Analysis of Metal Contaminants and Mercury Speciation in Fishes from the Slave and Athabasca Rivers

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ABSTRACT

The Slave and Athabasca are two connected rivers impacted by a variety of anthropogenic activities such as oil sands extraction, metal mining, pulp mills and agriculture. Concerns have been raised regarding the health of these two rivers especially the Athabasca River which runs through areas of oil sands development. The health of fish in these rivers is one of the primary concerns due to the cultural and economic importance of the fish to local community members. Metal contaminants in fish can have an impact on fish health and can pose a risk to the health of consumers of fish, including humans. This thesis investigates metals in five fish species (burbot, goldeye, northern pike, walleye, and whitefish) from sites along the Slave and Athabasca Rivers during four seasons (summer, fall, winter, and spring). A suite of 25 metals were analyzed by ICP-MS and the majority of the metal concentrations showed little location associated variability nor were they detected at concentrations of concern. One metal, Hg, was detected at concentrations of concern and four metals (As, Se, Tl, and V) demonstrated statistically significant variations in concentrations between sampling sites with greater concentrations in the sites on the lower Slave River compared to the upper Slave River, Athabasca River, and Peace River sites. The concentrations of these metals were not of sufficient magnitude to be of concern to fish or human health, but the trend is of interest due to concerns regarding industrial activities on the Athabasca River. Mean Hg concentrations in fish muscle exceed Health Canada consumption guidelines in 2.6% of fish groups separated by species, location, and season. These concentrations exceeded subsistence advisory Hg guideline concentrations in 47.4% of fish groups. The magnitude of Hg concentrations was not new information as other researchers have found similar concentrations in fish in the region and fish consumption advisories are already in place for the Athabasca River due to Hg concerns. The two species of Hg found in fish are Hg(II) and methylmercury. Methylmercury is the predominant form of Hg in fish and has the potential to biomagnify, increasing concern for fish and human health. A method to analyze for the two Hg species was developed utilizing sodium tetraethylborate derivatization with headspace solid-phased microextraction (SPME) followed by gas chromatography and orbitrap mass spectrometry (GC-Orbitrap MS) analysis. The use of GC-Orbitrap MS allows for the scanning of a wide range of mass/charge (m/z) at high resolution (>200,000). This resolution and scan range were utilized to quantify each Hg species and Hg

isotopes. The percent of total Hg represented by methylmercury in a subsample of the fish collected from the Slave and Athabasca Rivers were found to be 82.4% for goldeye, 90.2% in northern pike, 87.2% in walleye, 92.3% in whitefish, and 87.5% in burbot. Isotope patterns of Hg were also determined for these samples though the method was not sensitive enough to detect subtle differences in stable isotope patterns. Mercury concentrations are nearing, and in certain circumstances exceeding, Canadian guidelines. Overall, metal concentrations, with the exception of Hg, in the Slave and Athabasca Rivers do not appear to be at levels of concern for fish or human health at this time. The trend of four metals being greater in the lower Slave River provides an interesting opportunity for further research into metal chemodynamics.

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LIST OF ABBREVIATIONS

AAS – Atomic absorption spectroscopy

AED – Atomic emission detection

amu – Atomic mass unit

ANOVA – Analysis of variance

BB - Burbot

CCME – Canadian Council of Ministers of the Environment

CRM – Certified reference material

dm – Dry mass

DMT – Dimethyl thallium

EtHg - Ethylmercury

EtEtHg – Ethyl-ethylmercury

EtMeHg – Ethyl-methylmercury

FAPES – Furnace atomization plasma excitation spectrometry

FC – Fort Chipewyan

FF – Fort Fitzgerald

FM – Fort MacKay

FMU – Fort McMurray

FPD – Flame photometric detector

FR – Fort Resolution

FS – Fort Smith

GC – Gas Chormatography

GE – Goldeye

ICP-MS – Inductively coupled plasma mass spectrometry

LOD – Limit of detection

LOQ – Limit of quantification

MeHg – Methylmercury

MeOH-KOH – Methanolic potassium hydroxide

MIP-AES – Microwave induced plasma atomic emission spectrometry

MS – Mass spectrometry

m/z – mass/charge

$NaBEt_4$ – Sodium tetraethylborate

NOAEL – No observable adverse effects limit

NP – Northern pike

NPRI – National Pollutant Release Inventory

OSPW – Oil Sands Process-affected Water

PAHs – Polycyclic aromatic hydrocarbons

PCDDs – Polychlorinated dibenzodioxins

PCDFs – Polychlorinated dibenzofurans

PDMS -- Polydimethylsiloxane

PP – Peace Point

QA/QC – Quality assurance and quality control

RAMP – Regional Aquatics Monitoring Program

RfD – Reference dose

SAGD – Steam-assisted gravity drainage

SeMeth -- Selenomethionine

SIM – Selected ion monitoring

SPME – Solid-phase microextraction

SRDP – Slave River and Delta Partnership

TEL – Tetraethyl lead

THF – Tetrahydrofuran

UL – Tolerable upper intake level

US EPA – United States Environmental Protection Agency

WE - Walleye

WF - Whitefish

wm – wet mass

PREFACE

This thesis is presented in manuscript-style according to the requirements set by the College of Graduate Studies and Research. Chapter 1 is a general introduction, Chapters 2 and 3 are organized as manuscripts for publication in scientific journals, and Chapter 4 is a general discussion and conclusion. Thus, there is some repetition between the introduction and materials and methods sections in each chapter. References cited in each chapter are combined and listed in the References section of the thesis.

CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Anthropogenic activities can lead to significant changes to the natural environment and the extent of these changes is not always understood. One region where anthropogenic activities are a major concern are the Peace and Athabasca Rivers which combine to form the Slave River. These activities have raised concerns about contaminants entering the aquatic environment. Contaminants such as metals, polycyclic aromatic hydrocarbons (PAHs), and pulp mill effluents are a concern for both fish and human health in the region. The area has been the focus of significant interest due to industrial activity and its cultural and subsistence value to First Nations and Metis communities. This interest has driven researchers to investigate the contaminant levels and their potential impacts on the health of the environment. Pulp mill effluents and related contaminants have been studied in the Peace, Slave, and Athabasca rivers (Muir and Lockart 1993; Muir and Lockhart 1994; Peddle et al., 1995; Muir and Pastershank, 1997; McMaster et al., 2006). Polycyclic aromatic hydrocarbons (PAHs) are of interest in the Athabasca and Slave Rivers due to their association with petroleum and combustion sources which has led to many investigations into environmental contamination, including in fish (Van den Heuvel et al., 1999; Smits et al., 2000; Colavecchia et al., 2004; Gurney et al., 2005; Fleeger et al., 2007; Wayland et al., 2008; Kelly et al, 2009; Ohiozebau et al., 2016a; Ohiozebau et al., 2016b). Oil sands process-affected water (OSPW) is generated from the processing of oil sands bitumen and is stored on site in tailing ponds. The effects of OSPW on fish has been researched to determine potential effects of release of stored OSPW to the Athabasca River (Peters et al. Colavecchia et al., 2004, 2007; He et al., 2012). Metals potentially from oil sands aerial deposition and leaching have been studied in the Athabasca River (Squires, 2005; Kessler and Hendry, 2006; Fedorak and Coy, 2006; Kelly et al., 2010; Puttaswamy et al., 2010, Kirk et al., 2014). Mercury (Hg) is one metal that is of particular concern in fish and has been studied in the Athabasca region since the 1970s (Lutz and Hendzel, 1976; Moore et al., 1986; Moore et al., 1986; Donald et al., 1996; Evans et al., 2012). Studies have investigated metals such as Hg and As in the Slave River and Great Slave Lake due to their proximity to mining activities (Murdoch et al., 1989; Murdoch et al., 1992; Grey et al., 1995; McCarthy et al., 1997; Evans et al., 1998; Evans et al., 2013; Chetelat et

al., 2015; Cott et al., 2016; Schuh et al., 2018).In addition to these research endeavors, the Regional Aquatics Monitoring Program (RAMP), a joint industry, government, non-government organization, and community member program, began operating in the Athabasca region in 1997. The program transitioned into the Joint Oil Sands Monitoring Program in 2016.The Athabasca and Slave River regions have been the subjects of many research endeavors aimed at understanding the fate and effects of contaminants in these relatively unique Northern Canadian aquatic systems. Much has been discovered about potential impacts of exposure to these contaminants, but more research is required to understand the extent of exposure and environmental concentrations of contaminants in these complex environments.

1.2 Location of Interest

The Athabasca, Slave, and Peace Rivers are three of the largest rivers in Canada. Their tributaries rise in the Rocky Mountains of Alberta and British Columbia as well as areas of northern Saskatchewan. The Athabasca River flows through oil sands developments in Alberta and other developments, including coal mining, forestry and pulp mills, and agriculture. The Peace River is potentially affected by agricultural uses and hydroelectric power development, and it receives effluents from industries such as pulp and paper manufacturing. There are currently six pulp mills on the Peace River with five releasing effluents and two major power generating stations situated near Bennet Dam in British Columbia (Mackenzie River Basin Board, 2003). The Slave River's primary water sources are the Peace River and the Athabasca River which flows through the west end of Lake Athabasca, which in turn receives a large portion of its inflow from the Athabasca River. The Slave river flows into the Northwest Territories where it empties into the Great Slave Lake, providing approximately 75% of the inflow into the lake and serves as the headwaters of the Mackenzie River (Sanderson et al., 2012).

The Slave and Athabasca rivers are of great interest due to their proximity to extensive industrial activity, primarily oil sands operations, and due to the number of northern communities that rely on the two rivers for food, water, and transportation. Concerns have been raised about possible environmental impacts on these rivers and some research suggests that contaminants related to industry are entering the system.

1.2.1 Oil Sands Development

One of the largest industries potentially impacting the Slave and Athabasca region and causing concerns among its residents are the oil sands extraction operations. There are three major oil sands deposits in Alberta: the Athabasca, Peace River, and Cold Lake deposits (Allen, 2008; Honarvar et al., 2011) These oil sand deposits cover an area of 142 000 km^2 within Alberta (ERCB, 2010). Oil sands are mined for bitumen, which is a viscous mixture of hydrocarbons, which is then refined into usable petroleum products. Of the bitumen in the Alberta oil sands, only 18% is in shallow oil sand deposits within 75m of the surface and are thus extractable using open surface mining (Alberta Department of Energy, 2005). Bitumen not accessible via surface mining is extracted using *in situ* steam assisted gravity drainage (SAGD) or related technologies. Though only 18% of bitumen is surface mineable, surface mining operations accounted for 47% of the extraction operations in the region as of 2015 (Government of Canada, 2015). Commercial development of oil sands in the Athabasca region began in 1967 (Dillon et al., 2011). The investment and development in oil sands projects began to rapidly increase in the 1990s and investment peaked in 2014 (Dillon et al., 2011; Hussey et al., 2018) As of 2013, 895 km^2 of land had been disturbed for surface mining. Currently, oil sands companies are storing all OSPW effluents from bitumen extraction and the total liquid surface area of tailings ponds is 88 km^2, with a total area including pond associated structures of 220 km^2, and the total volume of tailings reported by the mine operators is 975.6 million m^3 (Government of Alberta, 2018). Oil sands extraction has altered a large area of land in the region and the extent of all the potential impacts is not yet fully understood. Measuring the impacts of potential contaminant releases can be difficult due to a lack of information on natural historical background levels of contaminants and since no monitoring programs began in the region until decades after oil sands operations began (Dillon et al., 2011).

1.2.2 Contaminants of Concern and Potential Sources

The Athabasca and Slave River regions and their headwaters have many different anthropogenic activities that can lead to contaminants entering the aquatic environment. These industries include but are not limited to petroleum extraction, mining activities, and pulp mills. These activities have been associated with contaminants of concern to fish and human health such as metals, PAHs, OSPW, and pulp mill effluents.

There are multiple potential anthropogenic sources of metals to the aquatic environment in the Athabasca and Slave regions. These potential sources include aerial deposition and leaching from oil sands activities and other legacy metal mining activities, such as gold mining on the Great Slave Lake and copper/mixed metal mining at Pine Point near Fort Resolution. A study investigating metal concentrations in fish from water bodies near the Pine Point mine found no evidence of increased metal concentrations due to the Pine Point Mine (Evans et al., 1998). Previous studies also found that contaminants are entering the Athabasca River through aerial deposition (Kelly et al., 2010; Kirk et al., 2014). Kelly et al. (2010) analyzed snowpack in the Athabasca region for contaminants and found 13 metals (Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn), all of which are considered priority pollutants by the US-EPA. Since their concentrations were greater near upgraders and oil sands operations compared to the upstream and far-field sampling locations, these contaminants have been suggested to be released from oil sands operations.

Oil sands coke has been found to have the potential to leach metals such as V, Ni, Cu, Mn, and Mo at levels exceeding Canadian guidelines for the protection of aquatic life (Squires, 2005; Kessler and Hendry, 2006; Fedorak and Coy, 2006; Puttaswamy et al., 2010). As of 2014, there were approximately 90 million tons of coke requiring disposal (Alberta Energy Regulator, 2015). One of the larger oil sands companies active in the Athabasca region, Syncrude, produces approximately two million tons of coke annually (ERCB, 2009).

Arsenic is commonly found in significant concentrations in gold deposits, therefore, mobilization of As is a concern with gold mining activities such as the former Giant Mine on the shore of Yellowknife Bay on the Great Slave Lake, which operated from 1948-2004 (Straskraba and Moran, 1990; Cott et al., 2016). During the life of the mine, nearly 260,000 tonnes of arsenic trioxide (As_2O_3) waste was generated with 237,000 tonnes having been captured and stored (Jamieson, 2014; Wrye, 2008). This resulted in approximately 20,000 tonnes being released into the surrounding environment primarily through emissions from the mine's roaster stacks. Some studies have found elevated arsenic levels in surface waters and sediment in Yellowknife Bay (Jackson et al., 1996; Mace, 1998; Mudroch et al., 1989). Lake whitefish and burbot collected near the Giant Mine site generally had greater concentrations of As compared to

the surrounding area including near Hay River on the southern side of the Great Slave Lake (Cott et al., 2016).

Polycyclic aromatic hydrocarbons (PAH) can enter the environment from both natural sources, such as forest fires and natural hydrocarbon seeps, and via anthropogenic activities, such as organic combustion and petroleum extraction and combustion (Peters et al., 2005; Boehm et al., 2007). The oil sands being a large petroleum deposit can therefore lead to both natural and anthropogenic release of PAHs into the environment. Increased deposition of PAHs was found in snowpack near two upgrading facilities in the Athabasca region providing evidence of airborne release of PAHs in the region (Kelly et al., 2009). PAHs have been found in organisms in the Athabasca region including fish and aquatic insects (Van den Heuvel et al., 1999; Smits et al., 2000; Colavecchia et al., 2004; Gurney et al., 2005; Fleeger et al., 2007; Wayland et al., 2008; Ohiozebau et al., 2016a; Ohiozebau et al., 2016b).

Currently, oil sands companies are not permitted to discharge OSPW and have to store OSPW in large ponds, but it is likely that in the future OSPW will need to be released to the environment. Metals are one of the constituents of OSPW and can be found at varying concentrations depending on factors such as source, extraction method, and ore quality. Analysis of metals in OSPW has found instances of individual metals exceeding Canadian Council of Ministers of the Environment (CCME) guidelines which could be problematic if OSPW is released (Allen, 2008; Li et al., 2014; Zhang, 2016). Results of laboratory studies have found that exposure of fish larvae to OSPW or waste water pond sediments can cause craniofacial, spinal, and cardiovascular deformities, premature hatching, incomplete hatching, decreased hatching success, reduced size, and increased larval mortality (Colavecchia et al., 2004; Peters et al., 2007; He et al., 2012). Methods to detoxify OSPW are being investigated but an efficient and cost-effective method has not been identified to date.

Pulp mills releasing effluent to the Peace River could lead to potential negative effects downstream, including on the Slave River. Various studies have shown that exposure of wild fish to pulp mill effluents can cause increased hepatic mixed-function oxygenase activities, increased liver size, and a decrease in gonad size and sex steroid concentrations (Reviewed in McMaster et al., 2006). Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans (PCDDs/PCDFs) are also a concern in pulp mill effluents and have been detected in Peace,

Athabasca, and Slave River fish in samplings from 1992-1994 (Muir and Lockart 1993; Muir and Lockhart 1994; Peddle et al., 1995; Muir and Pastershank, 1997; McMaster et al., 2006). Improvements in technology and regulation have significantly reduced the release of PCDDs and PCDFs which has led to a decrease in concentrations since the early 1990s (Muir and Pastershank, 1997). Pulp mill effluents have also been shown in laboratory exposures to reduce egg production and time to first spawning, in fathead minnows (Reviewed in Parrott et al., 2006). Mercury was used in pulp and paper mill processes prior to 1970 and could have led to potential environmental release of Hg in the Peace River during that time (Donald et al., 1996)

Overall, the Slave and Athabasca Rivers have significant industrial activities that are potentially leading to impacts by multiple types of contaminants from different sources. This thesis will focus on the potential impacts and quantification of metal concentrations in fish relevant to the local peoples of the region. In addition to the metal analysis, general fish health and PAHs screening methods for fish were investigated and results are available in Ohiozebau et al. (2016a; 2016b).

1.2.3 Native Fish Species

Five native fish species were of interest to this study: northern pike (*Esox lucius*), goldeye (*Hiodon alosoides*), walleye (*Sander vitreus*), whitefish (*Coregonius clupeaformis*), and burbot (*Lota lota*). These five species were selected due to their cultural and dietary/economic significance to local communities.

Northern pike are commonly found in vegetated lakes, quiet pools and backwaters of creeks and rivers (Page and Burr, 2011). They are solitary, highly territorial, and usually do not undertake long migrations though some may move larger distances. (Morrow, 1980). Northern Pike from the lower Slave River were found to have sulfur isotope ratios consistent with being river residents (Carr et al, 2017). The typical size range of northern pike is 46 to 76 cm in length and 0.9 to 4.3 kg (Scott and Crossman, 1973; Ontario Ministry of Natural Resources and Forestry, 2018) Northern pike spawn in the spring after the ice melts and move inshore or to marshy areas to spawn (Scott and Crossman, 1973). The spawning activities usually occur during the day (Morrow, 1980). Northern pike are voracious predators and their trophic level has been estimated as 4.31 (Vander Zanden et al., 1997). A Slave River gut content study found that

resident northern pike feed primarily on other fish including benthic species, such as flathead chub, Arctic lamprey, burbot and shallow dwelling species such as trout-perch, emerald shiner, ninespine stickleback, and younger northern pike (Little et al., 1998). Gut contents also show aquatic invertebrates such as zygopteran nymphs and amphipods. Terrestrial vertebrates were also found though both the invertebrates and terrestrial vertebrates comprised a much lesser portion of the gut contents than fish (Little et al., 1998).

Goldeye are smaller pelagic fish with an average length of 30.5 cm and average weight of 450 g (Fisheries and Oceans Canada, 2016A). Spawning occurs in the spring shortly after ice break up usually in May to early July and spawning activities last for 3 to 6 weeks (Scott and Crossman, 1973). They are nocturnal fish. Some populations of goldeye migrate upstream in spring for spawning and feeding and migrate back downstream in the fall (Scott and Crossman, 1973). Goldeye are carnivorous fish on the 3rd trophic level. The stomach contents of goldeye captured on the Slave River show they eat primarily aquatic invertebrates such as plecopterans, corixids, and branchiopoda. Terrestrial insects were commonly found in goldeye guts as well. Rodents and plant material were found as well but to a much lesser degree than invertebrates and insects. (Little et al., 1998).

Whitefish inhabit large lakes and large rivers and can enter brackish waters though they are primarily lake dwellers (Morrow, 1980; Page and Burr, 2011). The average length of whitefish is approximately 38 cm and can reach up to 50 cm with a weight of 2 kg (Scott and Crossman, 1973; Fisheries and Oceans Canada. 2016B). They are migratory fish and the general trend of their migration is from deep to shallow water in the spring, shallow to deep water in the summer. They migrate to shallow spawning areas in the fall, and back to deep water post spawn (Morrow, 1980). Separate populations can form in the same lake if large enough (Morrow, 1980). Whitefish populations on the Slave River are migratory and sulfur isotope analysis of whitefish from the lower Slave River showed their population contained both river and lake residents (Little et al., 1998, Carr et al., 2017). Whitefish are a carnivorous fish on the 3rd trophic level. Studies have found that in the Salt River, a smaller river that runs into the Slave River north of Fort Smith, juvenile whitefish ate almost exclusively aquatic invertebrates with small amounts of ninespine stickleback and plant material. The most commonly consumed invertebrates were ostracods, corixids, trichopteran larvae, and gastropods. (Little et al., 1998)

The stomach contents of the Salt River juvenile whitefish were similar to other reported whitefish diets (Scott and Crossman, 1973).

Walleye prefer large shallow lakes with high turbidity but can also be found in medium and large rivers such as the Slave and Athabasca Rivers (Frimodt, 1995; Etnier and Starnes, 1993). Walleye can migrate due to food availability and water temperature fluctuations and they also migrate to smaller tributary rivers or shallow shoals for spawning (Scott and Crossman, 1973). Sulfur isotope analysis of walleye in the lower Slave River indicated walleye in the region were lake dwellers (Carr et al., 2017). Spawning occurs in spring or early summer with northern populations more likely to spawn later than more southern populations (Scott and Crossman, 1973). Walleye are carnivorous fish on the 4th trophic level and their trophic level has been estimated to be 4.33 (Vander Zanden et al., 1997). Walleye primarily feed at night and a gut content study found that Slave River walleye primarily eat other fish such as ninespine stickleback, small northern pike, and trout-perch (Little et al., 1998; Scott and Crossman, 1973). Aquatic invertebrates, such as plecopterans, nymphs, and amphipods, were found in walleye guts as well but to a lesser degree than fish. Adult walleye are typically in the range of 35 to 80 cm and 1 to 8 kg (Anderson and Neumann, 1996; Hartman, 2009). The size of walleye can differ greatly depending on the temperature of water thus more northern walleye, such as those in NWT and northern Alberta, will be smaller than average. The NWT average weight is approximately 2.3 kg (Northwest Territories Tourism, 2018B).

Burbot are the only member of their order, Gadiformes, which live in freshwater. The average size of burbot is 1 to 3 kg and 30 to 60 cm (McPhail and Paragamian, 2000). Spawning occurs during the winter, typically January to March, beneath the ice of lakes and rivers (Scott and Crossman, 1973). They are primarily fished for in the winter through ice fishing, though they can be caught in other seasons as well. Burbot are nocturnal feeders and typically hunt for prey along or near the sediment (Scott and Crossman, 1973). They are a carnivorous fish on the 4th trophic level. Burbot collected in a different Slave River study were found to have small goldeye and lake whitefish in their stomachs but the data was limited due to most captured adults having empty stomachs (Little et al., 1998). Juvenile burbot collected from the Little et al. (1998) study had amphipods, ninespine stickleback, juvenile longnose sucker, and plecopteran nymphs among their stomach contents. (Little et al., 1998).

1.3 Metals

1.3.1 Metals of Concern

There are five metals of concern for this study, Hg, Tl, As, Se, and V. Mercury is an element and can be found naturally in the environment. Environmental mercury concentrations can be increased by anthropogenic activities such as mining, hydroelectric power developments, waste incineration, chlor-alkali production, and fossil fuel extraction and emissions (Bodaly et al., 1984; Garcia and Carignan, 1999; Qi et al., 2000; Ferraz and Afonso, 2003; Landis et al., 2004; Mukkerjee et al., 2004; Lockhart et al., 2005; Kelly et al., 2006; Kidd et al., 2012). Global anthropogenic emissions of Hg account for approximately 2200 tons per year (Pacyna et al., 2006) and natural emissions of Hg are estimated between 1800-5800 tons per year globally (Bergan et al., 1999; Shia et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002; Gustin, 2003; Yin et al., 2010).

There are three species of mercury that are most prevalent in the environment: metallic Hg, divalent Hg(II), and methylmercury (MeHg). Two of the Hg species can be found in fish, Hg(II) and MeHg, though Hg in fish is primarily in the form of MeHg (Bloom, 1992; Lasorsa and Allen-Gil, 1995; Jackson et al., 2008). Mercury is converted into MeHg in aquatic environments such as lakes and estuaries through methylation by sulfate reducing bacteria in sediment and water (Das et al., 2009). Methylmercury biomagnifies up food webs, leading to greater concentrations in the upper trophic levels of aquatic ecosystems (Baeyens et al., 2003). Methylmercury biomagnification can lead to Hg concentrations becoming problematic for upper trophic level species and terrestrial consumers of fish such as wildlife and humans. Given the concern for negative effects on human health, Health Canada has set a general Hg guideline in fish of 0.5 µg/g (Health Canada, 2007).

Mercury has seven stable isotopes ranging in mass from 196 to 204. These stable isotopes have varying natural abundances specific to each isotope. These stable isotopes can be changed by natural processes in specific ways that may be characteristic of the source of the Hg (Ridley and Stetson, 2007; Bergquist and Blum, 2007; Jackson et al., 2008; Bergquist and Blum, 2009; Das et al., 2009; Salters and Odom, 2009; Yin et al., 2010). The ability to detect subtle changes

in Hg isotope ratios could be a valuable tool in differentiating or determining the sources of Hg in environmental samples such as fish.

The first reported Hg analysis in the oil sands region was in 1975 with fish sampled from 16 sites between Fort McMurray and Lake Athabasca (Lutz and Hendzel, 1976). Whole body Hg concentrations were determined in walleye, northern pike, and whitefish which are species of interest to this study. In the 1980's, dorsal muscle Hg concentrations were determined in fish collected from lakes and rivers in Alberta including a site near Suncor and another site near Lake Athabasca (Moore et al., 1986). Similar sites to the 1975 sampling were sampled again in 1992 and fillet Hg concentrations were determined (Donald et al., 1996). Mean concentrations of Hg detected in fish from these studies ranged from 0.27-0.43 µg/g (Lutz and Hendzel, 1976; Moore et al., 1986; Donald et al., 1996), which is below the Health Canada general Hg guideline (Health Canada, 2007). Timoney and Lee (2009) analyzed the Hg concentration data from the 1975, 1980 and 1992 studies and found that concentrations in walleye muscle tissue increased over time. Evans et al. (2012) also reviewed these samplings with the addition of unpublished Department of Fisheries and Oceans data and theorized that due to differences in the tissues analyzed and the lengths of fish sampled, the Hg levels in the region were not increasing as presumed.

Thallium is a poorly studied metal with the potential for relatively great toxic effects. It is possibly the least understood of the metals that occur in the environment. Tl is naturally found in trace amounts in the Earth's crust at concentrations between 0.1-1.7 mg/kg (Kazantsis, 2000). Starting in 1920, Tl's primary use was as a rodenticide and pesticide, which continued for 45 years before it was banned by the US EPA (Nriagu, 1998). Tl is currently not a widely used metal in industrial activities, but there are over 150 uses and potential applications for Tl listed in the cumulative index of 'Chemical Abstracts' (Peter, 2004). Current uses of Tl and Tl-containing products include low-temperature thermometers, ceramic semiconductors, scintillation counters, optical lenses, and specialized electronic research equipment (Arzate, 1998; Ramsden, 2002; United States Environmental Protection Agency, 2002b). In the United States, 60-70% of Tl is used in the electronics industry (United States Environmental Protection Agency, 2002b). Currently, demand for Tl in industry is relatively small, but due to its use in electronics and possible future technology demand for Tl in industry could increase greatly (Nriagu, 2003).

Major industries that cause mobilization of Tl are sulfide ore mining and smelting, extraction and burning of fossil fuels and potash related industries. Tl can be volatilized during these processes or released in wastewater. Tl that is volatilized and released in aerial emissions can end up in aquatic systems. Emissions can deposit directly into aquatic systems or can deposit onto terrestrial areas. Deposition to terrestrial environments can be transported to aquatic systems through surface water runoff. Global production TL is estimated to be approximately 15 tons per year, whereas, an estimated 2000-5000 tons per year are mobilized by other industrial processes (Kazantzis, 2000).

Arsenic is a naturally occurring element that can found in mineral deposits such as sulphide minerals which can lead to the significant release of As into the environment (Murdoch and Clair, 1986). Arsenic concentrations in freshwater are generally in the range of 0.15-0.45 µg/L though there can be site-specific concerns in bodies of water impacted by mining activities (Bissen and Frimmel, 2003a; Bissen and Frimmel, 2003b). Waterborne As is primarily in the arsenate and arsenite forms with arsenite being the more toxic of the two (Cervantes et al., 1994; Hughes et al., 2011). In addition, As can be methylated into monomethylarsinic acid, dimethylarsinic acid, and trimethlyarsine oxide by microorganisms (Ridley et al., 1977; Woolson, 1977; Cullen and Reimer, 1989; Gadd, 1993). Organic forms of As generally demonstrate low toxicity (Gochfeld, 1995).

Arsenic in fishes, exists primarily in organic forms, and contrary to some other organometals, As does not appear to biomagnify (United States Environmental Protection Agency,2003; Williams et al. 2006). Inorganic As is the primary concern for human health which can lessen the risk of negative effects since As is primarily found as organic forms in fish (Rasmussen and Menzel, 1997; Kovendan et al., 2013). Arsenobetaine is the most abundant form of organic As in fish and increased levels of arsenobetaine can be detected in human urine after consuming fish (Morita and Edmonds, 1992; Phillips, 1990; Goessler et al., 1998; Lintschinger et al., 1998; Ritsema et al., 1998; Tsalev et al., 1998) There is an As guideline for fish protein in Canada of 3.5 ppm (Health Canada, 2018). Arsenic accumulation appears to be lowest in fish muscle tissue compared to other fish tissues with the US EPA finding fillet As concentrations to be on average 86% of whole body As in 10 species studied (Gilderhus, 1966; Maher et al., 1999;

Suner et al., 1999; Pedlar and Klaverkamp, 2002; United States Environmental Protection Agency, 2002a).

Selenium is a nonmetal/metalloid naturally found in the earths crust that can exist as inorganic selenite and selenate or organic compounds such as selenomethionine (SeMeth) (Fan et al., 2002; Janz, 2011). Natural background concentrations of Se in aquatic ecosystems are typically low with concentrations in the 0.01 -0.1 μg/L, but background concentrations can range anywhere from 5-50 μg/L (Maher et al., 2010). Selenium is prevalent in surface waters due to natural sources such as weathering and anthropogenic sources such as agriculture runoff, coal fired power plants and fly ash, mining and milling operations, and combustion of fossil fuel (Lemly and Smith 1987; Sappington, 2002). Selenium is essential to proper physiological functions in fish and fish require 0.1-0.5 μg Se/g dm in their diet (Hodson and Hilton, 1983; Lemly, 1997a, 1997b; Hamilton, 2004). Even though Se is an essential element, Se can be toxic to aquatic organisms when dietary concentrations exceed 3.0 μg Se/g dm (Lemly, 1997a; Hamilton, 2004).

Aquatic Se tends to become bound in sediment, reducing the available Se in the water column; however, Se can be remobilized and cycled back into food chains. Inorganic Se species are taken up by primary and secondary producers where they are converted to organoselenides such as SeMeth which is then transferred through the food chain to fish (Fan et al., 2002; Maher et al., 2010; Stewart et al., 2010; Janz, 2011). Dietary intake of SeMeth is the main source leading to bioaccumulation of Se in fish to toxic levels (Lemly and Smith, 1987). Se concentrations can increase up to several thousand-fold between uptake of Se from water to primary producers, leading to transfer of toxic levels to more sensitive organisms such as fish (Lemly and Smith, 1987; Skorupa, 1998; Stewart et al., 2010; Janz, 2011). The US EPA has set Se guidelines for the protection of aquatic life for fish tissue at 8.5 μg/g dm for whole body and 11.3 μg/g dm in muscle tissue (USEPA, 2016).

Vanadium is not found as metallic vanadium naturally but is found as vanadates in conjunction with other metals such as copper, lead, or iron (Environment and Climate Change Canada, 2016). There are currently no mining activities specifically for V in Canada, but it enters the environment from other industrial activities such as the extraction and burning of fossil fuels

(Environment Canada and Health Canada, 2010). The primary commercial form of V is vanadium pentoxide (V_2O_5) and under 10,000 tonnes was commercially used annually in 2006 and the majority was used in the production of alloys for steel manufacturing (Environment Canada and Health Canada, 2010, Environment and Climate Change Canada, 2016). It is considered persistent but not bioaccumulative under criteria set by the Government of Canada (Government of Canada, 2000, Environment and Climate Change Canada, 2016).

Vanadium is an essential trace element for some aquatic organisms and potentially for fish though the data is limited in fish (Nielsen, 1991; Markert 1994; Watanabe et al., 1997). Though it is potentially essential for fish health, V has been shown to inhibit Na-K-ATPase activity in fish gills (Bell and Sargent, 1979). It has been shown to be toxic with chronic deleterious effects (growth and survival) in fish (American flagfish, fathead minnow, and brook trout) at water concentrations ranging from 140-610 µg/L (Kimball, 1978; Holdway and Sprague, 1989; Ernst and Garside, 1987). Monitoring data for V in Canada has found concentrations between 0.001-16.1 µg/L which is less than toxic concentrations which makes V toxicity more of an isolated or site-specific concern (Environment Canada and Health Canada, 2010).

1.4 Objectives and Hypotheses

The overall objective of this study was to characterize metal concentrations in fish collected from the Slave and Athabasca Rivers and to establish a potential gas chromatography (GC) Orbitrap mass spectrometry (MS) method for mercury speciation and mercury isotope analysis.

Objective 1: Characterize spatial variation of metal concentrations in muscle tissues of fish collected from the Slave and Athabasca Rivers.

> Null-Hypothesis 1 (H_01): There are no statistically significant spatial variations in metal concentrations in muscle tissues of fish collected from the Slave and Athabasca Rivers.

Objective 2: Characterize the mercury speciation in fish from field sites in the Slave and Athabasca Rivers utilizing GC Orbitrap MS.

Null-Hypothesis 2 ($H_0$2): There is no statistical difference in mercury speciation in fish among the field sites in the Slave and Athabasca Rivers.

Objective 3: Characterize the mercury stable isotope ratios in fish from the Slave River and Athabasca Rivers utilizing GC Orbitrap MS.

Null-Hypothesis 3 ($H_0$3): There is no statistical difference in mercury stable isotopes in fish among the field sites in the Slave and Athabasca Rivers.

CHAPTER 2: CONCENTRATIONS OF METALS IN FISHES FROM THE ATHABASCA AND SLAVE RIVERS OF NORTHERN CANADA

2.0 Preface

This chapter discusses the collection and analysis of 25 metals in five species of fish collected from the Slave and Athabasca Rivers during four sampling seasons. The results were statistically analyzed for spatial and temporal trends. A simple risk assessment was done on metals of interest to determine the potential risk to human consumers. These samples were further analyzed and discussed in Chapter 3.

This Chapter will be submitted to Environmental Toxicology and Chemistry under joint authorship with Ehimai Ohiozebau, Garry Codling, Erin Kelly, John P. Giesy, and Paul D. Jones. Figures, tables, and references have been formatted to adhere to the thesis style. References for this chapter have been compiled and listed in the reference section for the thesis.

- Brett Tendler participated in collection of all the fish samples, prepared the fish tissue for total metal analysis, performed data analysis, and wrote the manuscript.
- Ehimai Ohiozebau participated in the collection of the fish samples and reviewed the manuscript.
- Garry Codling participated in the collection of some of the fish samples and reviewed the manuscript.
- Erin Kelly (Government of the Northwest Territories) aided in the development of the study, provided introduction and development of relationships with community members, provided site and local knowledge, reviewed manuscript.
- John P. Giesy aided in the development of the study and reviewed the manuscript.
- Paul D. Jones provided funding to conduct the research, developed the study, participated in the collection of all the fish samples, assisted with the data analysis, and reviewed the manuscript.
- Funding was provided by The Boreal Songbird Initiative, the Government of the Northwest Territories, Aboriginal and Northern Development Canada (ANDC) and the Canadian Water Network (CWN)

- First Nations and Metis communities provided assistance in collecting fish samples and performing fish health assessment.

2.1 Abstract

There is growing concern about the possible effects of exploitation of the Alberta Oil Sands on the ambient environment, including possible effects on populations of fishes in the Athabasca River and further downstream in Lake Athabasca and the Slave River. In this study, concentrations of metals in dorsal muscle tissue of five fishes (goldeye, northern pike, walleye, whitefish, and burbot) from the Slave, Peace, and Athabasca Rivers were quantified. A suite of 25 metals (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn) were analyzed. Most metals exhibited no significant variations in concentration among locations. There were five metals, As, Hg, Se, Tl, and V, concentrations of which exhibited significant variations among locations and were of sufficient magnitude to be of interest. Concentrations of Hg did not vary significantly among locations though Hg was of interest due to it being detected at concentrations of concern and the use of the selected fishes as a local food source. Concentrations of As, Se, Tl, and V in dorsal muscle of certain fishes in the Slave River were greater than those in the same tissues and species in the Peace and Athabasca Rivers. This phenomenon was most prevalent with Tl and to a lesser extent As and Se. However, concentrations were not of concern for human consumers.

2.2 Introduction

The Slave and Athabasca Rivers are two of the largest rivers in the in Canada. Their tributaries rise in the Rocky Mountains of Alberta and British Columbia as well as areas of northern Saskatchewan. The Slave River provides approximately 75% of the inflow into the Great Slave Lake (Sanderson et al., 2012). The Slave River's primary sources of water are the Peace River and Lake Athabasca, which receives a large portion of its inflow from the Athabasca River. The Athabasca River flows through oil sands developments in Alberta and other developments, including coal mining operations, forestry operations such as sawmills and pulp mills, and agriculture. The Peace River is affected by agricultural uses and receives effluents from industries such as pulp and paper and hydroelectric power. There are currently six pulp mills on the Peace River with five releasing effluents and two major power generating stations situated near Bennet Dam in British Columbia (Mackenzie River Basin Board, 2003).

Due to proximity to industrial activity, primarily oil sands operations, the health of the Athabasca River and the downstream Slave River are of interest to local, northern communities who rely on these two rivers for food, water, and transportation. Public concerns have been raised about possible environmental effects on these rivers from legacy and emerging industries and results of some research suggest that contaminants related to industry are entering the proximate aquatic system and potentially reaching downstream locations. These concerns also extend to potential impacts on human health as fish are an important food source for communities along the Athabasca and Slave River. There are fish consumption advisories for the Athabasca River and Lake Athabasca due to Hg concentrations in fish (Government of Alberta, 2016). Previous studies have found that contaminants are entering these rivers through aerial deposition (Kelly et al., 2009; Kelly et al., 2010, Kirk et al., 2014). Kelly et al., (2009; 2010) analyzed snowpack in the Athabasca region for contaminants and found polycyclic aromatic hydrocarbons, which can be associated with fossil fuel production, and 13 metals (Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn), all of which are considered priority pollutants by the US-EPA. Since their concentrations were greater near upgraders and oil sands operations compared to the upstream and far-field sampling locations, these contaminants have been suggested to be released from oil sands operations. Currently, industries are regulated to not discharge oil sands process-affected water (OSPW), but in the future it is likely that OSPW will

need to be released to the general environment. Oil sands process-affected waters can contain varying concentrations of metals depending on parameters such as source, extraction method, and ore quality and analysis of OSPW samples has found concentrations of some metals exceeding CCME guidelines (Allen, 2008; Li et al., 2014; Zhang, 2016). Results of studies conducted in the laboratory have found exposure of fish larvae to OSPW or waste water pond sediments can cause craniofacial, spinal, and cardiovascular deformities, premature hatching, incomplete hatching, decreased hatching success, reduced size, and increased larval mortality (Colavecchia et al., 2004; Peters et al., 2007; He et al., 2012). Local anglers have suggested that there are an increased number of lesions, tumours, and deformities in fishes of the Athabasca and Slave Rivers. However, currently, there is a lack of numerical data to either support or refute these claims.

Given all of the activities currently ongoing in the Athabasca region and uncertainties associated with these activities, an investigation into the contaminant levels in populations of fishes in the Athabasca and Slave Rivers was performed. Results of organic chemical contamination and condition of fishes have been previously reported (Ohiozebau et al 2015, 2016). Presented here are the findings of the investigations into metal contaminants in the muscle of five native fish traditionally eaten by local community members in the region that cover varying trophic levels.

2.3 Materials and Methods

2.3.1 Collection of Fishes

Five species of fish, including northern pike (*Esox lucius*), walleye (*Sander vitreus*), whitefish (*Coregonus clupeaformis*), goldeye (*Hiodon alosoides*), and burbot (*Lota lota*) were collected from the Athabasca and Slave rivers in 2011/2012, as previously described (Ohiozebau et al 2015; Ohiozebau et al 2016). Each sampling event consisted of capturing and dissecting up to the target of 30 fish of each species from each of the five locations in 2011 and seven locations in 2012. Four sampling events took place during the summer, fall, and winter of 2011 and the spring of 2012. Original sampling locations for the 2011 and 2012 samplings were Fort McMurray (FMU) and Fort Mackay (FM) on the Athabasca River, Fort Chipewyan (FC) on Lake Athabasca, and Fort Smith (FS) and Fort Resolution (FR) on the Slave River (Figure 1).

Two additional sites were sampled in the spring of 2012 at Peace Point (PP) on the Peace River and Fort Fitzgerald (FF) on the Slave River. Peace Point was added to improve understanding of potential differences on the Peace River, which is a major head water for the Slave River.

Fish were captured using gill nets from common local fishing sites and transferred, on ice, back to processing facilities. Fish were subjected to a detailed external and internal assessment before tissue samples were collected. Dorsal muscle tissues were stored in 125 mL amber jars at -18 °C. These samples were also analyzed for PAHs (Ohiozebau et al., 2015; Ohiozebau et al., 2016).

2.3.2 Quantification of Metals

The first ten fish of each species during each sampling period were subjected to metal analysis. The total number of fishes analyzed for each species, location, and sampling period is listed in Table 2.1 and 2.2. Freeze dried, muscle of fishes was prepared by digestion of 0.1 g tissue with nitric acid (69%) and hydrogen peroxide (20%) in Nalgene Vials. Digestates were evaporated at 75 °C using a hot plate and 5 mL of nitric acid (2%) was then added to preserve samples. Samples were filtered using 0.45 µm polyethersulfone syringe filter (VWR) and transferred into an 8 mL Nalgene vial until analysis was performed. Blank samples and Tort-2 lobster hepatopancreas (NRC, Ottawa, ON, Canada), a certified reference material, were used for analysis and they were subjected to all the same laboratory procedures as the samples of fish muscle. All glassware and laboratory equipment was carefully cleaned with soap and water, then soaked in an acid bath for a minimum of four hours, and lastly rinsed three times with reverse-osmosis water and Nano-pure water. Analyses were performed using an inductively-coupled plasma mass spectrometer (X Series II, Thermo Electron, Mississauga, ON, Canada). The metals analyzed were silver (Ag), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), tin (Sn), strontium (Sr), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn).

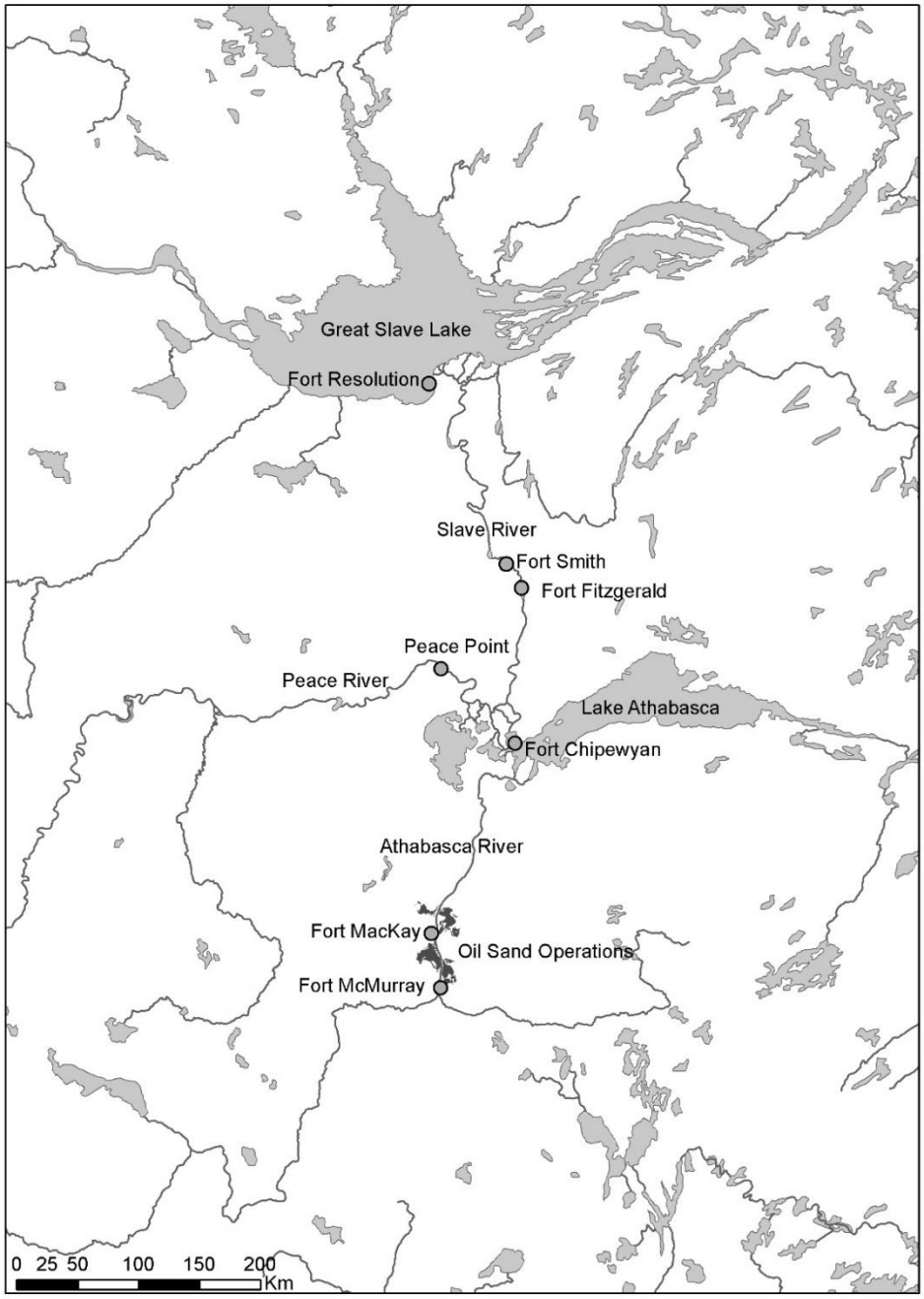

Figure 2.1: Map of the sampling locations and other areas of interest along the Slave, Athabasca, and Peace Rivers. Map created using ArcMap 10.4 (Environmental Systems Research Institute, Redlands, CA, USA). Sampling locations were Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR).

2.3.3 Statistics

Normality of data was checked by use of the Kolmogorov-Smirnov test and homogeneity of variance was checked by use of Levine's test. This data set contained data that met the assumptions of normality, but also some that even after $\log_{10}$ transformation did not meet the assumptions of normality. Therefore, less powerful non-parametric statistics were used for all data. Data was separated by species and sampling period and spatial differences were analyzed using a Kruskal-Wallis test followed by post hoc Dunn's test. A Bonferroni correction was applied to the Dunn's tests to reduce the likelihood of false positives. All statistical analysis was performed using SPSS Version 24 (IBM SPSS Statistics, Armonk, NY, USA). Differences were considered statistically significant at $p < 0.05$. This made it more difficult to demonstrate a difference if in fact there was one. That is there was a bias toward false negatives. All metals data for fish muscle tissue is reported as wet mass (wm). Dry mass (dm) metal concentrations will be converted using an 80% water content assumption which was the approximate water content of the fish muscle freeze dried for analysis.

2.4 Results and Discussion

Overall, 623 fish from four sampling periods were subjected to metal analysis of which 150 were goldeye, 154 were northern pike, 141 were walleye, 125 were whitefish, and 53 were burbot. All five species were collected during the summer, fall, and spring samplings. Burbot were the only species collected during the winter sampling. Four of the fish species (goldeye, northern pike, walleye, and whitefish) were collected in sufficient numbers during each sampling period to perform further statistical analysis. The number of burbot collected was limited with 34 of 53 captured being from Fort Resolution. As such, burbot were not included in further statistical analysis. Variations in the size of fish analyzed can have a significant effect on metal concentrations; however, no statistical difference in size between sites was found.

The majority of the metals (Ag, Al, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Sr, U, and Zn) analyzed in fish muscle tissue varied little among locations and few metals were detected at sufficient concentrations to be of concern (Table 2.1 and 2.2). Concentrations of five metals (Hg, As, V, Se, and Tl) either varied among locations or were present at concentrations considered to be of interest. The results for these five metals are in Tables 2.3-2.6

and Figures 2.2-2.6. Statistically significant differences are noted in Tables 2.3-2.6. These five metals have been associated with extraction and upgrading of bitumen by oil sands operations in Alberta (Kelly et al., 2009; Gomez-Bueno et al., 1981). Apart from Hg, the concentrations of these metals (As, V, Se, and Tl) were not considered to be of concern.

2.4.1 Mercury

Concentrations of Hg were not significantly different among locations (Figure2.2); However, in some locations mean concentrations of Hg exceeded the Health Canada guideline for general consumption (500 ng/g wm) or the subsistence consumption advice (200 ng/g wm) recommended by Health and Welfare Canada which is now integrated into Health Canada (Wheatley, 1979; Health Canada, 2007). The consumption guideline and advice for Hg are based on total mercury, not methylmercury, which is the chemical species of mercury predominately found in muscle of fishes (Bloom, 1992). The general Health Canada guideline (500 ng/g wm) was exceeded in 2.6% of the mean concentrations separated by species/season/locations (2/76). These exceedances occurred in walleye collected from Fort McMurray during the summer sampling and walleye collected from Fort Smith during the fall. The subsistence advice (200 ng/g wm) was exceeded in 46.7% of samples (36/77). Exceedances of the subsistence advice were most prevalent in northern pike (13/17), and walleye (13/16), and were less frequent but still common in goldeye (9/16). Fewer exceedances (1/12) were observed for burbot and there were no exceedances in whitefish. The greatest concentrations of mercury were measured in upper trophic level species, northern pike and walleye, which is consistent with the ability of methylmercury to be biomagnified (Watras and Bloom, 1992).

Concentrations of Hg in fish collected from the Athabasca and Slave Rivers in this study were relatively consistent with past measurements. Mean concentrations of Hg in northern pike and walleye from the Slave River, sampled in 1988-1990, were 340 ng/g wm for both species (Grey et al. 1995). Furthermore, northern pike and walleye sampled between 1990-1993 in the Slave River, had median concentrations of 187-296 ng/g wm and 202-261 ng/g wm, respectively (McCarthy et al. 1997). The majority of measured Hg concentrations were below the Health Canada general guideline for Hg in fish and should not pose significant risks to the mean consumer but could pose risks to those consuming more than mean amounts of fish such as

Table 2.1: Mean concentration of metals in muscle from goldeye and northern pike from sampling sites along the Slave, Athabasca, and Peace Rivers. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Goldeye																										
Location	Season	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	Summer	10	34	1.66	209	41.1	61.3	32.3	1.09	3.83	5.03	70.3	200	4.83	255	183	17.7	7.62	2.34	0.43	704	34.4	679	2.67	19.2	5.13	3.82
FM		10	38	0.81	51.8	56.6	35.2	20.7	1.99	0.58	2.82	88.8	211	3.13	228	139	14.6	3.71	1.6	0.27	457	109	937	2.37	49.4	5.75	3.32
FC		9	37	2.23	224	55.8	17.5	23.9	0.22	0.25	2.55	66.5	124	2.16	209	134	11.7	5.41	4.72	0.51	770	227	403	3.93	4.56	3.06	2.66
FS		10	29	4.22	225	60.4	1.92	249	0.35	2.72	12.1	54.4	185	4.56	233	462	15.6	33.1	3.72	0.81	588	80.0	4770	3.58	4.01	11.7	4.46
FR		2	38	0.72	1330	41.2	79.2	12.7	1.07	0.76	0.04	151	203	3.34	224	132	27.8	7.49	1	0.27	748	136	111	3.1	0.41	9.52	3.09
FMU	Fall	1	39	**<0.01**	121	12.4		58.7	0.1	2.12	3.46	0.06	119	3.25	226	199	5.12	0.06	2.55	0.13	142	0.62	992	0.01	1.64	3.67	3.52
FM		10	36	0.14	108	17.8	52.7	23.3	0.66	0.96	2.77	24.5	195	3.59	194	155	12.7	5.34	0.77	0.42	538	2.38	458	1.56	0.83	3.39	2.58
FC		9	37	2.19	132	30.8		67.4	0.74	1.9	4.65	22.9	126	2.81	188	264	7.77	8.16	0.38	0.61	518	13.1	1810	0.82	0.69	4.94	2.85
FS		10	35	0.84	167	35.4		11.5	0.41	2.85	2.67	60.8	151	3.08	159	128	13.8	10.8	4.96	0.32	844	0.63	308	1.9	108	2.64	2.34
FR		10	36	0.44	184	43.6	11.6	11.4	0.24	2.32	2.24	56.1	149	2.84	249	122	18.3	11.2	1.72	0.6	818	18.9	202	3.06	2.82	6.71	2.62
FMU	Spring	11	33	2.02	263	27.0		59.9	0.09	11.2	11.3	643	310	8.09	264	238	71.2	8.85		0.67	631	1.6	1089	3.17	7.74	8.46	5.30
FM		9	27	1.27	307	32.7		85.5	0.08	4.3	18.7	532	378	9.29	76.9	310	76.9	11.2		0.42	601	2.96	2000	3.08	0.41	9.12	5.57
FC		10	35	0.32	383	48.2	56.6	105		0.48	10.0	44.0	195	4.22	126	335	9.93	11.1		0.57	542	**<0.01**	1200	3.7	1.87	6.65	3.39
PP		9	40	0.02	6.53	26.0	19.7	66.4		0.01	3.28	34.3	157	3.09	260	150	1.75	9.36		0.21	408	**<0.01**	581	2.41	25.4	1.75	2.40
FF		10	26	2.29	243	32.8	162	75.0		1.84	5.63	31.8	208	5.29	78.3	264	7.66	2.87		6.13	488	3.96	1570	1.77	8.32	7.55	4.39
FS		10	35	0.68	220	20.7	72.4	17.8		2.65	3.29	24.4	668	3.83	133	116	21.7	86.6		0.03	682	1.88	280	2.84	3.57	2.12	2.62
FR		10	36	3.69	76.0	38.2	164	81.7		12.3	3.35	52.9	161	3.66	143	169	14.6	1.4		0.39	636	0.01	993	4.83	0.21	12.7	3.83
Northern Pike																										
Location	Season	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	Summer	10	57	1.32	618	62.5	54.3	72.3	0.65	2.15	2.38	75.4	112	3.06	230	359	16.6	13.9	2.65	0.46	246	65.9	774	3.51	57.8	5.14	3.71
FM		10	61	1.01	104	31.8	55.1	9.78	0.46	2.20	17.1	69.5	98.2	1.40	176	153	10.7	3.79	0.82	0.45	137	105	83.3	2.04	4.67	3.15	3.28
FC		10	67	2.21	81.92	68.8	20.3	3.55	0.78	0.43	1.41	120	88.1	1.92	195	105	20.0	2.82	0.78	0.53	357	151	76.8	5.00	2.80	4.81	3.03
FS		11	69	1.40	0.22	126	0.22	14.9	0.31	0.49	0.70	22.7	144	1.78	232	111	14.7	2.06	0.66	1.97	370	101	87.7	8.46	3.07	7.31	3.51
FR		11	67	7.22	144	141	16.7	13.6	0.79	2.17	1.07	143.3	291	2.59	175	83.4	16.8	7.16	23.76	0.72	360	247	106	11.0	4.41	2.77	5.42
FMU	Fall	3	72	<0.01	49.8	9.68	67.6	3.26	3.01	0.17	0.82	17.8	103	1.17	266	100	14.6	0.13	2.95	0.44	272	0.61	39.4	1.54	0.69	3.11	3.03
FM		9	68	0.03	143	15.5	23.5	10.5	0.47	0.45	0.92	34.9	145	1.50	400	119	18.0	7.80	1.86	0.44	210	4.00	98.7	1.23	0.15	3.65	2.72
FC		9	78	1.12	275	31.3	9.05	4.65	0.72	5.59	1.39	8.43	151	1.62	302	108	9.60	8.51	20.0	0.81	288	5.09	41.5	1.60	0.30	4.43	3.16
FS		10	70	0.81	413	94.9	40.7	10.8	0.71	0.49	1.13	38.2	97.9	1.41	338	87.5	16.0	1.53	65.3	0.68	375	4.06	121	4.60	2.13	2.60	2.52
FR		10	68	0.44	277	159	0.21	9.27	1.09	1.46	2.41	35.8	181	2.20	247	91.2	11.3	5.00	1.12	1.01	398	0.63	121	7.91	4.81	2.94	3.38
FMU	Spring	8	72	0.23	170	32.6		13.3	0.09	0.34	4.38	344	265	2.54	486	104	34.9	4.68		0.61	280	0.18	175	2.70	0.28	4.39	4.13
FM		4	69	0.15	195	32.0		6.22	0.08	2.09	3.22	178	132	2.00	252	98.6	36.7	0.33		0.28	215	4.04	92	3.26	0.04	2.85	3.76
FC		10	63	0.95	150	42.1	0.25	114		0.20	5.66	13.9	147	2.08	217	382	15.9	0.62		0.03	233	0.01		6.66	165	6.18	3.04
PP		10	70	0.84	208	30.9	40.1	43.9		1.14	2.01	99.0	131	2.92	243	150	7.16	17.2		0.22	285	0.40	201	4.57	0.85	1.04	2.48
FF		9	73	0.32	523	59.5	42.1	27.2		0.26	2.21	62.9	137	2.56	222	147	12.1	5.43		0.44	257	**<0.01**	151	3.76	0.21	11.12	6.13
FS		10	74	1.09	237	130	81.4	90.2		0.86	3.51	9.94	290	1.49	275	182	7.27	12.9		0.61	316	12.6	938	6.64	0.97	1.53	3.70
FR		10	67	0.57	134	120	74.9	88.9		0.01	1.93	39.9	152	1.94	180	223	15.8	8.64		4.26	288	1.28	834	13.2	0.10	3.95	3.93

Table 2.2: Mean concentration of metals in muscle from walleye (WE), whitefish (WF), and burbot (BB) from sampling sites along the Slave, Athabasca, and Peace Rivers. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Walleye

Location	Season	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	Summer	10	52	2.05	71.1	48.2	52.8	18.3	0.36	0.59	1.79	50.8	113	1.92	512	113	13.3	12.3	1.65	0.48	354	40.2	200	3.84	2.34	5.00	2.84
FM		10	45	1.20	10.7	44.9	54.2	12.9	0.84	0.52	2.45	115	144	2.10	262	123	20.7	5.79	0.71	0.26	296	74.4	175	4.51	15.4	4.09	2.98
FC		10	51	1.83	221	59.7	0.22	19	1.19	1.18	2.15	137	347	2.74	195	97.2	20.6	10.8	35.1	0.67	433	165	202	8.37	0.65	6.41	3.36
FS		10	37	1.52	291	56.3	0.21	74.2	0.86	1.87	5.11	186	103	2.75	234	150	35.3	22.7	1.34	0.83	448	69.4	609	10.9	22.3	8.60	2.67
FMU	Fall	3	42	1.15	181	35.7		14.7	0.11	0.04	1.72	0.06	129	1.36	169	153	7.76	2.23	0.30	1.37	302	0.65	595	5.71	0.70	5.57	2.22
FM		10	46	1.23	319	20.6	31.0	1.80	0.69	0.30	2.80	7.41	137	1.78	274	55.4	9.97	1.62	24.4	0.89	293	90.6	50.6	3.76	9.52	2.69	2.25
FC		5	50	1.24	555	30.5		6.41	0.65	0.04	2.04	22.4	107	2.92	122	91.4	12.0	2.80	11.4	0.67	409	61.2	59.0	6.59	1.37	3.10	2.32
FS		10	49	0.20	250	90.4	9.73	109	0.21	0.91	5.58	35.5	226	3.67	505	107	25.0	10.6	7.23	0.77	509	12.4	653	16.5	6.20	5.41	4.58
FR		10	47	0.61	140	55.4	0.20	3.50	0.34	2.82	5.85	30.1	123	1.47	272	56.1	15.4	4.35	1.07	0.56	455	4.21	34.3	15.7	14.4	3.50	2.79
FMU	Spring	7	47	2.30	187	25.9		24.7	0.09	3.11	4.69	609	196	4.55	308	125	806	20.8		0.66	325	4.91	495	5.38	0.12	6.05	3.86
FM		10	44	2.03	373	31.5		6.71	0.08	1.63	3.08	432	196	3.60	312	95.4	57.38	7.05		0.64	323	3.95	84.0	10.7	1.41	5.30	3.75
FC		8	49	0.54	114	32.6	4.05	27.9		1.23	2.71	24.0	327	2.70	232	120	7.83	18.4		0.31	321	0.01	641	10.6	306	3.13	3.21
PP		9	53	1.22	73.3	24.0	66.9	9.45		3.36	1.60	107	361	2.86	260	79.4	354	33.3		0.43	384	13.9	38.4	6.56	7.99	3.71	2.72
FF		10	56	0.98	295	32.5	82.5	11.7		1.08	1.40	5.86	139	1.60	244	117	30.4	33.0		0.07	376	0.01	92.1	6.29	4.33	1.23	2.80
FS		10	56	0.75	264	95.7	23.4	7.25		0.49	1.60	52.7	168	3.89	284	79.4	13.3	2.43		1.08	336	0.01	37.1	19.26	2.39	2.70	2.65
FR		9	47	2.13	258	67.8	55.2	16.8		3.44	1.73	28.4	199	3.47	223	103	13.1	3.67		1.12	370	38.9	103	18.84	0.07	3.98	3.24

Whitefish

Location	Season	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FM	Summer	10	42	1.28	261	72.2	26.6	0.92	0.63	2.55	13.9	208	155	8.94	46.1	185	44.0	6.52	0.99	0.72	460	109.4	130	1.8	3.95	6.01	3.09
FC		10	41	0.92	55.1	118	0.28	62.8	0.77	0.99	6.95	52.0	142	2.24	36.1	139	18.1	6.52	1.68	0.86	337	0.75	452	2.59	1.19	10.5	3.38
FS		7	41	1.31	74.9	132	0.21	40.2	0.45	0.64	3.86	70.0	117	2.40	37.9	151	26.1	4.06	2.46	9.14	400	74.0	481	4.47	30.3	11.2	2.57
FR		10	39	7.31	162	89.4	0.22	57.5	0.12	0.4	4.21	147.1	157	1.75	42.5	144	16.8	11.92	3.08	0.17	457	381.9	814	3.64	1.3	5.58	2.79
FMU	Fall	9	42	0.30	78.8	12.6	23.6	6.22	0.55	0.89	5.59	17.6	235	3.00	101.6	144	16.9	2.67	15.2	0.54	305	2.04	124	1.37	1.82	5.85	2.36
FM		10	40	1.22	132	29.6		0.47	0.67	0.26	3.09	3.88	145	1.81	31.5	143	8.42	4.08	49.2	0.57	308	17.8	49.9	1.07	1.96	2.39	2.06
FC		10	39	0.42	153	37.3	29.8	10.2	1.35	1.13	4.48	75.1	131	1.76	49.2	191	12.8	2.41	0.24	0.66	333	0.7	509	0.57	0.68	7.22	2.62
FS		10	41	0.91	61.8	107	0.21	16.7	0.73	0.93	9.88	20.3	121	1.98	49.5	122	18.4	6.48	8.93	0.96	440	54.4	354	3.72	0.82	5.94	2.35
FR		10	44	0.28	297	230	53.6	93.2	0.62	2.74	2.03	63.1	115	2.93	106	176	31.2	6.5	1.11	0.92	478	53.3	842	3.78	4.53	13.6	2.48
FMU	Spring	4	42	0.01	243	39.1		4.01	0.10	0.01	12.4	340	140	2.56	85.8	158	40.9	4.58		0.36	234	0.01	239	1.54	2.19	7.77	3.35
FM		2	38	2.11	143	17.8		3.81	0.10	1.06	14.0	202	147	2.52	63.5	167	19.7	0.37		0.26	308	3.83	323	1.47	0.08	5.2	5.55
FC		10	43	0.23	371	72.2	38.4	28.5		0.01	12.9	76.1	165	2.17	47.8	209	6.87	30.3		4.26	249	0.01	99.3	3.45	298	6.26	2.83
FF		8	45	0.61	348	58.2	69.9	42.2		0.01	14.2	52.8	190	3.96	84.5	203	12.2	7.14		0.29	278	0.16	332	3.22	0.14	5.32	3.42
FS		5	41	1.02	24.1	71.1	38.3	45.8		1.13	5.19	16.2	128	1.50	49.3	167	8.44	10.7		0.35	348	0.01	512	5.01	399	13.2	2.43
FR		10	40	2.98	79.4	108	107	39.6		7.41	5.38	32.9	150	3.00	50.2	142	7.24	2.07		1.47	309	10.0	417	3.19	0.73	7.9	2.54

Burbot

Location	Season	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	Summer	3	41	1.85	6.32	99.7	27.4	33.7	0.26	2.41	3.37	189	184	2.61	112	140	35.9	10.3	0.47	0.74	384	71.7	470	1.84	0.08	9.65	4.88
FC		1	56	1.89	77.5	61.6	0.18	2.95	0.09	0.04	3.73	0.05	159	0.84	61.6	140	0.06	9.06	1.02	0.44	483	732.2	110	3.28	1.04	0.77	3.40
FS		3	48	2.32	93.8	221	26.7	2660	0.24	2.84	13.9	130	185	4.12	149	473	32.4	39.3	3.10	1.09	322	140.8	6450	2.23	1.86	20.4	5.31
FR		10	62	1.03	60.8	188	42.0	139	0.24	0.40	1.78	78.7	127	1.71	112	169	14.1	3.21	1.10	0.17	290	86.7	484	3.17	0.06	4.97	3.15
FM	Fall	2	55	2.16	177.6	51.1		9.18	0.10	1.76	2.76	2.45	137	2.51	127	155	7.66	0.93	15.4	0.33	272	0.58	131	0.01	0.29	3.77	3.16
FC		3	58	0.16	78.1	43.5		13.5	0.09	0.74	3.07	16.7	120	2.42	56.2	161	9.86	5.31	272	1.51	358	107.8	107	0.93	1.09	2.65	2.50
FS		3	61	**<0.01**	305	141		220	0.92	19.4	3.52	0.05	99	2.64	154	218	7.83	7.12	17.4	1.11	412	32.7	1473	0.99	0.67	3.07	2.84
FR		8	62	0.73	659	111	45.3	25.6	0.47	2.17	35.1	47.8	142	2.98	185	215	19.3	11.4	14.2	1.16	378	49.8	178	1.63	0.79	7.10	2.97
FR	Winter	10	64	2.62	423	151	0.17	13.3	0.09	0.96	0.83	19.8	127	1.63	158	115	13.7	1.80	1.91	0.67	301	43.2	75.2	3.51	1.00	3.35	3.17
FMU	Spring	3	39	0.98	258	92.5		238	0.06	1.03	8.32	151	290	4.50	109	421	29.0	0.31		0.36		0.01	1720	2.39		8.31	5.96
FS		1	74	0.01	0.87	90.8		7.04		0.01	2.93	0.02	176	2.37	368	358	1.97	0.35		1.07	439	0.01	57.11	1.58		5.14	3.80
FR		6	63	0.27	0.36	132	158.4	51.5		1.12	2.85	109	145	3.30	104	188	13.6	1.92		0.64	281	4.8	67.82	2.33	1.84	3.77	3.35

subsistence fish consumers given the greater number of exceedances of the Hg subsistence advice.

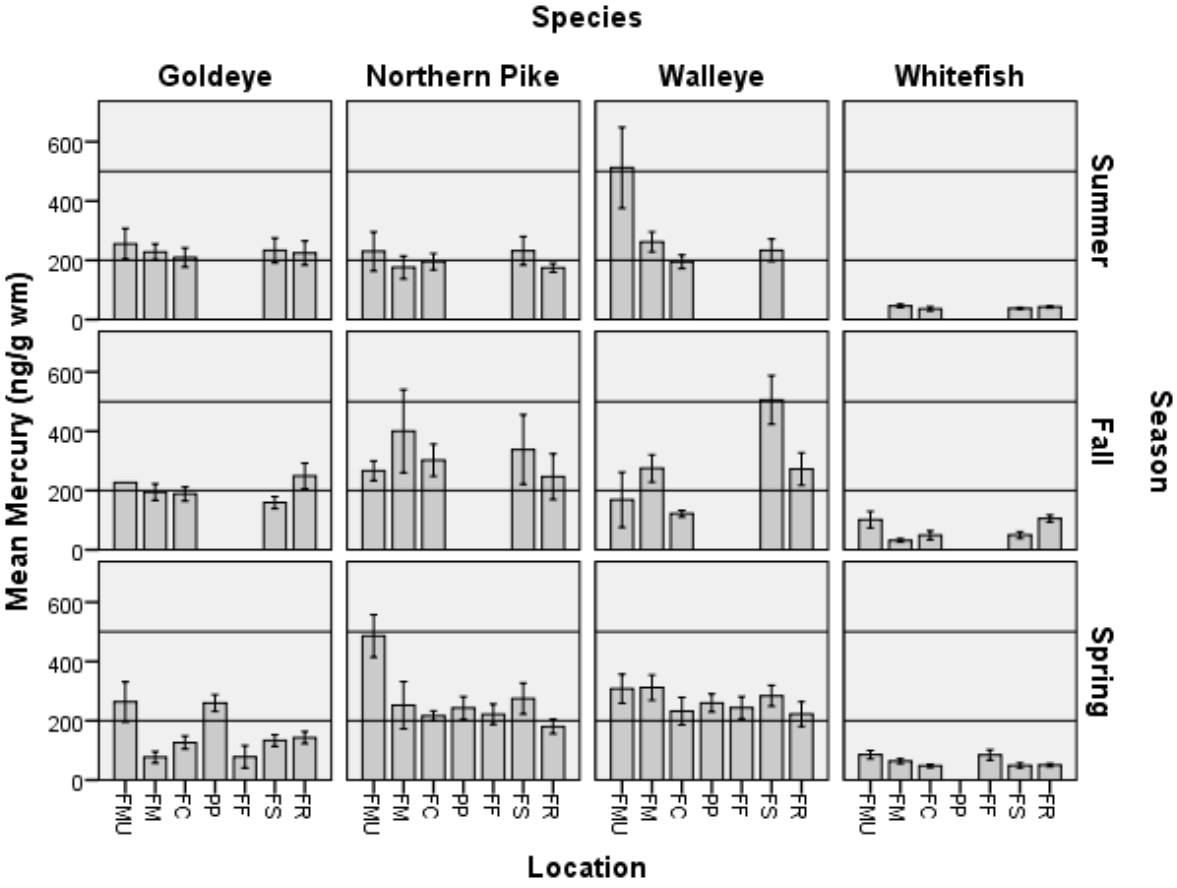

Figure 2.2: Mean concentrations of mercury in fish muscle tissue from sampling sites along the Slave and Athabasca Rivers. The error bars represent one standard error. Graphs are separated by species (top) and season (right side). The horizontal lines on the graphs represent the Health Canada guidelines with the upper line representing the general guideline and lower representing the subsistence advice.

2.4.2 Arsenic

Concentrations of As were greater in northern pike in the lower Slave River (FR and FS) compared to the upper Slave River (FF) and Athabasca River (FMU, FM, and FC) (Figure 2.3, Table 2.3). This trend was consistent for northern pike across summer, fall, and spring samplings. Concentrations of As in whitefish followed a similar trend to northern pike, though it was not as significant. The trend in whitefish was most pronounced for the sampling in the fall with concentrations of As being significantly different between the upper Slave River and

Athabasca Rivers. Concentrations of As in whitefish collected during the spring sampling from the lower Slave River sites, were not significantly different from those in the upper Slave River and Fort Chipewyan sites, but were significantly different from the sites on the Athabasca River. Goldeye and walleye did not exhibit the same pattern as northern pike and whitefish. As concentrations were significantly less in goldeye than in northern pike, walleye, and whitefish.

Arsenic in fishes, exists primarily in organic forms, and contrary to some other organometals, As does not appear to biomagnify (United States Environmental Protection Agency 2003; Williams et al. 2006). Inorganic As is the primary concern for human health. One possible explanation for greater concentrations of As in the lower Slave River is industrial activity on the Great Slave Lake, in particular gold mining. Gold was discovered on the northern shore during the 1930s which lead to the development of two major gold mines, Giant Mine (1948-2004) and Con Mine (1938-2003) (MRBB, 2003). Arsenic is commonly found in significant concentrations in gold deposits, therefore, mobilization of As is a concern with gold mining activities (Straskraba and Moran, 1990). Arsenic concentrations in locations on Great Slave Lake were less than those in the Giant Mine effluent receiving waters with As concentrations of 190 ng/g wm compared to 490 ng/g wm (Cott et al., 2016). Whitefish As concentrations in Fort Resolution increased to 230 ng/g wm in the fall compared to 89.4 ng/g wm and 108 ng/g wm in summer and fall respectively. Fish species such as whitefish are known to migrate upstream during the fall and could be a source of movement of As upstream into the Slave River (Morrow, 1980).

Mean concentrations of As, calculated for each location during each season, in northern pike ranged from 9.68-126 ng/g wm and those in whitefish ranged from 12.6-230 ng/g wm. These concentrations are similar or less than values found in some other studies. Another study investigated trace metals in David Lake, Delta Lake, and Unknown Lake in northern Saskatchewan for possible contamination from the Key Lake uranium facility (Kelly, 2007). David Lake was the reference lake, Delta Lake was the low exposure lake, and Unknown Lake was the high exposure lake. The study analyzed muscle of juvenile, northern pike for trace metals. Mean concentrations of As in juvenile northern pike were 26.6 ng/g wm in David Lake, 154 ng/g dm in Delta Lake, and 856 ng/g wm in Unknown Lake. Concentrations of As in whitefish collected from two northern Saskatchewan lakes, Montreal and Reindeer Lake, were

380, 40, and 36 ng/g dm in Montreal Lake and 728, 273, and 104 ng/g wm in Reindeer Lake, during the fall of 2008 and summer and fall of 2009, respectively (Hursky and Pietrock, 2012).

The Health Canada guideline for As in fish protein is 3.5 ppm (µg/g) (Health Canada, 2018). The guideline is for the edible form of the fish which can be both dry and wet mass. Hazards posed by observed concentrations of As measured in fishes during this study were di minimis for human health, as the determined mean concentrations in all fish was less than 0.25µg/g wm.

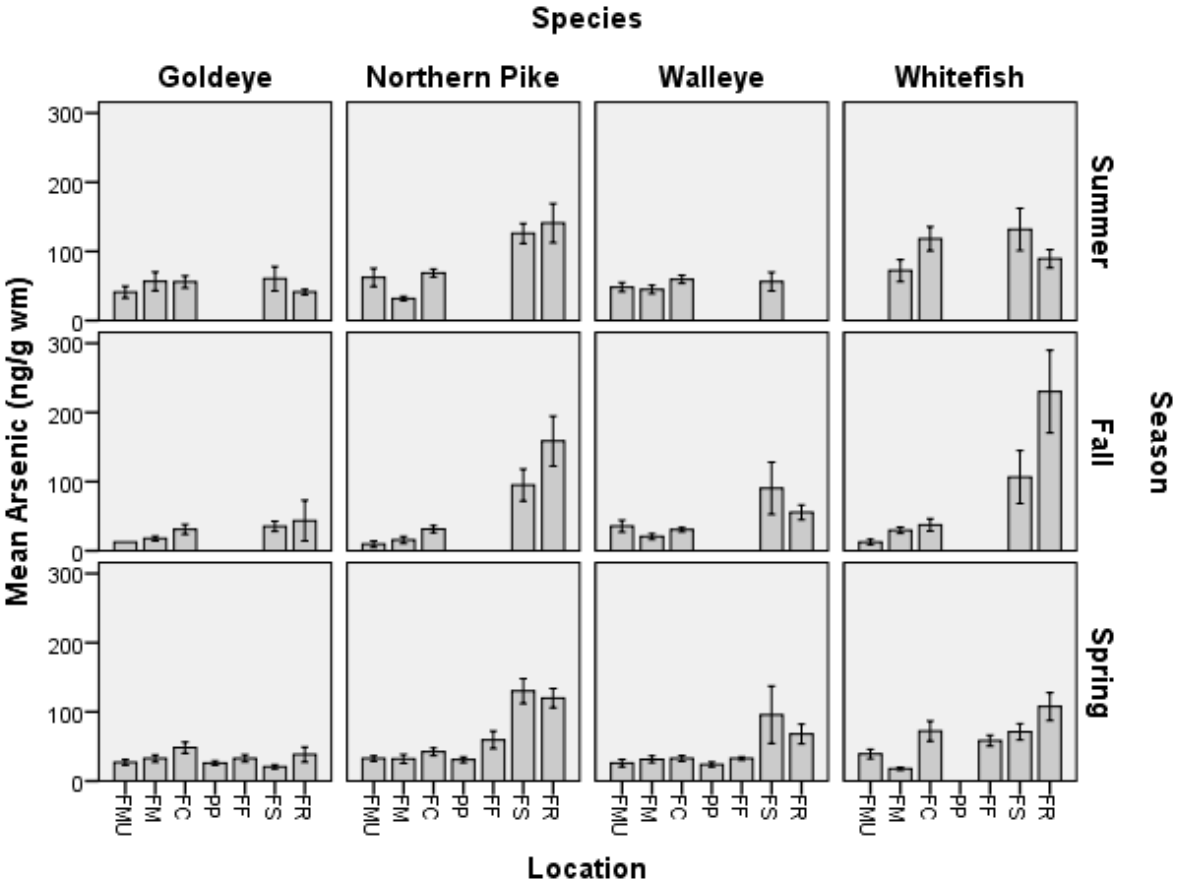

Figure 2.3: Mean concentrations of arsenic in fish muscle tissue from sampling sites along the Slave and Athabasca Rivers. The error bars represent one standard error. Graphs are separated by species (top) and season (right side).

Table 2.3: Mean concentration of arsenic in fish muscle tissue from sampling sites along the Slave, Athabasca, and Peace Rivers. Locations sharing a letter show no statistically significant difference ($p>0.05$) in mean arsenic concentrations. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), and whitefish (WF).

Summer 2011					
Species	Mean Arsenic Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	41.1	56.6	55.8	60.4	41.2
NP	62.5 B	31.8 A	68.8 B	126 C	140 C
WE	48.2	44.9	59.7	56.3	
WF		72.2 A	118 B	132 AB	89.4 AB
Fall 2011					
Species	Mean Arsenic Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	12.4	17.8	30.8	35.4	43.6
NP	9.68 A	15.5 A	31.3 A	94.9 B	159 B
WE	35.7	20.6	30.5	90.4	55.4
WF	12.6 A	29.6 B	37.3 B	107 C	230 C

Spring 2012							
Species	Mean Arsenic Concentration by Location (ng/g wm)						
	FMU	FM	FC	PP	FF	FS	FR
GE	27	32.7	48.2	26	32.8	20.7	38.2
NP	32.6 A	32.0 A	42.1 A	30.9 A	59.5 A	130 B	120 B
WE	25.9 A	31.5 A	32.6 A	24.0 A	32.5 A	95.7 B	67.8 B
WF	39.1 AB	17.8 A	72.2 AB		58.2 AB	71.1 AB	108 B

2.4.3 Vanadium

Concentrations of V exhibited trends that were similar to those observed for As, with concentrations in goldeye greater in the lower Slave River (Figure 2.4, Table 2.4). Concentrations of V in northern pike and walleye were not significantly different among locations. Concentrations of V were greater in whitefish in the lower Slave River, but only in fall when concentrations at Fort Resolution were greater than those in whitefish from locations on the Athabasca. Due to its association with oil sands operations in Alberta, V was of particular interest in this study. Appreciable concentrations of V can be found in petroleum coke fly ash (Gomez-Bueno et al., 1981).

Mean concentrations of V, calculated for each location during each season, in northern pike and whitefish collected during this study ranged from 1.04-11.12 ng/g wm and 2.39-13.6 ng/g wm, respectively. These concentrations are comparable or potentially less than concentrations reported previously. Walleye, northern pike, whitefish, and burbot collected during a 1992 and 1993 sampling from sites near Fort Resolution found V concentrations in all muscle samples less than their detection limit of 100 ng/g wm (Lafontaine, 1997; Sanderson et al., 1997). The detection limit of 100 ng/g wm is considerably greater than the measured concentrations from the 2011 and 2012 fish muscle samples. Vanadium concentrations in fish muscle from this study were also less than V concentrations from other northern locations. Mean concentrations of V in juvenile northern pike from David Lake were 22.4 ng/g wm, while those in Delta Lake were 26.4 ng/g wm and 21.4 ng/g wm in Unknown Lake (Kelly 2007). Concentrations of V in fishes from lakes in northern Saskatchewan in the fall of 2008 and summer and fall of 2009 were 18, 14, and 15 ng/g wm in fishes collected from Montreal Lake and 16, 13, and 14 ng/g wm in fishes collected from Reindeer Lake (Hursky and Pietrock, 2012).

There is no guideline for safe concentrations of V in edible muscle of fishes consumed by humans. There is a Health Canada guideline for tolerable upper intake levels (UL) for V, which is 1.8 mg/day (Health Canada, 2010). The UL is defined as: greatest mean daily intake that is likely to pose no risk of adverse effects to almost all individuals of a specified life-stage and gender (Health Canada, 2010). The greatest mean concentration of V was found in whitefish collected from near Fort Resolution during the fall. To exceed the UL, an adult would need to consume more than 132 kg/day of whitefish muscle from this location. The typical portion of fish muscle for an adult is 150 g (Health Canada, 2007). Concentrations of V in fishes collected during this study pose di minimis risk to human consumers.

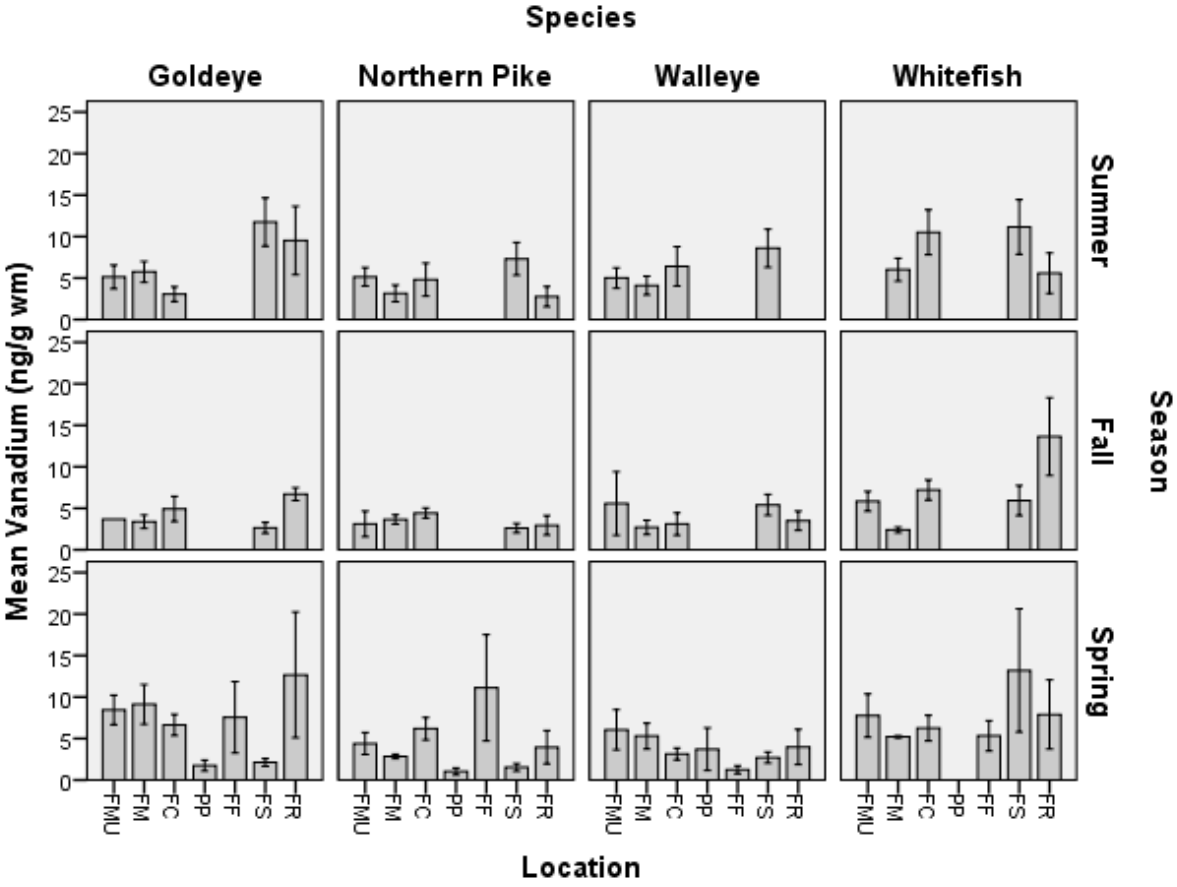

Figure 2.4: Mean concentrations of vanadium in fish muscle tissue from sampling sites along the Slave and Athabasca Rivers. The error bars represent one standard error. Graphs are separated by species (top) and season (right side).

Table 2.4: Mean concentration of vanadium in fish muscle tissue from sampling sites along the Slave, Athabasca, and Peace Rivers. Locations sharing a letter show no statistically significant difference ($p>0.05$) in mean vanadium concentrations. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), and whitefish (WF).

Summer 2011					
Species	Mean Vanadium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	5.13	5.75	3.06	11.7	9.52
NP	5.14	3.15	4.81	7.31	2.77
WE	5.00	4.09	6.41	8.60	
WF		6.01	10.5	11.2	5.58

Fall 2011					
Species	Mean Vanadium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	3.67 AB	3.39 A	4.94 AB	2.64 A	6.71 AB
NP	3.11 AB	3.65 AB	4.43 B	2.6 B	2.94 B
WE	5.57	2.69	3.1	5.41	3.5
WF	5.85 AB	2.39 A	7.22 B	5.94 AB	13.63 B

Spring 2012							
Species	Mean Vanadium Concentration by Location (ng/g wm)						
	FMU	FM	FC	PP	FF	FS	FR
GE	8.46 C	9.12 C	6.65 C	1.75 A	7.55 ABC	2.12 AB	12.7 BC
NP	4.39 AB	2.85 AB	6.18 B	1.04 A	11.1 AB	1.53 A	3.95 AB
WE	6.05	5.3	3.13	3.71	1.23	2.7	3.98
WF	7.77	5.2	6.26		5.32	13.2	7.9

2.4.4 Selenium

Concentrations of Se were greater in goldeye, northern pike, walleye, and whitefish collected from the lower Slave River during fall compared to these species collected from the upper Slave River and Athabasca River (Figure 2.5, Table 2.5). This gradient in concentrations of Se was observed only in fall. It is not apparent why the Se concentration were greater in the lower Slave River relative to the upper Slave River, Peace River, and Athabasca River sites only during the fall sampling. Concentrations of Se were significantly greater in goldeye, relative to those in other species, with mean concentrations of 614 ng/g wm, while concentrations in other species ranged from 292-375ng/g wm. Concentrations of Se in northern pike were also significantly less than Se concentrations in goldeye and walleye.

Mean concentrations of Se, calculated for each location during each season, in muscle of northern pike collected during the study, results of which are reported here, ranged from 137-398 ng/g wm, while those in whitefish ranged from 234-478 ng/g wm. A study investigating metals in the Athabasca River, Lake Athabasca, and the Slave River before merging with the Peace River found similar mean Se concentrations in fish muscle tissue with mean Se concentrations ranging from150-420 ng/g in northern pike and 350-410 ng/g wm in whitefish (Lutz and Hendzel, 1976). These ranges of concentrations of Se are similar to those reported previously for fishes from locations with limited industrial impact but considerably less than those in fishes from lakes near the uranium mine at Key Lake, Saskatchewan. Mean concentrations of Se in juvenile northern pike from David Lake were 136 ng/g wm while those in muscle of fishes from in the David Lake and Unknown Lake were 3380 ng/g wm and 4580 ng/g wm, respectively (Kelly 2007). During fall of 2008, summer and fall of 2009, concentrations of Se in whitefish from northern Saskatchewan lakes were 132, 156, and 154 µg/g wm in Montreal Lake and 302, 408, and 320 ng/g wm in Reindeer Lake, respectively (Hursky and Pietrock, 2012).

There is no guideline for safe concentrations of Se in fish muscle consumed by humans. There is a Health Canada guideline for tolerable upper intake levels for Se of 400 µg/day for adults, 150-280 µg/day for children aged 5-11 years, and a range of 90-150 µg/day for children aged 1-4 years (Health Canada, 2010). The greatest mean concentration of Se in muscle of fishes from any location was 844 ng/g wm in goldeye collected from Fort Smith during fall of 2011. An adult consumer would need to consume more than 474 g/day of goldeye muscle tissue from this location to exceed the UL. Children aged 5-11 years would need to consume 178-333 g of goldeye muscle from Fort Smith in fall to exceed the UL. Children aged 1-4 would need to consume 107-178 g/day of goldeye muscle from Fort Smith to exceed the UL. Health Canada recommends 40 g/day for adults, 33 g/day for 5-11 year old children and 20 g/day for 1-4 year old children as representative rates of consumption for subsistence consumers of fish (Health Canada, 2007). Concentrations of Se would be di minimis for healthy human consumers.

Selenium can be a concern for the health of aquatic life including fish and dietary intake can be an important route of exposure (Lemly and Smith, 1987). Due to these concerns, the US EPA has set Se guidelines for protection of aquatic life in fish muscle at 11.3 µg/g dm (USEPA, 2016). The guideline when converted to wm using an average moisture content of 80% would be

2.26 µg/g wm. The greatest mean Se concentration in muscle tissue from this study was 844 ng/g wm which is below the US EPA guideline, therefore, these Se concentrations are unlikely to negatively impact aquatic life.

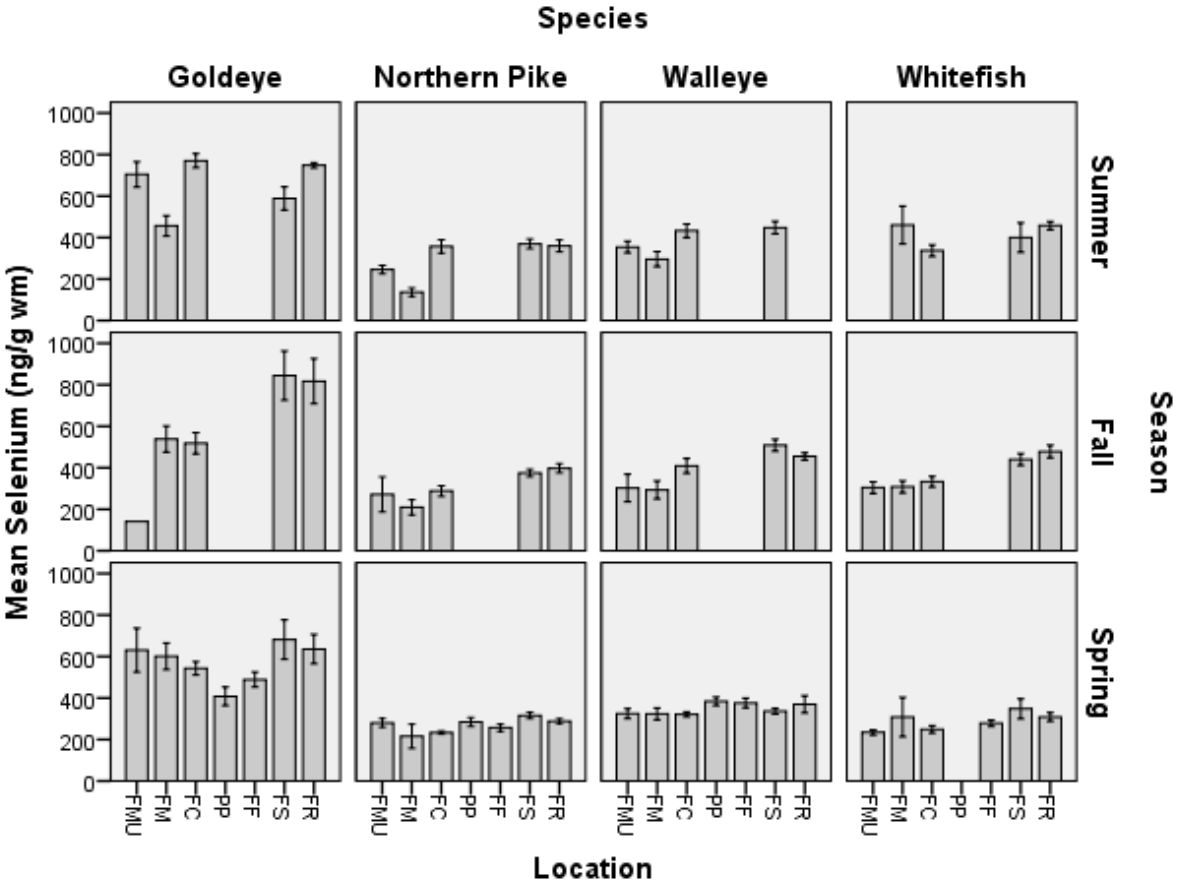

Figure 2.5: Mean concentrations of selenium in fish muscle tissue from sampling sites along the Slave and Athabasca Rivers. The error bars represent one standard error. Graphs are separated by species (top) and season (right side).

Table 2.5: Mean concentration of selenium in fish muscle tissue from sampling sites along the Slave, Athabasca, and Peace Rivers. Locations sharing a letter show no statistically significant difference ($p>0.05$) in mean selenium concentrations. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), and whitefish (WF).

Summer 2011					
Species	Mean Selenium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	704 B	457 A	770 B	588 AB	748 B
NP	246 B	137 A	357 C	370 C	360 C
WE	354 AB	296 A	433 AB	448 B	
WF		460 AB	337 A	400 AB	458 B
Fall 2011					
Species	Mean Selenium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	142 A	538 AB	518 A	844 B	818 AB
NP	271 ABC	210 A	288 AB	375 BC	398 C
WE	302 A	293 A	409 AB	508 B	455 B
WF	305 A	308 A	332 A	440 B	478 B

Spring 2012							
Species	Mean Selenium Concentration by Location (ng/g wm)						
	FMU	FM	FC	PP	FF	FS	FR
GE	630.6	600.7	542.5	408.2	488.5	682.0	635.8
NP	280 AB	215 AB	233 A	285 B	257 AB	316 B	288 AB
WE	324.8	323.5	321.2	383.9	376.0	336.1	369.9
WF	234.1	308.0	249.1		278.0	348.4	308.8

2.4.5 Thallium

There appears to be a strong spatial distribution of Tl along the Slave and Athabasca Rivers. Concentrations of Tl were greater at the lower Slave River sites than in the upstream Slave River and Athabasca sites (Figure 2.6, Table 2.6). The trend was most significant for higher trophic level species, such as northern pike and walleye, but was still observable for lower trophic species, goldeye and whitefish. This spatial trend in concentrations was observed during each sampling period though not for all species. Goldeye did not show statistically significant location associated variability during the summer sampling but did for the fall and spring samplings. Mean Tl concentrations were greater in upper trophic level species, northern pike and walleye, with mean Tl concentrations in northern pike and walleye ranging from 1.23-13.2 ng/g

wm and 3.76-18.8 ng/g wm respectively. Mean Tl concentrations in muscle from the lower trophic species, goldeye and whitefish, were 0.01-4.83 ng/g wm and 0.57-5.01 ng/g wm respectively.

There is no specific Canadian guideline for protection of health of humans established for ingestion of Tl in fish tissue. The CCME guideline for Tl in sediment is based on a reference dose (RfD) of 0.07 µg/kg per day that has been set by the US EPA (Canadian Council for Ministers of the Environment, 1999). This reference dose was based on a no observed adverse effect level (NOAEL) of 0.2 mg/kg, body mass per day determined from results of a study in which rats were fed Tl in the diet and to which a safety factor of 3000 was applied (Stoltz et al., 1986). The US EPA has since removed this RfD due to uncertainties with the study, upon which it was based (United States Environmental Protection Agency, 2009). To exceed this RfD to stay consistent with CCME and the greatest mean concentration of Tl observed during this study, a consumer would need to eat in excess of 254g wm of walleye muscle per day.

Differences in concentrations of Tl in water at each location could explain differences in concentrations observed in muscle of fishes. While samples of water were not collected during this assessment of fish, there were other monitoring operations ongoing in these regions. Government of the Northwest Territories have an ongoing water quality monitoring program which collects samples at Fort Smith, Fort Resolution, and the Great Slave Lake and Environment Canada collects water samples at Fort Fitzgerald. The Regional Aquatics Monitoring Program monitors water quality parameters along the Athabasca River. One observation of this data was that there are a considerable number of samples for which concentrations of Tl were less than the limit of quantification (LOQ). At some locations, as much as 40.4% of samples were less than the LOQ for Tl. At some locations, as much as 72.7% concentrations of Tl in sediments were less than the LOQ. Proportions of concentrations that were less than the LOQ and differences in those detection limits between monitoring programs make it difficult to compare between locations. Fort McMurray, Fort MacKay, and Fort Fitzgerald had similar mean total Tl concentrations in water of 0.05-0.068 µg/L. The mean concentration of total Tl in water at Fort Smith was at 0.19µg/L. It is possible that this could explain differences in concentrations of Tl observed in fishes, but there were only five measurements at Fort Smith. Conclusions based on such a small sample size might be biased.

Also, two of the concentrations of Tl in water from Fort Smith were less than the LOQ. This result is similar to the 40.2% non-detects in water samples from other locations. The collection of more monitoring data at Fort Smith could improve the understanding of Tl concentrations in the water.

Although, thallium was found in snowpack at greater concentrations near oil sands operations compared to far field samples, Tl was not found at greater concentrations in fish from sites in closer proximity to oil sands operations (Kelly et al., 2010). It is unclear why concentrations of Tl were greater in fishes from the lower Slave River compared to those in fishes of the upper Slave River and Athabasca River. It is possible that differences in oxidation state or other speciation phenomena could affect bioavailability in the upper Slave River which could result in differential accumulation efficiencies between the upper and lower stretches of the Slave River. Thallium has two oxidation states, Tl^{1+} and Tl^{3+}. Tl^{1+} has limited ability to form organic complexes in aquatic environments (O'shea, 1972). This lack of complex formation leads to greater bioavailability of Tl^{1+}. Tl^{3+} readily forms complexes in the aquatic environment which can lead to a reduction in bioavailability (Ralph and Twiss, 2002). It is possible that Tl^{1+} is the predominant species of Tl in the lower Slave River leading to greater uptake of Tl in fish.

Greater concentrations of TL in fishes of higher trophic levels, such as, walleye and northern pike, are also of interest. Greater concentrations in higher trophic level species suggest there is potential for trophic magnification of Tl. If Tl is biomagnifiying, it could be evidence of an organic form of Tl being the dominant species of Tl being incorporated into these fishes. The most likely organic form of Tl would be dimethyl thallium (DMT). It has been shown in laboratory experiments that benthic organisms in freshwater sediments are able to biomethylate inorganic Tl to DMT (Schedlbauer and Heumann, 2000).

Walleye and northern pike have a smaller home range than do the other species studied. This might indicate that the source or cause of the increased Tl concentrations is in the lower Slave River. This source of Tl could be due to natural differences in geology of the lower Slave River compared to the upper Slave River and Athabasca River. Another possibility is industrial activities in regions surrounding the lower Slave River and Great Slave Lake. There is a former lead-zinc mine at Pine Point on the southern side of Great Slave Lake. There are also two gold mines on the northern shore which add to the industrial footprint on the Great Slave Lake. The

presence of mining industries could lead to increased Tl concentrations due to potential liberation of Tl as the land is disturbed. The presence of mines in the region could indicate a greater likelihood for increased background concentrations due to baseline geology.

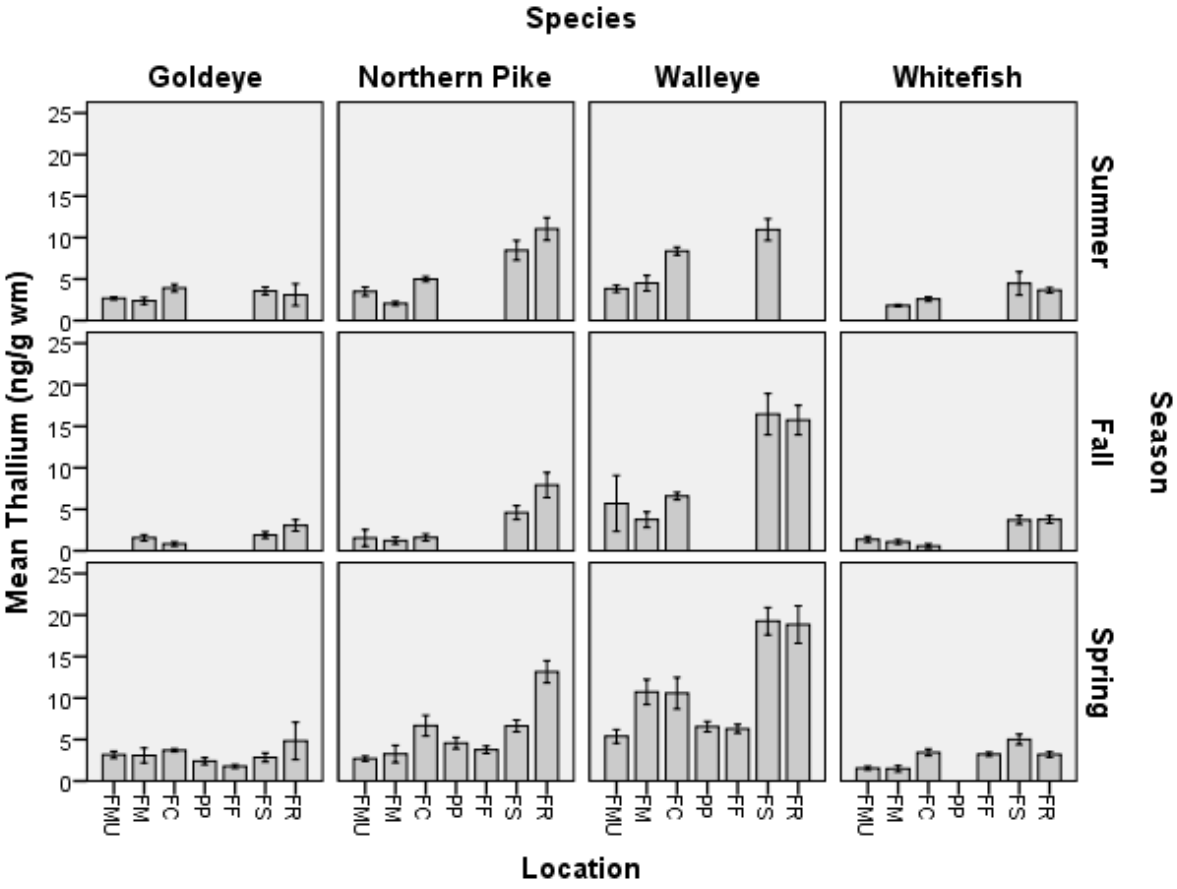

Figure 2.6: Mean concentrations of thallium in fish muscle tissue from sampling sites along the Slave and Athabasca Rivers. The error bars represent one standard error. Graphs are separated by species (top) and season (right side).

Table 2.6: Mean concentration of thallium in fish muscle tissue from sampling sites along the Slave, Athabasca, and Peace Rivers. Locations sharing a letter show no statistically significant difference ($p>0.05$) in mean thallium concentrations. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), and whitefish (WF).

Summer 2011					
Species	Mean Thallium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	2.67	2.37	3.93	3.58	3.1
NP	3.51 A	2.04 A	5.00 B	8.46 C	11.03 C
WE	3.84 A	4.51 A	8.37 B	10.9 B	
WF		1.8 A	2.59 B	4.47 B	3.64 B
Fall 2011					
Species	Mean Thallium Concentration by Location (ng/g wm)				
	FMU	FM	FC	FS	FR
GE	0.01 A	1.56 AB	0.82 A	1.9 AB	3.06 AB
NP	1.54 A	1.23 A	1.6 A	4.60 B	7.91 AB
WE	5.71 A	3.76 A	6.59 A	16.5 B	15.7 B
WF	1.37 A	1.07 A	0.57 A	3.72 B	3.78 B

Spring 2012							
Species	Mean Thallium Concentration by Location (ng/g wm)						
	FMU	FM	FC	PP	FF	FS	FR
GE	3.17 AB	3.08 AB	3.7 B	2.41 AB	1.77 A	2.84 AB	4.83 AB
NP	2.7 A	3.26 A	6.66 B	4.57 AB	3.76 A	6.64 B	13.2 C
WE	5.38 A	10.7 C	10.6 BC	6.56 ABC	6.29 AB	19.3 D	18.8 D
WF	1.54 A	1.47 A	3.45 B		3.22 B	5.01 B	3.19 B

Concentrations of Tl in fish measured during this study were generally less than those in fish from other regions. Lake Trout from Lake Michigan had mean concentrations of 141 ng /g wm (Lin et al., 2001). In another study which investigated trace metals in David Lake, Delta Lake, and Unknown Lake in northern Saskatchewan for possible contamination from the Key Lake uranium facility, concentrations of Tl were 6.5, 26.2 and 32.4 ng/g wm, respectively (Kelly, 2007). In the current study the greatest concentration of Tl observed in northern pike from the Slave River was 13.2 ng/g wm, greater than in the Saskatchewan reference lake but less than lakes nearer the Key Lake uranium facility.

There is evidence of industry related deposition of metals in the Athabasca region (Kelly et al., 2010, Kirk et al., 2014), but it does not appear that this deposition is leading to increased

metal concentrations in fish muscle tissue to levels of concern or greater than downstream locations. While concentrations of Tl in tissues of fishes would not be toxic to the fishes or consumers, including humans, this phenomenon offers an opportunity to further investigate the environmental chemodynamics of this poorly understood element.

2.5 Conclusions

Concentrations of metals in fishes from the Slave, Athabasca, and Peace Rivers were relatively consistent and less than those in fishes from other regions. Only four metals (As, Se, V, Tl) showed location related variations in concentration and one metal (Hg) was found at concentrations that may approach human consumption guidelines. However, it is of note that there are significant seasonal differences in the concentrations of metals in fish muscle. These observations might be due to migration and reproductive patterns of fishes as well as to seasonal alterations in metal inputs. The mercury concentrations in the sampled fish are not a novel development and have been investigated previously and should continue to be monitored given the concentrations approach and on occasion exceed levels of concern. Regarding the other metals analyzed, while not currently at concentrations of concern for human consumers, the increased concentration of some metals in the lower Slave River warrant continued vigilance in the face of ever-increasing upstream development.

Acknowledgments

The authors would like to thank the First Nations and Métis communities of Fort Resolution, Fort Smith, Fort Chipewyan, Fort Mackay, and Fort McMurray and the Territorial, Provincial, and Federal governments for the assistance during sample collection and processing which made this work possible. The authors would also like to thank the members of the Slave River and Delta Partnership (SRDP) who were instrumental in the coordination and completion of the sampling in the Slave River and delta. Prof. Giesy was supported by the Canada Research Chair program, the 2012 "High Level Foreign Experts" (#GDT20143200016) program, funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences and a Distinguished Visiting Professorship in the School of Biological Sciences of the University of Hong Kong.

CHAPTER 3: MERCURY SPECIATION BY AUTOMATED DERIVATIZATION AND HEADSPACE SPME EXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY ORBITRAP MASS SPECTROMETRY

3.0 Preface

The analysis from Chapter 2 found five metals to have results worth investigating further. Four of the metals (Tl, As, Se, and V) had spatial trends of interest with greater concentrations in fish during certain sampling seasons in the Slave River relative to the Athabasca River. The fifth metal, Hg, did not have spatial trends of note but it was found at concentrations of concern. The concentrations of Hg in fish were approaching the Health Canada guideline for consumption. This chapter will focus on improving upon Hg speciation methods through use of high-resolution mass-spectrometry and modern autosampler technologies.

This Chapter will be submitted to Environmental Toxicology and Chemistry under joint authorship with John P. Giesy, and Paul D. Jones. Figures, tables, and references have been formatted to adhere to the thesis style. References for this chapter have been compiled and listed in the reference section for the thesis.

- Brett Tendler participated in collection of all the fish samples, developed the analytical method, prepared the fish tissue for mercury speciation analysis, performed data analysis, and wrote the manuscript.
- John P. Giesy provided the analytical instrument and research space and reviewed the manuscript.
- Paul D. Jones provided funding, the analytical instrument, and research space to conduct the research, developed the analytical method, participated in the collection of all the fish samples, assisted with the data analysis, and reviewed the manuscript.

3.1 Abstract

Mercury concentrations in fish can be of significant concern for human consumers with methylmercury causing the greatest concern. There are two species of Hg that are found in fish, methylmercury and inorganic Hg. Determining the concentrations of each Hg species is an important factor in determining potential risk posed by Hg in fish. A method for Hg speciation using sodium tetratethylborate derivatization followed by Headspace (HS) Solid-phase Microextraction (SPME), Gas Chromatography and Orbitrap Mass Spectrometry (GC-Orbitrap MS) analysis was developed. The use of the GC Orbitrap MS allows for quantification of the different Hg species, and for the complete Hg isotope profile. The isotopes and their patterns can be used to identify and confirm analytes of interest. The observed mercury isotope patterns from these analyses had near perfect alignment with the theoretical isotope patterns based on the known natural abundance of Hg isotopes. The ability to detect the stable isotopes opens up the possibility of comparing stable isotope profiles between samples with further optimization of the method. In addition, identification and quantification of other metal species is possible with this method as tetraethyl lead was identified as a significant methodological artifact in the chromatograms produced from these analyses. Muscle samples of fish collected from the Slave and Athabasca rivers (Fall Sampling. Species: goldeye, northern pike, walleye, whitefish, burbot) were analyzed using the new mercury speciation technique. Concentrations for both methylmercury and inorganic mercury were quantified. In fish muscle, methylmercury was expected to account for almost the entirety of the total Hg concentration with inorganic Hg accounting for a minimal proportion. We found the mean MeHg percentage for goldeye to be 82.4% of total Hg, 90.2% in northern pike, 87.2% in walleye, 92.3% in whitefish, and 87.5% in burbot.

3.2 Introduction

Environmental Hg levels are of concern for both human and environmental health. One of the primary forms of Hg of concern is MeHg due to its propensity to biomagnify in foodwebs, leading to greater Hg concentrations in higher trophic level organisms such as fish which then can be consumed by humans (Baevens et al., 2003). Due to its toxicity and potential health effects, Health Canada has set a Hg guideline for general consumption of fish at 500 ng/g wm (Health Canada, 2007). Mercury can also be found in the elemental form, Hg, and as the inorganic ion, Hg^{2+}. Anthropogenic releases of Hg are not typically in the form of MeHg but are usually as inorganic Hg species that can subsequently methylated in water and sediment by sulfate reducing bacteria (Das et al., 2009). Inorganic Hg can also be found in fish, though, the majority of Hg in fish is MeHg (Bloom, 1992; Lasorsa and Allen-Gil, 1995; Jackson et al., 2008). It has been shown that Hg can be methylated into MeHg in fish tissues, but the extent is limited leading to the majority of MeHg being from external sources (Wang et al., 2013). Mercury guidelines for fish tissue assume all Hg in fish tissue is MeHg which is a conservative approach that may overestimate risk if Hg comprises a greater percentage of total Hg. Given the ability of MeHg to biomagnify and its greater toxicity, it is important to be able to analyze tissues, primarily fish tissues, for the presence of these two Hg species.

Other researchers have investigated Hg speciation and this research will look to expand on previous SPME methods (Cai and Bayona, 1995; Moens et al., 1997; He et al., 1998; Beichert et al., 2000; Rodil et al., 2002; Grinberg et al., 2003; Yang et al., 2003). These methods used borate reagents such as sodium tetraethylborate, sodium tetraphenylborate, sodium tetrapropylborate, and potassium tetrahydroborate to derivatize Hg compounds. Previous Hg speciation methods commonly use solvent based extraction methods such as toluene extraction followed by butylation or dichloromethane extraction followed by back extraction to water before ethylation (Qian et al., 2000). The use of borate derivatization with SPME limits the amount of solvent used and simplifies the process. Derivatization was followed by SPME extraction before analysis using GC-ICP-MS, GC-atomic absorption spectrometry (AAS), GC-MS, microwave-induced plasma emission spectrometry (MIP-AES), or furnace atomization plasma emission spectrometry (FAPES).These detectors were adequate for the quantification of Hg species but are limited in the amounts of data able to be collected relative to modern

advances in mass spectrometry technologies, specifically with regards to Orbitrap mass spectrometers. Orbitrap mass spectrometers are capable of scanning a wide range of mass/charge (m/z) in each scan with ultra-high resolution which can greatly increase the quantity of data extracted from each sample run. Previous SPME Hg methods analyzed various sample types including stock standards, fish tissues, fish CRM, mink skin and hair, water, soil, and sediment CRMs. Borate derivatization methods have also been used for analysis of other metals including As, Pb, Se, and Sn which may allow for simultaneous analysis of these metals in addition to Hg (Reviewed by Zahariadis, 2013).

Borate derivatization and SPME have been valuable additions to organometal analysis and in particular to Hg and MeHg analysis. This project assesses the advantages of modern advances in MS technology by using ultra high-resolution MS and automates derivatization and SPME through the use of a modern robotic sampler interfaced directly to the GC-MS system to simplify and reduce the steps that require human involvement reducing variability and potential human errors.

3.3 Materials and Methods

3.3.1 Analyzed Samples

In the fall of 2011, five species of fish (burbot, goldeye, northern pike, walleye, and whitefish) were collected from seven locations along the Slave and Athabasca Rivers. Fish were collected by gill net and subjected to health assessments prior to sample tissue collection. The collection methods, sample collection, and health assessments are described further in Ohiozebau et al. (2015), Ohiozeabau et al. (2016), and Tendler et al. (In Preparation). A subsample of the fish collected during the fall of 2011 were analyzed. The subsample included the first five fish sampled of each species from three locations (Fort Resolution, Fort Chipewyan, and Fort MacKay). When less than five individuals of a species were sampled at a location, all individuals sampled were analyzed. The specific number of samples for each species and location is listed in Table 3.1.

3.3.2 Sample Preparation

Sample preparation was modified from existing methods described in Cai and Bayona (1995), Grinberg et al (2003), and Yang et al (2003). Subsamples of each fish muscle sample were freeze dried. For digestion, 0.5g of dry sample was weighed and added to a sample vial to which 20mL of 20% (m/v) methanolic potassium hydroxide (MeOH-KOH) was added. A smaller mass of tissue could be used to accommodate the amount of tissue available though the tissue to MeOH-KOH ratio was maintained. The vial containing the tissue sample and MeOH-KOH was then placed in an ultrasonic bath (VWR Ultrasonic Cleaner 250D) at room temperature for a total of five hours with agitation by vortex mixer at 2.5 hours. The digestates were stored at 4°C until analysis. For analysis, 0.5mL of the digestate was added to a 20mL glass headspace vial along with 10mL of 1M sodium acetate buffer solution. The pH of the sodium acetate solution used depends on which species of Hg analyzed as the effectiveness of the derivatization reaction of MeHg and Hg(II) is pH dependent. Both MeHg and Hg reacted with $NaBEt_4$ between pH 5 and 6. For this method, a pH of 5.35 produced an optimal response for MeHg and a pH of 5.85 produced and optimal response for inorganic Hg. Derivatization can be performed either manually or by autosampler prior to analysis, both approaches are discussed here. For manual derivatization, the vial was capped and 100µL of 10% sodium tetraethylborate ($NaBEt_4$) in tetrahydrofuran (THF) solution was added using a syringe through the septum of the headspace vial cap. The automated derivatization is performed by the autosampler and the $NaBEt_4$ is stored in a cooled tray at 4°C to prevent degradation of the solution. Tetrahydrofuran without stabilizer(s) must be used for this analysis. Previously described methods used $NaBEt_4$ dissolved in water at 1% but the solution showed appreciable degradation within 24 hours at 4°C. Sodium tetraethylborate has a significantly longer shelf life when dissolved in THF and can be stored at 4°C in the dark for a period of up to four weeks without a decrease in derivatization efficiency (Schubert et al., 2000). Tetrahydrofuran was sparged using helium for 10 minutes before preparation of the $NaBEt_4$ solution. Once the $NaBEt_4$ vial is opened, it is placed under a flow of helium gas to prevent reagent degradation. The appropriate volume of sparged THF is added to the $NaBEt_4$ to make up the 10% $NaBEt_4$ solution. The solution was transferred to an amber headspace vial, any remaining air in the vial was purged with helium, and the vial was capped.

3.3.3 GC-Orbitrap MS Analysis

Analysis was performed on a Q Exactive-GC Orbitrap with an RSH autosampler and a Trace 1310 GC (Thermofisher Scientific). The GC was equipped with a DB5MS Column (60m, 0.25mm ID, 0.1 um film thickness). Derivatized samples were transferred to the incubation station and incubated at 40°C with agitation for two mins. While the sample is still in the incubation station, the SPME fibre is inserted into the headspace of the sample vial for 20 mins to allow the adsorption of sample to the fibre while the sample is continually agitated. The SPME fibre was an 85µm carboxen-Polydimethylsiloxane (PDMS) fibre (Supelco). After adsorption, the SPME fibre was transferred to the GC injection port where the sample is desorbed from the fibre at 280°C for 0.8 mins. The SPME fibre is conditioned for two mins prior to adsorption and 25 minutes post-desorption at 280°C. Carrier gas flow for the GC was 1 mL/min with a splitless time of 1.5 mins. The initial GC temperature was 60°C, held for 10 mins. The first ramp phase increased temperature by 10°C/min until reaching 150°C which was immediately followed by the second ramp phase of 25°C/min until a final temperature of 270°C was reached and held for five mins. The total run time was 28 minutes.

The MS was operated in full scan mode with a scan range of 125-300 m/z, and mass resolution of 60,000 (FWHM). The source temperature was set to 250°C and the transfer line temperature was 285°C. Data was acquired and analyzed using Xcalibur 4.0 software (Thermo Fisher Scientific).

3.3.4 Method Validation

Concentrations were determined using standard curves created by analyzing MeHg and Hg standards (Alfa Aesar) and using the sum total peak area for all fragments and isotopes of MeHg or Hg. The MeHg standard curves had r^2 values of 0.992, 0.993, 0.996, and 0.974 and the Hg standard curves had r^2 values of 0.997 and 0.992. Blanks, check standards, and certified reference materials were included in the analytical runs to ensure quality assurance and quality control (QA/QC). Dorm-4 (National Research Council Canada, fish protein homogenate) was the certified reference material (CRM). Dorm-4 has a certified concentration for MeHg of 0.355 µg/g dm and a total Hg of 0.412 µg/g. Dorm-4 recovery for MeHg was 92.1% ±5.8% (n=6) and for Hg recovery it was 104.9% ± 8.9% (n=5). The blanks showed minimal to no background Hg

concentrations with the greatest blank having a calculated concentration of 0.001 µg/g Hg and a peak area of 5229 counts compared to 467220 counts in the lowest standard (0.1 µg/g Hg).

The MeHg and Hg peaks were confirmed in two ways. The first was running standards of each and determining retention time using the m/z of derivatized MeHg or Hg and using this information for unknown samples. The second was using the isotope ratios of the analyte of interest, in this case Hg. These isotopes and their patterns can be used to identify and confirm the analyte of interest. The observed mercury isotope pattern from these analyses had near perfect overlap with the theoretical isotope pattern. (Figure 3.1, Figure 3.2).

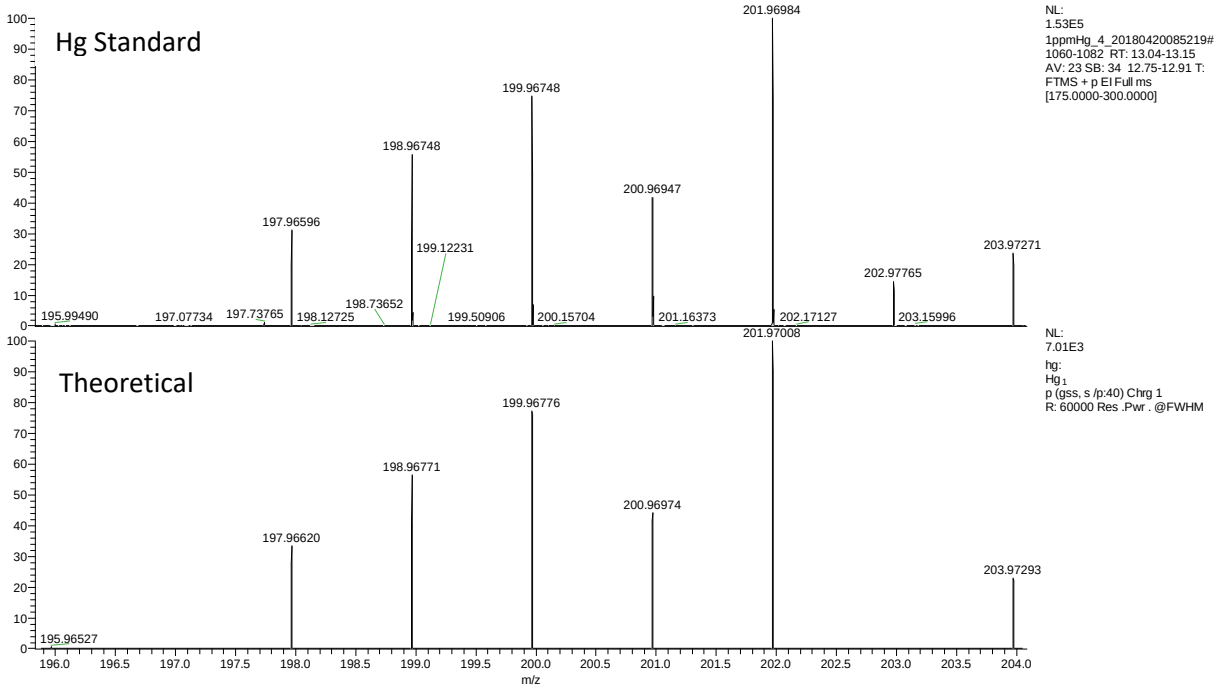

Figure 3.1: Comparison of an Extracted Ion Chromatogram produced by Headspace (HS) Solid-phase Microextraction (SPME) Gas Chromatography Orbitrap Mass Spectrometer (GC-Orbitrap MS) analysis of a mercury (Hg) standard to the theoretical distribution of mercury (Hg) isotopes produced by Xcalibur software. Y-axis represents relative abundance of specific mass/charge.

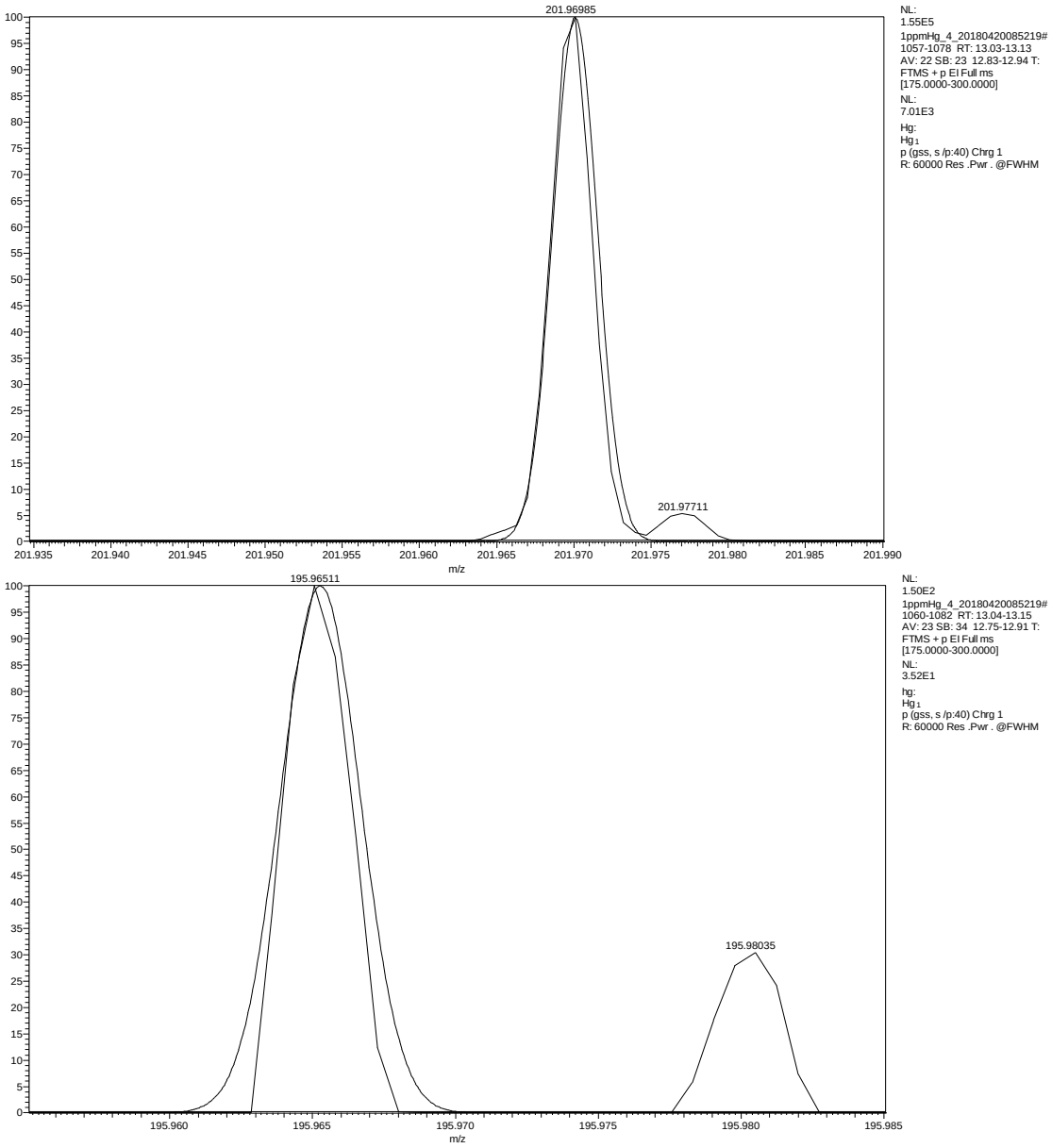

Figure 3.2: Mass accuracy comparison of an Extracted Ion Chromatogram produced by Headspace (HS) Solid-phase Microextraction (SPME) Gas Chromatography Orbitrap Mass Spectrometer (GC-Orbitrap MS) analysis of a mercury (Hg) standard to the theoretical distribution of the most abundant (202 Hg) and least abundant (196 Hg) stable mercury (Hg) isotope produced by Xcalibur software. Y-axis represents relative abundance of specific mass/charge.

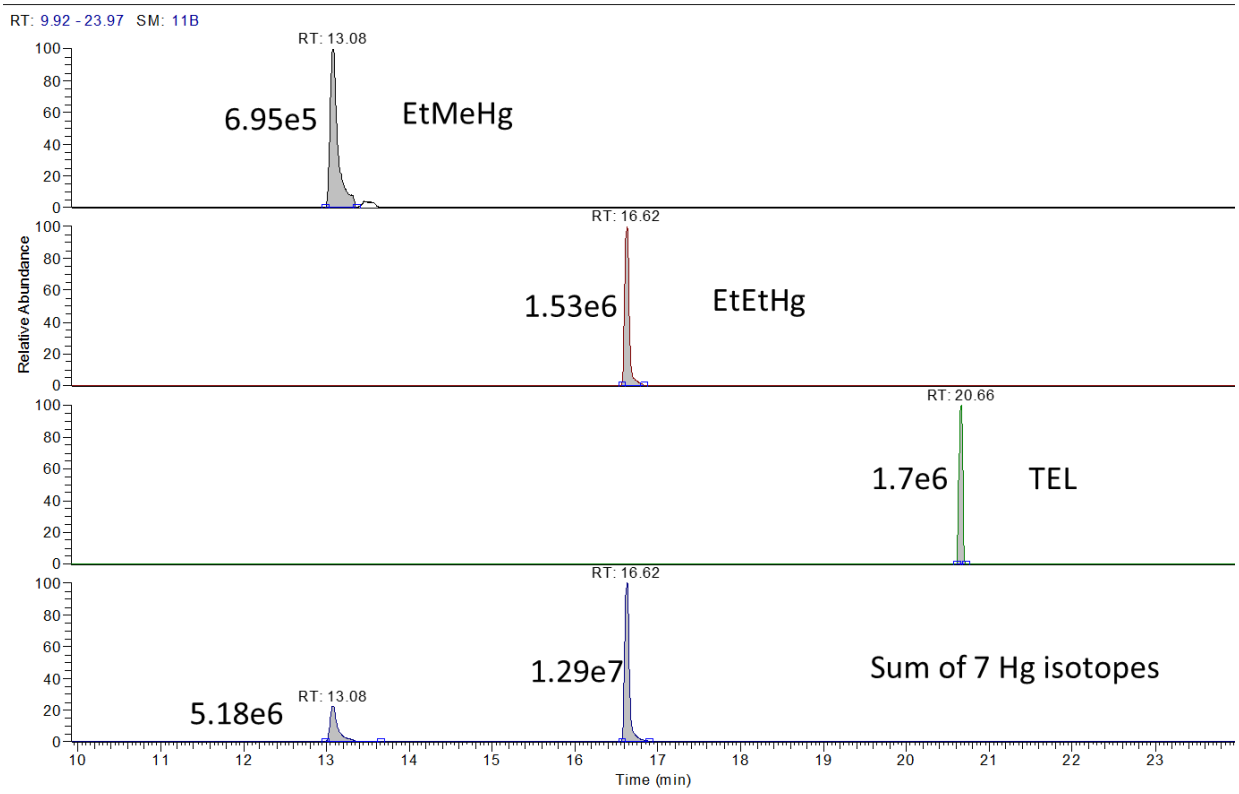

Figure 3.3: Chromatograms produced by Headspace (HS) Solid-phase Microextraction (SPME) Gas Chromatography Orbitrap Mass Spectrometer (GC-Orbitrap MS) analysis of a mercury (Hg) standard. The peaks represent the analytical signal for ethyl-methylmercury (EtMeHg), ethyl-ethylmercury (EtEtHg), tetraethyl lead (TEL), and the sum of the seven Hg isotopes. Y-axis represents relative abundance of the specific mass/charge. X-axis represents the retention time.

3.3.5 Statistics

Normality of data and homogeneity of variance were checked using the Kolmogorov-Smirnov test and Levine's test respectively. Data set passed the assumptions of normality and therefore, parametric tests could be used. Differences in MeHg percentage among species were tested utilizing a 1-way ANOVA followed by a post-hoc Tukey test. Mercury isotope ratios differences were also tested using a 1-way ANOVA followed by a post-hoc Tukey test. All statistical analysis was performed using SPSS Version 24 (IBM SPSS Statistics, Armonk, NY, USA). Differences were considered statistically significant at $p < 0.05$.

3.4 Results and Discussion

3.4.1 Mercury Speciation

A subset (Fall sampling. Species: goldeye, northern pike, walleye, whitefish, burbot. Locations: Fort Resolution, Fort Chipewyan, Fort Mackay.) of the Slave and Athabasca River fish tissue samples were analyzed using the newly developed mercury speciation method. Concentrations for both methylmercury and inorganic mercury were quantified (Tables 3.2 and 3.3). The GC-orbitrap MS total Hg value (MeHg + inorganic Hg) compared somewhat well to the ICP-MS total Hg value from previous analysis of this group of samples (Tendler et al., In Preparation) (Table 3.1). There were differences with maximum mean concentration difference of 219%. The differences between the ICP-MS and the GC-orbitrap MS methods showed a positive bias in the GC-orbitrap MS method. This could be due to different subsamples of the main sample being used but that is unlikely given the consistency of the positive bias. Mass discrimination could be another explanation for the positive bias due to the use of greater m/z values (up to 246 for MeHg and up to 260 for Hg) in the quantification of MeHg and Hg. Mass discrimination is caused by ions of different masses having different ionization and transmission efficiencies in the MS (Wood et al., 1978). The ICP-MS analysis used ^{202}Hg for quantification whereas the GC-orbitrap MS method utilized 21 m/z ranging from 196-248 for MeHg and 14 m/z ranging from 196-260 for Hg.

Limits of detection (LOD) were calculated for each standard curve using the formula $LOD = 3s_{y/x}/b$ where $s_{y/x}$ is the standard error of the regression and b is the slope of the regression. The method limits of detection for the MeHg analysis were 0.12, 0.16, 0.19, and 0.41 µg/g dm with an average of 0.22 µg/g dm. These correspond to 1.50, 1.96, 1.29, and 5.02 ng of MeHg in the headspace vials and final concentrations of 0.14, 0.18, 0.22, and 0.47 ng MeHg/mL in the headspace vials. The limits of detection for the Hg analysis were 0.17 and 0.23 µg/g dm with an average of 0.20 µg/g dm. These correspond to 2.08 and 2.81 ng of Hg in the headspace vials and final concentrations of 0.20 and 0.26 ng Hg/mL in the headspace vials.

Table 3.1: Comparison of mean concentration of mercury in fish muscle tissue using two analytical methods, Headspace SPME followed by GC-Orbitrap MS and ICP-MS. Locations Fort MacKay (FM), Fort Chipewyan (FC), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), whitefish (WF) and burbot (BB).

Location	Species	n	Total Hg (µg/g dm)	ICP-MS Hg Total (µg/g dm)	% Difference
FM	BB	2	1.25	0.69	81.4
	GE	5	2.84	1.05	170.2
	NP	5	2.24	1.76	27.0
	WE	5	2.63	1.44	82.0
	WF	5	0.28	0.17	64.2
FC	GE	5	2.60	1.02	155.0
	NP	5	3.55	1.34	164.2
	WE	5	1.74	0.62	178.9
	WF	5	0.21	0.25	-16.8
FR	BB	5	1.32	0.75	75.6
	GE	5	2.19	1.25	74.6
	NP	5	2.53	0.79	218.9
	WE	5	2.47	1.26	95.5
	WF	5	0.44	0.52	-15.3

Previous borate derivatization SPME analysis methods for MeHg/Hg calculated their LOD using the standard deviation of analyzed blanks except for Rodil et al. (2002) which used $LOD = 3s_{y/x}/b$. Calculating the LOD using the standard deviation of blanks can lead to a lower calculated LOD than using $LOD = 3s_{y/x}/b$. For comparison of LOD between these methods, the absolute LOD will be used due to differences in the quantities of tissue, methanolic KOH, buffer, and $NaBEt_4$ used for each method. Absolute LODs were calculated for studies which reported method LOD using the method information provided.

The absolute LOD values for this method fall within a similar range as previous borate derivatization methods with their absolute LOD for MeHg ranging between 0.11-2.2 ng and one at 26 ng (Cai and Bayona, 1995; Moens et al., 1997; He et al., 1998; Rodil et al., 2002; Grinberg et al., 2003; Yang et al., 2003). Three of these methods also analyzed for Hg simultaneously and had absolute LOD of 0.07, 0.8, and 8.6 ng (Cai and Bayona, 1995; Rodil et al., 2002; Grinberg et al., 2003). For the most part the absolute LOD were all within an order of magnitude but the method LOD for analyzed tissue varied to a greater degree due to amount of tissue and buffer used. The method LOD for Hg by ICP-MS ranged from 0.081-0.15 ng/g which allows the ICP-

MS to detect lower Hg concentrations, but the data is limited to total Hg and does not provide speciation data.

The limit of detection for this method is adequate for analyzing fish muscle tissue for Hg compared to the Health Canada Hg guidelines of 500 ng/g wm (approximately 2.5 µg/g dm) given that MeHg is the primary concern for human consumption of fish tissue. The limit of detection could be further improved by experimenting with digestion and extraction parameters.

In previous studies methylmercury accounted for almost the entirety of the total Hg concentration in fish tissue samples with inorganic Hg accounting for a minimal concentration. Other Hg speciation studies found average MeHg in fish to typically be greater than 80% with some having found greater than 95% MeHg though there are instances of MeHg percentages less than 80% and one instance in whitefish as low as 25% (Akagi and Nishimura, 1991; Akagi et al, 1994; Malm et al., 1995; Hylander et al., 2000; Jackson et al., 2008; Marrugo-Negrete et al., 2008; Carrasco et al., 2011). In the current study the mean MeHg percentage (MeHg/Total Hg x 100%) were: 82.4% in goldeye, 90.2% in northern pike, 87.2% in walleye, 92.3% in whitefish, and 87.5% in burbot. MeHg percentages were found to be statistically different among species by 1-way ANOVA ($p=0.036$) and a post-hoc Tukey test found goldeye to be significantly different ($p=0.02$) from whitefish. The whitefish value may be inflated due to Hg concentrations in whitefish being generally low. This could lead to Hg(II) concentrations being below detection leading to an increased MeHg percentage. Though not statistically different, goldeye appear to be lower than northern pike, walleye, and burbot. An increased sample size could be required to statistically verify the possible differences. MeHg percentages were not found to be statistically different by 1-way ANOVA between sites for each species.

Methylmercury generally comprises a greater percentage of total Hg as trophic level increases (Carrasco et al., 2011). This is mostly consistent with the mean MeHg percentages from this analysis with goldeye, 3rd trophic level, being lower than northern pike, burbot, and walleye which are on the 4th trophic level. Whitefish are on the 3rd trophic level but have the highest mean MeHg percentage which does not fit with the relationship between trophic level and MeHg percentage. This could potentially be explained by the generally lower concentrations of Hg in whitefish leading to non-detects for inorganic Hg. This contention is further supported by whitefish with greater concentrations of Hg seeming to have lower MeHg percentages.

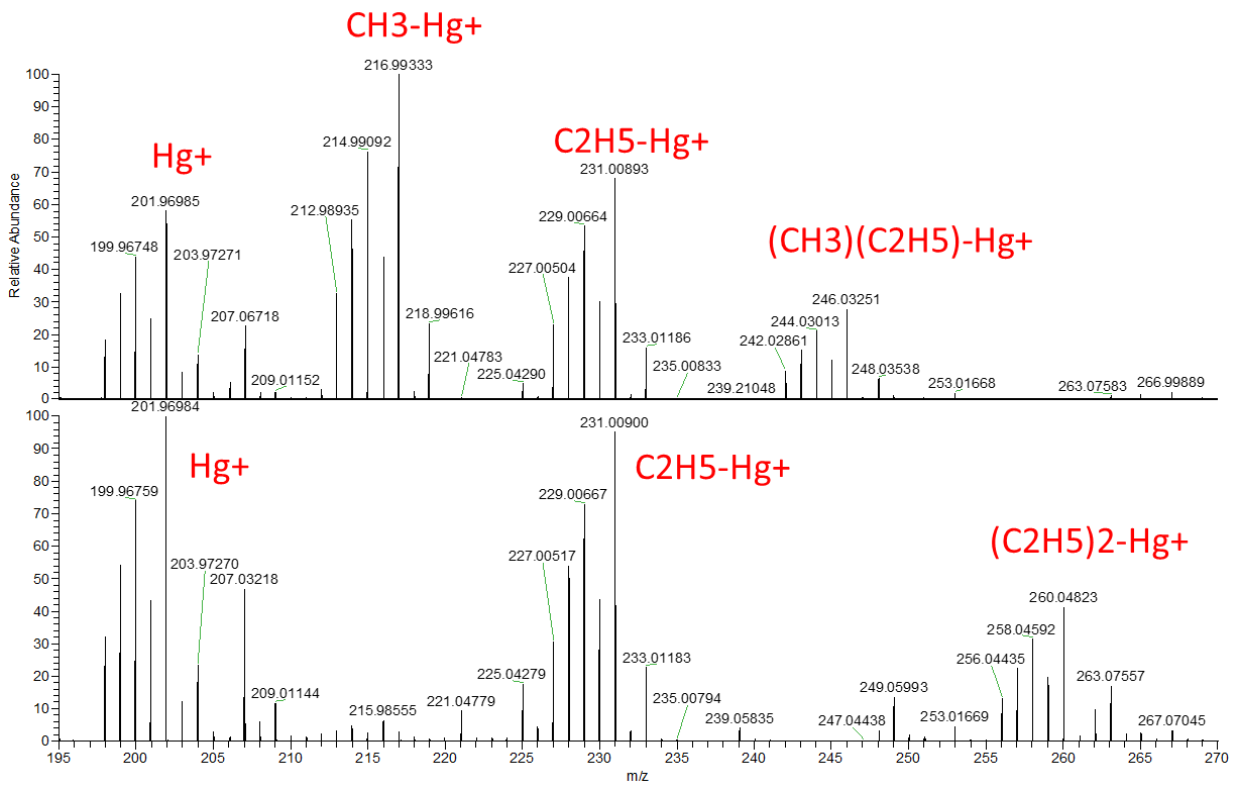

Figure 3.4: Extracted Ion Chromatogram produced by Headspace (HS) Solid-phase Microextraction (SPME) Gas Chromatography Orbitrap Mass Spectrometer (GC-Orbitrap MS) analysis of a mercury (Hg) standard. The peaks represent the analytical signal for the specific mass/charge (m/z) during the extracted scan. The upper scan represents the parent compound, ethyl-methylmecury, and its fragments, ethylmercury, methylmercury, and mercury. The lower scan represents the parent compound, ethyl-ethylmercury, and its fragments, ethylmercury and mercury. Y-axis represents relative abundance of the specific mass/charge.

Table 3.2: Comparison of mean concentration of methylmercury (MeHg) and inorganic mercury (Hg) in fish muscle tissue analyzed using Headspace SPME followed by GC-Orbitrap MS and ICP-MS. Locations Fort MacKay (FM), Fort Chipewyan (FC), and Fort Resolution (FR). Species are goldeye (GE), northern pike (NP), walleye (WE), whitefish (WF) and burbot (BB).

Species	Location	n	MeHg (µg/g dm)	Standard Deviation	Hg (µg/g dm)	Standard Deviation
BB	FM	2	1.07	0.24	0.19	0.24
	FR	5	1.16	0.38	0.16	0.08
GE	FM	5	2.37	0.87	0.46	0.19
	FC	5	1.84	1.06	0.36	0.14
	FR	5	1.84	1.38	0.35	0.14
NP	FM	5	2.07	0.53	0.21	0.20
	FC	5	3.39	1.11	0.16	0.25
	FR	5	3.90	2.58	1.10	1.9
WE	FM	5	2.09	0.73	0.54	0.47
	FC	5	1.57	0.88	0.17	0.17
	FR	5	2.19	1.86	0.28	0.27
WF	FM	5	0.26	0.30	0.03	0.03
	FC	5	0.21	0.11	0.002	0.002
	FR	5	0.36	0.13	0.08	0.05

3.4.2 Stable Isotopes of Mercury

The use of the GC Orbitrap MS allows for the collection of data regarding all mass/charge (m/z) values in the specified range in each scan with high mass resolution (60,000). This scan range and resolution allowed us to quantify Hg isotopes in the samples (Figures 3.4). Hg has seven stable isotopes with nominal masses: 196, 198, 199, 200, 201, 202, and 204 amu though 196 accounts for only approximately 0.15% of stable Hg and is typically not used in stable isotope analysis. The ability to detect the stable isotopes opens up the possibility of comparing stable isotope profiles between samples. Natural Hg isotope ratios have been found to have significant variation which could prove valuable for understanding Hg sources (Bergquist and Blum, 2009) The use of isotope profiles is frequently used with elements such as carbon, nitrogen, oxygen, and lead (Chételat et al., 2015). Other studies have investigated Hg stable isotope analysis and have made progress and discoveries into factors affecting Hg stable isotope profiles (Ridley and Stetson, 2007; Bergquist and Blum, 2007; Jackson et al., 2008; Das et al., 2009; Salters and Odom, 2009; Yin et al., 2010).

Photoreduction of waterborne Hg(II) and MeHg to elemental Hg can lead to the enrichment of odd Hg isotopes (199 and 201) over the even (196, 198, 200, 202, and 204) isotopes (Bergquist and Blum, 2007) This can lead to fish from different rivers or lakes having different enrichment of odd Hg isotopes due to differences in the amount of photoreduction occurring in the different bodies of water.

There is a relationship in Δ^{199}Hg and Δ^{201}Hg values and trophic position such as primary, secondary, or tertiary consumers (Jackson et al., 2008; Das et al., 2009). The ratios of $Me^{199}Hg/ Me^{202}Hg$ and $Me^{201}Hg/ Me^{202}Hg$ were used as surrogates for Δ^{199}Hg and Δ^{201}Hg. These ratios were subjected to a 1-way ANOVA to test for differences in the ratios between species. There were no statistical differences ($p=0.297$) found between species for $Me^{199}Hg/ Me^{202}Hg$ but there were statistical differences ($p=0.001$) for $Me^{201}Hg/ Me^{202}Hg$. Tukey post-hoc analysis found whitefish were statistically different than goldeye ($p=0.004$), northern pike($p=0.004$), and walleye ($p=0.005$). This is partially consistent with the relationship to trophic level though goldeye would be expected to be lower than northern pike and walleye as well. There being no difference in $Me^{199}Hg/ Me^{202}Hg$ does not align with the trophic level relationship either. Another explanation could be that whitefish are a migratory species and that at least some proportion of the fish sampled were likely resident in the Great Slave Lake which could lead to a different isotope ratio.

Unfortunately, this method would require further optimization in order to confidently compare isotope profiles between samples. The standard deviation within the same standard was not sufficient to confidently be able to detect subtle changes in isotope ratios (Table 3.4). The standard deviations were smaller in the largest standard compared to the second largest standard which could indicate increased precision as the concentration of MeHg and Hg increase. This opens the possibility of improvements in the method leading to the ability to detect more subtle differences in the isotope ratios between samples.

Table 3.3: Comparison of mean isotope ratios of the two greatest standards for Hg and MeHg and the theoretical isotope ratio of Hg. Ratios are calculated relative to ^{202}Hg. Standard deviation is listed in parentheses for each standard. ^{196}Hg was not included due to low abundance and frequency of non-detection.

		Isotope Ratio (^{x}Hg/^{202}Hg)				
	n	198	199	200	201	204
Theoretical		0.338	0.570	0.778	0.443	0.230
1µg/g MeHg	6	0.271 (0.051)	0.525 (0.027)	0.738 (0.023)	0.401 (0.017)	0.188 (0.008)
2µg/g MeHg	4	0.29 (0.008)	0.519 (0.027)	0.733 (0.023)	0.395 (0.017)	0.19 (0.009)
1.6µg/g Hg	5	0.290 (0.027)	0.502 (0.040)	0.723 (0.016)	0.394 (0.054)	0.188 (0.011)
3.6µg/g Hg	3	0.313 (0.010)	0.562 (0.017)	0.741 (0.006)	0.429 (0.007)	0.201 (0.004)

3.4.3 Applications to other Organometallics

Borate derivatization techniques have been used in the analysis of multiple organometallics including As, Hg, Pb, Se, and Sn analysis (Reviewed by Zahariadis, 2013). These methods used various borate derivatization reagents such as $NaBh_4$, $NaBPh_4$, $NaBPr_4$, and $NaBEt_4$ and detectors such as MS, AAS, AED, ICP-MS, and flame photometric detector (FPD). Borate derivatization followed by SPME has been used for simultaneous determination of organic Hg, Pb, and Sn compounds. In the current study, analytes other than MeHg and Hg(II) were not studied but it is possible that other organometallics might be able to be derivatized by $NaBEt_4$ and were detected within the scan range (125-300 m/z). Quantification of detected metals would not be possible retroactively but could be quantified in future analytical runs through additional metal standards.

Tetraethyl lead (TEL) was identified in all chromatograms produced from these analyses through use of the library search function of Xcalibur (Figure 3.3). The TEL peak appeared in all chromatograms which is likely due to background levels of Pb which would complicate attempts to quantify TEL and other Pb analytes.

The majority of Se compounds were below our scan range. Derivatized diethyl selenide has a m/z of 137.9942 and was identified in the DORM-4 reference material analyzed. Selenium standards were not used to confirm the retention time of Se analytes but the isotope pattern

(Figure 3.5) of the analyzed diethyl selenide matched up with the theoretical pattern increasing confidence in the identification.

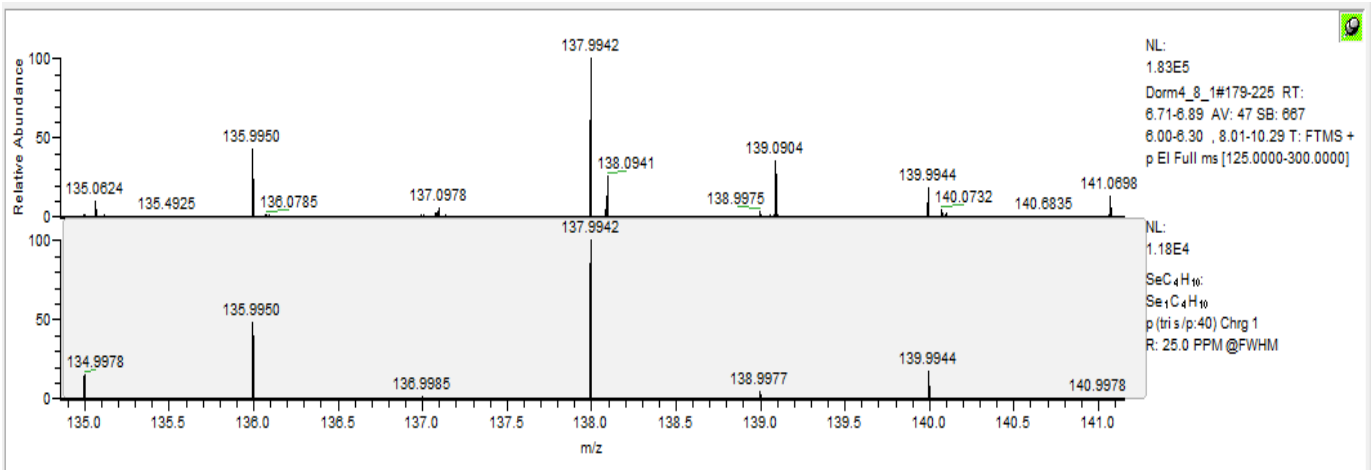

Figure 3.5: Comparison of an Extracted Ion Chromatogram produced by Headspace (HS) Solid-phase Microextraction (SPME) Gas Chromatography Orbitrap Mass Spectrometer (GC-Orbitrap MS) analysis of diethylselenide in DORM-4 certified reference material to the theoretical distribution of diethylselenide isotopes produced by Xcalibur software. Y-axis represents the relative abundance of the specific mass/charge.

Arsenobetaine is the prevalent species of As found in fish tissues including the CRM DORM-4 where it accounts for approximately 57% of the total As. Arsenobetaine does not appear to be derivatized by borate reagents such as the one used in this method. Other methods derivatized As species such as arsine, monomethylarsine, dimethylsarsine, trimethylarsine but not arsenobetaine (Pantsar-Kallio and Korpela, 2000). In the DORM-4 samples, a peak with arsine m/z was present but with As having only one stable isotope and the absence of As standards, confirmation was not possible.

3.5 Conclusions

This method was able to successfully quantify both MeHg and inorganic Hg in fish muscle tissue. The percentage of total Hg that was MeHg was similar though on the lower end of other studies with percentages ranging from 82.4% to 92.3%. This is consistent with the assumption that MeHg comprises the majority of total Hg in fish muscle. The ability to differentiate between Hg species in fish could be a valuable tool in risk assessment as currently it is assumed all Hg is MeHg in fish tissue leading to conservative risk estimates.

Previous borate derivatization SPME methods which utilized MS detectors were limited in the number of ions that could be used for quantification in selective ion monitoring mode (SIM). The first use of borate derivatization SPME for Hg analysis used two ions each for MeHg (217 and 246) and Hg (231 and 260) (Cai and Bayona, 1995). Other uses of MS as the detector for similar analysis used one and three isotopes (Moens et al., 1997; Yang et al., 2000). The use of ultra high-resolution MS allowed the use of full scan on the MS instead of SIM. Full scan allowed the use all isotopes for each fragment or parent of the Hg species which was 28 ions, seven isotopes each for one parent and three fragments, for MeHg and 21 ions, seven isotopes each for one parent and two fragments for Hg. The use of all the ions can limit potential impacts of skewed isotope ratios or fragmentation differences between samples. The ability to simultaneously scan for all isotopes with high-resolution allows for the determination of each Hg isotope which can be compiled into the stable isotope profile for the sample. With some optimization, the stable isotope profiles could be adequately sensitive for comparison of profiles between samples. The comparison of isotope profiles of Hg could be used to identify potential sources of Hg as specific environmental processes can lead to enrichment of specific Hg isotopes which could be unique to certain environments.

One drawback of this method is the durability of the SPME fibre. The SPME fibre has an approximate lifespan of 80-100 sample runs. There is also potential for loss of sensitivity as the fibre nears the end of its lifespan. Frequent check standards and visual inspections can limit potential impacts of fibre degradation.

Overall, this method looked to improve upon the existing Hg methods utilizing ultra high-resolution MS, automated derivatization and SPME, and the use of THF as the solvent for $NaBEt_4$.

CHAPTER 4: GENERAL DISCUSSION

4.1 Discussion

The Athabasca and Slave River regions may potentially be impacted by anthropogenic activities such as oil sands extraction, metal mining, agriculture and pulp mills. The Slave and Athabasca rivers are also of great importance to local communities for cultural, economic, and sustenance reasons. There have been concerns raised about the potential impacts these anthropogenic activities could be having on the health of the Athabasca and Slave Rivers. One major concern is loading of specific metals in fish populations that are a key portion of the culture and diet of community members.

The objective of this research was to investigate metal contaminants in fish species of importance to local community members from the Slave and Athabasca Rivers. In order to accomplish this objective, a suite of 25 metals was analyzed in five different species of fish (burbot, goldeye, northern pike, walleye, and whitefish), collected from five sites (Fort McMurray, Fort Mackay, Fort Chipewyan, Fort Smith, and Fort Resolution) along the Slave and Athabasca Rivers during four sampling periods (Summer, Fall, Winter, and Spring). A Peace River site and an additional Slave River site were added during the fall and spring samplings. There were limited location associated trends in the levels of metals detected in fish and the majority of these metals were not detected at concentrations of interest or concern. Four metals (As, Se, Tl, and V) had location associated trends and one metal (Hg) was detected in fish tissue at concentrations of concern. The concentrations of As, Se, Tl, and V were greater in lower Slave River sites compared to upper Slave, Athabasca and Peace River sites. This trend was not apparent in all species or all samplings and had varying significance between the metals. Thallium had the most significant trend followed by As. Given, the increased aerial deposition of metals near oil sands operations observed in other studies (Kelly et al., 2010; Kirk et al., 2014) this trend in metal concentrations was not expected. The concentrations of these four metals were compared to relevant guidelines or subjected to simple risk assessments and *de minimis* risk was found.

Mercury was detected in fish at concentrations of concern for human health. Mercury concentrations did not have correlation to any of the sampling locations. The Hg concentrations

were a concern as there were 2/76 mean Hg concentrations exceeded Health Canada consumption guidelines (500 ng/g wm) when samples were separated by location, species, and sampling season (Health Canada, 2007). The mean Hg concentrations had 36/76 exceedances of the subsistence advice for Hg of 200 ng/g wm (Wheatley, 1979). Exceedances were most frequent in northern pike and walleye which is consistent with the biomagnification potential of MeHg (Baeyans et al., 2003).

One common theme among the metal data was the difference in specific metal concentrations (As, Se, Tl, and V) in lower Slave River compared to the upper Slave River and Athabasca River. Fish migration could be a factor with other studies indicating whitefish and walleye populations in the lower Slave River are a mix of river residents and Great Slave Lake residents and northern pike are only river residents (Carr et al., 2017). Migration from the Great Slave Lake could be blocked by the series of 4 river rapids upstream of Fort Smith, preventing or at least deterring, lake resident fish from migrating further upstream. This could explain certain metal concentration differences between Fort Smith and Fort Fitzgerald which are closer together, geographically than Fort Smith and Fort Resolution.

Mean As concentrations in certain species from this study were found to be greater in the lower Slave River than the upper Slave River and the Athabasca River. All mean concentrations of As were less than the Health Canada guideline for fish protein of 3.5 ppm (µg/g) (Health Canada, 2018). One potential explanation for this phenomenon is mining operations on the Great Slave Lake. Environmental As releases have been related to gold mining activities which are present on the Great Slave Lake (Straskraba and Moran, 1990; Cott et al., 2016; Schuh et al., 2018). Concentrations of As in lake whitefish were found to be 490 ng/g wm in Baker Pond, connected to the Great Slave Lake by Baker Creek, which was the receiving environment for effluent from the Giant Mine on the northwest corner of Great Slave Lake (Cott et al., 2016). Arsenic concentrations in the same study were 190 ng/g wm in Yellowknife Bay which is near Giant Mine but is part of the Great Slave Lake and 190 ng/g wm near Hay River which is on the southeast corner of the lake. Given the difference in As concentration between Baker Pond and Yellowknife Bay and the similar As concentrations between Yellowknife Bay and Hay River, Giant Mine does not appear to have increased As concentrations in the Great Slave Lake whitefish. The concentrations of As in whitefish from Fort Resolution and Fort Smith ranged

from 71.1-230 ng/g wm which is considerably lower than fish collected in close proximity to the receiving waters of the mine effluent and similar to the whitefish collected in Yellowknife Bay and near Hay River. It is possible that migratory populations of white fish from the Great Slave Lake were a portion of the whitefish collected in this study. Whitefish migrate to shallow spawning grounds in the fall which coincide with the most pronounced difference in whitefish As concentrations in the lower Slave River compared to upper Slave River and Athabasca River (Morrow, 1980). There are sets of rapids upstream of Fort Smith which could provide a barrier to further upstream migration of whitefish which could explain lower concentrations in the upper Slave River.

Arsenic concentrations in northern pike followed the same trend in all three of the sampling periods. The cause of this trend is less apparent than for whitefish. Northern pike are piscivores and it is possible they consume the migrating Great Slave Lake whitefish which leads to the elevated As concentrations. This theory does not agree with a Slave River gut content study which did not find significant quantities of whitefish in northern pike guts (Little et al, 1998). The sampling for the gut content study may not have coincided with whitefish migration through the Slave River which could explain the absence of whitefish in northern pike stomachs. Northern pike are territorial fish and do not typically undertake significant migrations, so it is unlikely norther pike are migrating from areas of greater As contamination (Morrow, 1980).

Concentrations of V were greater in whitefish in the lower Slave River during the fall sampling when concentrations at Fort Resolution were greater than those in whitefish from locations on the Athabasca. Whitefish migration from the Great Slave Lake could be an explanation for seasonal differences as stable sulfur isotope analysis suggests the whitefish population at Fort Resolution consists of a mix of river residents and lake migrants (Carr et al., 2017).

The rapids upstream of Fort Smith may be a contributing factor as well. River rapids are sections of increased turbulence and water velocity with typically shallower water levels. River rapids lead to aeration of the water and the turbulence can keep particulates suspended. The rapids could be increasing the bioavailability of metals that are typically bound in sediment. The increase in bioavailability would be in effect downstream of the rapids but not upstream which is consistent with the concentration differences between Fort Smith and Fort Fitzgerald. Aeration

of sediment slurries has been shown to affect speciation of Cd and exposure of freshwater sediments to oxygen has resulted in both increases (Ni, Pb, Cu, Cd, Zn) and decreases (Fe, Mn) of metal mobility (Kersten and Foerstner, 1986). Oxidation of dredged sediment can significantly affect metal mobility (Calmano et al., 1993; Forstner, 1995; Tack et al., 1996). Sediment bound Se can become bioavailable through oxidation (Lemly and Smith, 1987). Rapids would aerate a relatively small distance of river and its sediment but the change in oxygenation could affect the sediment and particulate being carried from upstream. This could lead to fish that prefer to reside near the rapids due to habitat or prey opportunity to be in waters with the potential for greater metal bioavailability.

In these northern rivers flow is lower during the winter which could lead to less sediment disturbance in the winter. This could lead to an influx of metals during the spring when river flows increase dramatically due to snow melt. Snow melt could also lead to an influx of metals from aerial deposition that had accumulated on the snow. Snowmelt can also lead to increased dilution as the flow increases. An influx of metals during snowmelt does not immediately agree with the increase in fall concentrations unless there is a delay in the metal influx reaching the fish such as requiring uptake into food or requiring time to reach the new equilibrium. If this is the case, there would be an expected trend of increased metal concentrations in summer to a lesser degree than fall. A more plausible scenario would be an influx in bioavailable metal concentrations as flow increases due to snow melt, followed by a decrease as the increased flow carries the water, particulates, and metals onward to the Great Slave Lake, among the 30 million metric tons of sediment which is carried through the Slave River to the Great Slave Lake each year (Mollard, 1981).

Thallium had the most significant location associated trend among the metals analyzed. It is a poorly understood metal and the reason for greater concentrations in the lower Slave River is not apparent. Biomethylation of Tl to DMT by benthic organisms is possible in sediments (Schedlbauer and Heumann, 2000). Sediment bound Tl would not be available or have reduced availability for uptake into fishes. Disturbances caused by the rapids upstream of Fort Smith could mobilize sediment bound Tl which could have been methylated into DMT. Dimethylthallium is an organic form of Tl and could have greater potential for bioaccumulation similar to some other organometallics.

Selenium concentrations were greater in goldeye than the other species sampled. Northern pike had significantly lower concentrations than goldeye and walleye. One potential cause of the greater Se concentrations in goldeye is dietary differences. Goldeye consume greater quantities of invertebrates than northern pike and walleye, which are primarily piscivores as adults. Selenium has been shown to bioconcentrate from water to primary producers which are more directly consumed by goldeye (Lemly and Smith, 1987; Skorupa, 1988; Stewart et al., 2010; Janz, 2012). It is possible that Se is transferring from the goldeye diet at greater rates than walleye, and northern pike. Whitefish diets are similar to goldeye which doesn't explain the greater concentrations of Se in goldeye tissues though the migratory nature of whitefish could explain the differences. Selenium can be a major concern for fish health and dietary concentrations exceeding 3.0 µg/g dm, approximately 15 µg/g wm, can be toxic to aquatic organisms. The mean concentrations of Se were well below this concentration with the greatest mean concentration of Se being 0.844 µg/g wm.

The trends in Se and V are not as pronounced as the trend for Tl and As. Increasing the data set either through increasing the sample size by analyzing collected samples or adding sampling seasons could provide more confidence in the potential trends and insight into potential causes.

Geological differences could be another explanation for the metal concentration differences. The sampling locations covered a significant distance and it is plausible differences in geology could lead to the differences in metal concentrations. There are reasons to doubt geological differences as an explanation. Geological differences wouldn't necessarily explain why there are differences only in certain seasons. There is not a large distance between Fort Smith and Fort Fitzgerald though there are significant differences between the metal concentrations at each location. Fort Fitzgerald has metal concentrations in line with the Athabasca River locations whereas Fort Smith has concentrations similar to Fort Resolution which is further from Fort Smith than Fort Fitzgerald.

It is possible that continued expansion of oil sands activities is not leading to increasing metal concentrations in fish relative to previous fish samplings possibly due to improvements in the emissions technology and stricter emission guidelines leading to lower metal concentrations in the emissions. National Pollutant Release Inventory data has reported annual emissions to air,

water, and land from oil sands extraction companies from Fort McMurray for a suite of chemicals including metals of interest to this research, As, Hg, Se, and V. Overall, Hg emissions have decreased from 34 kg in 2000 to 6.3 kg in 2017.The greatest annual Hg emission was in 2007 with emissions of 82 kg. Mercury emissions had a noticeable decrease between 2013, 2014, and 2015 with emissions of 60 kg, 31 kg and 9.9 kg respectively. The number of reporting operations decreased from four to three in 2015 which would have contributed but the total emissions decreased by approximately 50% between 2013 and 2014 without a decrease in the number of reporting operations. Vanadium emissions appear to have had a significant reduction event as well with a reduction of 18 metric tonnes in 1995 to 6.4 metric tonnes in 1996. There was only one reporting facility between 1993 and 2000 which eliminates facility differences in the emission reduction. Arsenic emissions have also decreased with per capita emissions decreasing from 35 kg per reporting operation in 2002 to 20.4 kg per reporting operation in 2017. The major drop appears to have occurred in the reporting between 2005 and 2006 where the number of reporting operations increased from two to four with emission increasing from 78 kg to 98 kg. Arsenic emissions did have spikes in 2007 and 2010 which brought per capita emissions to pre-2007 levels. Selenium emissions have increased according to the NPRI data. Selenium emissions have increased from 86 kg in 2009 to 205 kg in 2017. An additional facility began reporting in 2011 which coincides with the beginning of the Se emission increase which would indicate increasing oil sands development could lead to greater Se emissions. The NPRI has data beginning in 1993 for V, 2000 for Hg, 2002 for As, and 2006 for Se. The large-scale development of the oil sands in the Athabasca region began in 1964 which leaves a gap of 30 or more years lacking emissions reporting. There does appear to be improvement in the emissions of some metal from individual oil sands operations, but the total emission amount is still greatly impacted by the number of functioning operations which would indicate increasing operations in the region would likely counteract improvements in metal emissions. Reported emissions may be lower for Hg and V but the extent of emissions such as leaching from coke could be leading to unaccounted for releases of these metals.

Although, metals have been demonstrated to be entering the Athabasca/Slave river system (Kelly et al., 2010, Kirk et al., 2014) and there are reported releases of metals from oil sands companies in the National Pollutant Release Inventory (NPRI), they may not appreciably be entering the resident fish populations. Determining possible impacts of oil sands extraction

can be quite difficult as there is little to no baseline information from before the extraction of bitumen from the oil sand deposits began. There were also no significant environmental monitoring activities until the Regional Aquatics Monitoring Program (RAMP) began in 1997. There were some individual sampling efforts before RAMP such as the Hg samplings of walleye in 1975,1984, and 1992 with mean Hg concentrations of 0.27-0.43 µg/g wm (Lutz and Hendzel, 1976; Moore et al., 1986; Donald et al., 1996). These Hg concentrations are similar to the concentrations from this research which had mean Hg concentrations in walleye ranging from 0.122-0.512 µg/g wm.

Industrially impacted areas with high metals concentrations in sediment cores do not necessarily lead to higher concentrations in fish (Harrison and Klaverkamp, 1990; Outridge et al, 2011; Evans and Talbot, 2012). Rivers near the copper and zinc smelter in Flin Flon MB had sediment Hg concentrations of 2690 to 9220 ng/g compared to lakes approximately 70 km distant which had sediment concentrations of 30-220 ng/g. Mercury concentrations in northern pike fillets were greater in the lakes, with fillet concentrations of 0.47µg/g compared to 0.09 µg/g in the close lakes.

Metal speciation plays an important role in metal chemistry and can impact toxicity and bioavailability. There are two mercury species of interest in fish, MeHg and Hg(II) (Bloom, 1992; Lasorsa and Allen-Gil, 1995; Jackson et al., 2008). Understanding the speciation of Hg is important due to the greater potential for toxicity and biomagnification of MeHg relative to Hg(II) (Baeyens et al., 2003). The importance of speciation was the driving factor in the development of the Hg speciation method for this research.

There were three areas of interest in developing the speciation method. The primary goal was to differentiate and quantify Hg and MeHg. The secondary objectives were quantifying Hg isotopes and the addition of automation to pre-injection sample preparation. The speciation method was successful in differentiating and quantifying Hg and MeHg. The absolute LOD for this method was comparable to other borate derivatization methods discussed in Chapter 3 (Cai and Bayona, 1995; Moens et al., 1997; He et al., 1998; Rodil et al., 2002; Grinberg et al., 2003; Yang et al., 2003). The LOD is sufficient for analyzing fish tissue for compliance with Health Canada guidelines (Health Canada, 2007). There was potential for positive bias in this method

when compared to total Hg analysis by ICP-MS of the same fish samples. The exact reasons for the positive bias are unknown but could be due to subsample differences or mass discrimination.

This method was able to analyze for each of the Hg isotopes in both Hg and MeHg but was not sufficiently sensitive for comparison of isotope ratios between samples. The Hg isotope analysis does show potential for method improvements, which are discussed later, leading to sufficient sensitivity for isotope comparisons. The ability to simultaneously detect all of the stable isotopes allowed the use of peak areas for all isotopes in quantification of MeHg and Hg which limits potential variability due to differences in isotope ratios.

The automation of pre-injection sample preparation was successful. Derivatization, vial transport, incubation, and SPME sampling were all able to be automated utilizing the modern autosampler equipped to the GC-orbitrap MS. Autosampler method development software was used to set up the automation which allowed the design of a fully customizable step by step procedure. The two significant advantages to using automated pre-injection sample preparation are reduction of variability in sample preparation and reduction in labor required for sample preparation. The primary disadvantages of automation are the up-front time investment into developing and testing the autosampler method and added cost of additional equipment, maintenance, and potential increase in instrument related downtime due to additional working pieces.

Previous investigations into Hg speciation found that MeHg was the dominant species of Hg in fish and had found MeHg percentages greater than 90% (Akagi and Nishimura, 1991; Akagi et al, 1994; Malm et al., 1995; Hylander et al., 2000; Marrugo-Negrete et al., 2008). The MeHg percentages found were similar to previous findings, with percentages of 82.4%, 90.2%, 87.2%, and 92.3% for goldeye, northern pike, walleye, and whitefish, respectively. Research since then has found instances where MeHg percentages were lower in fish, with one study finding a MeHg percentage as low as 25% in whitefish (Jackson et al., 2008: Carrasco et al., 2011). The lower MeHg percentages in fish tissue could be due to advances in analytical techniques leading to an increased ability to detect Hg(II) which is generally present at lower concentrations than MeHg. Given that Hg(II) is less toxic than MeHg, it could be a positive for Hg(II) to comprise a greater percentage of Hg in fish though MeHg is still the dominant species and of more concern.

4.2 Conclusion

The majority of metals analyzed in this study did not show elevated concentrations or spatial trends over the course of the study period. Four metals (Tl, As, Se, and V) had location associated variability to differing degrees and one other metal, Hg, had concentrations that exceeded Health Canada general guidelines for 2/76 sampling groups separated by species, location, and season. The subsistence consumption advisory level was exceeded in 36/76 sampling groups. These exceedances are a potential health concern for residents of the Slave and Athabasca River regions who rely on fish for sustenance. Mercury concerns are not new for this region and consumption advisories are in place for the Athabasca River and Lake Athabasca (Government of Alberta, 2016). Overall, the metal analysis provides data for a region with significant potential industrial impacts and environmental health concerns expressed by the local population.

The Hg speciation method succeeded in differentiating between MeHg and Hg and has sufficient sensitivity to analyze fish tissue for MeHg and Hg relative to Canadian guidelines. The method provides valuable speciation information for a metal that is a human health concern in fish. The method in its current state would need further optimization to adequately detect differences in isotope ratios between samples. There is potential for this method to simultaneously analyze for multiple metals and organometals as evidenced by detection of MeHg, Hg, TEL, and diethylselenide. Further research utilizing specific standards and optimization of sample preparation and reaction pH would be required.

4.3 Future Work

4.3.1 Total Metal Analysis

Continuing the fish sampling in the Slave and Athabasca Rivers to establish a longer timeline of metal concentrations would be valuable in determining any changes or trends related to metals in fish. Determining trends or any significant time related changes such as increases or decreases in metal concentrations is difficult with the current sampling data covering a period of 1-3 years. It is possible but in order to see subtle changes, years more sampling would be required. The addition of other types of samples such as water, sediment, invertebrates, and small

fish would add value and increase the data obtained from these endeavors. Adding these other sample types would allow fish concentrations to potentially be compared and linked to other contaminant sinks or sources.

4.3. Mercury Speciation

There are potential improvements to the Hg speciation method that could be investigated. One option is to increase the amount of Hg in the headspace vial. There are two ways to accomplish this. The first is to increase the amount of tissue digested which comes with a potential downside of incomplete digestion. The other option is to increase the amount of digestate added to the buffer. This would require additional pH correction to counteract the increase in pH due to the KOH in the digestate. One of the other borate derivatization methods used 2mL of digestate added a final volume in the headspace vial of 10 mL (Rodil et al., 2002). This is an increase of approximately 4-fold in the amount of digestate in the headspace vial if 2 mL of digestate was adopted in this method. Increasing the Hg in the headspace vial should lead to a greater amount of Hg in the vapor phase which will get adsorbed onto the SPME fibre. This should increase the amount of Hg which will be detected by the detector increasing the analytical signal. By increasing the signal, the detection limit will be improved allowing quantification at lower concentrations. If the detection limit is lowered, it will improve our ability to quantify inorganic Hg which is found at significantly lower concentrations in fish than MeHg. Improving detection limits will also improve our ability to investigate the potential of this method to do Hg stable isotope analysis. Certain Hg isotopes, 196 and to a lesser degree 204, are at considerably lower concentrations than the other isotopes (198, 199, 200, 201, and 202) and can fall below the detection limit. The non-detection of these isotopes makes it difficult to compare between samples when these potentially important data points are unavailable.

The derivatization of Hg was greatly impacted by the pH of the solution during reaction and slight fluctuations in pH could impact the efficiency of the derivatization. Investigating the pH of the solution and potential improvements to the buffering ability of the solutions could lead to increased consistency in the analysis. It is also possible that investigating and improving pH control of the reaction could lead to being able to analyze for both MeHg, Hg(II), and potentially other organometallics during the same analytical run. Improvements in the detection limit could

also come into play here where choosing a pH that improves the efficiency of the lower concentration species which also keeps the reaction consistent for the other analytes could allow the analysis of multiple analytes during the same analysis. Specific pHs could still be used when a single analyte is of interest or if detection limit of a single analyte needs to be improved.

The use of an internal standard could improve the method. Two potential internal standards could be isotopically labelled ethylmercury or phenylmercury. In order to use unlabelled ethylmercury, a different borate reagent such as sodium tetraphenylborate would need to be used. The method would not likely need to be changed and the sodium tetraphenylborate could be swapped for $NaBEt_4$. This leaves phenylmercury as a simpler choice for an internal standard. The internal standard would undergo all the same processes as MeHg or Hg and thus could be used to correct for sample to sample variation such as digestion and derivatization efficiency and SPME fibre sorption.

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APPENDIX: SUPPLEMENTARY MATERIAL

Table A1: Mean concentration and standard deviation of metals in muscle from goldeye from sampling sites along the Slave, Athabasca, and Peace Rivers. The upper value is the mean and the lower value is the standard deviation. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Summer																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	10	34	1.66	209	41.1	61.3	32.3	1.09	3.83	5.03	70.3	200	4.83	255	183	17.7	7.62	2.34	0.43	704	34.4	679	2.67	19.2	5.13	3.82
		4	2.22	338	27.1	70.3	60.7	1.80	8.63	4.15	74.5	94	3.02	163	219	15.0	10.4	3.29	0.68	194	71.8	1245	0.58	36	4.50	1.65
FM	10	38	0.81	51.8	56.6	35.2	20.7	1.99	0.58	2.82	88.8	211	3.13	228	139	14.6	3.71	1.60	0.27	457	109	937	2.37	49.4	5.75	3.32
		2	0.84	85.5	42.7	27.3	53.1	2.66	1.06	3.30	128.5	193	2.51	85.2	112	18.5	5.62	2.28	0.26	156	131	2266	1.27	152	4.02	1.33
FC	9	37	2.23	224	55.8	17.5	23.9	0.22	0.25	2.55	66.5	124	2.16	209	134	11.7	5.41	4.72	0.51	770	227	403	3.93	4.56	3.06	2.66
		1	2.81	340	26.1	16.5	25.3	0.30	0.37	2.04	136	28.0	1.29	96.7	46.6	11.9	5.10	5.95	0.42	100	341	471	1.33	6.681	2.69	0.42
FS	10	29	4.22	225	60.4	1.92	249.0	0.35	2.72	12.1	54.4	185	4.56	233	462	15.6	33.1	3.72	0.81	588	80.0	4770	3.58	4.01	11.7	4.46
		4	8.55	389	55.7	3.86	292.7	0.40	4.89	21.1	77.7	82.8	2.09	132	459	12.6	74.6	4.34	0.84	176	109	6159	1.47	11.673	9.22	1.94
FR	2	38	0.72	1330	41.2	79.2	12.7	1.07	0.76	0.04	151	203	3.34	224	132	27.8	7.49	1.00	0.27	748	136	111	3.1	0.41	9.52	3.09
		2	0.92	1883	5.4	111.7	13.4	1.35	1.01	0.001	38	11.0	1.3	57.2	59.4	7.91	8.67	1.41	0.38	17.7	191	80.8	1.87	0.58	5.82	0.23
Fall																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	1	39	**<0.01**	121	12.4		58.7	0.10	2.12	3.46	0.06	119	3.25	226	199	5.12	0.06	2.55	0.13	142	0.62	992	0.01	1.64	3.67	3.52
FM	10	36.20	0.14	108	17.8	52.7	23.3	0.66	0.96	2.77	24.5	195	3.59	194	155	12.7	5.34	0.77	0.42	538	2.38	458	1.56	0.83	3.39	2.58
		1	0.31	227	10.6	28.7	25.5	1.17	1.72	1.89	42.8	98.4	1.85	87.8	79.1	10.7	9.57	1.31	0.32	200	4.91	456	1.17	1.32	2.54	0.47
FC	9	37	2.19	132	30.8		67.4	0.74	1.90	4.65	22.9	126	2.81	188	264	7.77	8.16	0.38	0.61	518	13.1	1810	0.82	0.69	4.94	2.85
		2	2.89	176	21.4		158.4	1.25	5.57	4.78	68.2	31.7	0.84	71.1	339	10.4	8.84	0.83	0.32	152	37.2	4244	0.77	0.68	4.541	1.43
FS	10	35	0.84	167	35.4		11.5	0.41	2.85	2.67	60.8	151	3.08	159	128	13.8	10.8	4.96	0.32	844	0.63	308	1.9	108	2.64	2.34
		2	2.07	190	22.8		30.9	0.97	7.26	1.79	119	50.8	1.28	64.3	120	20.5	18.0	11.1	0.28	375	0.05	830	1.22	337.1	2.06	0.42
FR	10	36	0.44	184	43.6	11.6	11.4	0.24	2.32	2.24	56.1	149	2.84	249	122	18.3	11.2	1.72	0.60	818	18.9	202	3.06	2.82	6.71	2.62
		1	0.7	116	93.1	28.0	12.6	0.23	2.07	1.87	48.2	34.7	1.32	136	53.9	8.65	17.7	5.43	0.50	343	57.7	238	2.16	7.03	2.45	0.56
Spring																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	11	33	2.02	263	27.0		59.9	0.09	11.2	11.3	643	310	8.09	264	238	71.2	8.85		0.67	631	1.60	1089	3.17	7.74	8.46	5.30
		3	3.92	152	12.7		92.5	0.04	20.0	7.3	820	180	3.49	224	233	98.1	13.7		1.29	352	3.513	1512	1.40	24.2	5.91	1.90
FM	9	27	1.27	307	32.7		85.5	0.08	4.30	18.7	532	378	9.29	76.9	310	76.9	11.2		0.42	601	2.96	2000	3.08	0.41	9.12	5.57
		5	2.78	220	15.4		105.7	0.04	5.19	12.3	817	313	5.59	58.7	278	104	17.0		0.47	192	8.32	2573	2.66	0.436	7.13	2.10
FC	10	35	0.32	383	48.2	56.6	104.7		0.48	10.0	44.0	195	4.22	126	335	9.93	11.1		0.57	542	0.01	1200	3.7	1.87	6.65	3.39
		3	0.72	404	25.6	113.4	101.9		1.40	5.9	70.2	101	2.15	69.5	217	12.4	13.1		0.76	101	0.002	1182	0.60	2.93	4.02	1.09
PP	9	40	0.02	6.53	26.0	19.7	66.4		0.01	3.28	34.3	157	3.09	260	150	1.75	9.36		0.21	408	**<0.01**	581	2.41	25.4	1.75	2.40
		2	0.04	19.07	10.2	42.5	90.0		0.00	2.63	26.0	95.1	1.13	89.3	89.6	3.19	16.7		0.21	141		708	1.30	59.9	2.08	0.42
FF	10	26	2.29	243	32.8	162.4	75.0		1.84	5.63	31.8	208	5.29	78.3	264	7.66	2.87		6.13	488	3.96	1570	1.77	8.32	7.55	4.39
		7	3.97	657	15.3	171.9	69.7		2.68	3.63	44.5	94.4	3.03	113	119	6.34	2.37		17.0	108	11.9	1894	0.65	12.5	12.9	2.14
FS	10	35	0.68	220	20.7	72.4	17.8		2.65	3.29	24.4	668	3.83	133	116	21.7	86.6		0.03	682	1.88	280	2.84	3.57	2.12	2.62
		5	1.54	601	8.8	77.6	27.2		5.12	2.40	60.3	1254	1.95	61.0	42.6	42.3	173		0.08	300	5.94	408	1.68	9.40	1.47	0.96
FR	10	36	3.69	76.0	38.2	164	81.7		12.3	3.35	52.9	161	3.66	143	169	14.6	1.40		0.39	636	0.01	993	4.83	0.21	12.7	3.83
		6	8.72	194.1	34.0	280	99.0		30.0	1.89	74.2	37.1	1.07	63.4	125	7.83	1.92		0.43	223	0.002	1085	7.10	0.28	24.0	2.61

Table A2: Mean concentration and standard deviation of metals in muscle from northern pike from sampling sites along the Slave, Athabasca, and Peace Rivers. The upper value is the mean and the lower value is the standard deviation. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Summer																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	10	57	1.32	618	62.5	54.3	72.3	0.65	2.15	2.38	75.4	112	3.06	230	359	16.6	13.9	2.65	0.46	246	65.9	774	3.51	57.8	5.14	3.71
		20	1.40	1649	41.6	83.1	109	1.04	4.45	3.47	96.8	23.3	3.02	208	305	16.2	29.9	2.37	0.41	63.7	89.3	1150	1.67	93.0	3.51	1.00
FM	10	61	1.01	104	31.8	55.1	9.78	0.46	2.20	17.1	69.5	98.2	1.40	176	153	10.7	3.79	0.82	0.45	137	105	83.3	2.04	4.67	3.15	3.28
		10	1.47	164	9.69	75.0	15.1	0.64	5.76	50.4	108	19.7	1.04	122	76.3	15.6	4.36	0.96	0.48	62.3	145	84.2	0.75	11.1	3.16	1.00
FC	10	67	2.21	81.9	68.8	20.3	3.55	0.78	0.43	1.41	120	88.1	1.92	195	105	20.0	2.82	0.78	0.53	357	151	76.8	5.00	2.80	4.81	3.03
		9	3.66	138	18.1	29.2	3.19	1.86	0.58	1.27	225	27.6	1.70	86.6	16.3	37.1	8.03	1.05	0.30	101	316	17.7	1.02	4.83	6.30	0.61
FS	11	69	1.40	0.22	126	0.22	14.9	0.31	0.49	0.70	22.7	144	1.78	232	111	14.7	2.06	0.66	1.97	370	101	87.7	8.46	3.07	7.31	3.51
		8	1.58	0.02	47.7	0.02	11.7	0.41	0.67	0.79	26.7	70.2	0.64	159	49.1	13.1	3.66	0.87	1.91	76.5	118	57.8	3.90	6.78	6.51	0.80
FR	11	67	7.22	144	141	16.7	13.6	0.79	2.17	1.07	143	291	2.59	175	83.4	16.8	7.16	23.8	0.72	360	247	106	11.0	4.41	2.77	5.42
		9	9.67	110	93.3	36.9	15.2	0.95	4.02	1.23	207	429	2.32	49.4	27.0	21.6	6.64	74.0	0.67	94.0	290	183	4.48	13.6	4.02	0.00
Fall																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	3	72	<0.01	49.8	9.68	67.6	3.26	3.01	0.17	0.82	17.8	103	1.17	266	100	14.6	0.13	2.95	0.44	272	0.61	39.4	1.54	0.69	3.11	3.03
		14	0	84.2	8.08	.	5.64	2.96	0.23	1.01	12.9	23.6	0.12	57.8	20.9	9.26	0.14	5.10	0.11	146	0.02	22.4	1.74	0.65	2.67	1.64
FM	9	68	0.03	143	15.5	23.5	10.5	0.47	0.45	0.92	34.9	145	1.50	400	119	18.0	7.80	1.86	0.44	210	4.00	98.7	1.23	0.15	3.65	2.72
		13	0.10	200	14.9	40.4	26.9	1.09	0.63	0.84	55.2	85.3	0.71	420	89.3	14.5	19.2	5.47	0.36	108	10.1	261	1.31	0.18	1.65	0.51
FC	9	78	1.12	275	31.3	9.05	4.65	0.72	5.59	1.39	8.43	151	1.62	302	108	9.60	8.51	20.0	0.81	288	5.09	41.5	1.60	0.30	4.43	3.16
		5	3.15	452	15.1	12.5	6.41	1.21	13.9	1.39	13.5	120	0.88	162	17.8	11.7	10.1	51.8	0.30	76.6	13.3	45.0	1.25	0.18	1.78	1.71
FS	10	70	0.81	413	94.9	40.7	10.8	0.71	0.49	1.13	38.2	97.9	1.41	338	87.5	16.0	1.53	65.3	0.68	375	4.06	121	4.60	2.13	2.60	2.52
		11	1.41	977	72.9	57.2	22.7	1.14	1.04	0.71	66.9	24.8	0.38	372	28.7	18.7	2.71	163	0.36	56.8	11.0	227	2.62	2.44	1.79	0.35
FR	10	68	0.44	277	159	0.21	9.27	1.09	1.46	2.41	35.8	181	2.20	247	91.2	11.3	5.00	1.12	1.01	398	0.63	121	7.91	4.81	2.94	3.38
		11	0.83	387	114	0.01	19.0	1.96	2.35	2.61	97.9	124	1.50	244	31.3	11.6	7.49	3.51	0.64	69.7	0.03	177	4.82	12.0	3.70	0.46
Spring																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	8	72	0.23	170	32.6		13.3	0.09	0.34	4.38	344	265	2.54	486	104	34.9	4.68		0.61	280	0.18	175	2.70	0.28	4.39	4.13
		13	0.63	85.7	10.5		11.8	0.03	0.96	1.45	564	166	1.63	202	26.0	49.2	7.17		0.64	59.3	0.49	48.6	0.86	0.36	3.71	1.20
FM	4	69	0.15	195	32.0		6.22	0.08	2.09	3.22	178	132	2.00	252	98.6	36.7	0.33		0.28	215	4.04	92	3.26	0.04	2.85	3.76
		18	0.29	94.9	12.7		4.15	0.03	3.24	0.48	176	17.5	0.60	160	11.9	24.6	0.05		0.24	117	8.07	16.1	2.07	0.06	0.53	1.12
FC	10	63	0.95	150	42.1	0.25	114		0.20	5.66	13.9	147	2.08	217	382	15.9	0.62		0.03	233	0.01		6.66	165	6.18	3.04
		7	2.99	164	16.9	0.72	171		0.41	5.72	25.6	83.8	0.84	51.4	611	10.7	0.03		0.10	23.8			3.96	170	4.22	0.67
PP	10	70	0.84	208	30.9	40.1	43.9		1.14	2.01	99.0	131	2.92	243	150	7.16	17.2		0.22	285	0.40	201	4.57	0.85	1.04	2.48
		13	1.19	621	12.4	44.2	113		2.15	1.30	153	54.6	2.70	116	223	9.03	20.8		0.35	63.7	1.2	502	2.06	1.10	1.23	0.78
FF	9	73	0.32	523	59.5	42.1	27.2		0.26	2.21	62.9	137	2.56	222	147	12.1	5.43		0.44	257	**<0.01**	151	3.76	0.21	11.1	6.13
		9	0.61	1279	40.0	60.0	63.6		0.80	2.77	85.6	64.8	2.29	109	184	11.3	6.83		0.44	54.2		364	1.41	0.36	20.2	9.80
FS	10	74	1.09	237	130	81.4	90.2		0.86	3.51	9.94	290	1.49	275	182	7.27	12.9		0.61	316	12.6	938	6.64	0.97	1.53	3.70
		12	2.20	391	56.9	71.9	82.6		2.35	1.57	17.9	284	0.68	165	106	11.5	17.0		0.44	47.0	39.9	913	2.283	2.31	1.45	1.72
FR	10	67	0.57	134	120	74.9	88.9		0.01	1.93	39.9	152	1.94	180	223	15.8	8.64		4.26	288	1.28	834	13.2	0.10	3.95	3.93
		7	0.95	199	43.9	101	140		0.00	1.82	39.4	33.6	0.56	77.5	221	11.2	15.3		8.79	34.7	4.03	1233	4.19	0.12	6.34	0.86

Table A3: Mean concentration and standard deviation of metals in muscle from walleye from sampling sites along the Slave, Athabasca, and Peace Rivers. The upper value is the mean and the lower value is the standard deviation. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Summer																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	10	52	2.05	71.1	48.2	52.8	18.3	0.36	0.59	1.79	50.8	113	1.92	512	113	13.3	12.3	1.65	0.48	354	40.2	200	3.84	2.34	5.00	2.84
		10	2.06	183	20.8	35.2	26.9	0.58	1.13	2.18	61.8	28.1	2.17	431	120	11.8	13.3	1.89	1.02	87.6	52.3	370	1.31	7.08	3.89	0.48
FM	10	45	1.20	10.7	44.9	54.2	12.9	0.84	0.52	2.45	115	144	2.10	262	123	20.7	5.79	0.71	0.26	296	74.4	175	4.51	15.4	4.09	2.98
		11	1.74	22.4	19.6	40.3	17.0	1.27	1.01	2.92	138	50.5	1.75	107	53.6	23.2	7.74	1.06	0.27	113	115	262	2.95	35.0	3.58	0.37
FC	10	51	1.83	221	59.7	0.22	19.0	1.19	1.18	2.15	137	347	2.74	195	97.2	20.6	10.8	35.1	0.67	433	165	202	8.37	0.65	6.41	3.36
		3	3.34	216	18.1	0.03	27.1	2.07	1.92	2.20	238	536	2.02	71	19.5	31.7	14.3	84.9	0.67	104	347	333	1.47	1.04	7.50	1.27
FS	10	37	1.52	291	56.3	0.21	74.2	0.86	1.87	5.11	186	103	2.75	234	150	35.3	22.7	1.34	0.83	448	69.4	609	10.94	22.3	8.60	2.67
		8	1.46	594	43.2	0.01	134	1.64	3.15	11.9	282	24.9	1.60	119	105	36.0	38.8	1.06	0.79	96.7	111	1341	4.10	62.7	7.28	0.58
Fall																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	3	42	1.15	181	35.7		14.7	0.11	0.04	1.72	0.06	129	1.36	169	153	7.76	2.23	0.30	1.37	302	0.65	595	5.71	0.70	5.57	2.22
		11	1.99	243	14.6		24.8	0.01	0.00	0.83	0.00	26.0	0.14	161	158	0.30	1.88	0.51	1.25	115	0.03	962	5.85	0.62	6.63	0.30
FM	10	46	1.23	319	20.6	31.0	1.80	0.69	0.30	2.80	7.41	137	1.78	274	55.4	9.97	1.62	24.4	0.89	293	90.6	50.6	3.76	9.52	2.69	2.25
		5	2.50	904	12.9	.	2.95	1.24	0.81	5.56	14.5	72.1	0.67	146	16.4	9.58	1.89	44.3	1.26	137	136	30.9	2.96	28.5	2.72	0.64
FC	5	50	1.24	555	30.5		6.41	0.65	0.04	2.04	22.4	107	2.92	122	91.4	12.0	2.80	11.4	0.67	409	61.2	59.0	6.59	1.37	3.10	2.32
		3	2.58	794	7.06		8.04	1.21	0.00	0.90	43.9	34.2	1.85	25.1	42.5	4.86	2.30	22.9	0.41	79.4	69.4	33.2	1.01	2.31	3.03	0.26
FS	10	49	0.20	250	90.4	9.73	109	0.21	0.91	5.58	35.5	226	3.67	505	107	25.0	10.6	7.23	0.77	509	12.4	653	16.5	6.20	5.41	4.58
		6	0.46	431	119	21.3	187	0.31	1.18	10.2	37.2	197	3.06	260	86.1	15.6	14.5	13.4	0.25	90.1	24.1	1139	7.88	9.89	3.97	2.48
FR	10	47	0.61	140	55.4	0.20	3.50	0.34	2.82	5.85	30.1	123	1.47	272	56.1	15.4	4.35	1.07	0.56	455	4.21	34.3	15.7	14.4	3.50	2.79
		7	1.55	162	33.8	0.02	7.60	0.72	6.29	13.9	44.0	22.8	0.49	173	14.0	11.0	6.21	2.52	0.13	53.4	9.82	18	5.61	27.1	3.62	0.38
Spring																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	7	47	2.30	187	25.9		24.7	0.09	3.11	4.69	609	196	4.55	308	125	806	20.8		0.66	325	4.91	495	5.38	0.12	6.05	3.86
		3	2.46	136	14.4		56.9	0.03	7.19	4.30	1169	127	4.78	129	107	1881	31.5		1.19	63.0	7.21	1170	2.15	0.12	6.39	1.29
FM	10	44	2.03	373	31.5		6.71	0.08	1.63	3.08	432	196	3.60	312	95.4	57.4	7.05		0.64	323	3.95	84.0	10.7	1.41	5.30	3.75
		3	6.12	398	15.3		7.66	0.04	2.92	1.02	719	78.2	2.84	134	30.5	89.4	11.0		0.51	91.3	5.49	24.8	4.78	4.01	4.91	0.61
FC	8	49	0.54	114	32.6	4.05	27.9		1.23	2.71	24.0	327	2.70	232	120	7.83	18.4		0.31	321	0.01	641	10.6	305.62	3.13	3.21
		7	0.95	172	11.6	10.4	68.7		3.46	2.74	29.5	461	1.98	131	27.6	3.56	43.5		0.53	32.3	0.00	1055	5.36	626	1.99	0.87
PP	9	53	1.22	73.3	24.0	66.9	9.45		3.36	1.60	107	361	2.86	260	79.4	354	33.3		0.43	384	13.9	38.4	6.56	7.99	3.71	2.72
		9	2.51	121	9.90	120	11.3		7.99	0.73	233	708	1.56	90.1	32.1	832	89.8		0.92	59.5	31.7	24.9	1.88	10.00	7.68	0.90
FF	10	56	0.98	295	32.5	82.5	11.7		1.08	1.40	5.86	139	1.60	244	117	30.4	33.0		0.07	376	0.01	92.1	6.29	4.33	1.23	2.80
		6	1.53	585	7.45	66.9	23.3		3.41	1.09	18.5	55.5	1.90	118	116	58.8	98.5		0.20	72.3	0.00	167	1.65	7.50	1.51	0.65
FS	10	56	0.75	264	95.7	23.4	7		0.49	1.60	52.7	168	3.89	284	79.4	13.3	2.43		1.08	336	0.01	37.1	19.3	2.39	2.70	2.65
		3	1.74	438	131	28.9	8.80		1.51	2.29	50.0	66.0	5.99	111	37.8	18.3	3.18		1.79	41.4	0.00	10.5	5.22	4.54	2.11	0.65
FR	9	47	2.13	258	67.8	55.2	16.8		3.44	1.73	28.4	199	3.47	223	103	13.1	3.67		1.12	370	38.9	103	18.8	0.07	3.98	3.24
		9	4.55	426	42.5	84.3	37.6		10.2	1.42	30.5	95.4	3.01	125	38.3	17.6	6.20		1.28	124	113	174	6.76	0.16	6.33	1.20

Table A4: Mean concentration and standard deviation of metals in muscle from whitefish from sampling sites along the Slave, Athabasca, and Peace Rivers. The upper value is the mean and the lower value is the standard deviation. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Summer																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FM	10	42	1.28	261	72.2	26.6	0.92	0.63	2.55	13.9	208	155	8.94	46.1	185	44.0	6.52	0.99	0.72	460	109	130	1.80	3.95	6.01	3.09
		4	1.74	355	50.0	31.3	1.36	1.09	5.95	21.1	284	42.1	18.4	18.7	110	53.0	6.23	0.55	0.67	287	154	26.5	0.45	5.85	4.34	0.67
FC	10	41	0.92	55.1	118	0.28	62.8	0.77	0.99	6.95	52.0	142	2.24	36.1	139	18.1	6.52	1.68	0.86	337	0.75	452	2.59	1.19	10.5	3.38
		3	1.59	95.5	55.1	0.06	161	1.21	1.49	5.63	107	37.5	0.87	23.0	63.8	18.6	7.62	2.33	0.74	89.0	0.16	621	0.85	1.88	8.54	0.96
FS	7	41	1.31	74.9	132	0.21	40.2	0.45	0.64	3.86	70.0	117	2.40	37.9	151	26.1	4.06	2.46	9.14	400	74.0	481	4.47	30.3	11.2	2.57
		3	1.39	160	80.8	0.02	71.9	0.40	0.75	2.42	152	53.0	1.64	7.22	31.7	32.7	5.14	4.44	23.1	187	93.4	636	3.73	78.4	8.71	0.51
FR	10	39	7.31	162	89.4	0.22	57.5	0.12	0.40	4.21	147	157	1.75	42.5	144	16.8	11.9	3.08	0.17	457	382	814	3.64	1.30	5.58	2.79
		2	10.6	145	41.6	0.02	124	0.05	0.67	2.40	156	132	1.49	11.3	35.4	25.9	3.29	3.50	0.20	60.7	422	1816	0.99	2.77	7.71	0.78
Fall																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	9	42	0.30	78.8	12.6	23.6	6.22	0.55	0.89	5.59	17.6	235	3.00	102	144	16.9	2.67	15.2	0.54	305	2.04	124	1.37	1.82	5.85	2.36
		4	0.59	99.3	11.1	20.7	7.79	1.05	0.89	6.15	19.1	243	3.75	83.1	32.2	11.8	4.14	31.1	0.48	83.9	4.34	181	1.02	3.28	3.53	0.77
FM	10	40	1.22	132	29.6		0.47	0.67	0.26	3.09	3.88	145	1.81	31.5	143	8.42	4.08	49.2	0.57	308	17.8	49.9	1.07	1.96	2.39	2.06
		2	2.25	236	14.1		1.47	1.79	0.68	2.30	11.2	113	1.00	18.1	34.1	2.50	6.89	155	0.30	93.2	37.4	22.8	0.82	2.66	1.11	0.52
FC	10	39	0.42	153	37.3	29.8	10.2	1.35	1.13	4.48	75.1	131	1.76	49.2	191	12.8	2.41	0.24	0.66	333	0.70	509	0.57	0.68	7.22	2.62
		3	0.73	233	28.5	23.3	27.3	2.19	1.96	3.76	137	47.3	0.70	47.9	96.4	14.5	1.70	0.56	0.47	80.8	0.06	1450	0.80	0.49	3.85	0.36
FS	10	41	0.91	61.8	107	0.21	16.7	0.73	0.93	9.88	20.3	121	1.98	49.5	122	18.4	6.48	8.93	0.96	440	54.4	354	3.72	0.82	5.94	2.35
		2	1.20	89.4	121	0.01	36.0	1.96	1.41	13.3	29.0	45.9	0.53	35.5	48.7	12.2	6.71	16.0	1.20	88.4	63.9	837	1.67	1.67	5.72	0.42
FR	10	44	0.28	297	230	53.6	93.2	0.62	2.74	2.03	63.1	115	2.93	105.8	176	31.2	6.50	1.11	0.92	478	53.3	842	3.78	4.53	13.63	2.48
		3	0.48	376	189	137	210	1.59	3.10	3.72	66.6	42.8	2.28	36.5	75.4	9.89	8.02	1.70	0.47	96.6	63.5	2010	1.40	4.42	14.8	0.25
Spring																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	4	42	0.01	243	39.1		4.01	0.10	0.01	12.4	340	140	2.56	85.8	158	40.9	4.58		0.36	234	0.01	239	1.54	2.19	7.77	3.35
		2	0.00	123	13.8		4.23	0.04	0.00	1.97	656	18.8	2.60	28.2	24.1	67.2	8.42		0.37	25.3	0.00	39.4	0.44	3.87	5.21	0.43
FM	2	38	2.11	143	17.8		3.81	0.10	1.06	14.0	202	147	2.52	63.5	167	19.7	0.37		0.26	308	3.83	323	1.47	0.08	5.20	5.55
		2	2.98	52.7	3.13		2.05	0.01	1.50	6.53	250	20.2	1.13	11.5	50.3	8.04	0.04		0.37	134	5.41	15.0	0.52	0.11	0.19	1.38
FC	10	43	0.23	371	72.2	38.4	28.5		0.01	12.9	76.1	165	2.17	47.8	209	6.87	30.27		4.26	249	0.01	99.3	3.45	298	6.26	2.83
		6	0.36	751	45.7	57.6	40.4		0.00	5.45	192	74.5	1.19	16.6	97.2	7.05	56.8		12.8	56.3	0.00	50.8	1.30	716	4.88	0.65
FF	8	45	0.61	348	58.2	69.9	42.2		0.01	14.2	52.8	190	3.96	84.5	203	12.2	7.14		0.29	278	0.16	332	3.22	0.14	5.32	3.42
		8	0.59	984	22.2	88.2	85.3		0.00	13.0	71.0	93.8	4.01	50.0	140	13.8	11.9		0.69	42.5	0.42	470	0.70	0.22	5.17	1.01
FS	5	41	1.02	24.1	71.1	38.3	45.8		1.13	5.19	16.2	128	1.50	49.3	167	8.44	10.7		0.35	348	0.01	512	5.01	399	13.2	2.43
		1	1.60	52.5	26.3	57.4	37.7		1.68	5.25	22.4	40.8	0.40	18.0	43.5	9.61	12.1		0.44	107	0.00	424	1.40	779	16.6	0.26
FR	10	40	2.98	79.4	108	107	39.6		7.41	5.38	32.9	150	3.00	50.2	142	7.24	2.07		1.47	309	10.01	417	3.19	0.73	7.90	2.54
		3	4.86	105	63.5	205	105		17.8	4.35	52.4	106	1.66	18.0	62.7	11.1	2.81		3.20	65.2	31.6	996	0.99	1.34	13.1	0.54

Table A5: Mean concentration and standard deviation of metals in muscle from burbot from sampling sites along the Slave, Athabasca, and Peace Rivers. The upper value is the mean and the lower value is the standard deviation. Concentrations are in ng/g wet mass unless otherwise stated. Locations are Fort McMurray (FMU), Fort MacKay (FM), Fort Chipewyan (FC), Peace Point (PP), Fort Fitzgerald (FF), Fort Smith (FS), and Fort Resolution (FR). N= number of individuals analyzed.

Summer																									
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	3	41	1.85	6.32	99.7	27.4	33.7	0.26	2.41	3.37	189	184	2.61	112	140	35.9	10.3	0.47	0.74	384	71.7	470	1.84	0.08	9.65	4.88
		3	0.81	10.6	48.0	38.0	11.0	0.26	3.72	2.70	156	32.9	1.33	29.4	16.6	21.9	5.40	0.43	0.24	78.5	10.2	76.8	0.04	0.07	1.09	0.40
FC	1	56	1.89	77.5	61.6	0.18	2.95	0.09	0.04	3.73	0.05	159	0.84	61.6	140	0.06	9.06	1.02	0.44	483	732	110	3.28	1.04	0.77	3.40
FS	3	48	2.32	93.8	221	26.7	2660	0.24	2.84	13.9	130	185	4.12	149	473	32.4	39.3	3.10	1.09	322	141	6450	2.23	1.86	20.37	5.31
		10	0.45	153	256	45.9	4555	0.25	4.21	24.0	143	72.5	1.09	93.4	505	20.6	68.0	3.17	0.02	61.4	66.9	10933	0.73	3.22	7.46	2.94
FR	10	62	1.03	60.8	188	42.0	139	0.24	0.40	1.78	78.7	127	1.71	112	169	14.1	3.21	1.10	0.17	290	86.7	484	3.17	0.06	4.97	3.15
		5	1.33	86.4	30.9	57.3	423	0.31	0.63	2.48	93.6	28.8	1.02	43.2	59.9	18.0	4.36	0.92	0.20	39.4	186	1243	1.89	0.18	4.21	0.48
Fall																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FM	2	55	2.16	178	51.1		9.18	0.10	1.76	2.76	2.45	137	2.51	127	155	7.66	0.93	15.4	0.33	272	0.58	131	0.01	0.29	3.77	3.16
		1	3.05	34.1	25.7		2.12	0.00	2.44	0.29	3.38	13.7	0.36	41.4	9.22	1.23	0.28	21.7	0.01	29.6	0.00	5.31	0.00	0.35	0.51	0.90
FC	3	58	0.16	78.1	43.5		13.5	0.09	0.74	3.07	16.7	120	2.42	56.2	161	9.86	5.31	272	1.51	358	108	107	0.93	1.09	2.65	2.50
		3	0.28	135	15.4		8.78	0.01	0.69	0.82	21.9	8.6	1.61	7.26	84.5	3.27	1.78	243	0.90	30.0	69.9	43.0	0.27	0.94	0.94	0.21
FS	3	61	**<0.01**	305	141		220	0.92	19.4	3.52	0.05	98.9	2.64	154	218	7.83	7.12	17.4	1.11	412	32.7	1473	0.99	0.67	3.07	2.84
		5		527	81.8		166	1.42	33.1	2.01	0.00	26.4	1.76	61.5	14.5	2.01	7.05	30.2	0.72	134	29.1	1251	0.71	0.59	1.95	0.64
FR	8	62	0.73	659	111	45.3	25.6	0.47	2.17	35.14	47.8	142	2.98	185	215	19.3	11.4	14.2	1.16	378	49.8	178	1.63	0.79	7.10	2.97
		5	1.38	985	61.9	71.6	39.8	0.81	2.19	95.6	48.2	31.5	0.72	113	37.6	10.1	10.1	20.2	1.04	52.0	46.1	254	0.50	0.89	2.55	0.61
Winter																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FR	10	64	2.62	423	151	0.17	13.3	0.09	0.96	0.83	19.8	127	1.63	158	115	13.7	1.80	1.91	0.67	301	43.2	75.2	3.51	1.00	3.35	3.17
		4	5.74	687	41.8	0.02	29.3	0.01	1.68	0.78	22.7	31.0	0.60	123	24.7	13.0	2.22	4.03	0.32	32.4	63.9	38.5	0.87	0.83	2.12	0.78
Spring																										
Location	N	Length (cm)	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe (µg/g)	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Tl	U	V	Zn (µg/g)
FMU	3	39	0.98	258	92.5		238	0.06	1.03	8.32	151	290	4.50	109	421	29.0	0.31		0.36		0.01	1720	2.39		8.31	5.96
		3	1.69	143	29.2		315	0.04	1.77	3.82	223	215	2.32	13.0	570	10.6	0.07	.	0.32		0.00	2283	0.13		1.90	1.94
FS	1	74	0.01	0.87	90.8		7.04		0.01	2.93	0.02	176	2.37	368	358	1.97	0.35		1.07	439	0.01	57.1	1.58		5.14	3.80
FR	6	63	0.27	0.36	132	158	51.5		1.12	2.85	109	145	3.30	104	188	13.6	1.92		0.64	281	4.76	67.8	2.33	1.84	3.77	3.35
		3	0.36	0.09	50.9	215	106		2.73	2.37	188	44.8	1.51	40.3	43.8	10.6	2.68		0.78	50.1	11.6	40.8	0.61	3.47	4.08	1.20

Table A6: Analyzed concentrations of methylmercury (MeHg) and inorganic mercury (Hg) in muscle from goldeye (GE), northern pike (NP), walleye (WE), whitefish (WF), and burbot (BB) from Fort Resolution. Concentrations are in µg/g dry mass.

Sample ID	Location	Species	MeHg Concentration	Hg Concentration	Total Hg	ICP-MS Total Hg	%MeHg
FR091	FR	BB	1.72	0.19	1.91	0.82	89.9
FR194			0.71	0.06	0.77	0.22	92.6
FR197			1.26	0.26	1.52	1.47	83.0
FR199			1.19	0.19	1.38	0.72	86.2
FR202			0.93	0.09	1.02	0.52	90.8
FR079		GE	0.89	0.17	1.07	0.51	83.8
FR080			1.05	0.29	1.34	2.05	78.5
FR081			1.69	0.31	2.00	0.89	84.3
FR082			1.32	0.42	1.75	2.14	75.7
FR083			4.26	0.53	4.79	0.67	88.8
FR089		NP	10.35	4.53	14.88	4.65	69.6
FR090			1.59	0.34	1.93	0.72	82.2
FR092			5.67	0.02	5.69	1.41	99.6
FR095			0.96	0.14	1.10	0.45	87.6
FR096			0.93	0.46	1.40	0.58	66.8
FR097		WE	2.04	0.50	2.53	0.94	80.4
FR099			5.35	0.63	5.98	1.67	89.4
FR100			1.93	0.01	1.93	0.99	99.7
FR167			0.99	0.16	1.16	1.59	85.8
FR193			0.65	0.10	0.76	1.14	86.2
FR155		WF	0.30	0.13	0.43	0.23	70.6
FR164			0.36	0.13	0.50	0.58	72.9
FR168			0.58	0.11	0.68	0.78	84.5
FR169			0.33	0.02	0.35	0.43	93.3
FR170			0.22	0.03	0.24	0.59	89.6

Table A7: Analyzed concentrations of methylmercury (MeHg) and inorganic mercury (Hg) in muscle from goldeye (GE), northern pike (NP), walleye (WE), whitefish (WF), and burbot (BB) from Fort MacKay (FM) and Fort Chipewyan (FC). Concentrations are in µg/g dry mass.

Sample ID	Location	Species	MeHg Concentration	Hg Concentration	Total Hg	ICP-MS Total Hg	% MeHg
FC161	FC	GE	2.15	0.46	2.61	1.30	82.2
FC162			1.09	0.32	1.41	0.54	77.4
FC163			0.43	0.13	0.57	-	76.5
FC164			3.00	0.43	3.43	1.17	87.4
FC166			2.53	0.43	2.96	1.08	85.4
FC108		NP	6.38	0.61	6.99	1.82	91.3
FC109			1.59	0.06	1.65	0.69	96.6
FC110			4.28	0.03	4.32	0.95	99.2
FC151			1.92	0.09	2.01	2.35	95.8
FC152			2.78	0.01	2.79	0.92	99.5
FC160		WE	0.53	0.00	0.53	0.46	100.0
FC201			1.80	0.06	1.86	0.61	96.6
FC202			1.21	0.28	1.49	0.60	81.0
FC203			2.91	0.08	2.99	0.87	97.4
FC204			1.40	0.41	1.81	0.58	77.4
FC170		WF	0.34	0.00	0.35	0.81	100.0
FC171			0.28	0.00	0.28	0.14	100.0
FC172			0.11	0.00	0.11	0.08	100.0
FC173			0.09	0.00	0.09	0.24	100.0
FC174			0.20	0.01	0.21	0.14	97.4
FM165	FM	BB	0.90	0.36	1.25	0.53	71.6
FM172			1.24	0.02	1.26	0.85	98.6
FM103		GE	3.83	0.42	4.26	0.93	90.0
FM105			2.10	0.16	2.27	0.60	92.8
FM107			2.08	0.60	2.68	0.89	77.7
FM129			2.36	0.64	3.00	1.10	78.6
FM133			1.51	0.46	1.98	1.73	76.6
FM136		NP	2.16	0.14	2.30	3.34	93.9
FM149			1.43	0.21	1.63	2.67	87.4
FM158			2.46	0.49	2.94	1.11	83.4
FM159			2.68	0.02	2.70	0.83	99.4
FM121		WE	1.52	0.32	1.85	0.70	82.4
FM122			1.28	0.01	1.28	0.66	99.3
FM140			2.06	0.42	2.49	2.97	83.0
FM144			3.06	1.27	4.33	1.52	70.7
FM151			2.53	0.67	3.20	1.37	79.0
FM099		WF	0.18	0.03	0.21	0.17	86.9
FM106			0.11	0.00	0.11	0.08	100.0
FM108			0.11	0.01	0.11	0.11	92.9
FM110			0.09	0.01	0.10	0.10	94.3
FM111			0.80	0.08	0.88	0.39	90.4