hg concentrations at these study sites.

Figure 4.1: Box and whisker plot of log-methylmercury (MeHg) in food web compartments in the study rivers and streams. The box represents the median and 25th and 75th percentiles, and the whiskers the 5th and 9th percentiles of data. Fish Hg is plotted as total mercury (THg) assuming that 95-99% of mercury in fish is of the MeHg form.

Bioaccumulation factors have been calculated between water and fish in other freshwater (Watras and Bloom 1992, Southworth et al. 2004, DeForest et al. 2007) and marine (Baeyens et al. 2003, Hammerschmidt and Fitzgerald 2006) systems. BAF in freshwater streams in the southeastern United States were determined for Hg in-redbreast sunfish to be between 3.15 and 6.81 with a mean of 4.81 (Southworth et al. 2004); these values are generally lower than the fish BAF reported here. Watras and Bloom (1992) present data on BAF of 6.0-6.5 in age 1+ yellow perch in in Minnesota, US. These values are comparable to those calculated for my young-of-the-year trout-perch (5.69), 1+ trout-
perch (5.90), and pearl dace (6.31). DeForest et al. (2007) present a mean BAF of MeHg in both freshwater and saltwater animals, from zooplankton to small- and large-bodied fish species, of 6.36. Some of the BAF presented for biota in streams and rivers in this study were above this value in small-bodied fish (Tables 3.2 and 3.3), which suggests that the bottom-up processes that promote the production and mobilization of Hg in the subarctic system are very efficient.

The small-bodied fish used to calculate BAFs among these study sites were far-removed from direct sources of contamination. Even those values calculated for sites that have not been directly impacted by the physical and hydrological modifications associated with the activities of the De Beers Victor Mine (which does not produce, use, or discharge Hg as part of any of its processes) were high (5.57-6.44). The BAFs for benthic invertebrates were also very high (5.57) and similar to those in fish, and because BAFs are strongly influenced by trophic position (Watras and Bloom 1992), this suggests that benthic invertebrates among our study sites were grazing on similar food sources to fish. This food source is likely organic matter and primary producers. These values are especially concerning because DeForest et al. (2007) report the minimum chronic toxicity threshold for a BAF of MeHg in wildlife to be 6.34 and the maximum threshold, 7.66. The context within which these BAF are generated should be carefully considered, as an environment with high water MeHg could result in low BAF but levels of MeHg toxic to wildlife. The mean BAFs that were calculated between water and fish were within this threshold range at site 6 (North Granny Creek) and very close at site 2 (Attawapiskat River), site 7 (South Granny Creek), and site 8 (Tributary 5A). Site-specific BAF may be used to determine limits for Hg in water (Southworth et al. 2004, Riva-Murray et al. 2013b), and so the values identified in this study could be useful in the assessment of targets and regulation measures for Hg in fishes in the subarctic.

4.3 Environmental change and mercury in subarctic aquatic food webs

The subarctic is especially vulnerable to climate and land-use change (Tarnocai 2006, Stern et al. 2012), and one of the many potential consequences is the impact of rising temperatures on Hg in surface waters. MeHg production is driven by the metabolism of
anaerobic bacteria (Schaefer and Morel 2009), which is enhanced as environmental temperatures increase (Bodaly et al. 1993, Ullrich et al. 2001). Bodaly et al. (1993) identify temperature as the primary factor that governs Hg in fish. Although not accounted for in this study, future research should consider temperature as a factor in studies on Hg in northern aquatic food webs. If soil and water temperatures increase with climate warming, it is likely that Hg in water will increase in response. Land-use disturbance in peatlands is also known to enhance methylation of Hg (Zillioux et al. 1993, Heyes et al. 2000), and the subarctic is currently experiencing land-use modification pressures due to resource extraction.

An illustration of the potential impact of climate change on surface water Hg levels and fish tissue Hg has been developed from the data presented here and calculated BAFs (Figure 4.2). The purpose of this illustration is to project potential changes in Hg in higher trophic level biota in response to changes in Hg in water. It could also be used to monitor changes in bioaccumulation over time. This figure is based on the assumption that the mean BAF that were calculated in this study will remain stable with increases to water column MeHg levels, and that biota will increase approximately proportionally to water.

Presented here are two scenarios: current (based on mean water column MeHg (dissolved) across the study sites = 0.0001 µg/L) and a 3-fold increase (water = 0.0003 µg/L). Acknowledging that there is uncertainty associated with any numerical calculation, each scenario includes a projection for the 25th, 50th, and 75th percentiles of data. Pearl dace are the fish with highest body burdens of mercury in this study. Under the current scenario, pearl dace Hg ranges from 68 µg/kg to 304 µg/kg, but under the 3X scenario, a situation that is very possible, then the range of fish tissue Hg could increase to 204 µg/kg (25th percentile) to 913 µg/kg (75th percentile). This tissue concentration would fall far above the guideline for commercial sale of fish in Canada of 500 µg/kg (Lockhart et al. 2005). Presented in Table 4.1 are water concentration values that would be needed for small-bodied fish to reach the guidelines for subsistence (200 µg/kg) and commercial sale, based on the projection illustration.
There may be implications of high BAFs on higher trophic levels (large-bodied fish) at these study sites, but assumptions cannot be made based on data from this study. That said, unpublished data (De Beers, 2010) on Hg in walleye and Northern pike can be used to illustrate potential Hg changes in these fishes with increases to water MeHg. Mean Hg in walleye (313.35 µg/kg) results in a BAF of 6.50 and mean Hg in Northern pike (533.13 µg/kg) a BAF of 6.73. With a 3-fold increase to current water MeHg concentration, fish tissue could increase to 940.04 µg/kg and 1599.38 µg/kg in walleye and Northern pike, respectively. These levels are well above the consumption guideline for food fishes. This illustration suggests that small changes in Hg at the bottom of a food web can have big implications at the top in this previously understudied environment.

**Table 4.1:** Based on mercury BAFs, mean water concentrations required to increase fish tissue Hg concentrations to the Canadian subsistence (200 ug/kg) and commercial sale (500 ug/kg) guidelines. Presented in the table are 25<sup>th</sup>, 50<sup>th</sup>, and 75<sup>th</sup> percentiles of possible values. Current mean water MeHg values are 1.0<sup>µ</sup>g/L.

<table>
<thead>
<tr>
<th>Guideline</th>
<th>Percentile</th>
<th>YOY Trout-Perch</th>
<th>1+ Trout-Perch</th>
<th>Pearl Dace</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 ug/kg</td>
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<td>6.1&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.8&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>10.3&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>6.9&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>5.3&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sale)</td>
<td>75&lt;sup&gt;th&lt;/sup&gt;</td>
<td>8.1&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>3.8&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>1.6&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Figure 4.2: Illustration of potential increase in fish tissue in relation to increases in water methylmercury (MeHg) based on bioaccumulation factors (BAFs) for our study site. The ‘Current’ figure was developed using data from our study. ‘3X’ represents an increase to water MeHg concentrations of 3-fold (0.0003 µg/L). The boxes represent the 25th, 50th, and 75th percentiles of data. The horizontal lines represent the Canadian subsistence (dotted, 200 ug/kg) and commercial fishing (solid, 500 ug/kg) guidelines.
Chapter 5

5 Conclusion

The primary objectives of this study were: (1) to evaluate the spatial variability in THg and MeHg in water, sediment, and biota within and across a range of subarctic streams and river reaches of the Hudson Bay Lowland, and (2) use the data from objective 1) combined with mercury data from northern forage fishes to calculate bioaccumulation factors for these northern lotic ecosystems, and assess the impact of potential future changes in water MeHg concentrations on trophic transfer and bioaccumulation in these fishes.

The first comprehensive dataset of MeHg in a subarctic aquatic food web is presented. The findings of this study show that Hg is variable among rivers and streams of the Hudson Bay Lowland, and there is also small-scale variability in the food web compartments within these water bodies. The characterization of MeHg in this food web demonstrates that, overall, Hg transfers predictably and efficiently from one level to the next. The illustration suggests that small increases in Hg at the bottom of this food web can result in high Hg concentrations in higher-level organisms.

The characterization of the bioavailable MeHg in the food web is incomplete due to spatial heterogeneity of Hg in this system. Fish Hg may be more intricately linked to the abiotic food web in these rivers and streams. For example, the control of temperature on Hg methylation is well understood (Bodaly et al. 1993, Stern et al. 2012), and slight increases in water temperature is suggested as one possible mechanism for increases in food web MeHg. As such, Environmental Effects Monitoring programs should continue to monitor changes in in-stream abiotic conditions alongside water and fish Hg.

The Hudson Bay Lowland is a peatland- and river-dominated region of northern Canada that is characterized by cold and short growing seasons, a low topographic gradient, permanent water saturation, and a range of permafrost conditions (Sjörs 1959, Roulet et al. 1994, Whittington et al. 2012). This region is located in an extreme climate zone, one that is forecasted to undergo severe climate changes over the next century (Tarnocai
In addition to climate change, land-use modification from resource exploration and extraction will contribute to environmental pressure on northern ecosystems. The bioavailability of MeHg to biota is directly linked to MeHg production and mobilization (Lehnherr et al. 2012a), and disturbance through the modification of natural ecosystems, e.g., mining activities, is known to increase this mobilization in wetlands (Heyes et al. 2000). As aquatic ecosystem stability is imperative to longevity of fish populations, physical alterations at these sites may alter food webs and, subsequently, the bioaccumulation and uptake of Hg by biota (Bhavsar et al. 2010). Although it is difficult to predict future trends in climate and Hg dynamics in subarctic aquatic food webs, Figure 4.2 provides a possible scenario for increases in Hg.

The application of science to policy is invaluable in efforts to mitigate the effects of climate and land-use changes in the north, especially for First Nations communities who rely on food fishes as a commodity and for sustenance. This research is the very first comprehensive study of MeHg in food webs in the subarctic. This unique and vast region is undergoing significant ecological change and in order to effectively manage freshwater aquatic ecosystems and fish stocks in light of projected climate and land-use change scenarios, an understanding of the baseline trends in Hg and the underlying science is critical.
References


IPCC. 2007. Climate change 2007: the physical science basis: working group I contribution to the fourth assessment report of the IPCC. Cambridge University Press.


Appendices

**Appendix 1:** Physical characteristics of the study sites. --- indicates that no data is available.

<table>
<thead>
<tr>
<th>Water Body</th>
<th>Site No.</th>
<th>Stream Order</th>
<th>Drainage Basin Area (km²)</th>
<th>Runoff (mm/day)</th>
<th>Mean Width (m)</th>
<th>Mean Depth (m)</th>
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<tbody>
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<td>---</td>
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<td>1.2</td>
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<td>1.27</td>
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<td>0.6</td>
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<tr>
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<td>29.9</td>
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<td>0.7</td>
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Appendix 2: Summary of the number of samples (n) collected, range of values, mean (\(\bar{x}\)), and coefficient of variation (CV) for total mercury (THg) and methylmercury (MeHg) concentrations in food web compartments from all sites. Mean Hg values include \(\pm 1\) standard deviation (SD). --- indicates that no data is available.

2a: Water

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (ng/L)</th>
<th>MeHg (ng/L)</th>
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</thead>
<tbody>
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<td>Range</td>
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<td>13</td>
<td>1.11-2.28</td>
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<td>5</td>
<td>14</td>
<td>1.07-2.02</td>
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<tr>
<td>6</td>
<td>23</td>
<td>1.13-2.95</td>
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<tr>
<td>7</td>
<td>3</td>
<td>1.48-1.69</td>
</tr>
<tr>
<td>8</td>
<td>16</td>
<td>0.87-2.38</td>
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</table>

2b: Sediment

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<tr>
<th>Site</th>
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<tbody>
<tr>
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<td>Range</td>
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<td>5</td>
<td>21.55-25.33</td>
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<td>5</td>
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<td>4</td>
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</tr>
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<td>9</td>
<td>21.15-129.02</td>
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<td>8</td>
<td>15</td>
<td>6.89-115.38</td>
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</table>
### 2c: Plants, seston, and algae (grouped)

<table>
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<th>MeHg (µg/kg)</th>
</tr>
</thead>
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</tr>
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<td>1</td>
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<tr>
<td>3</td>
<td>12</td>
<td>4.99-28.81</td>
</tr>
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<td>4</td>
<td>9</td>
<td>4.40*-53.74</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5.50-49.50</td>
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<tr>
<td>6</td>
<td>3</td>
<td>64.91-116.86</td>
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<tr>
<td>7</td>
<td>5</td>
<td>5.21-63.80</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>3.85-37.92</td>
</tr>
</tbody>
</table>

### 2d: Benthic invertebrates

<table>
<thead>
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<th>MeHg (µg/kg)</th>
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</thead>
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<td>3</td>
</tr>
<tr>
<td>8</td>
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</table>
### 2e: Trout-perch (young-of-year and 1+ years of age)

<table>
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<th>Site</th>
<th>Young-of-Year THg (µg/kg)</th>
<th>1+ THg (µg/kg)</th>
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</thead>
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<td>Range</td>
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<td>49</td>
<td>6-79</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>33-112</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>18-84</td>
</tr>
<tr>
<td>4</td>
<td>-----</td>
<td>-----</td>
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<td>-----</td>
</tr>
<tr>
<td>6-8</td>
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### 2f: Pearl dace

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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
</tr>
<tr>
<td>1-3</td>
<td>-----</td>
</tr>
<tr>
<td>4</td>
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<td>5</td>
<td>41</td>
</tr>
<tr>
<td>6</td>
<td>107</td>
</tr>
<tr>
<td>7</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
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</tbody>
</table>
**Appendix 3:** Percent methylmercury (MeHg) of total mercury (THg) in food web compartments from all sites, including range of values, mean (\(\bar{x}\)) concentration with ± 1 standard deviation (SD), and the coefficient of variation (CV). --- indicates that no data is available.

### 3a: Water

<table>
<thead>
<tr>
<th>Site</th>
<th>MeHg (%)</th>
<th>n</th>
<th>Range</th>
<th>(\bar{x} \pm SD)</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td></td>
<td>14</td>
<td>1.41-5.50</td>
<td>3.21(\pm 1.09)</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>11</td>
<td>1.77-7.16</td>
<td>4.55(\pm 1.88)</td>
<td>0.41</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>10</td>
<td>2.00-12.51</td>
<td>6.52(\pm 3.57)</td>
<td>0.55</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>22</td>
<td>1.71-45.49</td>
<td>6.69(\pm 9.78)</td>
<td>1.46</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>3</td>
<td>0.87-5.87</td>
<td>3.41(\pm 2.50)</td>
<td>0.73</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>15</td>
<td>0.97-6.45</td>
<td>3.72(\pm 1.64)</td>
<td>0.44</td>
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</table>

### 3b: Sediment

<table>
<thead>
<tr>
<th>Site</th>
<th>MeHg (%)</th>
<th>n</th>
<th>Range</th>
<th>(\bar{x} \pm SD)</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>4</td>
<td>0.69-1.73</td>
<td>0.98(\pm 0.50)</td>
<td>0.51</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>5</td>
<td>0.21-1.27</td>
<td>0.60(\pm 0.47)</td>
<td>0.78</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>5</td>
<td>0.89-1.30</td>
<td>1.06(\pm 0.16)</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>10</td>
<td>0.12-5.05</td>
<td>2.47(\pm 1.63)</td>
<td>0.66</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>9</td>
<td>0.20-22.67</td>
<td>5.65(\pm 7.09)</td>
<td>1.25</td>
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<tr>
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<td></td>
<td>9</td>
<td>0.35-6.99</td>
<td>3.59(\pm 1.99)</td>
<td>0.55</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>9</td>
<td>0.00-71.30</td>
<td>12.30(\pm 24.12)</td>
<td>1.96</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>15</td>
<td>0.00-6.77</td>
<td>1.90(\pm 1.95)</td>
<td>1.03</td>
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</table>
### 3c: Plants

<table>
<thead>
<tr>
<th>Site</th>
<th>MeHg (%)</th>
<th>n</th>
<th>Range</th>
<th>$\bar{x}$ ± SD</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>2</td>
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<td>---</td>
<td>15.59</td>
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</tr>
<tr>
<td>3</td>
<td></td>
<td>11</td>
<td>0.11-45.01</td>
<td>17.37±13.06</td>
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<td>3.85-21.43</td>
<td>9.62±27.29</td>
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### 3d: Algae

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<th>$\bar{x}$ ± SD</th>
<th>CV</th>
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<td>11.57-14.62</td>
<td>13.09±2.15</td>
<td>0.16</td>
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</table>
Appendix 4: Summary of the number of samples (n) collected, range of values, mean (\(\bar{x}\)), and coefficient of variation (CV) for total mercury (THg) and methylmercury (MeHg) concentrations in individual compartments of plants, seston, and algae from all sites. Mean Hg values include ± 1 standard deviation (SD). --- indicates that no data is available.

4a: Plants

<table>
<thead>
<tr>
<th>Site</th>
<th>THg (µg/kg)</th>
<th>MeHg (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>---</td>
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<tr>
<td>2</td>
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</tr>
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<td>3</td>
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<td>6</td>
<td>0.00-7.10</td>
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<td>5.50-9.64</td>
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<td>3.85-21.43</td>
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### 4b: Seston

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<th>Range</th>
<th>( \bar{x} \pm SD )</th>
<th>CV</th>
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<td>12.08</td>
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<td>2.92</td>
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### 4c: Algae

<table>
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<th>Site</th>
<th>THg (µg/kg)</th>
<th>MeHg (µg/kg)</th>
<th>n</th>
<th>Range</th>
<th>( \bar{x} \pm SD )</th>
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</tbody>
</table>
Curriculum Vitae

Name: Ashley L. Warnock

Post-secondary Education and Degrees:
University of Toronto, Mississauga, Ontario
2005-2010 HBSc with Distinction

Honours and Awards:
Northern Scientific Training Program
2011-2012, 2012-2013
Graduate Student Teaching Award
2012-2013
125th Anniversary Scholarship
2010-2012
Dean’s Excellence Award in Experiential Learning
2009-2010
Howard F. Andrews Memorial Award in Geography
2008-2009

Related Work Experience
Teaching Assistant
Western University
2010-2013
Research Assistant
University of Toronto, Western University
2009-2013
Society of Graduate Students’ Vice President Academic
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2011-2012

Publications: