Evaluating the concentrations of mercury, priority pollutant trace elements, and polycyclic aromatic compounds in traditionally harvested plant and animal foods of the Bigstone Cree Nation in Alberta, Canada

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Abstract

Traditional foods consumed by Indigenous communities consist of locally-harvested, nutrient-dense animal and plant species. These foods are associated with social, health, and economic benefits for the Indigenous communities, and have often been shown to have higher nutritional value than store-bought foods. Nevertheless, these foods may also contain environmental contaminants. In particular, research in Alberta has shown that the oil sands industry releases elevated levels of multiple essential and non-essential trace elements, considered as priority pollutant elements (PPE), as well as a group of organic pollutants including polycyclic aromatic compounds (PACs) in abiotic matrices such as rivers, soils, sediments, and snowpacks. Thus, release of these contaminants from the oil sands industry into the environment is a concern in local and scientific communities. There has been limited research focusing on measuring these contaminants and nutrients in wild plants, animals, and in animal organ tissues, all of which are consumed as traditional foods by Indigenous communities, including the Bigstone Cree Nation, who are living in close proximity to the oil sands developments in Alberta. The overall objective of this thesis is to determine and compare concentrations of key contaminants and nutrients (can also be toxic if consumed/accumulated in excess) in various food groups (plants and animals, and animal organ tissues) of traditional importance to the Bigstone Cree Nation. The specific objectives are addressed in three chapters: (1) determining the concentrations of total mercury (THg), methylmercury (MeHg), selenium (Se)— thought to protect against Hg toxicity—, and ratios of selenium to mercury (Se:THg) in a comprehensive suite of traditional foods of the Bigstone Cree Nation (Chapter 2); (2) investigating the concentrations of essential and non-essential PPE such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), thallium (Tl),

and zinc (Zn) in a variety of traditional food samples, including multiple plants and animal tissues/organs (Chapter 3); (3) quantifying various classes of PACs including the 16 U.S. EPA priority polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and dibenzothiophenes—sulfur-containing PACs— in these traditional plant and animal foods (Chapter 4). Results of Chapter 2 indicated that compared to the Health Canada and U.S. EPA guidelines of 0.5 μg g^{-1} wet weight (w.w.) and 0.3 μg g^{-1} w.w. for THg (respectively), the levels of THg and MeHg were generally low in plants and animals where none of the samples exceeded the guideline limits. The lowest Se:THg ratios belonged to aquatic animal species (i.e., fish and duck), regardless of tissue type, which could be related to a higher uptake of THg, mostly in the form of MeHg in the aquatic environment. Nonetheless, Se was in molar excess relative to Hg for all the traditional foods (Se:THg ratio >1), suggesting a potentially sufficient amount of Se associates with Hg and mitigates its toxicity. In Chapter 3, the concentrations of PPE showed variations that were dependent on species, tissue, and trace elements. In plants, concentrations of PPE declined in the following order: Zn > Cu > Ni > Cr ~ Pb > As ~ Cd > Ag ~ Tl, while in animals, the order was Zn > Cu > Cd > Cr ~ As ~ Ni ~ Pb ~ Ag (Tl was below the detection limit in all animal samples). Overall, essential PPE concentrations were found to be higher compared to non-essential PPE. This could be related to different uptake rate, homeostasis processes, assimilation of trace elements, and trace elements' primary target tissue/organ. In Chapter 4, among different classes of PACs, alkylated PAHs predominated and accounted for between 63% and 95% of total PAC (∑PAC), while the 16 U.S. EPA priority PAHs accounted for 4% to 36% of ∑PAC. The DBT levels were the lowest and only represented <1% to 14% of ∑PAC in the traditional foods. Results of this chapter shed light on the importance of including a more persistent and potentially more toxic group of PACs, the alkylated PAHs, which are comparatively a less studied class of

PACs than the parent PAHs in the research of traditional food items, particularly in communities residing in close proximity to oil sands extracting activities. The novel contribution of this thesis is that it provides baseline concentration data which was previously lacking for most plants and wildlife species, and also for animal organ tissues either consumed or used for traditional medicinal purposes by the Bigstone Cree Nation residing in Canada's boreal forest in close proximity to Alberta's oil sands developments. At this time, levels of contaminants found in these traditional foods do not pose a public health concern. Since previous studies have already shown elevated levels of contaminants in abiotic matrices in close proximity to the Alberta oil sands developments where Indigenous communities reside, the baseline concentrations from this thesis will be useful for future comparisons of the levels of contaminants and nutrients in traditional foods collected/harvested within oil sands development regions.

Résumé

Les aliments traditionnels consommés par les communautés autochtones consistent en des espèces animales et végétales riches en nutriments récoltées à partir des ressources locales. Ces aliments sont associés à des avantages sociaux, sanitaires et économiques pour les communautés autochtones et se sont souvent avérés avoir une valeur nutritionnelle plus élevée que les aliments traditionnels du marché. Néanmoins, ces aliments peuvent également contenir des contaminants environnementaux. En particulier, des recherches en Alberta ont montré que l'industrie des sables bitumineux libère des niveaux élevés de multiples oligo-éléments essentiels et non essentiels considérés comme des éléments polluants prioritaires (EPP) par l'Agence Américaine de Protection de l'Environnement (US APE), ainsi qu'un groupe des polluants organiques, y compris les composés aromatiques polycycliques (CAP) dans les matrices abiotiques telles que les rivières, les sols, les sédiments et les accumulations de neige. Ainsi, le rejet de ces contaminants de l'industrie des sables bitumineux dans l'environnement est une préoccupation dans les communautés locales et scientifiques. Il y a eu peu de recherches axées sur la mesure de ces contaminants et nutriments dans les plantes sauvages, les animaux et les tissus d'organes animaux, qui sont tous consommés comme aliments traditionnels par les communautés autochtones, y compris la nation crie de Bigstone, qui vivent à proximité de l’industrie des sables bitumineux en Alberta. L'objectif général de cette thèse, dirigée par la communauté, était de déterminer et de comparer les concentrations de contaminants et de nutriments (peuvent également être toxique s’ils sont consommés/accumulés en excès) clés dans divers groupes d'aliments (plantes et animaux, et tissus d'organes animaux) d'importance traditionnelle pour la nation crie de Bigstone. Des objectifs spécifiques ont été abordés dans trois chapitres: (1) déterminer les concentrations de mercure total (HgT), de méthylmercure (MeHg), de sélénium

(Se) - censées protéger contre la toxicité du Hg - et le ratio sélénium / mercure (Se: HgT) dans une gamme complète d'aliments traditionnels de la nation crie de Bigstone (Chapitre 2); (2) étudier les concentrations d'EPP essentiels et non essentiels tels que l'arsenic (As), le cadmium (Cd), le chrome (Cr), le cuivre (Cu), le plomb (Pb), le nickel (Ni), l'argent (Ag) , le thallium (Tl) et le zinc (Zn) dans une variété d'échantillons d'aliments traditionnels, y compris de multiples plantes et tissus/organes d'animaux (Chapitre 3); (3) pour quantifier les diverses classes de CAP, y compris les 16 hydrocarbures aromatiques polycycliques (HAP) prioritaires de l'U.S. APE, les HAP alkylés et les dibenzothiophènes (CAP contenant du soufre) dans ces aliments traditionnels d'origine végétale et animale (Chapitre 4). Les résultats du Chapitre 2 indiquent que, par rapport aux recommandations de Santé Canada et de l'APE des États-Unis, respectivement de 0.5 $\mu g\ g^{-1}$ poids humide pour le HgT et de 0.3 $\mu g\ g^{-1}$ poids humide pour le HgT, les niveaux de HgT et de MeHg étaient généralement faibles dans les plantes et les animaux donc aucun des échantillons ne dépassait les limites de la recommandation. Le rapport Se: HgT le plus bas ont été mesurées chez les espèces aquatiques (c.-à-d. poissons et canards), quel que soit le type d'organe, ce qui pourrait être expliqué par une absorption plus élevée de HgT, principalement sous forme de MeHg dans le milieu aquatique. Néanmoins, le Se était en excès molaire par rapport au Hg dans tous les aliments traditionnels (rapport Se: HgT > 1), ce qui suggérait potentiellement suffisamment de Se pour s'associer au Hg et atténuer sa toxicité. Au chapitre trois, différentes concentrations d'EPP ont été observées selon des espèces, des tissus et des oligo-éléments. Chez les plantes, les concentrations d'EPP ont diminué dans l'ordre suivant: Zn > Cu > Ni > Cr ~ Pb > As ~ Cd > Ag ~ Tl, tandis que chez les animaux, l'ordre était Zn > Cu > Cd > Cr ~ As ~ Ni ~ Pb ~ Ag (Tl était en dessous de la limite de détection dans tous les échantillons d'animaux). Dans l'ensemble, les concentrations essentielles d'EPP étaient plus élevées que celles des EPP non

essentiels. Cela pourrait être lié à différents taux d'absorption, processus d'homéostasie et assimilation des oligo-éléments et des principaux tissus/organes cibles des oligo-éléments. Dans le Chapitre 4, parmi les différentes classes de CAP, les HAP alkylés prédominaient et représentaient entre 63% et 95% du total des CAP (∑CAP), tandis que les 16 HAP prioritaires de l'APE des États-Unis représentaient 4% à 36% du ∑CAP. Les niveaux de DBT étaient les plus bas et ne représentaient que <1% à 14% du ∑CAP dans les aliments traditionnels. Les résultats de ce chapitre mettent en lumière l'importance d'inclure un groupe plus persistant et potentiellement plus toxique de CAP, les HAP alkylés, en tant que classe de CAP relativement moins étudiée que les HAP parentes dans la recherche sur les produits alimentaires traditionnels, en particulier dans les communautés résidant à proximité des activités d'extraction des sables bitumineux. La contribution originale de cette thèse est qu'elle a fourni des données de concentration de base qui faisaient défaut pour la plupart des espèces végétales et fauniques, et des organes animaux consommés ou utilisés à des fins alimentaires / médicinales traditionnelles par la Nation crie de Bigstone résidant dans la forêt boréale du Canada et à proximité des activités d'extraction des sables bitumineux en Alberta, au Canada. À ce point, les niveaux de contaminants trouvés dans ces aliments traditionnels ne posent pas de problème de santé publique pour la Nation crie de Bigstone. Des études antérieures avaient montré des niveaux élevés de contaminants dans les matrices abiotiques, ce qui peut être problématique pour les communautés résidant à proximité des activités/développements des sables bitumineux. Ainsi, les concentrations de base de cette thèse seront utiles pour les futures comparaisons des niveaux de contaminants et de nutriments dans les aliments traditionnels chassé/récoltés dans les régions de développement des sables bitumineux.

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This thesis is dedicated to the Bigstone Cree Nation.

Contribution to Knowledge

This thesis fills important knowledge gaps and contributes to the advancement of knowledge as follows:

I investigated variation in concentrations of total mercury (THg), methylmercury (MeHg), selenium (Se), and selenium to mercury ratios (Se:THg), and priority pollutant elements (PPE). In total, I assessed the concentrations of eleven out of thirteen trace elements listed as PPE by the United States Environmental Protection Agency (U.S. EPA) under the Clean Water Act (currently, there is no such a list as Canadian guideline levels) in different species of plant and animal samples and various tissues including muscle and organs in animals consumed as traditional foods of the Bigstone Cree Nation in Alberta, Canada, who live in close proximity to oil sands activities. Additionally, I evaluated and compared the distribution profiles of various classes of polycyclic aromatic hydrocarbons (PACs) including the 16 U.S. EPA priority polycyclic aromatic hydrocarbons (PAHs) listed by U.S. EPA, alkylated PAHs, and dibenzothiophenes (DBTs) in the traditional foods of the Bigstone Cree community.

Research on traditional foods and Indigenous communities residing in the boreal forest and close to oil sands development is limited. This study moves beyond traditional quantitative measurements of THg and MeHg in muscle tissues of aquatic organisms to analyze and compare the relationship between Hg and Se—as an element that may have positive associations with Hg and therefore mitigates its toxicity— in a wide variety of traditional plants, animals and the animal organ tissues. This study provides an improved understanding that measuring concentrations of not only THg but also MeHg, and potential associations with Se, will convey a more comprehensive approach to toxicological studies. This thesis greatly expands upon PPE data that is mostly available on abiotic matrices in the Athabasca oil sands region and provides

baseline PPE data for a variety of traditional plants and wildlife species for which it is lacking around the Alberta oil sands region. Regarding various classes of PACs, since the U.S. EPA identified the list of the 16 priority PAHs four decades ago most research has been conducted on these priority PAHs. Thus, research on more toxic congeners of PACs such as alkylated PAHs is not well-established. In line with this, most risk assessment studies in oil sands regions of Alberta on abiotic and biotic matrices including soil, water, and fish have been conducted on the 16 U.S. EPA priority PAHs, despite the fact that alkylated PAHs are more prevalent near major oil sands production than the 16 U.S. EPA priority PAHs. This research strengthens the comprehensive toxicological profiling of PAHs by measuring more toxic congeners of PAHs, including alkylated ones that are relatively less studied, in traditional foods of Indigenous communities inhabiting regions adjacent to large industrial activities, such as the Bigstone Cree Nation. The findings of this thesis will help better understand the importance of screening the levels of trace elements and various classes of PACs in these traditional foods as they are regularly consumed by the community for their medicinal or nutritional purposes.

Contribution of Authors

This thesis comprises of three result chapters authored by the candidate and intended for publication. Chapter 2 was designed and developed by the candidate with conjugation with Dr. Niladri Basu. The data for total mercury (THg) and methylmercury (MeHg) was generated in Dr. Basu's lab, while selenium (Se) data was obtained by the assistance of Ms. Hélène Lalande. Dr. Janelle Baker assisted in sample collections and shipments. Dr. Benjamin Barst provided assistance on methylmercury analysis as well as providing comments on the manuscript. Dr. Josie Auger as Chief and member of the Council of the Bigstone Cree Nation (2014-2018) supported the research at the time, and she had provided assistance in facilitating contacts within the community. The candidate was responsible for the study design, laboratory work, data analysis, interpretation of the data, discussion of the results, and preparation of the manuscript. The statistical analysis was conducted with the assistance of Dr. Jose Correa from the Department of Mathematics and Statistics. Dr. Melissa McKinney, the candidate's supervisor, provided constant guidance and advice on all aspects of the study, specifically writing, reviewing and editing. This chapter is co-authored by the candidate's supervisor, Dr. Melissa McKinney, and Drs. Benjamin Barst, Niladri Basu, Janelle Baker, and Josie Auger. This chapter was published in *Chemosphere* on February 21st, 2020 and is formatted in the style of this journal.

For chapter 3, the candidate was responsible for the study design, statistical analysis, and interpretation of the data, discussion of the results, and preparation of the manuscript. Laboratory work was conducted with the assistance and guidance of Ms. Hélène Lalande. This chapter is co-authored by the candidate's supervisor, Dr. Melissa McKinney, who provided detailed feedback on different aspects of the study. Dr. Niladri Basu covered the technical costs and Dr. Janelle Baker assisted with sample collections. Dr. Josie C. Auger facilitated contacts within the

community. This chapter is intended for submission to *Environmental Toxicology and Chemistry* and is formatted in the style of this journal.

For Chapter 4, laboratory analysis was carried out by the AXYS laboratory (AXYS Analytical Services Ltd., British Columbia, Canada) in which Dr. Niladri Basu covered the costs through the available findings allocated to this project. The candidate conducted sample preparation, statistical analysis, and interpretation of the data, discussion of the results, and preparation of the manuscript. Dr. Melissa McKinney provided constant guidance and feedback on the manuscript. Drs. Benjamin Barst, Janelle Baker, and Josie Auger provided feedback on the manuscript. This chapter is co-authored by the candidate's supervisor, Dr. Melissa McKinney, and collaborators including Drs. Benjamin Barst, Janelle Baker, and Josie Auger. This chapter was re-submitted to *Environmental Pollution* in November 13th, 2020 and is written in the format of this journal.

List of Abbreviations

Ag	Sliver
As	Arsenic
BDL	Below Detection Limit
Cd	Cadmium
Cr	Chromium
Cu	Copper
d.d.f.	Denominator of Degree of Freedom
DMA	Direct mercury analyzer
d.w.	Dry Weight
FFQ	Food Frequency questionnaire
GC-MS	Gas Chromatography-Mass Spectrometry
Hg	Mercury
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
InHg	Inorganic Mercury
IPR	Initial Precision and Recovery
MDL	Method Detection Limit
MeHg	Methylmercury
Ni	Nickel
OPR	Ongoing Precision and Recovery
PACs	Polycyclic Aromatic Compounds
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead

PMDL	Practical Method Detection Limit
ppb	Parts Per Billion
PPE	Priority Pollutant Elements
ppm	Parts Per Million
QA/QC	Quality Control/Quality Assurance
RSD	Relative Standard Deviation
Se	Selenium
Se:Hg	Selenium to Mercury Ratio
SRM	Standard Reference Material
SAGD	Steam Assisted Gravity Drainage
THg	Total Mercury
Tl	Thallium
TMDL	Theoretical Method Detection Limit
U.S. EPA	United States Environmental Protection Agency
w.w.	Wet Weight
WHO	World Health Organization
Zn	Zinc

Chapter 1. Introduction

1.1. General Introduction

High global demand for fossil fuel consumption has led to the development of large-scale mining industries such as the oil sands region located in northern Alberta, Canada. Canada's oil sands reserves are estimated to contain 171.0 billion barrels of crude oil, in which 166.3 billion barrels occur in the form of oil sands in Alberta (Natural Resources Canada, 2019). The oil sands reserves are located in three regions; Athabasca (the largest), Cold Lake, and Peace River (National Energy Board, 2018) where bitumen is extracted by traditional surface mining or *in-situ* (below the surface) mining in which the extraction is performed using steam assisted gravity drainage (SAGD) technology. Given the high energy demand, oil sands production is projected to increase by 58% from 2.8 million barrels per day in 2017 to 4.5 million barrels per day in 2040 (National Energy Board, 2018).

Recent studies on lakes, rivers, sediments, snowpacks, and lichens have shown that the oil sands industry releases elevated levels of contaminants, such as trace metals considered as priority pollutant elements (PPE) under the U.S. EPA's Clean Water Act, and a class of organic contaminants broadly known as polycyclic aromatic compounds (PACs), in the Athabasca oil sands region in Alberta, Canada (Giesy et al., 2010; Harner et al., 2018; Kelly et al., 2010; Kelly et al., 2009; Kurek et al., 2013; Landis et al., 2019; Parajulee and Wania, 2014; Schuster et al., 2015). These studies pointed out that reported emissions of contaminants estimated in environmental impact assessments or from the Regional Aquatic Monitoring Program (RAMP) in Alberta, industry, government and related agencies are likely underestimated (Kelly et al., 2010; Kelly et al., 2009; Kurek et al., 2013; Parajulee and Wania, 2014).

The PPE include antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). Some of these elements are categorized as essential (i.e., Cu, Se, and Zn) and possibly essential (presumed to be essential; i.e., Cr, and Ni) as requirements for proper human biological functioning, yet, elevated levels of these elements could be harmful to organisms (Zoroddu et al., 2019). The non-essential PPE (i.e., Sb, As, Be, Cd, Hg, Pb, Ag, and Tl) elements are not required for biological functioning in humans, and they could be toxic to organisms and humans even at low concentrations (Jaishankar et al., 2014; Zoroddu et al., 2019). PACs is a general term which includes different classes of polycyclic aromatic hydrocarbons (PAHs), most notably the 16 U.S. EPA priority PAHs and alkylated PAHs, and the sulfur-containing heterocyclic dibenzothiophenes (DBTs). PACs are well-known for their deleterious health effects, however, most research has been conducted on the 16 parent PAHs, while limited toxicological data is available on other classes of PACs such as alkylated PAHs which are more persistent in the environment and more toxic to wildlife and humans (Andersson and Achten, 2015).

With regard to contaminants released from the oil sands developments into the environment, research showed there was almost 3-fold increase in the deposition of several PPE—namely As, Pb and Hg—into the air from the oil sand activities between 2001 and 2008 (Kelly et al., 2010). Additionally, within 50 km of oil sands facilities in Alberta, the loading of PACs from airborne particulates onto the snowpacks was 391 kg in just over 4 months (Kelly et al., 2009). Studies in the oil sands regions of Alberta emphasised that release of PACs and the thirteen PPE are increased during the spring snowmelt and the washout of rainfall (Kelly et al., 2010; Kelly et al., 2009). They also concluded that the PPE are more widespread than PACs

since they were found up to 85 km from where they originated (Kelly et al., 2010; Kelly et al., 2009). Thus, release of contaminants derived from the oil sands industry may be a potent source of chemical contamination into surrounding ecosystems and could have potential negative consequences for both wildlife and humans (Tenenbaum, 2009). This is an issue of major concern for Indigenous communities reliant on traditional foods residing close to oil sands developments (Donaldson et al., 2012; Donaldson et al., 2010; Van Oostdam et al., 2005).

Given the limited knowledge of concentrations of key contaminants and nutrients in traditional foods of these communities adjacent to the oil sands, the overall objective of this thesis is to provide a baseline assessment of the levels of eleven out of thirteen PPE and various classes of PACs including the16 parent and alkylated PAHs, and DBTs in a broad variety of frequently consumed traditional foods (plants and animals) of the Bigstone Cree Nation located in close proximity to the major oil sands development in the Athabasca region of Alberta. Having this information will improve our understanding of the levels of PPE and various groups of PACs in a fulsome sampling of aquatic and terrestrial plants and animals and their organ tissues, which are consumed as important traditional food items. The results of this thesis will provide valuable insight to many communities, Indigenous or otherwise, who rely on non-seafood items.

In this thesis, I investigate and discuss three result chapters: Chapter 2 focuses on evaluating the concentrations of total mercury, methylmercury, selenium, and selenium:mercury molar ratios. The main objectives of this chapter are two-fold: 1) to determine the concentrations of total mercury (THg), methylmercury (MeHg), selenium (Se), and ratios of Se:THg in a comprehensive suite of traditional food of the Bigstone Cree Nation and; 2) to compare patterns in the associations between THg and Se among kidney, liver, muscle, and brain tissues of

animals. Chapter 3, quantifies the PPE including essential (Cr, Cu, Ni, and Zn) and non-essential trace elements (Ag, As, Cd, Pb, and Tl) with the focus to determine the concentrations of nine out of the thirteen elements listed as PPE under the U.S. EPA's Clean Water Act, specifically to quantify and compare the concentrations of trace elements in food groups (plant or animal), individual species, and tissue types (muscle versus organ). Chapter 4 evaluates the concentrations of various classes of PACs including the 16 U.S. EPA priority pollutants (parent or unsubstituted), alkylated PAHs, and dibenzothiophenes (DBTs) in a wide variety of traditional foods of the Bigstone Cree Nation. Here, I determined the levels of the 16 U.S. EPA priority PAHs, alkylated PAHs, and DBTs in traditional plant and animal foods. Additionally, this chapter characterizes the ring distribution profiles of the 16 U.S. EPA priority PAHs and alkylated PAHs in plant and animal species.

1.2. Literature review

1.2.1. Traditional foods

1.2.1.1. Value to Indigenous communities and contamination concerns

Traditional foods are considered as animal and plant species harvested from local resources (Donaldson et al., 2010). These foods have a significant importance in shaping and sustaining the culture, health, and well-being of Indigenous communities in Canada in several ways; (A) cultural identity: a community's traditional food choices are derived from generations of ancestors that came before them, while food-foraging activities, such as hunting, harvesting, and fishing allows its members to be physically, socially and spiritually engaged (Pufall et al., 2011); (B) socioeconomic status: traditional food sources may be the most affordable source of food for Indigenous communities (Chan et al., 2006); (C) nutritional and health benefits:

consumption of traditional foods can provide higher nutritional value than store-bought foods as they are important sources of fatty acids, vitamins, protein, and other essential nutrients (Gagné et al., 2012; Kenny et al., 2018). Research has indicated that in communities where consumption of traditional foods has diminished or been replaced with store-bought foods, Indigenous communities face nutritional deficiencies and are more prone to develop obesity, type 2 diabetes and cardiovascular disease (Donaldson et al., 2010; Kuhnlein and Receveur, 1996; Kuhnlein et al., 2004). Yet, increasing industrialization has led to spread of various contaminants including trace elements such as mercury (Hg), and a group of persistent organic pollutants such as polycyclic aromatic compounds (PACs) into the environment (Abdel-Shafy and Mansour, 2016; Eagles-Smith et al., 2018; Jaishankar et al., 2014; Lawal, 2017; Rhind, 2009). In particular, contaminants from industrial activities including the oil sands development are readily dispersed at elevated levels into the local abiotic matrices including soil, sediments, snowpacks, and rivers (Kelly et al., 2010; Kelly et al., 2009). Once deposited in these matrices, they may bioaccumulate in organisms via trophic transfer in food webs and consequently result in elevated concentrations among the various tissues of plant and animal species consumed by humans (Abdel-Shafy and Mansour, 2016; Eagles-Smith et al., 2018; Jaishankar et al., 2014; Lawal, 2017). Some Indigenous peoples, living near contaminant point sources have expressed concerns regarding potential contamination of their traditional foods (Baker, 2016; Baker and Westman, 2018).

1.2.1.2. Location of the Bigstone Cree Nation

The Bigstone Cree Nation with total population of 7,455 (Voyageur et al., 2013) and as a part of Treaty 8 agreement (Government of Canada, 1899) is located in northern Alberta, Canada, in close proximity to the Athabasca region, known as the largest and major oil sands

development region in Alberta. The community is surrounded by the boreal forest and particularly four lakes including the North and South Wabasca, Sandy, and Calling which provide unique wildlife habitats with an abundance of traditional foods including fish and wild game in the region (Figure 1.1) (Baker, 2018). This community contains six reserves with a massive land of 21,066 hectares (Voyageur et al., 2013). The majority of the community members prefer to harvest/collect food from the land over imported or store-bought food, however, being in close proximity to the oil sands development regions and influx of large-scale *in-situ* mining are important concerns of the community members (Baker, 2016). Therefore, they were keen to know about the levels of contaminants and nutrients in their traditional foods. The community members are observing changes in their wild food population including caribou distinction in the oil sands regions (Boutin et al., 2012). They have found several species of wild animals such as fish and ducks with deformities, cysts, and also being covered with a thick substance similar to bitumen (J. Baker, personal communication). Due to heavy industrial activities close to their traditional foods such as berry patches, they are travelling farther away from home in order to find food that are not close to oil sands development sites and the food they trust (Baker, 2016). Observing this changes in traditional foods made the community members anxious regarding the levels of contaminants in their foods where they have decided to perform a contaminant monitoring on their frequently consumed plants and animals. The community did not trust companies and government reports to perform a contaminant monitoring on their traditional food samples as research indicated environmental impact assessments in the oil sands regions are likely underestimated (Kelly et al., 2010; Kelly et al., 2009; Parajulee and Wania, 2014). Therefore, they have decided to send their traditional food samples to Center for Indigenous People's Nutrition and Environment (CINE) at McGill University.

Among research that has been conducted on contaminations of traditional foods in Indigenous communities in Canada, limited research has considered Indigenous perceptions of contaminants in traditional foods (Power, 2008). One of the important aspects of this thesis was to consider the Bigstone Cree Nation traditional ecological/environmental knowledge regarding the contamination of their foods as indicators to select frequently consumed traditional plants and animals for testing. Doing this is critically important considering the increasing production of oil sands developments in the region and the stress and anxiety that these developments put on Indigenous communities regarding the accessibility and safety (levels of contaminants) of their wild foods (Baker, 2016). Contamination of traditional foods also disrupt holistic properties of these foods. For examples, several plants such as Labrador tea are used regularly; hence, they are considered as food-medicine by the community members. Community members, notably elders, still consume variety of organ tissue-including liver, kidney, and brain, thus, these organs were also included in this study.

In the Indigenous believe system, food is sacred and must be harvested in a way that is available in the future (Berkes, 1999). Thus, food quality is a prime indicator of when and where to harvest/hunt. For examples, The Bigstone Cree members stopped harvesting berries grown in berry patches close to oil sands developments (Baker, 2016; Baker, 2020). The notion of traditional foods being contaminated is disruptive and has immense consequences on physical and mental well-being of Indigenous communities (Baker, 2016; Baker, 2020), as well as potential interruption of traditional families that are deeply rooted around harvesting and hunting of traditional foods (Parlee et al., 2006).

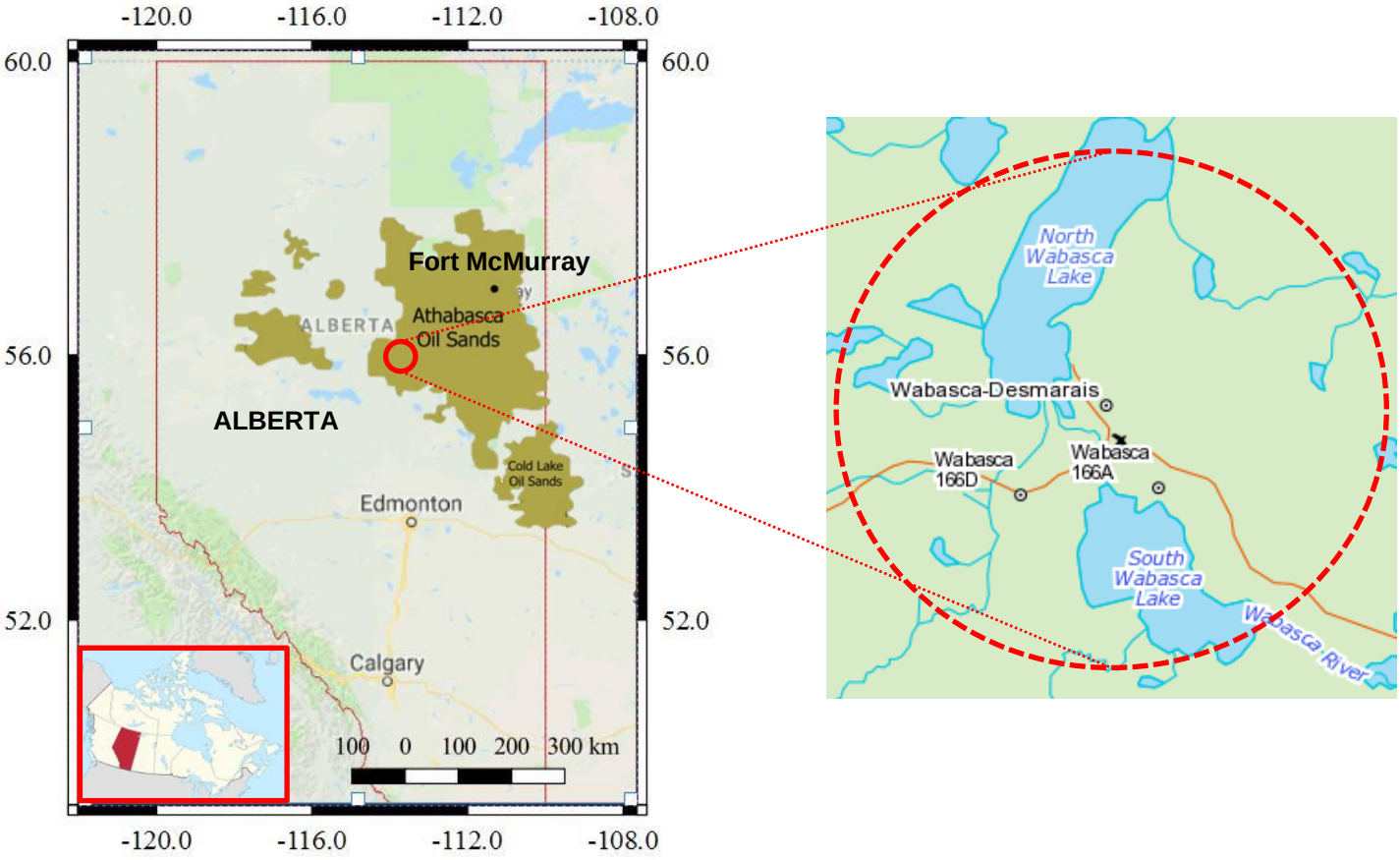

Figure 1.1. Map showing the location of the Bigstone Cree Nation territory (red dashed circle) in Alberta, Canada. General area of the Bigstone Cree Nation reserves' territory covers a significantly larger area (Golzadeh et al. 2020).

1.2.2. Contaminants in the environment and ecosystem

Although pollutants can be released into the environment via natural processes including volcanic eruptions, anthropogenic sources such as fossil fuels account for the majority of contaminants released into the environment (Jaishankar et al., 2014; Rhind, 2009). Contaminants such as PPE and PACs then deposit in terrestrial and aquatic environments and potentially cause

health risks to both wildlife and humans (Abdel-Shafy and Mansour, 2016; Ali and Khan, 2019). Deposition of contaminants in aquatic and terrestrial environment depends on several factors including; (1) microorganisms and/or organisms present that can uptake the contaminants; and (2) chemical and physical changes to the contaminant attributed to microbial activities or environmental conditions (Wright et al., 2018). For example, microorganisms could convert inorganic mercury (InHg) to methylmercury (MeHg), which is known as one of the most bioavailable forms of Hg that can be harmful to organisms and humans (Driscoll et al., 2013). Of all the PPE, research has indicated that Hg has the strong ability to bioaccumulate and biomagnify within organism and food webs (Driscoll et al., 2013). PACs are readily degraded, however they can also bioaccumulate in organisms and biomagnify in the ecosystems' food webs, depending on the amount and duration of exposure, uptake, and species ability to metabolize various congeners of PACs (Abdel-Shafy and Mansour, 2016). Exposure to contaminants can accumulate in various target tissues and organs depending on the species and their habitats (terrestrials vs. aquatic), diet composition, and state of development and age (Rhind, 2009), along with the chemical and physical properties of contaminants (Rhind, 2009). Effects of contaminants in animals and humans will depend on a given contaminant's uptake rate and its assimilation factor, which affects how they are degraded, excreted or metabolized by the body (Rhind, 2009).

1.2.2.1. Mercury

Mercury (Hg) is a global pollutant distributed throughout the environment by natural sources, as well as anthropogenic activities, specifically fossil fuel extraction and consumption (Pirrone et al., 2010; Streets et al., 2009). Atmospheric transport is the major pathway of Hg

emissions into the environment; hence, Hg can travel long distances and become deposited into the abiotic matrices including water, soil, and sediments (Driscoll et al., 2013). The three most common forms of Hg are elemental (Hg^0), inorganic (InHg: Hg^{1+} and Hg^{2+}) and organic Hg such as methylmercury (MeHg; CH_3Hg), which is a highly toxic form of Hg formed by the transformation of InHg by anaerobic bacteria (Driscoll et al., 2013). Once formed, MeHg bioaccumulates in organisms and biomagnifies in food webs (Driscoll et al., 2013), being readily available in aquatic and wetland habitats since methylation occurs under anoxic (low to no oxygen) conditions (Driscoll et al., 2013). Most research has focused on measuring total mercury (THg) in traditional foods (Evans and Talbot, 2012; Kinghorn et al., 2007) with the main focus being on seafood meats (i.e., muscle tissues). Therefore, limited research has been conducted on levels of MeHg as the more toxic form of Hg. A great deal of research being done on aquatic organisms found that humans are predominantly exposed to MeHg through eating aquatic organisms (Sheehan et al., 2014), however, recent studies are drawing attention to the fact that exposure to Hg can take place through consumption of other food sources, including organ tissues of terrestrial animals and rice (Gamberg et al., 2016; Zhao et al., 2019). Additionally, in most of the research conducted on aquatic organisms, MeHg has been usually measured in only the muscle tissues (i.e., meat). Therefore, limited data is available on measuring MeHg in organ tissues, especially in terrestrial animals which indicates a gap in knowledge in the occurrence and distribution of MeHg in food other than fish flesh (Chan and Ing, 1998; Chan et al., 1995; Evans and Talbot, 2012; Gamberg et al., 2016).

As top consumers in the food chain, humans likely face an elevated consumption of MeHg, which could pose a threat to their health, since MeHg (1) can easily cross the blood-brain barrier by forming a structure that mimics an amino acid called methionine (Clarkson and

Magos, 2006); (2) is highly stable; (3) is slowly eliminated (Bernhoft, 2012); and (4) can exhibit neurotoxic effects even at low concentrations, leading to cognitive disorders and other well-established deleterious health effects (Bjørklund et al., 2017). Not surprisingly, MeHg has been widely researched for its potential to accumulate in the central nervous system and subsequently have neurotoxic effects. Among several documented cases of Hg poisoning around the world, residents of Minamata, in Minamata Bay, Japan, began showing signs of extreme illness and death after consuming fish and shellfish in 1956; they experienced neurological symptoms, such as paralysis, sensory disturbance, deafness, speech impairment, and mental disorders, collectively referred to as Minamata disease (Ekino et al., 2007). This incident served as one of the first major instances in which MeHg was recognized as a neurotoxin with the central nervous system and the brain as its primary targets (Harada, 1995).

Communities with a staple source of traditional foods contaminated with Hg may still be at risk. Children are particularly at a higher risk for the toxic effects of Hg exposure, more so than adults, due to their developing systems and lower neurologic-effect threshold (Ha et al., 2017). Even during pregnancy, there has been data consistently showing that MeHg is transferred to the fetus via the placenta; in fact, the fetal cord's MeHg blood concentration is higher than the corresponding maternal concentration, at a ratio of approximately 1.7 (Stern, 2005). There is evidence from various regions worldwide of poorer neurological status and delayed development, as well as inferior performance on language, memory and attention tests in newborns previously exposed to MeHg *in utero* (Kim et al., 2016; Yorifuji et al., 2016; Yorifuji and Tsuda, 2016). A study by Jacobson et al. (2015) found that "children with cord Hg concentration of $\geq 7.5\mu g/L$ were four times as likely to have an IQ score of lower than 80, which is considered as the clinical cut-off for intellectual disability". A Nunavik study on Indigenous

communities in northern Canada revealed how subtle effects of chronic Hg exposure may extend to adults as well. This was based on a sample of 732 Inuit participants aged 18 or higher for which Hg exposure was correlated with a corresponding increase in blood pressure and pulse pressure, and consequently cardiovascular diseases (Valera et al., 2013; Valera et al., 2009).

1.2.2.2. Role of selenium in mercury mitigation

Selenium (Se) is an essential element that occurs in the environment from natural and anthropogenic sources (Mehdi et al., 2013). As a micronutrient, it is required for healthy metabolic and central nervous system functioning (Mehdi et al., 2013), providing protective effects to key organs such as the brain since it behaves as an antioxidant (Steinbrenner and Sies, 2013). Since the affinity of Hg to Se is several orders of magnitude greater than Hg to sulfur (thiol groups) (Khan and Wang, 2009), Se may have the ability to mitigate the toxicity of Hg by decreasing its bioavailability through a variety of mechanisms (Spiller, 2018); (1) it binds to InHg and forms an insoluble, stable and inert Se:Hg complex; (2) demethylation of MeHg to InHg is facilitated; (3) Hg absorption from the gastrointestinal tract into the blood stream may be reduced (Spiller, 2018). The Se:Hg binding in a biological system can also decrease Se storage, and cause Se deficiency since less Se will be available for biological functions (Spiller, 2018). Previous research has pointed out that in a biological system if Se is available in excess amount compared to Hg (i.e., Se:Hg molar ratio ≥ 1), then there may be positive associations between Se and Hg which reduces the toxicity of Hg in animals and humans who consume them (Peterson et al., 2009; Sormo et al., 2011).

1.2.2.3. Priority Pollutant Elements (PPE): essential and non-essential trace elements

Studies in the oil sands regions of Alberta have indicated elevated levels of trace metals, considered as PPE under the U.S. EPA's Clean Water Act, and include essential and non-essential trace elements except for Se. Trace elements —also known as heavy metals— are naturally occurring elements found throughout the earth's crust and rocks, however, most environmental contamination and human exposure arise from anthropogenic activities, such as fossil fuels operations and industrial production (Ali et al., 2019; Jaishankar et al., 2014; Rhind, 2009). Trace elements were originally defined as metallic elements of relatively high density in comparison to water, since metallic elements were originally grouped according to their physical density, and therefore were called heavy metals (Duffus, 2002). However, over time research demonstrated this trait as a poor predictor of their biologically adverse effects; therefore, other criteria, namely atomic weight and number, and different chemical properties or toxicity, were developed to functionally group these elements (Duffus, 2002). In classifying such metals, several terms predominate: light versus heavy metals (defined by molecular weight), essential versus non-essential, as well as toxic and trace metals/elements (Duffus, 2002). A more defined term is "trace element" because these elements could be present in trace concentrations (i.e., low ppb to < 10 ppm range) in various environmental matrices and they can be toxic even at trace amount (Tchounwou et al., 2012).

The essential and possibly essential PPE (i.e., required for bodily function) are involved in many biochemical and physiological regulatory functions for both animals and plants (Tchounwou et al., 2012; Zoroddu et al., 2019). They are important components of organometallic enzymes involved in various oxidation-reduction reactions (Jaishankar et al., 2014). However, if available in excess relative to an organism's body requirements, they can

disrupt normal biological functioning (Prashanth et al., 2015). Some elements such as Cr and Ni are known as possibly essential elements since they are presumed but not established to be essential for humans (Zoroddu et al., 2019). The determination of toxic versus optimal intake of essential trace elements depends on the regulation of the concentrations of these elements by homeostatic (regular physiological) processes in organisms (Aliasgharpour and Rahnamaye Farzami, 2013). By contrast, non-essential PPE could be toxic even at trace amounts (i.e., very low concentrations) since they are not required for bodily functions (Tchounwou et al., 2012). Physiological disruptions due to presence of trace elements can occur primarily through: (1) accumulation of toxic metals in key organs including kidney, liver and brain; and (2) exposure to toxic elements that may alter the biological function of micronutrients by displacing them and interfering with their vital roles in maintaining health (Jaishankar et al., 2014; Singh et al., 2011). PPE can cause major damage to cellular processes by displacing the essential elements (Flora et al., 2008). Oxidative stress can also occur as these elements have the ability to bind to DNA and nuclear proteins leading to deleterious health effects (Flora et al., 2008). Research indicates that the excessive amount of several trace elements (i.e., arsenic (As); cadmium (Cd); and lead (Pb)) in human food is associated with significant health issues, including cardiovascular, kidney, nervous system, and bone disease (Jaishankar et al., 2014). For example, studies on humans demonstrate that Cd toxicity can harm the lungs, kidneys, bones and cause renal dysfunction (Bernard, 2008; Satarug, 2018), while nickel (Ni) toxicity can cause damage to the lungs, nasal passages, and skin (Kim et al., 2015). Furthermore, another study measured Cd and Pb in the blood of mothers and children living close to a metal refinery in Germany, and revealed their blood contained elevated amounts of both non-essential trace elements compared with those living in rural areas (Wilhelm et al., 2005). Additionally, research has linked Pb exposure to

neurological disorders and behavioural abnormalities, concluding that long-term low-level Pb exposure in children may lead to their diminished intellectual/cognitive ability (Koller et al., 2004).

For Canada, research on essential and non-essential metals in traditional foods have focused mostly on measuring several trace metals, including Cd and Pb, such as those consumed by Baffin Inuit in the Arctic, for which metals concentrations exceeded those in corresponding market foods (Chan et al., 1995). The exposure assessments of these foods in Inuit adults (at least 20-years old) and children (3 to12-years old) revealed that some traditional foods such as ring seal meat were major contributors to Cd and Pb exposure in this community (Chan et al., 1995). After Kelly et al. (2010) drew attention to elevated levels of PPE in abiotic matrices including, rivers, soil, sediments, and snowpacks, in Alberta, recent research has started to look at levels of PPE in biotic matrices in the oil sands of the region, yet, this was limited to only several trace elements and species. In a recent study in First Nation communities in Alberta, Cd was measured in moose muscle and organs, including liver and kidney, which resulted in that consumption of moose liver and kidney should be limited compared with moose muscle in order to reduce health risk to the community members (McAuley et al., 2018a). Furthermore, another study measured Pb concentrations in grouse breasts, a subsistence traditional food in Indigenous communities in Alberta (McAuley et al., 2018b), and found that grouse shot with a gun containing lead bullets posed a significantly higher dietary risk compared to grouse that were not shot (McAuley et al., 2018b). Levels of various essential and non-essential trace elements were also detected in different species of berries in Alberta (Shotyk, 2020; Stachiw et al., 2019), which showed that the variation in concentrations of these elements was dependent on uptake by different species from soil, and/or atmospheric deposition on various parts of the plants (i.e.,

root, leaf, and fruit). Trace elements were also measured in various teas, including Labrador and mint tea, of First Nations communities in northern Alberta. In this study, various trace elements were measured in raw tea leaves and also in brewed tea and results showed that the concentrations of trace elements were lower in brewed tea than in raw tea leaves (McAuley et al., 2016). This finding is important since cooking/food preparation methods may affect the availability of trace elements in a given tissue and therefore, should be considered in studies evaluating exposure of contaminants from traditional plant samples.

1.2.2.4. Polycyclic aromatic compounds (PACs)

Polycyclic aromatic compounds (PACs) are a group of organic contaminants with a structure consisting of two to seven fused benzene rings in linear, clustered, or angular arrangements (Abdel-Shafy and Mansour, 2016; Lawal, 2017). Several thousands of individual congeners of PACs are formed from natural biological processes as well as the incomplete combustion of natural sources, such as forest and bush fires, or that of anthropogenic sources including various industries and motor-vehicle emissions (Abdel-Shafy and Mansour, 2016). Those PACs generated during the incomplete combustion of organic materials at high temperatures (i.e., 350°C to more than 1200°C) under low or no oxygen conditions include pyrogenic PACs, which contain 16 parent (or unsubstituted) polycyclic aromatic hydrocarbons (PAHs) listed by the U.S. EPA as priority compounds (Abdel-Shafy and Mansour, 2016). Unlike the parent PAHs, petrogenic PAHs are formed at lower temperatures (100–150°C) for millions of years over geologic time scales (Abdel-Shafy and Mansour, 2016). This group of PACs includes alkylated PAHs and the DBTs, that are sulfur-containing PACs which occur naturally in bitumen and other petroleum products (Abdel-Shafy and Mansour, 2016; Harner et al., 2018). Another important

factor in identifying the toxic profile of PACs are the number of benzene rings and molecular weight, because high-molecular weight PAHs (≥ 4 rings) persist longer in the environment due to their lower vapour pressure, lower volatility, higher hydrophobicity (more lipophilic, less soluble in water) and greater resistance to breakdown (e.g., low water solubility); hence, they can potentially bioaccumulate in organisms (Abdel-Shafy and Mansour, 2016; Lawal, 2017). Furthermore, some PACs can become much more toxic in the presence of ambient solar light compared with laboratory conditions (Giesy et al., 2010). Of the PACs, the 16 parent/unsubstituted PAHs are listed as the U.S. EPA priority list because they are readily found in the environment, thus making them the focus of many investigations to date. This has left other PACs including the alkylated PAHs that are more persistent in the environment relatively understudied (Andersson and Achten, 2015). This has likely led to a significant underestimation of the toxicity and risks of alkylated PAHs in biota, wildlife and humans. The environmental concerns about PACs are important since a recent study indicated that high levels are released into snowpacks, and the Athabasca river and its tributaries due to oil sands mining and processing in Alberta (Kelly et al., 2009). In Kelly et al. (2009) study, sampled snow indicated that PACs deposition increased near the oil sands upgrade facilities. The concentrations of PACs also increased in the Athabasca tributaries during spring, due to the melting of the snowpacks which may have toxic effects on fish embryos as several native species of fish in the Athabasca river spawn in spring and early summer in snow melting period.

Other than smokers and occupational exposure, ingestion is the primary way to encounter PACs and this accounts for 90% of the exposure in humans (Singh et al., 2018). Yet, risk assessments associated with human exposure to PACs remain limited since most studies have focused on measuring the 16 U.S. EPA priority PAHs in comparison with potentially more

harmful groups of PACs, such as the alkylated PAHs (Andersson and Achten, 2015). Studies on health effects of the 16 U.S. EPA priority PAHs are well-stablished with indication of some congeners being mutagenic and carcinogenic (Idowu et al., 2019). A review study on "health effects due to exposure to polycyclic aromatic hydrocarbons from the petroleum refining industry" indicated that PACs can affect health in multiple ways, including causing various cancers (lung, pleural, skin, bladder, prostate, stomach, myeloma, leukemia, and kidney) (Montaño Soto and Garza Ocañas, 2014), as well as preterm birth and pulmonary dysfunction (Montaño Soto and Garza Ocañas, 2014). Another study assessed the association between childhood hematologic cancer (lymphocytic leukemia) and residential proximity to oil and gas development. They determined that the demographic aged 5–24 years were more likely to be diagnosed with a hematological cancer than be diagnosed with a non-hematologic cancer when living within 16.1-kilometers of an active oil and gas development (McKenzie et al., 2017).

Studies on First Nations communities living close to oil sands development activities indicated low to negligible cancer risks based on PAHs measured in the air, soil and fish (Irvine et al., 2014; Ohiozebau et al., 2017). In this context, however, we should keep in mind that only the 16 U.S. EPA priority PAHs have been measured and not any alkylated PAHs, which are known to be more harmful to human health (Irvine et al., 2014; Ohiozebau et al., 2017). One study of cancer risk to First Nations' people from exposure to PAHs near *in-situ* bitumen extraction in Cold Lake, Alberta, measured the 16 U.S. EPA priority PAHs in soil and air for exposure from inhalation or inadvertent soil ingestion, finding negligible cancer risks associated with these levels of PAH exposure to this particular community (Irvine et al., 2014). Recently, the potential health risks posed by 16 U.S. EPA priority PAHs were investigated by measuring them in muscle tissues of fishes from the Athabasca and Slave Rivers, Canada; this work

concluded “the average lifetime risk of additional cancers for humans who consumed these fish” was deemed to be within an “acceptable” range (Ohiozebau et al., 2017). Unfortunately, research on alkylated PAHs in traditional foods in Canada is disproportionately limited. Thus, in order to have a comprehensive toxicological understanding of PACs, measurements of a more toxic class of PACs, including alkylated PAHs, should be included in future studies conducted in close proximity to the oil sands mining developments. Another critical factor to consider in toxicological research is interactions between essential and non-essential trace elements (i.e., Hg and Se). Having a more comprehensive approach in toxicology is important to help better understand the real-life exposure. Wildlife and humans are not only exposed to one contaminant but a pool of contaminants and nutrients that may have additive, synergic, or antagonistic effects. Thus, these interactions may imply different toxicological profiles.

This thesis had limitations in which risk of exposure through consumption of traditional foods and the source of contaminants release whether they are from the oil sands industry or long-range transport were not assessed.

Chapter 2. Evaluating the concentrations of total mercury, methylmercury, selenium, and selenium:mercury molar ratios in traditional foods of the Bigstone Cree in Alberta, Canada

2.1. Abstract

Traditional foods provide nutritional, social, and economic benefits for Indigenous communities; however, anthropogenic activities have raised concerns about mercury (Hg), especially methylmercury (MeHg), in these foods. This issue may be of particular concern for communities near large industrial activities, including the Bigstone Cree Nation adjacent to the Athabasca oil sands region, Canada. This community-led study sought to assess variation in THg and MeHg concentrations among traditional food types (plants or animals), species, and tissues (muscles, organs), and variation in concentrations of the micronutrient selenium (Se)—thought to protect against Hg toxicity—and Se:THg ratios. Thirteen plant and animal species were collected in 2015 by Bigstone Cree community members. We quantified THg, Se, and Se:THg ratios in 65 plant and 111 animal samples, and MeHg in 106 animal samples. For plants, the lichen, old man's beard (*Usnea* spp.), showed the highest concentrations of THg and Se (0.11 ± 0.02 and 0.08 ± 0.01 μg g^{-1} w.w., respectively) and also had a low Se:THg molar ratio. Concentrations of THg, MeHg, and Se differed among animal samples ($P < 0.010$), showing variation among species and among tissues/organs. Generally, concentrations of THg and MeHg were highest in aquatic animals, which also had relatively low Se:THg molar ratios. Overall results revealed substantial variation in the patterns of THg, MeHg, Se and Se:THg ratios across this comprehensive basket of traditional foods. Thus, measuring concentrations of THg alone,

without considering MeHg and potential associations with Se, may not adequately convey the exposure to Hg in traditional foods.

2.2. Introduction

Traditional foods, consisting of animals and plants harvested from natural resources, (Donaldson et al., 2010), have been directly linked to social, health, and economic benefits for Indigenous communities worldwide (Kuhnlein, 2015). Community consumption of these foods has often been shown to provide higher nutritional value than store-bought foods (Kuhnlein, 2015; Sheehy et al., 2015). Nonetheless, elevated levels of mercury (Hg) in traditional foods in Canada and elsewhere is the subject of on-going, and in some regions growing, concern both in local and scientific communities (Van Oostdam et al., 2005; Evans and Talbot, 2012; Juric et al., 2017). Although environmental Hg can come from natural sources, Hg is a global pollutant associated with anthropogenic activities, particularly fossil fuel extraction and use (Driscoll et al., 2013), and poses substantial risk to the environment and to human health (Eagles-Smith et al., 2018). Most studies on mercury in traditional foods have focused on measuring only total mercury (THg) (Chan and Receveur, 2000; Kinghorn et al., 2007; Evans and Talbot, 2012), and mainly in seafood meats (i.e., muscle tissues); thus, there is currently limited knowledge of the levels of the more toxic methylmercury (MeHg), as well as the relative levels of selenium (Se), which may confer antagonistic effects against Hg toxicity, in other traditional foods (Chan, 1998; Kehrig et al., 2009, 2013; Burger et al., 2013). Knowledge on the concentrations of MeHg and Se, and in species/organisms other than seafood, is important as many communities, Indigenous or otherwise, subsist on non-seafood items.

Most of the research concerning level of contaminants in traditional foods and Indigenous people has focused on Inuit and other Indigenous people in the Arctic (Van Oostdam et al., 2005; Donaldson et al., 2010), with far fewer studies investigating these foods in communities living in the boreal forest and close to oil sands developments (Evans and Talbot, 2012). It is thought humans are predominantly exposed to MeHg through eating aquatic organisms (Sheehan et al., 2014), yet some studies suggested human exposure to Hg can occur from consuming other food items, including different organ tissues of terrestrial animals and rice (Gamberg et al., 2016; Zhao et al., 2019). Nonetheless, MeHg is usually measured in muscle (i.e., meat) tissues of these aquatic foods, and even those studies examining tissues and foods other than fish muscle have focused on measuring total Hg (THg), leaving considerable uncertainty as to the occurrence and distribution of MeHg in muscle/organ tissues (Chan, 1998; Evans and Talbot, 2012; Gamberg et al., 2016). Moreover, in Canada, THg concentrations are generally compared to the Health Canada guideline of 0.5 $\mu g\ g^{-1}$ wet weight (w.w.) for edible (i.e., muscle/meat) parts of non-predatory fish/seafood (Health Canada, 2007). This value has been set to 0.3 $\mu g\ g^{-1}$, w.w. by the United States Environmental Protection Agency (U.S. EPA, 2001). However, while appropriate for fish muscle, this guideline level may be inappropriate for some organ tissues, such as kidney where Hg is mostly accumulated as inorganic mercury (InHg) (Chan, 1998). A guideline based on generalizing data from muscle to all other organ tissues may not necessarily provide the best information for dietary Hg exposure.

In contrast to Hg, selenium (Se) is a nutrient that is vital for metabolic (Mehdi et al., 2013) and central nervous system functioning because it behaves as an antioxidant capable of providing potential protective effects to, e.g., the brain (Steinbrenner and Sies, 2013). Furthermore, the affinity of Hg for Se is several orders of magnitude greater than its affinity for

sulfur (-thiol groups) (Khan and Wang, 2009). This might suggest a mitigating role of Se against Hg toxicity by decreasing Hg bioavailability that may also depend on the chemical forms of Hg and Se (Spiller, 2018). Therefore, there may be sufficient Se available in various tissues/organs to bind Hg to create an inert Se-Hg complex (Spiller, 2018). Strong positive correlations between Se and Hg in human organ tissues including thyroid, pituitary, kidney and brain were found in workers exposed to high amounts of InHg (Kosta et al., 1975). This would suggest that if more Hg enters these organs, more Se is retained, providing greater protection against Hg toxicity. Most studies to date have been limited to measuring Se in aquatic organisms and mainly in muscle tissues (Kehrig et al., 2009), similar to Hg studies, thus, the potentially protective effect of selenium (Se) among other foods (i.e., plants and terrestrial animals) and organ tissues is not well known (Chan, 1998; Bordeleau et al., 2016; Gamberg et al., 2016). Several studies have suggested that a tissue with Se:Hg molar ratio ≥ 1 may offer potential protective effects against Hg toxicity in animals species, as an excess amount of Se can bond with Hg, creating an inert Se-Hg complex, and potentially reducing the reactivity/toxicity of Hg (Peterson et al., 2009; Sørmo et al., 2011). Additionally, dietary selenium can potentially decrease Hg uptake in the intestinal tract (Spiller, 2018).

The importance of monitoring concentrations of key contaminants such as Hg, and its association with Se, in a more comprehensive suite of staple traditionally consumed items, including animal-based foods and medicinal plants (hereafter, collectively refer to as foods) is especially acute for Indigenous communities living close to major industrial activities, including the Bigstone Cree Nation near the Athabasca oil sands region in Alberta, Canada. The environment surrounding this development has been shown to contain elevated levels of several pollutants, including Hg, in water bodies, snowpack, and the atmosphere (Kelly et al., 2010; Bari

et al., 2014; Kirk et al., 2014). By considering not only the concentrations of THg, but also MeHg, Se, and Se:Hg molar ratios across a broad sampling of traditional foods, an improved understanding of Hg contamination in these community foods may be achieved. It should be noted that an assessment of exposure to Hg and MeHg from consumption of traditional foods was outside the scope of this study, as consumption data were not collected. The study design also did not permit a determination of the relative contribution of oil sands activities versus other sources including long-range transport, as precise sampling locations were not specified. Location of sampling is an important factor, as research in the oil sands regions indicated that samples taken within 25 km from the oil sands upgrading facilities have likely more concentrations of contaminants than samples taken farther away (i.e., within 150 km) (Studabaker et al., 2012). In this community-led participatory study, in which community members collected their often consumed traditional foods, we sought to answer three objectives: (1) to characterize THg, MeHg, and Se concentrations as well as Se:THg molar ratios in various traditional plant and animal foods consumed by the Bigstone Cree Nation, (2) to understand if THg, MeHg, and Se concentrations as well as Se:THg molar ratios varied across various tissue/organ types, and (3) to evaluate the correlations between THg and Se among kidney, liver, muscle, and brain tissues of animals.

2.3. Materials and Methods

2.3.1. Study site and field sampling

The Bigstone Cree Nation (BCN) is located in the boreal forest of central Alberta (320 km north of Edmonton), adjacent to four lakes—North Wabasca, South Wabasca, Sandy, and Calling (Figure 2.1.) in a wilderness region with abundant fish and wild game. It is also situated

among the largest oil sands reserves in Alberta, the Athabasca region, near the major oil sands operations based at Fort McMurray (Baker, 2018). At the request of community members with the support of Chief and Council, this study was jointly carried out by the Bigstone Cree Nation office and the Centre for Indigenous Peoples' Nutrition and Environment (CINE) at McGill University. Members of Bigstone Cree Nation were keen to participate in this research because they are concerned about the potential levels of contaminants in their foods given the heavy industrial extraction activity close to their territory (Baker, 2016; Baker and Westman, 2018). Frequently consumed plant and animal samples were identified via an internal community survey that estimated the annual consumption. The frequently consumed traditional foods were then collected by the community members from June to September 2015 and frozen, then shipped in November 2015 to the CINE laboratory. Upon arrival, all samples were stored frozen at –20 °C until analysis.

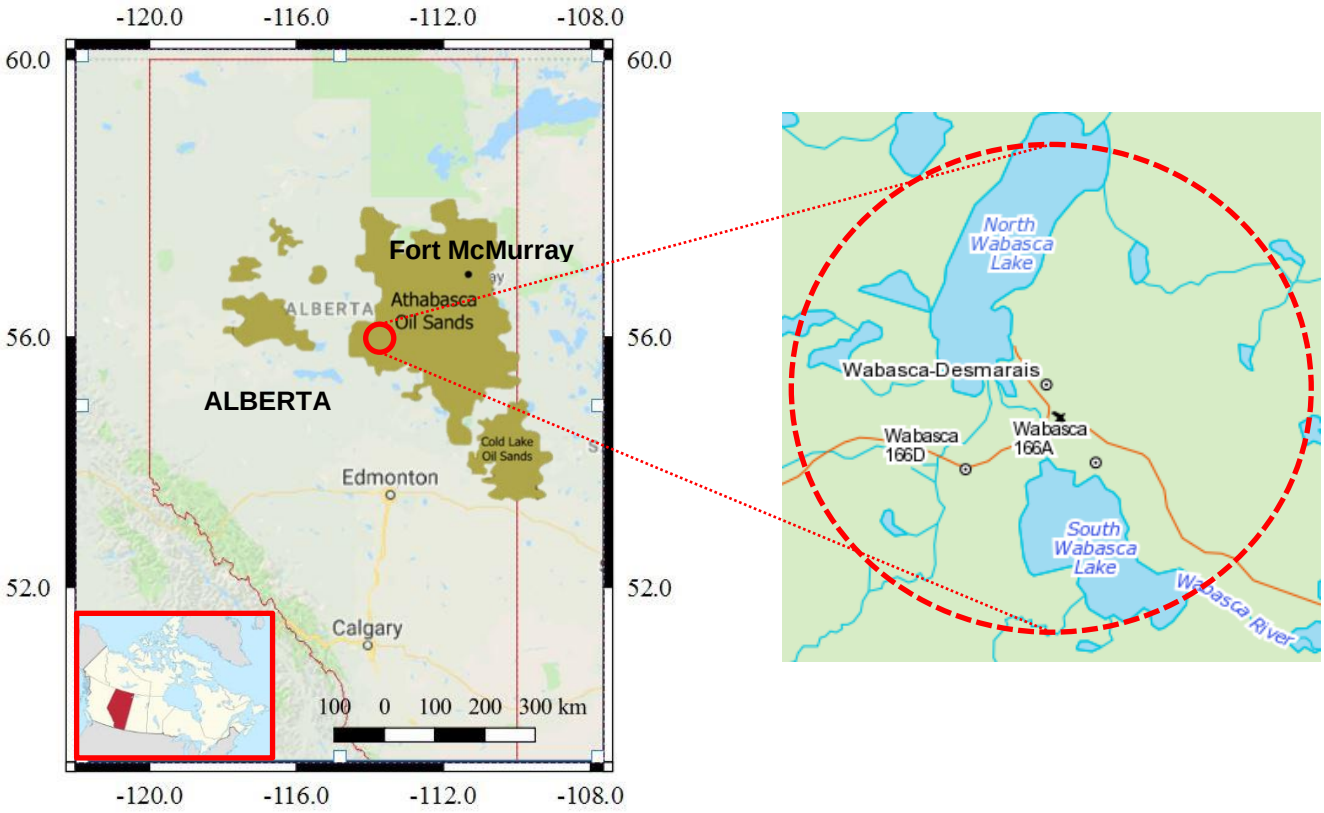

Figure 2.1. Map showing the location of the Bigstone Cree territory (red circle) in Alberta, Canada.

We subsampled different parts (i.e., leaves, roots, stems, and fruits) from individual aquatic and terrestrial plants samples of seven species: water lily, Labrador tea, rat root, mountain ash, mint, and old man's beard, a type of lichen (Table 2.1.). These plants are used mostly for medicinal purposes by the Bigstone Cree Nation. Additionally, berries from eight plant species were collected (i.e., 3 individual lingonberry, 3 individual cranberry, 3 individual rosehip, 3 individual highbush cranberry, 1 bunchberry, 1 blueberry, 1 bog cranberry, and 1 Saskatoon berry) and grouped as "berry".

Table 2.1. Plant samples of the Bigstone Cree. *N* represents the number of individual samples per species.

	Plant Samples	**Scientific name**	**Tissue**	***N***
Aquatic	**Water lily**	*Nymphaeaceae* spp.	Roots	10
Terrestrial	**Labrador tea**	*Rhododendron groenlandicum*	Leaves	10
	Berry		Fruits	16
	Lingonberry	*Vaccinium vitis-idaea*		3
	Cranberry	*Vaccinium* spp.		3
	Rosehip	*Rosa canina*		3
	Highbush cranberry	*Viburnum trilobum*		3
	Bunchberry	*Cornus canadensis*		1
	Blueberry	*Cyanococcus* spp.		1
	Bog cranberry	*Vaccinium oxycoccos*		1
	Saskatoon berry	*Amelanchier alnifolia*		1
	Rat root	*Acorus calamus* spp.	Roots	12
	Mountain ash	*Sorbus aucuparia*	Stems	9
	Mint	*Mentha* spp.	Leaves and stem	3
	Old man's beard	*Usnea* spp.	Whole tissue	5
	Total			65

Various species of animals were collected from both freshwater lake and terrestrial environments. Whitefish, mallard duck, grouse (3 ruffed grouse and 11 spruce hen), and snowshoe hare were received in whole form (skin/feathers on). Moose and black bear arrived already dissected by the community members. Since ruffed grouse and spruce hen share a similar diet, both could be reasonably grouped under “grouse”. Skin/feathers and bones were removed from the whole form animals and their muscle and organ tissues were used in our analyses (Table 2.2.).

Table 2.2. Animal samples of the Bigstone Cree Nation. *N* represents the number of each individual samples of that species.

	Animal Samples	**Scientific name**	**Tissue**	***N***
Aquatic	**Fish**		Muscle	6
	Whitefish	*Coregoninae clupeaformis*	Liver	5
	Duck		Muscle	7
	Mallard	*Anas platyrhynchos*	Liver	6
			Brain	7
Terrestrial	**Grouse**		Muscle	14
	Ruffed grouse	*Bonasa umbellus*	Liver	12
	Spruce hen	*Falcipennis canadensis*	Brain	12
	Hare		Muscle	10
	Snowshoe hare	*Lepus americanus*	Liver	10
			Kidney	10
	Moose		Muscle	3
	Moose	*Alces alces*	Rib-smoked	5
	Bear		Muscle	4
	American black bear	*Ursus americanus*		
	Total			111

All samples were weighed and then dried. Specifically, plant samples were sub-sampled and dried at 50°C for 24 h, and animal tissue samples were dissected and freeze-dried at –90 °C for 24 h with a Flexi-Dry^{TM}-MP unit (Kinetics, New York, USA). Thus, all measurements were performed on dried samples, however, moisture content was also determined for each sample, so that dry weight (d.w.) concentrations could be converted to wet weight (w.w.) equivalents (Supplementary Table S2.1. A, B).

2.3.2. Total mercury analysis

A total of 65 plant samples and 111 tissue samples of animal samples were analyzed for THg concentrations following U.S. EPA method 7473 (U.S. EPA, 2007) and as detailed in a

recent paper (Perkins et al., 2017). Briefly, 15–30 mg of dried sample was accurately weighed in a tared nickel analytical vessel or ceramic vessel (depending on the used equipment) and heated in an oxygenated decomposition furnace to release and quantify THg directly with mercury analyzers (DMA-80, Milestone and NIC MA-3000, Nippon Instruments, North America). Quality control measures included at least one blank, a sample replicate, and standard reference material (SRM) after every batch of 10 samples. The SRMs consisted of peach leaves (NIST-1547; National Institute of Standards and Technology) for plant samples and fish protein (DORM-4; National Research Council of Canada) for animal samples. Quality control data were acceptable according to the U.S. EPA guidelines, that is for plant samples, the measured concentration of THg in the NIST-1547 (n = 23) was 0.036 ± 0.003 μg g^{-1} (certified THg value 0.031± 0.007 μg g^{-1}), where the average recovery ranged from 110.3% to 118.7%. For animal samples, the measured concentration of THg in DORM-4 (n = 26) was 0.37 ± 0.01 μg g^{-1} (certified value for THg at 0.41± 0.05 μg g^{-1}), which indicated the average recovery ranged from 85.8% to 92.8%. Full QC details of SRMs are also provided in the Supplementary Information (Table S2.2. A). The accuracy and precision were similar between the two analyzers, and therefore these values were combined; however, detection limits differed between instruments and were calculated separately. The detection limits are provided in detail in Supplementary Information (Table S2.2. B).

2.3.3. Methylmercury analysis

The MeHg concentrations in 106 animal tissue samples were determined using gas chromatography-cold-vapour atomic fluorescence spectrophotometer (GC-CVAFS) with a Tekran 2700 unit (Tekran Instruments Corporation, Toronto, Canada), following the U.S. EPA

method 1630 (EPA, 1998) and as detailed elsewhere (Perkins et al., 2017). We tried to measure MeHg in plants, but their levels were extremely low, and we lacked robust reference material; furthermore, research has shown that THg in plants (mostly terrestrial species) occurs mostly as InHg (Patra and Sharma, 2000). Between 20–25 mg of a given dried sample was digested in 8 mL of 25% potassium hydroxide (KOH) in methanol for 4 h on a heat block. Samples were rotated every 10 minutes during the 4 h of digestion to prevent boiling and to ensure uniform temperature among the vials. Once cooled, the digest volume was increased to 30 mL with methanol and stored at –20 °C. For the analysis, 0.2–1 mL of sample digests, depending on initial mass, were added to ultrapure water (18.2 Ω) produced from a Milli-Q system (Millipore Corporation). The pH was adjusted to 4–4.5 with acetate buffer, then ethylation was performed using 1% sodium tetraethylborate. Standard reference materials—DORM-4 and DOLT-5, dogfish liver (National Research Council of Canada)—were likewise digested using the above procedure and simultaneously analyzed with the animal samples. Quality control samples included SRMs, reagent blanks, as well as initial and ongoing precision and recovery (IPR and OPR) samples after every 10 samples. Quality control data were deemed acceptable according to the U.S. EPA's guidelines. The mean measured concentration of MeHg in DORM-4 (n = 7) was 0.32 ± 0.02 μg g^{-1}, compared to the certified value of 0.36 ± 0.03 μg g^{-1}), while that of DOLT-5 (n = 5) was 0.13 ± 0.02 μg g^{-1}, compared to the certified value of 0.12 ± 0.06 μg g^{-1}. Specifically, the recovery of DORM-4 (n = 7) ranged from 80.3% to 97.7% of the certified value for MeHg, while that of DOLT-5 (n = 5) ranged from 85.1% to 117.5%. Full details on MeHg quality control and detection limits are provided in the Supplementary Information (Table S2.3. A, B), respectively.

2.3.4. Selenium analysis

Selenium was measured by inductively coupled plasma mass spectrometry (ICP-MS) following the U.S. EPA method 200.8 (EPA, 1994) from 65 plant and 111 animal tissue samples. Approximately 160 mg of sample was digested overnight with 2 mL of trace metal grade nitric acid (HNO_3). Samples were put on a dry digestion block at 125°C for 2 h, cooled, had 0.5 mL of trace metal grade hydrogen peroxide (H_2O_2) added, and then returned to the digestion block for another 3 h at 125°C. After cooling, samples were diluted to 50 mL with Milli-Q water, shaken, left to settle overnight, and then subjected to four times dilution prior to ICP-MS analysis. Quality control measures included blanks, an internal standard, replicate samples, and SRMs which were placed after every 10–15 samples. Quality control data were in the U.S. EPA's guideline's acceptable range and provided in the Supplementary Information (Table S2.4. A, B).

2.3.5. Data analysis

The concentrations of THg, MeHg, and Se were measured, and Se:THg molar ratios calculated per sample by dividing the associated concentrations (μg g^{-1}, w.w.) by their corresponding molecular weight (g mol^{-1}) as follows:

$$Molar\ ratio = \frac{\text{Concentration of Se } (\mu g\ g^{-1}\ \text{w.w.}) \,/\, \text{molecular weight } (78.90\ g\ mol^{-1})}{\text{Concentration of THg } (\mu g\ g^{-1}, \text{w.w.}) \,/\, \text{molecular weight } (200.59\ g\ mol^{-1})}$$

Due to our unbalanced and incomplete dataset, a mixed modelling approach with a compound symmetry covariance structure using restricted maximum likelihood (REML) was required, in which each animal specimen was designated as a random subject, because tissue types taken from the same individual cannot be considered independent of one another. Doing so ensured no pseudo-replication and inflation of statistical power, as the correct denominator degrees of freedom were used for testing the fixed effects of interest (using the Wald/*F* statistic).

A pair of mixed models was fitted to the data: one that compared food groups alone (i.e., plants with animals) and their species (nested within food group), and then another that compared only animal species and tissue type (tissues/organs nested within species). Fitted models were checked for normality of residuals and equal variances by visual checks of diagnostic plots. When these assumptions were violated, $\log_{10}$-transformation of the variables was sufficient to satisfy them in all cases. For significant effects in the mixed models, *post hoc* pairwise comparisons among factor levels were conducted using Tukey's honest significant difference (HSD) test with least squares (LS) means (Supplementary Table S2.5. A, B). We were also interested to see how Se and Hg uptake covaried within each tissue/organs of different animal species and therefore, to examine the association between Se and THg concentrations. To do this, non-parametric correlations were performed using Kendall's *tau* (τ) because of our low sample sizes.

In presenting and interpreting our results, fish and duck were considered as aquatic and the remainder of the animal species as terrestrial; however, for the analyses, all were grouped under "animal". Likewise, for plant samples: all species were terrestrial except water lily (aquatic) and for the analysis all were grouped under "plants". The concentrations of THg, MeHg, Se and Se:THg ratios were measured in not only muscle but also organ tissues (i.e., liver, kidney, and brain) because some community members (notably elders) still consume them. All statistical analyses were conducted in JMP Pro 13.2.0 or JMP 14.1.0 (SAS Institute Inc., 2018) for the Macintosh operating system. The level of statistical significance was set to $P < 0.05$. Hereafter, concentrations of THg, MeHg, and Se are reported as arithmetic mean ($\mu g\ g^{-1}$, w.w.) ± SE.

2.4. Results

2.4.1. Total mercury and methylmercury

Overall, the tissues traditionally consumed from animals had significantly higher mean THg concentrations than those of plants (mixed model, $F_{1, 153} = 6.0$, $P = 0.015$) ranging from 0.001 ± 0.000 μg g^{-1}, w.w. in water lily to 0.11 ±0.03 μg g^{-1}, w.w. duck liver, respectively. Interestingly, old man's beard, a lichen species, showed similar concentrations of THg (0.11 ± 0.02 μg g^{-1}, w.w.) as found in duck liver. The concentrations of THg differed significantly among species of plants (mixed model, $F_{11, 133} = 24.73$, $P < 0.001$), being 38- to 110- fold higher in old man's beard than in rat root and water lily (Figure 2.2.A). For animal species, the concentrations of THg varied significantly depending on the species (mixed model, $F_{5, 43} = 25.10$, $P < 0.001$) and harvested tissue/organ types (nested term, $F_{8, 58} = 17.73$, $P < 0.001$), being highest in duck liver, fish liver, hare kidney, fish muscle, and duck muscle ($P < 0.048$) and lowest in grouse liver, moose muscle and rib, grouse muscle and brain, hare and bear muscles ($P < 0.001$; Figure 2.2.B). The concentrations of THg in animal tissue/organs ranged from 0.003 ± 0.001 μg g^{-1}, w.w. in grouse liver, moose muscle and rib to 0.11 ± 0.03 μg g^{-1}, w.w. in duck liver, showing that duck liver had 37 times higher concentrations of THg compared to grouse liver, moose muscle and rib. Similarly, the MeHg concentrations differed significantly among species (mixed model, $F_{5, 46} = 60.77$, $P < 0.001$) and their tissue/organ types (nested term, $F_{8, 59} = 18.49$, $P < 0.001$; Figure 2.2.C), being highest in fish muscle, duck liver and muscle, and fish liver ($P < 0.001$) and lowest in grouse and hare muscles, grouse liver, moose and bear muscles ($P < 0.001$). The mean concentrations, MeHg ranged from 0.0002 ± 0.0000 μg g^{-1}, w.w. in grouse and hare muscle, 0.0003 ± 0.0000 μg g^{-1}, w.w. in grouse liver, and 0.0004 ± 0.0001 μg g^{-1}, w.w. in moose muscle to 0.07 ± 0.02 μg g^{-1}, w.w. in fish muscle. Generally, aquatic species (i.e., fish and duck)

had higher concentrations of both THg and MeHg in their muscle and organ tissues when compared with the traditionally consumed terrestrial species, the only exception being hare kidney, which had a high concentration of THg but not MeHg (Figures 2.2. B, C). Mean concentrations are fully detailed in Supplementary Information (Table S2.6. A, B).

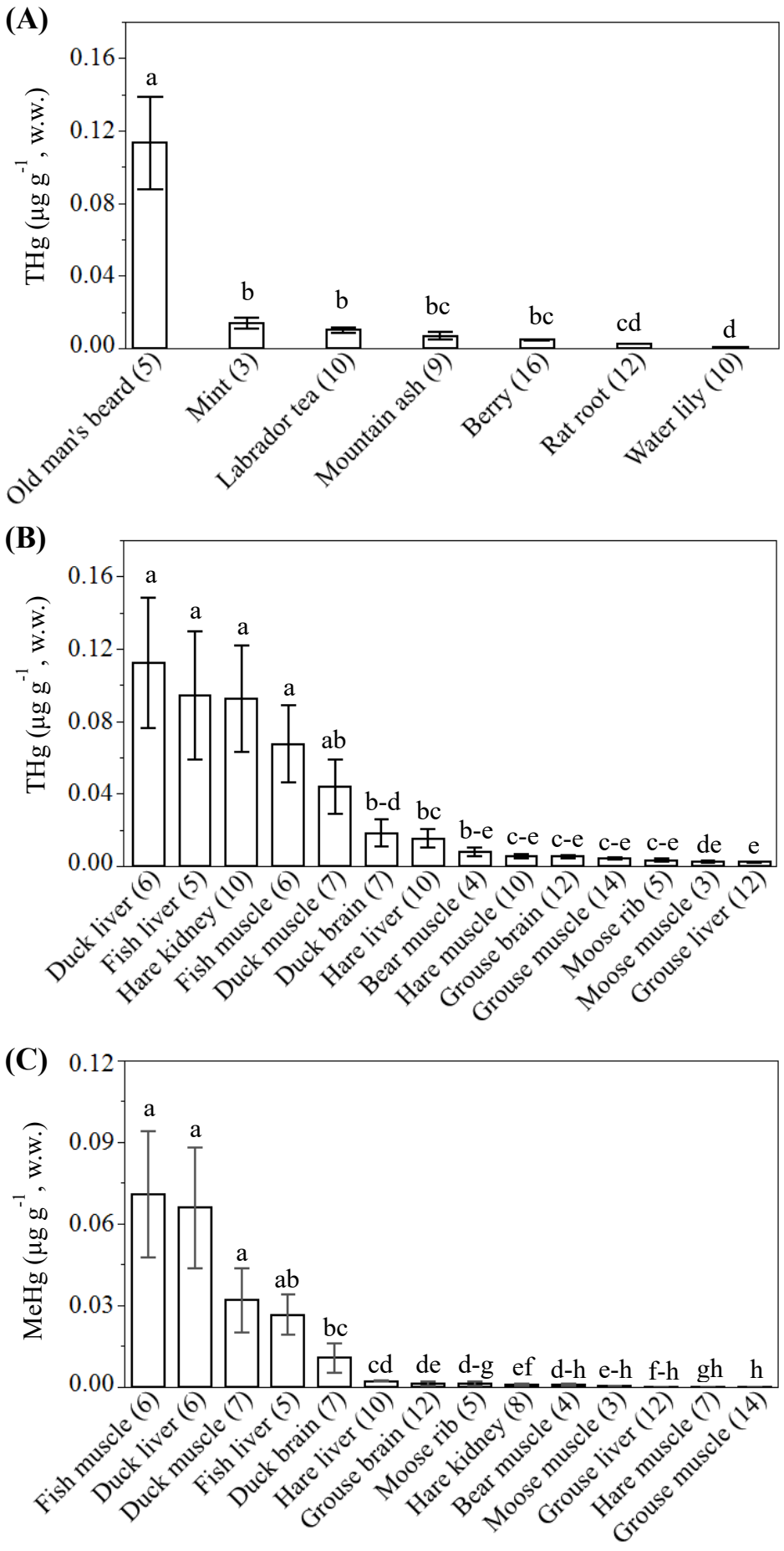
(A)
THg (µg g-1, w.w.)
0.16
0.12
0.08
0.04
0.00
a
b
b
bc
bc
cd
d
Old man's beard (5)
Mint (3)
Labrador tea (10)
Mountain ash (9)
Berry (16)
Rat root (12)
Water lily (10)
(B)
THg (µg g-1, w.w.)
0.16
0.12
0.08
0.04
0.00
a
a
a
a
ab
b-d
bc
b-e
c-e
c-e
c-e
c-e
de
e
Duck liver (6)
Fish liver (5)
Hare kidney (10)
Fish muscle (6)
Duck muscle (7)
Duck brain (7)
Hare liver (10)
Bear muscle (4)
Hare muscle (10)
Grouse brain (12)
Grouse muscle (14)
Moose rib (5)
Moose muscle (3)
Grouse liver (12)
(C)
MeHg (µg g-1, w.w.)
0.12
0.09
0.06
0.03
0.00
a
a
a
ab
bc
cd
de
d-g
ef
d-h
e-h
f-h
gh
h
Fish muscle (6)
Duck liver (6)
Duck muscle (7)
Fish liver (5)
Duck brain (7)
Hare liver (10)
Grouse brain (12)
Moose rib (5)
Hare kidney (8)
Bear muscle (4)
Moose muscle (3)
Grouse liver (12)
Hare muscle (7)
Grouse muscle (14)

Figure 2.2. Mean (± SE) concentrations of total mercury (THg) in (A) plant samples, (B) animal samples, and (C) concentrations of methylmercury (MeHg) in the same animal tissue samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada. Parenthetical numbers following the sample type denote sample size. Different lower-case letters indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other. Graphs shown with different y-axis scales.

2.4.2. Selenium

On average, mean Se concentrations were higher in the animals than in the plant samples, (mixed model, $F_{1, 144} = 195.17$, $P < 0.001$), ranging from 0.01 ± 0.00 μg g^{-1}, w.w. in water lily and mountain ash to 1.12 ± 0.03 μg g^{-1}, w.w. in fish liver. Within plants, the Se concentrations varied between 0.009 ± 0.002 μg g^{-1}, w.w. in mountain ash and 0.009 ± 0.001 μg g^{-1}, w.w. in water lily to 0.08 ± 0.01 μg g^{-1}, w.w. in old man's beard. Similar to THg, the Se concentration was significantly higher in old man's beard than in most other plant species, with corresponding fold changes up to 8 (mixed model, $F_{11, 120} = 3.92$, $P < 0.001$; Figure 2.3.A). In animal samples, the mean Se concentrations ranged from 0.09 ± 0.01 μg g^{-1}, w.w. in moose rib to 1.11 ± 0.27 μg g^{-1}, w.w. in fish liver, with fold changes up to 12, which clearly depended on the species (mixed model, $F_{5, 45} = 3.42$, $P < 0.010$) and harvested tissue/organ types (nested term, $F_{8, 59} = 12.33$, $P < 0.001$); fish and duck livers and hare kidney had the highest mean Se concentrations ($P < 0.001$), while the rest of the animal species and their muscle and organ tissues had similar mean Se concentrations (Figure 2.3.B). In general, organs (i.e., liver from fish and duck, and hare kidney)

contained greater Se than muscle tissues (Figure 2.3.B). For example, the mean Se concentration of hare kidney was three times higher than that of hare muscle.

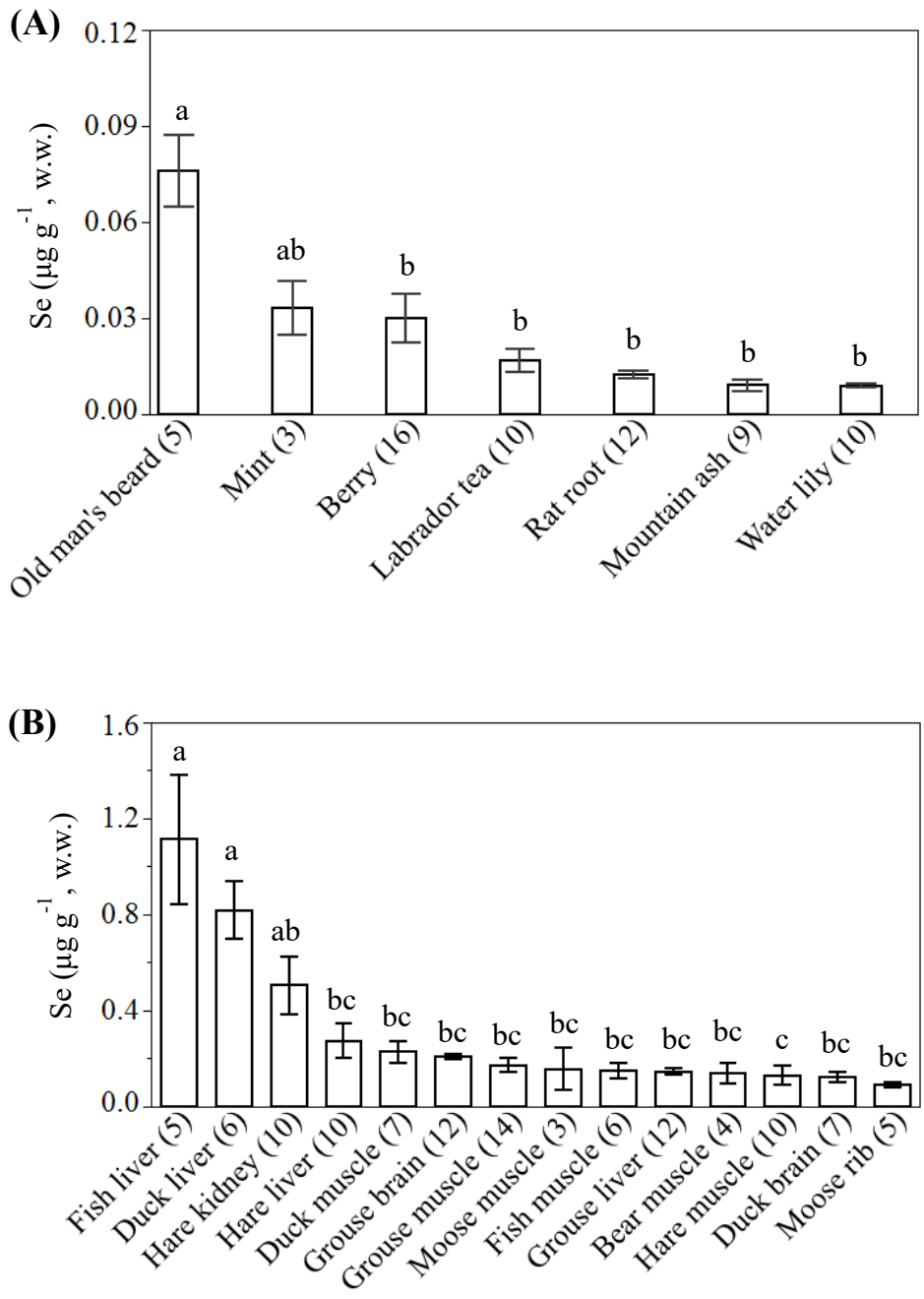

Figure 2.3. Mean (± SE) concentrations of selenium (Se) in (A) plant samples and (B) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada. Parenthetical numbers following the sample type denote sample size. Different lower-case letters indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other. Graphs shown with different y-axis scales.

2.4.3. Molar ratios of selenium:total mercury and correlations

On average, the Se:THg ratios were higher in the animals than in the plant samples (mixed model, $F_{1, 130} = 164.92$, $P < 0.001$); overall, the values obtained ranged from 1.84 ± 0.16 in old man's beard to 160.00 ± 57.52 in moose muscle. There were also significant differences among the plants (mixed model, $F_{11, 107} = 14.50$, $P < 0.001$), with higher Se:THg ratios in water lily, berry, rat root, and mint compared to old man's beard, Labrador tea, and mountain ash ($P < 0.001$; Figure 2.4.A), with ranges from 1.84 ± 0.16 in old man's beard to 25.11 ± 4.08 in water lily, corresponding to fold change of 14. The mean Se:THg ratios showed differences among animal species (mixed model, $F_{5, 45} = 19.29$, $P < 0.001$) and the harvested tissue/organ types (nested term, $F_{8, 59} = 7.36$, $P < 0.001$); where moose muscle, grouse liver, brain, and muscle, and moose rib were most elevated, while the lowest ratio belonged to fish muscle, hare kidney, duck muscle, and duck liver. The ratios obtained ranged between 10.00 ± 3.05 in fish muscle and 160.00 ± 57.52 in moose muscle in which moose muscle had 16 times higher Se:THg ratios that of fish muscle. In this respect, mean Se:THg ratios were generally higher in the terrestrial than the aquatic animals (Figure 2.4.B).

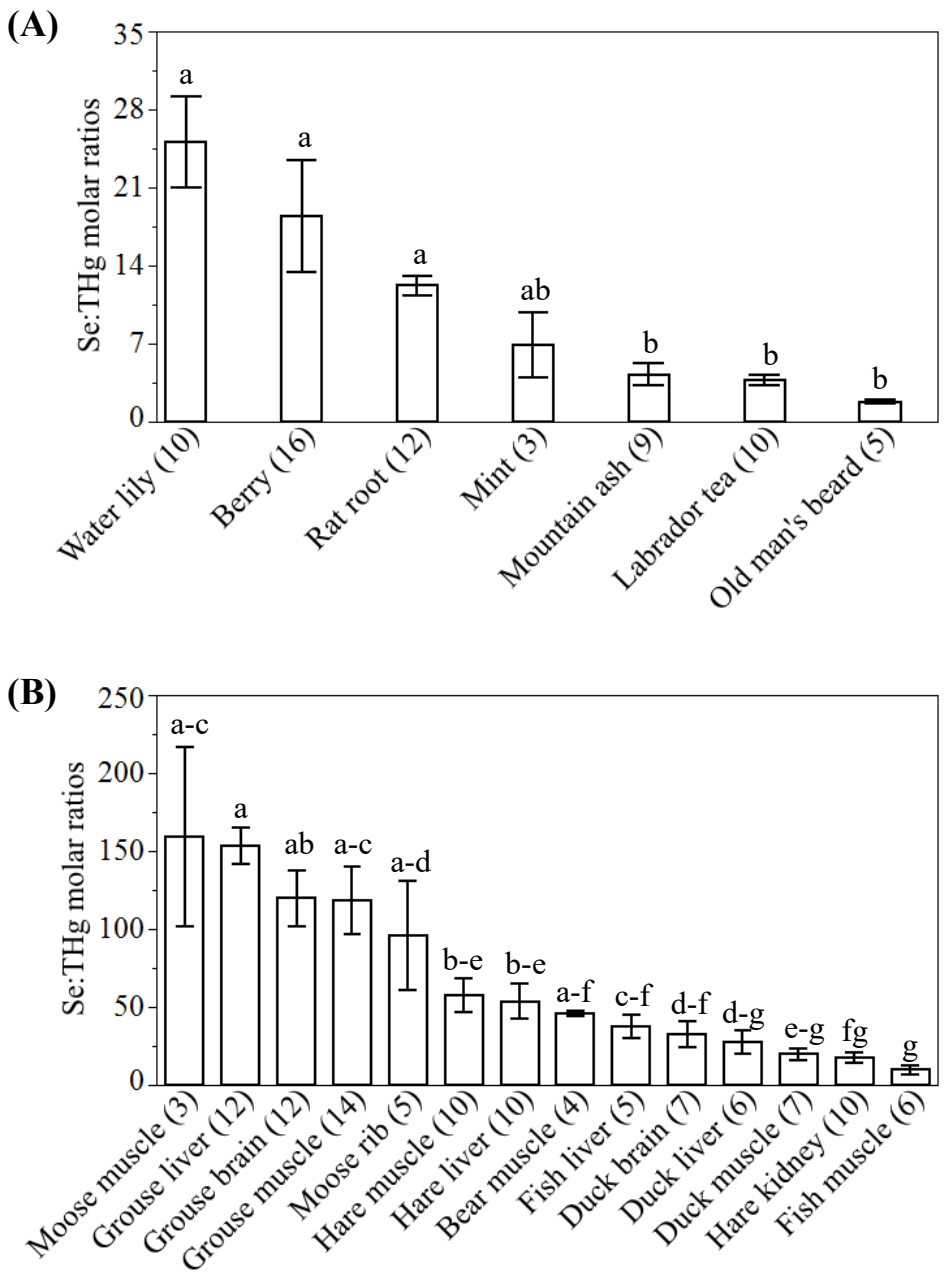

Figure 2.4. Mean (± SE) molar ratios of selenium: total mercury (Se:THg) in (A) plant samples and (B) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada. Parenthetical numbers following the sample type denote sample size. Different lower-case letters indicate significantly different mean values

based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other. Graphs shown with different y-axis scales.

Among all muscle and organ tissues of animal species in this study, there were strong, positive correlations between Se and THg concentrations for hare kidney ($\tau = 0.73$, $P = 0.003$, Figure 2.5.A), duck muscle ($\tau = 0.71$, $P < 0.024$, Figure 2.5.B), and hare liver ($\tau = 0.68$, $P < 0.005$, Figure 2.5.C). For other animal species muscle and organ tissues, the correlations were positive but not significant ($\tau > 0.06$, $P > 0.051$), except for fish muscle; it had a negative and non-significant correlation ($\tau = -0.45$, $P = 0.188$).

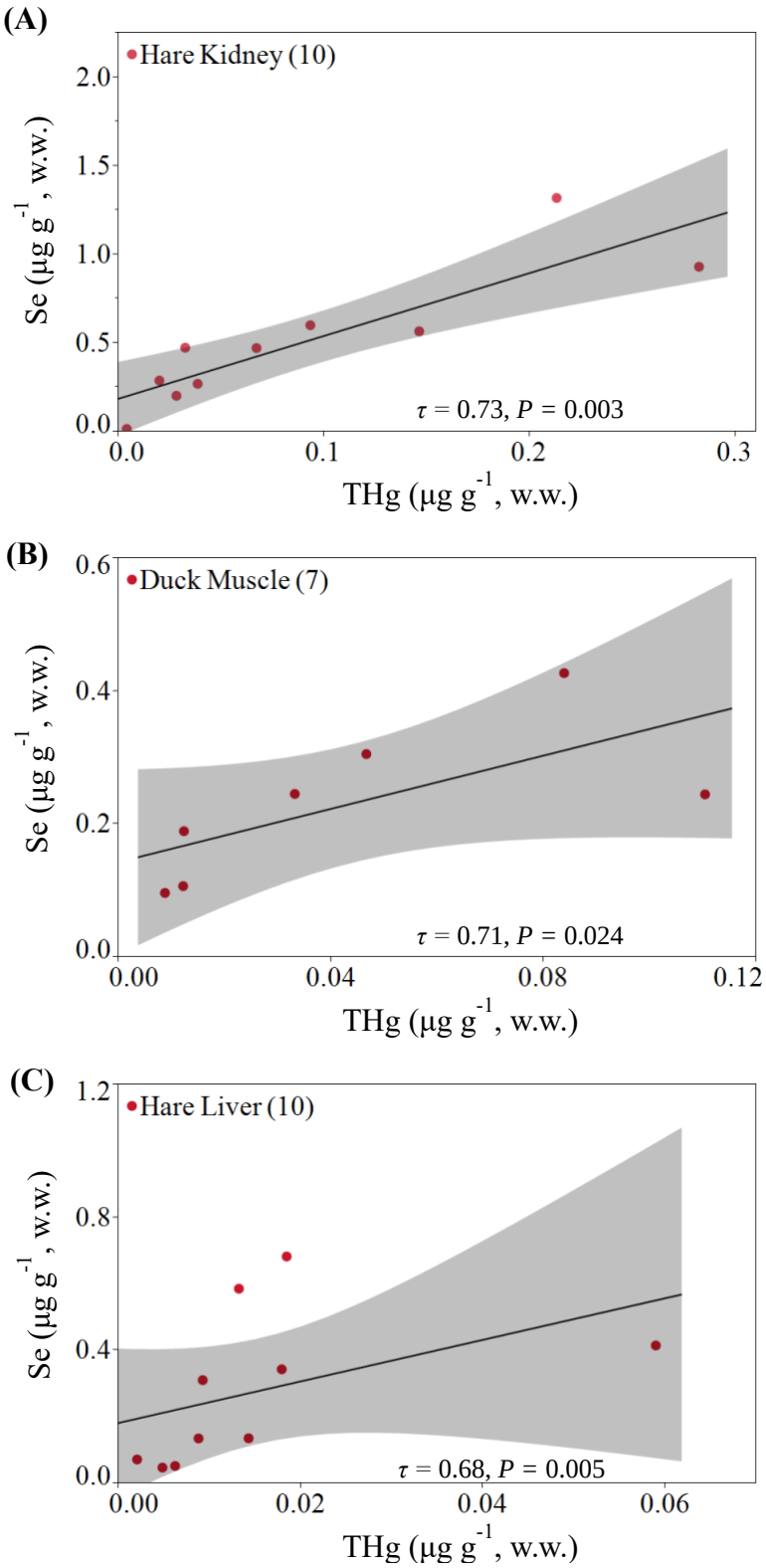
(A)
Hare Kidney (10)
Se (µg g-1, w.w.)
THg (µg g-1, w.w.)
τ = 0.73, P = 0.003
(B)
Duck Muscle (7)
Se (µg g-1, w.w.)
THg (µg g-1, w.w.)
τ = 0.71, P = 0.024
(C)
Hare Liver (10)
Se (µg g-1, w.w.)
THg (µg g-1, w.w.)
τ = 0.68, P = 0.005

Figure 2.5. Correlations between selenium (Se) and total mercury (THg) concentrations in (A) hare kidney, (B) hare liver, and (C) duck muscle tissues of animals collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada. Parenthetical numbers following the sample type denote sample size. Bivariate associations were examined with a non-parametric Kendall's *tau* (τ) correlation test.

2.5. Discussion

In general, animal samples had higher concentrations of THg compared to plant samples with the exception of the lichen, old man's beard, which also had low Se:THg ratios. Generally, animals living in or near aquatic systems (i.e., fish and duck) had the highest concentrations of THg and MeHg, and Se:THg ratios were also lower in the aquatic species than in most terrestrial species. We found that measuring THg concentrations alone may not always be a good indicator of dietary MeHg exposure or Se:THg ratios. This suggests a more careful approach is needed, which considers MeHg and Se:THg ratios to better assess the complexity of Hg exposures through food items, notably for Indigenous community members as substantial traditional food consumers. Traditional food consumption advisories, if not formulated and communicated effectively, could result in Indigenous communities limiting their consumption of traditional foods, yet remaining susceptible to other health issues (McAuley and Knopper, 2011). In comparing the Bigstone Cree Nation food samples to the available THg guidelines, our results indicated that none of the plant and animal samples exceeded the 0.5 μg g^{-1}, w.w. nor the 0.3 μg g^{-1}, w.w. THg guidelines set by Health Canada (Health Canada, 2007) and U.S. EPA (U.S. EPA, 2001), respectively. Additionally, the molar ratios of Se:THg were above 1 in all plant and animal samples, suggesting potentially sufficient Se to reduce the potential negative health

consequences of Hg exposure to the community members through the consumption of these traditional foods. However, it should be noted that we did not assess the risk of dietary exposure in the community, which would require additional data on food consumption (Chan et al., 1995).

Among the plant samples we examined, the lichen, old man's beard, contained higher THg concentrations relative to other plants. In a study of epiphytic lichen (*Hypogymnia physodes*) growing close to a chlor-alkali plant and a power plant in New Brunswick, Canada, their THg concentrations ranged from 0.088 ± 0.005 μg g^{-1}, d.w. to 0.148 ± 0.046 μg g^{-1}, d.w. (Sensen and Richardson, 2002). At our study site in Alberta, the mean THg concentration in old man's beard was on par with that (0.15 ± 0.04 μg g^{-1} d.w.). This may be due to accumulation of contaminants close to industrial activities, as research has suggested that THg concentrations of old man's beard (*Usena* spp.) were elevated in lichens close to a coal-fired power plant compared to the samples taken almost 100 km away from the power plant (0.52 vs. 0.06 μg g^{-1}, d.w.) (Jardine et al., 2009). This discrepancy could also be due to the different species of lichens investigated by researchers, since a study on epiphytic lichen (*Hypogymnia physodes*) distributed within 150 km of the Athabasca oil sands region developments, in Alberta, Canada, obtained a mean THg concentration of 0.14 ± 0.03 μg g^{-1} d.w. which was independent of spatial patterns (Blum et al., 2012). Old man's beard is primarily used as a disinfectant (urinary tract, kidney and bladder infections) (Ayer, 1995). Lichens are slow-growing terrestrial organisms without a cuticle or stomata, resulting in direct adsorption or absorption of nutrients and contaminants into their thalli (Garty, 2001). Consequently, lichens are often used as biomonitors of airborne metals, including Hg (Lodenius, 2013). The remaining plant samples showed low THg compared to the animals, likely related to the low trophic position of the plants and, therefore, limited THg biomagnification.

Elevated concentrations of THg and MeHg were found in tissues and organs including muscle and liver of aquatic animals, i.e., fish and duck, compared to terrestrial animals. This result may be linked to the abundance of microorganisms capable of converting InHg to MeHg in aquatic environments, leading to higher MeHg concentrations in aquatic than terrestrial ecosystems; fish and waterfowl then bioaccumulate Hg in the form of MeHg through greater contact with water and feeding on water-associated organisms (Driscoll et al., 2013). Indeed, more than 90% of the Hg in fish muscle occurs as MeHg (Watanabe et al., 2012), which is in line with our findings of 97.00 ± 6.14%. Yet, we found variation in THg and MeHg among muscle and organ tissues of the same animal species. For example, in hare, mean THg concentrations were higher in kidney than in liver and muscle, whereas MeHg concentrations were higher in hare liver and kidney than in hare muscle. In studies comparing muscle and organ tissues of various fish species, higher mean THg concentrations were found in liver than in muscle tissues (Baêta et al., 2006; Barst et al., 2016). Our findings for fish followed a similar result, but not statistically significant, perhaps due to insufficient statistical power to detect a difference due to low sample size. Similarly, a study of ducks (*Anas platyrhynchos*) from northwestern Poland found that mean THg concentrations in liver and kidney (0.25 ± 0.21 μg g^{-1}, d.w. and 0.27 ± 0.26 μg g^{-1}, d.w.) significantly exceeded that in muscle 0.13 ± 0.16 μg g^{-1}, d.w. (Kalisinska et al., 2013); however, this report did not include corresponding MeHg concentrations. Our results for duck did show that although its liver had higher concentrations of THg than its muscle (0.43 ± 0.13 μg g^{-1}, d.w. versus 0.16 ± 0.05 μg g^{-1}, d.w.), these were not significantly different. This discrepancy between our results and Kalisinska et al. (2013) could be due to a difference in the statistical analyses and their larger sample size used.

Recently, an investigation of traditional foods of four Anishnaabeg communities living near a copper smelter in the eastern Canadian boreal forest found that hare (*Lepus americanus*) liver tissues contained higher mean THg concentrations than muscle tissues (0.15 ± 0.62 μg g^{-1}, d.w. versus 0.05 ± 0.10 μg g^{-1}, d.w., respectively) (Bordeleau et al., 2016). Studies in mammals indicated that Hg in kidney is predominately present as InHg (Zalups, 2000). This corroborates our results since hare kidney had a low proportion of MeHg (1.09 ± 0.60 %). Overall, these studies are consistent with our results for terrestrial animals, in that muscle tissues generally contain lower concentrations of THg than the organ tissues (i.e., liver and kidney).

Concentrations of Se were highest in old man's beard relative to all other plant samples, as was the case for THg, probably because of similar biogeochemical and/or physiological factors driving uptake of the two elements. Moreover, research has suggested that, unlike for animals and humans, Se is not an essential element for plants, for which Se uptake depends on Se phytoavailability in local soil (White, 2016). Se uptake and retention is known to differ among various species of plants, which may also depend on soil physiological conditions (i.e., salinity and pH, presence of organic matter, and translocation mechanisms with a plant) (Zhao et al., 2005). For example, for epiphytic *Parmelia* lichens (mostly, *Parmelia sulcata* Taylor) growing in Portugal, mean Se concentrations ranged from 0.28 ± 0.08 μg g^{-1}, w.w. to 0.54 ± 0.30 μg g^{-1}, w.w. across locations, but they increased nearer to industrial activities (Ventura et al., 2005). We found a comparatively lower concentration of Se in lichen in our study (0.08 ± 0.02 μg g^{-1}, w.w.), likely due to lower atmospheric and soil Se concentrations in the environment (Kelly et al., 2010) where the Bigstone Cree Nation members took the samples or simply because of different lichen species were used in our study and that of Ventura et al. (2005). Among the animal samples we received as whole, multiple tissues/organs were harvested, and

the organ tissues (i.e., kidney and/or liver) showed significantly higher concentrations of Se than muscle tissues for fish, duck, hare, but not for grouse. This tissue distribution pattern was expected because kidney and liver are two key detoxifying organs wherein much metabolic processing to facilitate elimination occurs (Chen et al., 2006). Even with relatively high kidney concentrations of Hg, there is still an excess amount of Se to bind with almost all Hg passing through the kidney (Drasch et al., 1996). This may be why some organ tissues such as liver and kidney contain more Se than other tissues. Similar to our findings, research on walleye (*Stizosedion vitreum*) caught from boreal lakes around the Sudbury smelters in Ontario, Canada, found significantly higher concentrations of Se in liver (ranged: 3.0 ± 0.6 to 18.0 ± 2.0 μg g^{-1}, d.w.) than in muscle or brain (ranged: 1.2 ± 0.2 to 10 ± 1.0 μg g^{-1}, d.w. and 0.96 ± 0.20 to 6.1 ± 0.8 μg g^{-1}, d.w., respectively) (Yang et al., 2010).

Among food groups, animal samples had significantly higher Se:THg ratios than plant samples. Additionally, Se:THg ratios were higher in the terrestrial than aquatic animals. The latter results may be related to relatively higher concentrations of THg and MeHg in various tissues/organs of the aquatic species. Significant variation in Se:THg ratios among traditional foods of the Bigstone Cree Nation may be due to differing Se and Hg exposures and Se-Hg interactions in plants or various animal muscle and organ tissues. Research has indicated that the Se and Hg interaction is dependent on the chemical forms of Se and Hg (Dang and Wang, 2011). Others pointed out that this interaction may vary in different species due to varying metabolic pathways and enzyme systems (Khan and Wang, 2009). The moose muscle and rib had high Se:THg molar ratio and this could related to their diet of leaves, bark, pine cones, twigs, tree buds and shrubs (Shipley, 2010), all foods which should be low in THg. Moose also forage on aquatic plants such as water lilies (Fraser and Hristienko, 1983). As our plant results indicated,

water lily had the highest mean Se:THg ratio among the plant samples. Various tissues of grouse (i.e., liver, brain, muscle) also showed similarly high Se:THg ratios as the moose. This result may also be explained by animal diet, as grouse forage on berries, fruits, leaves, small insects and invertebrates (King, 1969), which are all low in THg. Therefore, diet could be an important factor in Se:THg ratios since Hg and Se uptake differ in various species and their tissues/organs. Conversely, the aquatic animal species, regardless of tissue, generally showed the lowest Se:THg ratios which could be related to higher uptake of THg, mostly in MeHg form. Even though the aquatic animals had low Se:THg ratios, all Bigstone Cree Nation traditional food samples (plants and terrestrial and aquatic animals and their tissues/organs) had Se:THg ratios above 1, suggesting potentially sufficient Se to associate with Hg. Nonetheless, when interpreting Se:Hg ratios, several uncertainties arise including surrounding the protective levels/ratios required among various organ tissues, and which organs are most sensitive in terms of adverse toxic effects (Burger et al., 2013). Overall, the patterns among all the traditional foods of the Bigstone Cree Nation were similar when comparing the concentrations of THg, MeHg, and Se:THg ratios, where old man's beard showed the highest THg and low Se:THg ratios. Also, liver and muscle tissues of aquatic species showed higher THg, MeHg, and generally lower Se:THg ratios. Therefore, in these cases only, measuring the concentrations of THg does reflect the patterns in concentrations of MeHg and Se:THg ratios. However, while hare kidney showed similarly elevated concentrations of THg and lower Se:THg ratios, as the aquatic species, concentrations of MeHg in hare kidney were much lower relative to the aquatic species. Thus, measuring THg alone may not always fully reflect MeHg concentrations depending on the species and tissues/organs evaluated.

Consistent with the notion of protective effects of Se toward Hg toxicity (Ralston, 2008; Sørmo et al., 2011), we found strong positive Se and THg correlations in hare kidney and liver, where most detoxification of xenobiotics occur; and also duck muscle. In a study in Northwest territory, Canada, the THg and Se in muscle tissues of wild-harvested fish species including whitefish from lakes in the Dehcho Region were found to be negatively correlated in muscle tissues (Reyes et al., 2017). This could be due to similar intraspecific variations in Hg and Se uptake (Reyes et al., 2017). In general, in our study, the Se and Hg correlations relied on low sample sizes and therefore, they had low statistical power.

Additional factors in traditional food use, not examined in the present study, could be important to an overall understanding of the issues surrounding Hg contamination in these foods. First, raw samples were mainly tested, whereas cooking methods have been shown to affect the eventual bioavailability of Hg in the human body (Bradley et al., 2017). Second, differences in specimen sizes of our animal species were not considered. For instance, larger fish may contain higher concentrations of MeHg due to bioaccumulation and biomagnification, in addition to a slow rate of elimination of MeHg relative to its dietary uptake, thus leaving less Se available, notably in the liver and brain, to protect against Hg toxicity (Sandheinrich and Wiener, 2011). Third, we did not differentiate Se speciation, which has been shown to be involved in antagonistic effects of Se on the bioaccumulation of Hg (Dang and Wang, 2011).

Since the Bigstone Cree Nation members are living close to oil sands development activities where production is projected to increase, we recommend on-going monitoring of THg, MeHg, and Se concentrations and Se:THg ratios in traditional/wild foods and biota. The findings of this study could also help others pursue exposure and risk assessments for a variety of traditional foods in Canada and elsewhere by having a better understanding of not only THg but

also MeHg, Se concentrations, and Se:THg ratio patterns/distributions among various food species relative to dietary consumption. This information could be obtained through food frequency questionnaires. We also recommend investigating speciation of Se to better understand the binding between Hg and Se in various muscle and organ tissues of different species of traditional foods.

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Linking Statement

In the previous chapter, I investigated variations in concentrations of total mercury (THg), methylmercury (MeHg), selenium (Se), and selenium to mercury ratios (Se:THg) of multi-species of plant and animal samples consumed as traditional foods of the Bigstone Cree Nation in Alberta, Canada, who live in close proximity of oil sands activities. Mercury and selenium are two out of thirteen of the trace elements listed as priority pollutant elements (PPE) by the United States Environmental Protection Agency (U.S. EPA) under the Clean Water Act. Research has indicated elevated levels of PPE in the surrounding environment of the Athabasca region in Alberta, Canada. In the next chapter, I assessed the concentrations of nine other PPE in various traditional food groups (plants versus animals) and various tissues including muscle and organs within animal species. This study greatly expands upon PPE data that is mostly available on abiotic matrices in the Athabasca oil sands regions and provided baseline PPE data for a variety of traditional plants and wildlife species for which it is lacking around the Alberta oil sands region. This study helped better understand the levels of trace elements in these regularly consumed traditional foods with medicinal, nutritional, and holistic purposes.

Chapter 3. Quantifying priority pollutant elements (PPE) in plant and animal samples consumed as traditional foods in traditional foods by the Bigstone Cree Nation in Alberta, Canada

3.1. Abstract

This study investigated the concentrations of nine elements considered as priority pollutants (PPE) by the U.S. Environmental Protection Agency Clean Water Act, including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), thallium (Tl), and zinc (Zn) in traditional plant and animal foods of the Bigstone Cree Nation, an Indigenous community adjacent to the Athabasca oil sands in Alberta, Canada. In plants, concentrations of PPEs declined in the following order: Zn > Cu > Ni > Cr ~ Pb > As ~ Cd > Ag ~ Tl, while in animals, the order was Zn > Cu > Cd > Cr ~ As ~ Ni ~ Pb ~ Ag (Tl < detection limit in animals). Considering essential trace elements in humans, Zn and Cu concentrations were similar in plants (15.2 ± 2.5 μg g^{-1} w.w. and 2.1 ± 0.3 μg g^{-1} w.w., respectively) and animals (21.8 ± 2.2 μg g^{-1} w.w. and 3.2 ± 0.3 μg g^{-1} w.w. respectively), while Ni and Cr showed higher concentrations in plants than in animals. For the non-essential PPEs, Cd concentrations were highest in animals, whereas Pb concentrations were highest in plants. Ag and Tl showed the lowest concentrations in both plants and animals. Concentrations of all PPEs were generally below published guidelines limits, where available.

3.2. Introduction

The oil sands development in northern Alberta, Canada, has raised concerns about the release of trace elements, considered to be priority pollutant elements (PPE) by the United States Environmental Protection Agency (U.S. EPA), into the surrounding environment (Bari et al., 2014; Gueguen et al., 2011; Kelly et al., 2010; Skierszkan et al., 2013; Wiklund et al., 2012). Some of these PPE (e.g., arsenic (As), cadmium (Cd), lead (Pb), silver (Ag), thallium (Tl)) consist of elements categorized as non-essential trace elements for the human body (i.e., only negative effects on function have been documented; (Zoroddu et al., 2019)). Other identified PPE are categorized as essential trace elements (e.g., copper (Cu), zinc (Zn)), or possibly as essential trace elements (chromium (Cr), nickel (Ni)); these elements are necessary at low concentration for human biological functioning, but become toxic at elevated levels relative to body requirements (Zoroddu et al., 2019). All of these PPE are taken up by plants and animals (Jaishankar et al., 2014; Rai et al., 2019) and can then be consumed as traditional foods and medicinal plants by local/Indigenous communities (Donaldson et al., 2010; McAuley et al., 2018a; Shotyk et al., 2020). Yet, locally harvested nutrient-dense animal and plant species also represent valuable sources of protein, vitamins, and minerals, and thus form a major part of healthy diets of such communities (Gagne et al., 2012; Kenny et al., 2018). Research on the levels of PPE in traditional foods in the boreal regions, such as northern Alberta, is limited, with most studies on this topic focusing on Arctic or near-Arctic regions (Donaldson et al., 2010). In addition, few studies have examined terrestrial plants and animals, despite their traditional importance to communities residing close to the oil sands developments (Graney et al., 2012; Graney et al., 2017; McAuley et al., 2018a; Shotyk, 2020; Shotyk et al., 2020; Stachiw et al., 2019).

Exposure of biota to essential and non-essential trace elements occurs naturally, although anthropogenic sources, such as fossil fuel installations, can be a major contributor to their environmental concentrations (Ali et al., 2019; Jaishankar et al., 2014). Essential trace elements are required for bodily function, acting as critical constituents of several organometallic enzymes (Prashanth et al., 2015). The determination of what is a toxic, versus optimal, intake of essential trace elements depends on the physiological requirements of an organism and on homeostatic processes that assist in regulating the concentrations of these elements to maintain them at optimal levels (Aliasgharpour and Rahnamaye Farzami, 2013). When present in excess, they can disrupt normal bodily functioning (Prashanth et al., 2015). Therefore, it is important to assess the concentrations of these essential elements in traditional foods, given that these foods are good sources of essential elements and minerals (Gagne et al., 2012; Kenny et al., 2018), but could contain essential elements at toxic concentrations as PPE due to anthropogenic activities. Unlike the essential trace elements, non-essential elements can be toxic even at the low ppb to < 10 ppm range (Tchounwou et al., 2012). These elements can disrupt normal bodily functions even at very low concentrations through accumulation in vital organs, including the kidney, liver, and brain, and alter the biological function of micronutrients by displacing them and interfering with their key roles in maintaining health (Jaishankar et al., 2014; Singh et al., 2011). Non-essential elements can further damage cellular processes through oxidative stress (Flora et al., 2008; Jaishankar et al., 2014).

Recent research has shown that the oil sands industry operations in Alberta, Canada have led to elevated concentrations of thirteen essential and nonessential trace elements—antimony (Sb), (As), beryllium (Be), (Cd), (Cr), (Cu), (Pb), (Hg), (Ni), (Ag), (Tl), and (Zn), but not selenium (Se)—considered to be priority pollutants by the U.S. EPA, within the region of the

Athabasca river and its tributaries, snowpacks, and soils/sediments (Kelly et al., 2010). In line with the findings of Kelly et al. (2010), recent research is now converging upon measuring the levels of PPE in wild plants and animals of the Athabasca region; however, this work so far remains limited to studies on lichens, moose, Labrador tea, fish, and berries (Landis et al., 2019; McAuley et al., 2018a; Shotyk, 2020; Shotyk et al., 2019; Shotyk et al., 2020; Stachiw et al., 2019). Landis et al. (2019) pointed out that distance from the main oil sands production operations is an important factor regarding the levels of trace elements, as the majority of these elements were deposited within 25 km from the oil sands upgrading facilities. McAuley et al. (2018a) found out that in general, among various tissues of moose, trace elements such as Cd showed higher concentrations in organ tissues including kidney and liver than moose muscle. Trace elements can be deposited on the surface of plants by dust or plants can uptake these elements from soil via roots (Shotyk, 2020; Shotyk et al., 2019; Shotyk et al., 2020; Stachiw et al., 2019). Research on Labrador tea and berries indicated that washing samples before analysis could reduce the concentrations of trace elements in these traditional food items (McAuley et al. 2016; Stachiw et al., 2019). Understanding the concentrations of essential and nonessential trace elements in a more fulsome sampling of community foods may be particularly important in this region of elevated environmental levels of PPE (Kelly et al., 2010). The Bigstone Cree Nation is a First Nation community located close to Fort McMurray, one of the major oil sands operations in Alberta. This community relies on traditional animal and plant foods consumed for their nutritional and medicinal values. The interpretation of concentrations measured in these traditional foods may be aided by comparison to guideline limits. Although there are no guideline limits for trace elements in most species of wild animals, the European Commission has provided guideline limits for trace elements, including Pb and Cd, for fish muscle, as well as

for the meat and offal of farm animals (European Commission, 2006). According to those guidelines, Pb and Cd should not respectively exceed 0.30 μg g^{-1} w.w. and 0.05 μg g^{-1} w.w., in fish muscle; and 0.10 μg g^{-1} w.w. and 0.05 μg g^{-1} w.w. in muscle tissues of farm animals. The European Commission (2006) guideline limits for Cd in organ tissues including kidney (1.0 μg g^{-1} w.w.) and liver (0.5 μg g^{-1} w.w.) have been also established. Additionally, the World Health Organization (WHO) has provided a guideline for several essential and nonessential trace elements, including As (5 μg g^{-1} w.w.), Cd (0.3 μg g^{-1} w.w.), Cr (2 μg g^{-1} w.w.), and Pb (10 μg g^{-1} w.w.) in raw herbal medicines in different countries such as Canada (WHO, 2007). The objective of this study was to determine the concentrations of nine out of the thirteen elements listed as PPE under the U.S. EPA's Clean Water Act, specifically to quantify and compare the concentrations of essential trace elements, including As, Cd, Cr, Cu, Ni, Pb, Ag, Tl, and Zn in food groups (plant or animal), individual species, and tissue types (muscle versus organ). Two other PPEs, Hg and Se, were previously assessed in traditional foods of the Bigstone Cree Nation, as described in detail by Golzadeh et al. (2020).

3.3. Materials and Methods

3.3.1. Study site and field sampling

This study was conducted through community-led participation, in which Bigstone Cree members collected frequently consumed traditional foods. The Bigstone Cree Nation identified all of these items as food worthy of study. Hereafter, traditional plant and animal samples are referred to as traditional foods for simplicity and as most items, including the medicinal herbs, are referred to as food by community members. Various teas are consumed with such regularly in the region that they are considered a form of food-medicine. Various organ tissues were also

used in this study, since some members of the Bigstone Cree Nation, notably elders, consume the organ tissues including liver, kidney, and brain.

The location of the Bigstone Cree Nation and associated field samplings were previously described in detail Golzadeh et al. (2020) (Supplementary Information, Figure S3.1.). In short, the Bigstone Cree Nation is located in central northern Alberta, Canada, in close proximity to the Athabasca oil sands region, the largest oil sands development region in Alberta. The region is rich in traditional foods, i.e., fish and wild game, given its location in the boreal forest and it being surrounded by four lakes: the North and South Wabasca, Sandy, and Calling (Baker, 2018). This research was conducted in collaboration with members of the Bigstone Cree Nation and the Centre for Indigenous Peoples' Nutrition and Environment (CINE) at McGill University. Based on an internal food survey within the community and their traditional knowledge, frequently consumed traditional plant and animal samples were collected by the community members from June to September 2015. Once collected, samples were frozen and shipped to CINE for analysis.

Seven species of aquatic and terrestrial plants were collected, with subsampling of plant leaves, root, stems, and fruits. Six of these species are mainly used by the community as medicinal plants, including water lily (*Nymphaeaceae* spp.), Labrador tea (*Rhododendron groenlandicum*), rat root (*Acorus americanus*), mountain ash (*Sorbus aucuparia*), mint *(Mentha* spp.), and lichen called "old man's beard (*Usnea* spp.)". We also received seven species of berries (all grouped as "berry"): lingonberry (*Vaccinium vitis-idaea*), cranberry (*Vaccinium spp.*), rosehip (*Rosa canina*), highbush cranberry (*Viburnum trilobum*), bunchberry (*Cornus canadensis*), blueberry (*Cyanococcus spp.*), bog cranberry (*Vaccinium oxycoccos*), and

Saskatoon berry (*Amelanchier alnifolia*) (sample sizes and moisture content provided in Supplementary Table S3.1.).

Traditional animal samples from the Bigstone Cree Nation territories were collected from lake and terrestrial environments, including whitefish (*Coregoninae clupeaformis*), mallard duck (*Anas platyrhynchos*), grouse including ruffed grouse (*Bonasa umbellus*) and spruce hen (*Falcipennis canadensis*), and snowshoe hare (*Lepus americanus*) as whole animals with skin/feathers on. Muscle, liver, kidney, and brain samples were dissected for analytical analyses. Additionally, community members had already dissected some animal samples, including several individual tissues of moose (*Alces alces*) and black bear (*Ursus americanus*). Moose rib samples were traditionally smoked by the community as well. Hereafter, ruffed grouse and spruce hen are grouped as "grouse" since they share a similar diet (sample sizes and moisture content provided in Supplementary Table S3.2.).

3.3.2. Trace element analysis

Each individual sample was weighed and dried. Plant samples were oven-dried at 50 °C for 24 hr, and various tissues of animal samples were freeze-dried at –90 °C for 24 h with a Flexi-Dry^{TM}-MP unit (Kinetics, New York, USA). To convert dry weight (d.w.) trace element concentrations to wet weight (w.w.) equivalents, the moisture content of each individual sample was determined gravimetrically. Trace elements were extracted and measured following the U.S. EPA's method 200.8 (EPA, 1994). Digestion of a 160 mg portion of each sample was done overnight using 2 mL of trace metal grade nitric acid (HNO_3). Next, the samples were placed on a dry digestion block at 125 °C for 2 h, then cooled to room temperature. A 0.5 mL aliquot of trace metal grade hydrogen peroxide (H_2O_2) was added to each sample, and then samples were

again placed on the digestion block (3 h at 125°C), and subsequently cooled. Ultrapure water (18.2 Ω) from a Milli-Q system (Millipore Corporation) was used to dilute samples to 50 mL. The samples were shaken, left to settle overnight, and finally subjected to four times dilution prior to analysis by inductively coupled plasma mass spectrometry (ICP-MS).

Quality control samples included blanks, replicate samples, and standard reference materials (SRM), which were placed every 10 to 15 samples. Peach leaves were used as the SRM for plant samples (NIST SRM 1547; National Institute of Standards and Technology) and for animal samples, fish protein was used (DORM-4; National Research Council of Canada). The average recovery rates of SRM 1547 (n = 4) and DORM-4 (n = 8) were calculated based on the certified value for available trace elements in each SRM as follows: As (NIST-1547: 274.1 ± 38.9%; DORM-4: 95.4 ± 0.0%); Cd (NIST-1547: 202.6 ± 30.2%; DORM-4: 109.8 ± 0.2%); Cr (NIST-1547: 86.4 ± 1.0%; DORM-4: 96.2 ± 1.4%); Cu (NIST-1547: 89.7 ± 0.8%; DORM- 4: 88.5 ± 0.5%); Pb (NIST-1547: 85.3 ± 1.2%; DORM-4: 71.6 ± 2.3%); Ni (NIST-1547: 135.6 ± 3.7%; DORM- 4: 93.5 ± 6.3%); and Zn (NIST-1547: 108.3 ± 7.9%; DORM-4: 98.6 ± 1.0%). The SRMs did not have certified values for Ag and Tl. Despite As and Cd having high recovery ranges in the plant SRM, their concentrations were used in the data analysis (Boulanger et al., 2019; Stachiw et al., 2019). The mean relative standard deviation (RSD) for replicate plant samples (n = 5) was 18.1 ± 8.0%, while that of animals (n = 11) was 13.4 ± 7.4%. Detection limits for each trace element were calculated as the mean value of reagent blank samples multiplied by 3× the SD (standard deviation), as follows: As (0.005 ± 0.019 μg L^{-1}), Cd (0.011 ± 0.008 μg L^{-1}), Cr (0.22 ± 0.30 μg L^{-1}), Cu (0.15 ± 0.03 μg L^{-1}), Pb (0.15 ± 0.16 μg L^{-1}), Ni (0.36 ± 0.28 μg L^{-1}), Ag (0.003 ± 0.002 μg L^{-1}), Tl (0.000 ± 0.005 μg L^{-1}), and Zn (2.62 ± 1.16 μg L^{-1}).

Sample concentrations were not blank corrected since blanks showed 10 or more times lower concentrations relative to the concentrations of samples.

3.3.3. Data analysis and treatment

In conducting data treatment, if the concentration of samples were below the detection limits, they were replaced by a value half the detection limits. Additionally, if the concentrations of ≥ 70% of a group of species was below the detection limit for given trace element, then the entire species was excluded from further analysis. Further details on trace elements with concentrations below the detection limits are presented in Supplementary Table S3.3. Several outliers in the Pb concentration of animal samples were detected and omitted from the analysis (Supplementary Table S3.4.).

We used a mixed modeling approach to compare the trace element concentrations, since the data set was unbalanced and incomplete due to small sample size and also variation among the samples. This approach used a compound symmetry covariance structure with restricted maximum likelihood (REML). For the animal data, each specimen was designated as a random subject, since tissue types taken from the same individual are not statistically independent of one another. This prevented pseudo-replication or inflation of statistical power, since the correct denominator degrees of freedom (d.d.f.) were used for testing the fixed effects of interest (using the Wald/*F* statistic, with d.d.f. approximated following the method by Kenward and Roger, 1997). For each trace element, a pair of mixed models was fitted to the data: one that compared food groups alone (i.e., plants with animals) and their species (nested within food group), and then another that compared only animal species and tissue type (tissues/organs nested within species). Fitted models were checked for normality of residuals and equal variances by visually

checking diagnostic plots. When these assumptions were violated, $\log_{10}$-transformation of the variables was sufficient to satisfy them in all cases. For significant effects in the mixed models, *post hoc* pairwise comparisons among factor levels were conducted using Tukey's honest significant difference (HSD) test with least squares (LS) means.

In interpreting our results, we grouped aquatic and terrestrial animal and plant species under "animals" and "plants" respectively. Collection and organization of data was done via Excel 2016 V. 16.25, and statistical analyses were conducted in JMP V. 14.1.0 (SAS Institute Inc., 2019). The results were considered statistically significant at $P < 0.05$. Hereafter, concentrations of essential and non-essential trace elements are reported as arithmetic mean ± SE in $\mu g\ g^{-1}$ w.w.

3.4. Results

Concentrations of PPE declined in the following order for plants: Zn > Cu > Ni > Cr ~ Pb > As ~ Cd > Ag ~ Tl, while in animals, the order was Zn > Cu > Cd > Cr ~ As ~ Ni ~ Pb ~ Ag with Tl being below the detection limit in all animal samples. The concentrations of Ag and Tl were mostly below the detection limit in plant and animal samples. Thus, the essential and possibly essential elements (Cr, Cu, Ni, and Zn) were generally higher than the non-essential elements (e.g., As, Cd, Pb, Ag, and Tl), although the distinction was somewhat less clear for animals than for plants.

3.4.1. Variation in the concentrations of Cr, Cu, Ni, and Zn

Considering the four essential and possibly essential PPE, i.e., Cr, Cu, Ni, and Zn, there were significant differences between animals and plants for three of them; Zn showed higher

concentrations in animal samples than plants, and Ni and Cr were higher in plants than animals (mixed model, food group: for Cr, $F_{1, 163} = 62.00$, $P < 0.001$; Ni, $F_{1, 155} = 361.50$, $P < 0.001$; Zn, $F_{1, 169} = 21.06$, $P < 0.001$). Zn had the greatest concentrations of all PPE in both animals and plants, but animals showed around 1.5 times higher Zn concentrations than plants (21.6 ± 2.1 μg g^{-1} w.w. versus 15.2 ± 2.5 μg g^{-1} w.w., respectively). Cu concentrations were not significantly different between plants and animals (mixed model, food group, $F_{1, 168} = 0.60$, $P < 0.443$). Concentrations of Ni were 16 times higher in plants than animals. For Cr, concentrations were around an order of magnitude lower than for Zn, and showed a similar pattern to Ni, in which plant concentrations were higher than animal samples (0.22 ± 0.07 μg g^{-1} w.w. versus 0.04 ± 0.00 μg g^{-1} w.w., respectively).

Comparing Cr within food groups, Cr concentrations varied significantly among plant species (mixed model, $F_{11, 105} = 9.38$, $P < 0.001$), being significantly higher in Labrador tea, old man's beard, and mint than in the other plant species ($P < 0.001$) (Figure 3.1.A). In contrast to plant samples, the Cr concentrations did not vary among animal species (mixed model, $F_{5, 49} = 1.51$, $P < 0.201$); however, the concentrations did show variability among tissue/organ of animal samples (nested term, $F_{8, 64} = 6.73$, $P < 0.001$), being highest in grouse brain and muscle, hare muscle, fish liver, moose muscle and rib, and duck liver and muscle than the rest of animal samples ($P < 0.001$) (Figure 3.1.B).

The Cu concentrations also differed significantly among the plant species (mixed model, $F_{11, 137} = 11.53$, $P < 0.001$), where mint showed the highest concentrations and the lowest concentrations belonged to water lily compared to the rest of species ($P < 0.001$) (Figure 3.1.C). The Cu concentrations also varied among animal species (mixed model, $F_{5, 46} = 11.51$, $P < 0.001$) and their harvested tissue/organ types (nested term, $F_{8, 61} = 32.37$, $P < 0.001$), with duck

liver and muscle and fish liver ($P < 0.001$) having an order of magnitude higher concentrations than fish muscle, which had the lowest Cu concentrations ($P < 0.001$) (Figure 3.1.D).

Likewise, the Ni concentrations varied significantly among the plant species (mixed model, $F_{6, 58} = 27.0$, $P < 0.001$); concentrations were higher in mint, mountain ash, old man's beard, Labrador tea, and berry than in water lily ($P < 0.001$) (Figure 3.1.E). The concentrations of Ni were also variable among animal species (mixed model, $F_{5, 52} = 4.43$, $P = 0.002$) and harvested tissue/organ types (nested term, $F_{8, 66} = 6.47$, $P < 0.001$); grouse brain, hare kidney, moose rib and muscle had higher levels than all other animal samples ($P < 0.001$) (Figure 3.1.F).

The levels of Zn also varied significantly among plant species (mixed model, $F_{11, 136} = 19.27$, $P < 0.001$), being highest in mountain ash, mint, old man's beard, and Labrador tea ($P < 0.001$) relative to other plants, while water lily had the lowest concentrations (Figure 3.1.G). Among the animal species, Zn concentrations varied depending on the species (mixed model, $F_{5, 49} = 15.50$, $P < 0.001$) and harvested tissue/organ types (nested term, $F_{8, 64} = 15.21$, $P < 0.001$), being highest in moose muscle and rib, bear muscle, and liver of fish, duck, and hare ($P < 0.001$), whereas the lowest concentrations belonged to duck muscle and brain, and fish and grouse muscle ($P = 0.001$) (Figure 3.1.H). Mean concentrations of essential trace elements in all plant and animal samples are fully detailed in Supplementary Information (Table S3.5.).

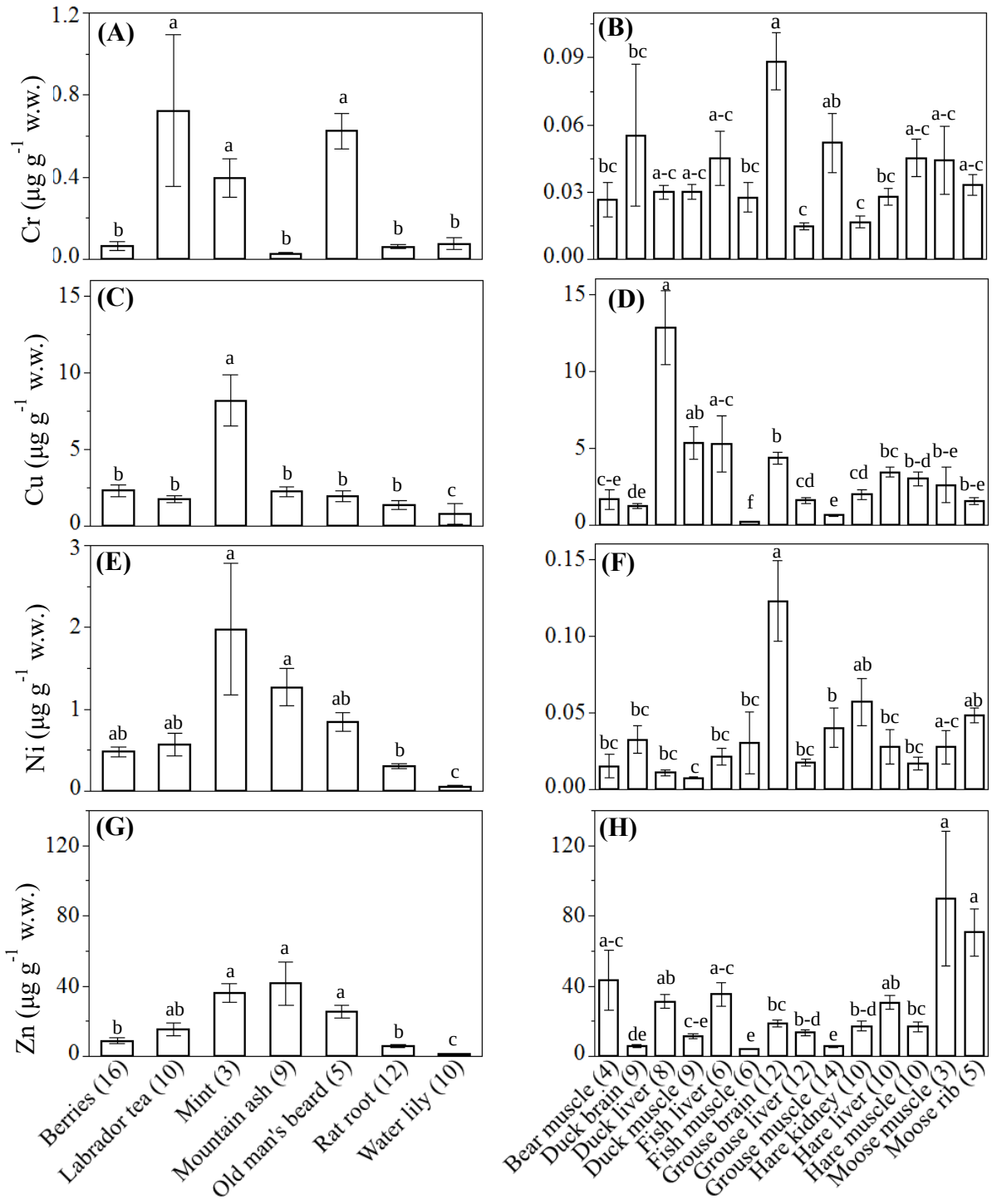

Figure 3.1. Mean ± SE concentrations (µg g^{-1} w.w.) of (A) and (B) chromium (Cr), (C) and (D) copper (Cu), (E) and (F) nickel (Ni), and (G) and (H) zinc (Zn) in important plant and animal

foods, respectively, of the Bigstone Cree Nation in Alberta, Canada in 2015. The number in brackets following the food type represents the sample size (*n*) where each sample was taken from an individual plant or animal species. Different lower-case letters within columns indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other. Note that the y-axis scales differ for Cr and Ni between plants and animals in order to be able to visualize them.

3.4.2. Variation in the concentrations of As, Cd, Pb, Ag, and Tl

There were significant differences among animals and plants for some of the non-essential element PPEs, including As, Pb, Ag, and Tl (mixed model, food group: for As, $F_{1, 104} = 9.30$, $P = 0.003$; Pb, $F_{1, 147} = 105.00$, $P < 0.001$; Ag, $F_{1, 142} = 5.11$, $P < 0.025$; Tl, $F_{1, 92} = 12.24$, $P < 0.001$). Pb showed the highest concentrations of the non-essential PPE in plants, and Pb concentrations were higher in plants compared to animals (0.18 ± 0.05 μg g^{-1} w.w. versus 0.03 ± 0.00 μg g^{-1} w.w.; mixed model, food group: Pb, $F_{1, 147} = 1.00$, < 0.001). The highest concentration of non-essential PPE in animals was Cd (0.5 ± 0.2 μg g^{-1} w.w.), although concentrations of Cd were not significantly different among animal and plant samples (mixed model, food group: Cd, $F_{1, 132} = 0.96$, $P = 0.33$). Concentrations of Ag and Tl were mostly lower than for all other PPE in both food groups (i.e., plants and animals) and were below the detection limits in most samples.

Concentrations of As varied significantly among plant samples (mixed model, $F_{6, 58} = 19.93$, $P < 0.001$), where old man's beard, Labrador tea, rat root, and mint had the highest concentrations and the lowest concentrations belonged to mountain ash and berry ($P < 0.001$) (Figure 3.2.A). For animal samples, its concentrations varied significantly among species (mixed

model, $_{2, 30}$ = 12.39, $P < 0.001$) and tissue/organ types harvested (nested term, $F_{5, 45} = 3.90$, $P = 0.005$). It was higher in fish liver and muscle, duck and grouse liver, and duck muscles ($P < 0.001$) than in duck brain, and grouse muscle and brain ($P < 0.001$). The concentrations of As were below the detection limit in bear muscle, hare kidney, liver, and muscle, moose muscle and rib (Figure 3.2.B).

Considering variation in Cd concentrations within food groups, Cd concentrations differed among plant (mixed model, $F_{10, 123} = 10.66$, $P < 0.001$) and animal species (mixed model, $F_{5, 47} = 16.93$, $P < 0.001$) and their tissue/organ types (nested term, $F_{5, 43} = 143.06$, $P < 0.001$). That is, among the plant samples, Cd concentrations were higher in mountain ash, old man's beard, and mint than in the rest of the plant samples (Figure 3.2.C); and within the animals Cd concentrations were higher in hare kidney ($P < 0.001$) than the reminder of samples ($P < 0.001$) (Figure 3.2.D).

The Pb concentrations varied significantly among the plant species (mixed model, $F_{11, 129} = 6.20$, $P < 0.001$), with the highest concentrations in old man's beard and mint and the lowest in water lily, mountain ash, berry, and rat root ($P < 0.001$) (Figure 3.2.E). In contrast, the concentrations of Pb were similar among all animal species (mixed model, $F_{5, 54} = 1.08$, $P = 0.377$) and tissue/organ types (nested term, $F_{8, 67} = 1.10$, $P = 0.371$) (Figure 3.2.F).

Considering Ag concentrations, they varied significantly among plant species (mixed model, $F_{6, 58} = 8.65$, $P < 0.001$) and were found to be highest in old man's beard, mint, and Labrador tea ($P < 0.001$) and lower in berry, rat root, and water lily ($P < 0.001$) (Figure 3.2.G). Unlike plant samples, the concentrations of Ag did not differ among animal species (mixed model, $F_{2, 28} = 0.80$, $P = 0.460$). Ag concentrations in most tissue/organs of animal samples including bear muscle, fish muscle, grouse brain, liver and muscle, hare kidney, liver and

muscle, and moose muscle and rib were below the detection limits; therefore, no statistical analysis was performed (Figure 3.2.H).

Lastly, Tl concentrations in both plant and animal samples were the lowest among all the non-essential elements. The Tl concentrations were below the detection limits in berry, mountain ash and water lily and also did not differ among the rest of the plant species (mixed model, $F_{3, 26} = 1.03$, $P < 0.39$) (Figure 3.2.I). Unlike the plant species, the concentrations of Tl in all animal species and their organ tissues were below detection limit (Figure 3.2.J). Details of mean concentrations of non-essential trace elements in all plant and animal samples are provided in Supplementary Information (Table S3.6.).

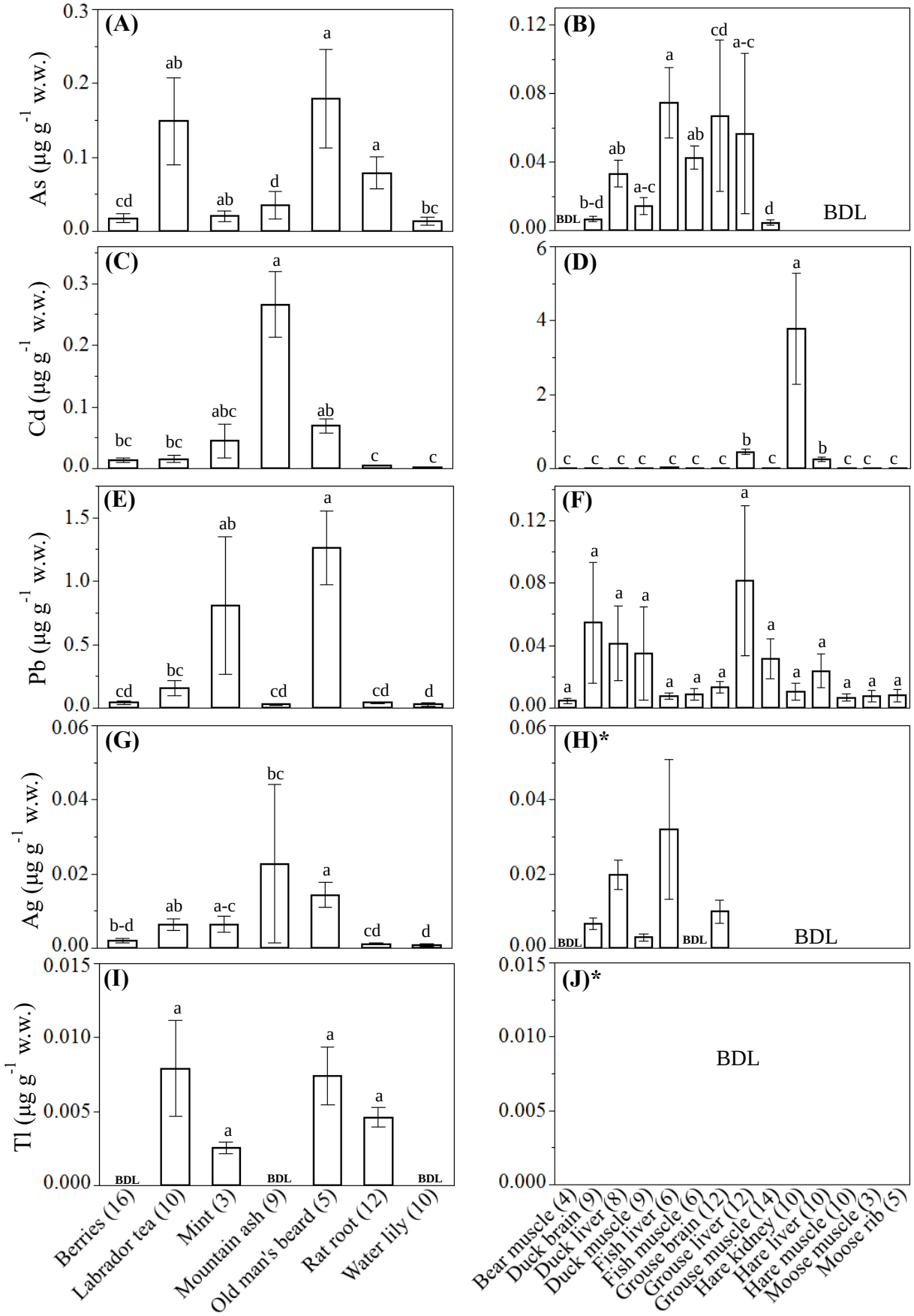
(A)
As (µg g-1 w.w.)
cd
ab
ab
d
a
a
bc
(B)
BDL
b-d
ab
a-c
a
ab
cd
a-c
d
BDL
(C)
Cd (µg g-1 w.w.)
bc
bc
abc
a
ab
c
c
(D)
c c c c c c c b c a b c c c
(E)
Pb (µg g-1 w.w.)
cd
bc
ab
cd
a
cd
d
(F)
a a a a a a a a a a a a a
(G)
Ag (µg g-1 w.w.)
b-d
ab
a-c
bc
a
cd
d
(H)*
BDL
BDL
BDL
(I)
Tl (µg g-1 w.w.)
BDL
a
a
BDL
a
a
BDL
(J)*
BDL
Berries (16)
Labrador tea (10)
Mint (3)
Mountain ash (9)
Old man's beard (5)
Rat root (12)
Water lily (10)
Bear muscle (4)
Duck brain (9)
Duck liver (8)
Duck muscle (9)
Fish liver (6)
Fish muscle (6)
Grouse brain (12)
Grouse liver (12)
Grouse muscle (14)
Hare kidney (10)
Hare liver (10)
Hare muscle (10)
Moose muscle (3)
Moose rib (5)

Figure 3.2. Mean ± SE concentrations (μg g^{-1} w.w.) of non-essential priority pollutant elements (PPE) in (A) and (B) arsenic (As); (C) and (B) cadmium (Cd); (E) and (F) lead (Pb); (G) and (H) silver (Ag); and (I) and (J) thallium (Tl) in the plant and animal samples of the Bigstone Cree Nation in Alberta, Canada in 2015. The number in brackets following the food type represents the sample size (*n*) where each sample was taken from an individual plant or animal species. Different lower-case letters within columns indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other. BDL denotes those samples below the detection limits. *, no robust statistical analysis possible for Ag and Tl concentrations in animal samples due to most or all samples being below detection limits. Note that the y-axis scales differ for As, Cd, and Pb between plants and animals in order to be able to visualize them.

3.5. Discussion

Among the essential/possibly essential PPE in both plants and animals, Zn showed higher concentrations than other elements including Cu, Ni, and Cr. This could be due to the fact that over 300 enzymes in an organism require Zn for regular functioning (McCall et al., 2000). The mean concentration of Zn was 1.5 times higher in the Bigstone Cree Nation's animals than plant samples as animal-based foods are generally a greater source of Zn than plant-based foods (Sloup et al., 2017), given that they contain certain amino acids that improve Zn absorption (Brown et al., 2001). Levels of Zn being higher than the rest of essential trace elements could be due to some trace elements being more naturally abundant (i.e., Zn) (Luoma and Rainbow, 2005). However, it could also reflect the abundance of some PPE in the ecosystem arising from industrial activities or long-range atmospheric transport that releases those pollutants into the

environment (Kelly et al., 2010; Steinnes and Friedland, 2006). Indeed, for the oil sands regions of Alberta, Canada, Kelly et al. (2010) indicated that concentrations of Cd, Cu, Ni, Pb, Ag, and Zn exceeded Alberta's guidelines for the protection of aquatic life in water collected from Athabasca River and its tributaries near or downstream of the oil sands developments. Among non-essential trace elements in the traditional plant and animal samples, Cd in animal samples showed 8.5 times higher concentrations than that of plants; whereas for Pb this pattern was reverse, showing that plant samples had 6.6 times higher concentrations than the animals. This difference could be explained by heavy metal transfer from abiotic matrices to organisms (i.e., for plants: soil to plant and atmospheric deposition of dust, and for animal: trophic transfer and uptake of contaminants through food chain), and physiology of species that influences the accumulation of trace elements (Ali and Khan, 2019).

Of the essential elements in plant samples Zn showed significantly higher mean concentrations compared to the rest of trace elements, generally ranked Cu > Ni > Cr. This descending pattern is in line with Stachiw et al. (2019) study where essential trace elements in unwashed berries (i.e., cranberry, lingonberry, and blueberry) collected from Fort McKay in the Athabasca oil sands region showed concentrations in the following rank: Zn (7.8 ± 1.9 μg g^{-1} d.w.) > Cu (3.1 ± 0.9 μg g^{-1} d.w.) > Ni (0.5 ± 0.4 μg g^{-1}, d.w.) > Cr (0.04 ± 0.24 μg g^{-1} d.w.) (Stachiw et al., 2019). Comparing our results with the same species of berries used in Stachiw et al. (2019), Zn and Cr concentrations in berries of the Bigstone Cree Nation were higher by 3- to 4- fold (Zn: 16.9 ± 5.4 μg g^{-1} d.w. and Cr: 0.15 ± 0.05 μg g^{-1} d.w., respectively), while Cu and Ni showed similar concentrations with (Cu: 4.2 ± 0.6 μg g^{-1} d.w. and Ni: 0.8 ± 0.1 μg g^{-1} d.w.). This discrepancy is possibly due to the different sampling locations where in the current study berries were collected from traditional sites that are also places the community members are concerned

about the concentrations of contaminants, whereas in Stachiw et al (2019), berries were not collected in relationship to First Nations people in the area (J. Baker, Personal communication). The Bigstone Cree Nation did not wish to share the locations where samples were taken. In regard with proximity to the oil sands among Stachiw et al (2019) and the current study, Fort McKay territory is much closer to the surface mining (open pit mines), while the Bigstone Cree Nation is in close proximity to major *in-situ* mining (using steam assisted gravity drainage system) near the berry patches (J. Baker, Personal communication). Interestingly, Stachiw et al. (2019) found out that, contaminants could be deposited in form of dust on the surface of plants (i.e., Cr) or taken up by the plants (i.e., Zn, Cu, Ni). The concentrations of Zn, Ni, Cu, and Cr in epiphytic lichens (*Hypogymnia physodes*) collected within a 150 km radius from oil sands activities (Landis et al., 2019) were 1.8- to 5.3- fold higher than that of the lichen, old man's beard, in our study (Zn: 46.6 ± 9.7 μg g^{-1} w.w. versus 25.3 ± 3.5 μg g^{-1} w.w.; Ni: 4.5 ± 2.8 μg g^{-1} w.w. versus 0.8 ± 0.1 μg g^{-1} w.w.; Cu: 3.9 ± 1.7 μg g^{-1} w.w. versus 1.9 ± 0.3 μg g^{-1} w.w.; and Cr: 2.7 ± 1.9 μg g^{-1} w.w. versus 0.62 ± 0.08 μg g^{-1} w.w.). This could, in part, be due to the differences between lichen species used in various studies. Distance to the oil sands could also play a role, however, the exact locations of the plant and animal samples collected by the Bigstone Cree for our study were confidential. Comparing our concentrations of essential/possibly essential elements with earth's crust abundance indicated that none of the Bigstone Cree Nation plant samples exceeded the upper continental earth's crustal abundance of Zn (67.0 μg g^{-1}), Cu (28.0 μg g^{-1}), Ni (47.0 μg g^{-1}), and Cr (92.0 μg g^{-1}) (Rudnick and Gao, 2003). This may suggest that there is no significant anthropic contribution to the levels of essential these elements (Stachiw et al., 2019).

Among the essential elements in animal samples, the rib, muscle, and liver tissues of several species showed the highest concentrations of Zn compared to kidney and brain tissues. This variation is perhaps due to different factors such as presence of certain amino acids, metabolic process, and the intake of metals from food/diet and other sources (Bawuro et al., 2018). Studies of essential trace elements in various terrestrial animal species in oil sands regions are limited, and therefore made it challenging to make comparison with various species in our study. Similar to the oil sands industry, elevated release of trace elements from copper smelters has been reported (Hu et al., 2019). A study of snowshoe hare in industrial regions of northwestern Quebec (< 150 km from a copper smelter) reported Zn concentrations in hare liver was 2.5 times higher than that of hare muscle at 31.1 ± 13.6 μg g^{-1} w.w. and 12.2 ± 11.0 μg g^{-1} w.w., respectively (Bordeleau et al., 2016). This is in line with our results for hare liver and muscle (30.7 ± 4.0 μg g^{-1} w.w. and 16.9 ± 2.9 μg g^{-1} w.w., respectively) which indicated liver tissue of hare accumulated almost twice higher concentrations of Zn than the muscle. The second most abundant essential trace element in Bordeleau et al. (2016) was Cu, in hare liver at 3.7 ± 2.1 μg g^{-1} w.w. and hare muscle at 2.7 ± 0.9 μg g^{-1} w.w., similar to our finding for hare liver of 3.4 ± 0.3 μg g^{-1} w.w. and for hare muscle of 3.0 ± 0.4 μg g^{-1} w.w. Zn being higher in liver than muscle could also be linked to metal detoxifications through metallothionines in the liver (Hogstrand and Haux, 1991). Levels of Cr and Ni were below detection limit in Bordeleau et al. (2016) study; however, we detected concentrations in hare liver (Cr: 0.028 ± 0.003 μg g^{-1} w.w.; Ni: 0.027 ± 0.011 μg g^{-1} w.w.) and muscle (Cr: 0.045 ± 0.008 μg g^{-1} w.w.; Ni: 0.016 ± 0.004 μg g^{-1} w.w.). This variation may be due to the amount of trace elements released from the oil sands development compared with the copper smelter industry that implemented filtering technology resulting in reduced emission of several trace elements (Savard et al., 2006).

For non-essential elements concentrations in plant samples, Pb at 0.18 ± 0.05 μg g^{-1} w.w. had higher concentrations than the rest of the non-essential trace elements. Comparing the concentrations of non-essential elements in old man's beard to those reported in various species of epiphytic lichens from the Athabasca oil sands region showed that the levels of As, Cd, Pb, and Tl in old man's beard were 2.2 to 5.4 times lower than that of Landis et al. (2019) study. That study did not report the concentrations of Ag, therefore, Ag levels could not be compared with our plant samples. In Stachiw et al. (2019), concentrations of Cd and Pb measured in wild berries at 0.008 ± 0.007 μg g^{-1} d.w. and 0.01± 0.00 μg g^{-1} d.w., respectively, were lower than those found for the Bigstone Cree Nation samples (Cd: 0.03 ± 0.01 μg g^{-1} d.w.; Pb: 0.09 ± 0.03 μg g^{-1} d.w.). As stated previously, this could be due to differences in the uptake rate of trace elements and distance from the oil sands activities as the Bigstone Cree Nation samples were collected in a closer proximity to Fort McMurray where the majority of *in-situ* oil sands developments occur. The mean concentration of Tl at 0.006 ± 0.004 μg g^{-1} w.w. in wild berries collected from reclaimed areas after open-pit oil sands (bitumen) mining in the same region (Shotyk, 2020), was higher than our results for Tl in which the concentrations were below the detection limit in berries. Concentrations of As, Pb and Ag in raw Labrador tea and mint used as traditional plants in two communities in northern Alberta, Canada, were as follows: for Labrador tea (As, 0.03 ± 0.02 μg g^{-1} d.w.; Pb: 0.05 ± 0.03 μg g^{-1} d.w.; Ag: BDL) and mint (As: 0.04 ± 0.02 μg g^{-1} d.w.; Pb: 0.06 ± 0.04 μg g^{-1} d.w.; Ag: BDL) (McAuley et al. 2016). Both Pb and Ag showed higher concentration in Labrador tea and mint of the Bigstone Cree Nation than that of McAuley et al. (2016). As showed similar concentrations in mint in both studies; however, its concentration was 4.9 times higher in Labrador tea of the Bigstone Cree Nation. This discrepancy could be due to field sampling regions since in McAuley et al. (2019) study, samples

were collected from Peace River oil sands region which is known as the smallest oil sands deposits in Alberta, where there may be fewer upgrading activities. Another likely contributing factor is where plant species were collected by the Bigstone community members, since distance to the nearest road or industrial activities may affect the concentrations of trace elements in plants (Modrzewska and Wyszkowski, 2014). It should be noted that Labrador tea and mint are usually consumed in the form of tea, in which concentrations of trace elements may be lower than in the raw vegetation (McAuley et al. 2016). Non-essential elements in the Bigstone Cree Nation plant samples resulted in that Ag and Tl showed concentrations below the earth's crust abundance, respectively; however, Pb levels in plant samples (0.18 ± 0.05 μg g^{-1} w.w.) showed elevated concentrations than that of the earth's crust (0.0005 μg g^{-1}). This indicates that some elements such as Pb could be emitted by the oil sands development into the surrounding area and then deposited on plants via dust (Stachiw et al., 2019).

Unlike plant samples, the highest concentrations of non-essential elements in animal samples belonged to Cd. Among the animal species of the Bigstone Cree Nation, Cd concentrations were higher in kidney compared to other animal tissues, likely as Cd is primarily stored in the kidney (Nordberg et al., 2015). Cd concentrations measured in moose from three First Nation communities in northern Alberta, Canada from 2012 to 2014 were found to be higher in kidney (9.2 ± 10.4 μg g^{-1} w.w.), followed by liver (2.0 ± 2.3 μg g^{-1}, w.w.), and lowest in muscle tissues (0.008 ± 0.006 μg g^{-1} w.w, similar to the current study at 0.006 ± 0.001 μg g^{-1} w.w..) (McAuley et al., 2018a). The First Nation Food, Nutrition and Environmental Study (FNFNES) for Alberta, Canada, reported average concentrations of As, Cd, and Pb at 0.004 μg g^{-1} w.w., 0.009 μg g^{-1} w.w., and 0.069 μg g^{-1} w.w. (respectively) for moose muscle (*Alcas alcas*) (Chan et al., 2016). For moose muscle in our study, As concentrations were below the detection

limit and Cd and Pb both showed concentrations that were 1.8 to 9.8 times lower than that of FNFNES. The FNFNES also reported average levels of As, Cd, and Pb in hare muscle at 0.03 μg g^{-1} w.w., 0.04 μg g^{-1} w.w., 4.2 μg g^{-1} w.w., respectively (Chan et al., 2016). As concentrations were below the detection limit in our hare muscle; Cd concentrations were 2.7 times higher, while Pb concentrations were lower at 0.007 ± 0.002 μg g^{-1} w.w., relative to the hare muscle results reported in FNFNES. Concentrations of Ag and Tl were relatively low compare to the rest of non-essential elements in both plant and animal samples. The non-essential metal variation among different species/organ tissues could be related to animals' assimilation and detoxification ability, feeding habits, bioavailability of trace elements in a given environment (i.e., water, soil, and sediments), structure and function of tissue in which metal accumulation occur (Ali et al., 2019).

Comparing our results for plants with established guideline values provided by the World Health Organization (WHO, 2007), we found that all plants samples had concentrations below the guideline levels for As (5 μg g^{-1} w.w.), Cd (0.3 μg g^{-1} w.w.), Cr (2 μg g^{-1} w.w.), and Pb (10 μg g^{-1} w.w.). The Pb and Cd concentrations in the Bigstone fish muscle (0.009 ± 0.003 μg g^{-1} w.w. and 0.001 ± 0.000 μg g^{-1} w.w., respectively) were more than an order of magnitude lower than the guideline limits for fish of 0.30 μg g^{-1} w.w. for Pb and 0.05 μg g^{-1} w.w. for Cd provided by the European commission (European Commission, 2006). All other animal muscle tissues concentrations in our study were also below the guidelines for Pb (0.1 μg g^{-1} w.w.) and Cd (0.05 μg g^{-1} w.w.) for meat/muscle of farm animals including bovine animals, sheep, pig and poultry (European Commission, 2006). Comparing the Bigstone Cree Nations kidney and liver samples to the European Commission (2006) guidelines for respective tissues in farm animals (kidney: 1.0 μg g^{-1} w.w.; and liver: 0.5 μg g^{-1} w.w.) revealed that hare kidney had 3.7 times concentrations

above the established guideline; however, none of the liver samples exceed the guideline limits. It should be noted that these guidelines are mostly established for farm animals and therefore, may not be appropriated for wild animals as research has indicated different accumulation patterns of trace elements in wild compared to farm animals (Minganti et al., 2010).

3.6. Conclusions

Consumption of traditional food provides many benefits to Indigenous communities including high nutritional value, however, elevated concentrations of several PPE in abiotic matrices in the oil sands region of Alberta, Canada (Kelly et al 2010) may compromise the higher nutritional value of these foods. Among plant and animal samples of the Bigstone Cree Nation, levels of essential trace elements were generally higher than that of non-essential elements. Concentrations were generally below guideline values; however, guideline values are not available for all elements and/or all tissue types/species. This study provides baseline PPE data to which future concentrations can be compared, given expected on-going increases in extractive activities in the region (National Energy Board, 2018). We thus recommend on-going monitoring to identify future changes in PPE concentrations in these traditional foods. Future studies should be designed to distinguish the extent to which PPE found in traditional foods is related to the oil sands industry, natural source, and/or arrive via long-range atmospheric transport. Results of this study could be used in comprehensive risk evaluation via food frequency consumption questionnaire and food and personal habit survey (i.e., smoking) to better evaluate the exposure risk through consumption of these traditional foods.

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Linking Statement

In the previous two chapters, I quantified and compared the concentrations of eleven priority pollutant elements (PPE) in various species of plant and animal samples of the Bigstone Cree Nation. The next chapter builds on evaluating and comparing distribution profile of another group of contaminants, polycyclic aromatic compounds (PACs), which their massive release from the oil sands industry in Alberta has been indicated by recent studies. Various classes of PAC include the 16 parent polycyclic aromatic hydrocarbons (PAHs) listed by U.S. EPA, alkylated PAHs, and dibenzothiophenes (DBTs). Since the U.S. EPA identified the list of the 16 parent PAHs, four decades ago, most research has been conducted on these priority PAHs. Thus, research on more toxic congeners of PACs such as alkylated PAHs is not well-established. In line with this, most research in oil sands regions of Alberta on abiotic and wildlife species has conducted on the 16 U.S. EPA priority PAHs, despite the fact that alkylated PAHs are more prevalent near major oil sands production than the 16 U.S. EPA priority PAHs. This chapter strengthened comprehensive toxicological profiling of PACs by measuring more toxic congeners of PAHs, including alkylated ones that are relatively less studied, particularly in traditional foods of the Bigstone Cree Nation inhabiting the oil sands development region.

Chapter 4. Alkylated polycyclic aromatic hydrocarbons are the largest contributor to polycyclic aromatic compound concentrations in traditional foods of the Bigstone Cree Nation in Alberta, Canada

4.1. Abstract

Rising global demand for energy promotes extensive mining of natural resources, such as oil sands extractions in Alberta, Canada. These extractive activities release hazardous chemicals into the environment, such as polycyclic aromatic compounds (PACs), which include the parent polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and sulfur-containing heterocyclic dibenzothiophenes (DBTs). In areas adjacent to industrial installations, Indigenous communities may be exposed to these PACs through the consumption of traditional foods. Our objective was to evaluate and compare the concentrations of total PACs (∑PAC), expressed as the sum of the 16 U.S. EPA priority PAHs (∑PAH), 49 alkylated PAHs (∑alkyl-PAH), and 7 DBTs (∑DBT) in plant and animal foods collected in 2015 by the Bigstone Cree Nation in Alberta, Canada. We analyzed 42 plant tissues, 40 animal muscles, 5 ribs, and 4 pooled liver samples. Concentrations of ∑PAC were higher in the lichen, old man's beard (*Usnea* spp.) (808 ± 116 ng g^{-1} w.w.), than in vascular plants, and were also higher in smoked moose (*Alces alces*) rib (461 ± 120 ng g^{-1} w.w.) than in all other non-smoked animal samples. Alkylated-PAHs accounted for between 63% and 95% of ∑PAC, while the concentrations of ∑PAH represented 4% to 36% of ∑PAC. Contributions of ∑DBT to ∑PAC were generally lowest, ranging from <1% to 14%. While the concentrations of benzo(a)pyrene (B[a]P) and ∑PAH4 (∑benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and B[a]P) in all samples were below guideline levels for human

consumption as determined by the European Commission, guideline levels for the more prevalent alkylated PAHs are not available. Given the predominance of alkylated PAHs in all food samples and the potentially elevated toxicity relative to parent PAHs of this class of PACs, it is critical to consider a broader range of PACs other than just parent PAHs in research conducted close to oil sands mining activities.

4.2. Introduction

Increasing worldwide demand for energy, especially for fossil fuels, promotes large-scale extractive industries, such as the well-known oil sands of Alberta, Canada. Canada is estimated to contain the third-largest crude oil reserves in the world, after Venezuela and Saudi Arabia, with oil reserves estimated at 171.0 billion barrels; 166.3 billion barrels of this are estimated to be present in the oil sands reservoirs in Alberta (National Resources Canada, 2017). These oil sands are located in three regions of Alberta: Athabasca (the largest), Cold Lake, and Peace River. Ongoing demand has led to the enormous growth of oil production in these regions, projected to increase by 58%, from 2.8 million barrels per day in 2017 to 4.5 million barrels per day in 2040 (National Energy Board, 2018).

This ongoing development may be a potent source of chemical contaminants released into surrounding ecosystems, leading to potential negative consequences for both wildlife and humans. Recent studies have indicated that the oil sands industry in Alberta releases elevated levels of multiple classes of contaminants, including polycyclic aromatic compounds (PACs) into lakes, rivers, sediments, and snowpack in the Athabasca oil sands region (Giesy et al., 2010; Kelly et al., 2009; Kurek et al., 2013; Parajulee and Wania, 2014; Schuster et al., 2015). This is an issue of concern for nearby communities that rely on traditional foods (wild plants and

animals harvested from local resources), which usually have higher nutritional value than store-bought foods, and provide key social, health, and economic benefits for Indigenous communities reliant on them (Gagné et al., 2012; Kuhnlein, 2015).

The PACs consist of thousands of components that are released into the environment from natural and anthropogenic sources including fossil fuel use (Abdel-Shafy and Mansour, 2016). One well-known sub-class of PACs, the polycyclic aromatic hydrocarbons (PAHs), are ubiquitous hydrophobic organic compounds consisting of two or more fused benzene rings varying widely in structure (Balmer et al., 2019). Alkylated PAHs consist of benzene rings with various numbers of alkyl substituents including methyl, ethyl, and propyl groups symbolized as C1, C2, and so on, which designate the number of carbon atoms on different locations of the benzene rings and thus, form different structures of alkylated PAHs (Achten and Andersson, 2015; Andersson and Achten, 2015). Dibenzothiophenes (DBTs) are sulfur-containing PACs and are components of bitumen and petroleum products (Harner et al., 2018). Those PACs generated at high temperatures (350°C to above 1200°C) during the incomplete combustion of fossil fuels and other organic materials are referred to as the pyrogenic PAHs (Abdel-Shafy and Mansour, 2016). The 16 parent (unsubstituted) PAHs listed by the United States Environmental Protection Agency (U.S. EPA) as priority compounds are highly represented in pyrogenic sources (Lima et al., 2005). By contrast, petrogenic PAHs form over geologic time scales at relatively low temperatures (100°C to 150°C); petrogenic sources, including bitumen and other petroleum products, tend to show high representation by the alkylated PAHs (Abdel-Shafy and Mansour, 2016). Both alkylated PAHs and DBTs could be considered as markers for PAC emissions from petrogenic sources (Schuster et al., 2015).

Most studies to date in the oil sands region, have focused on quantifying the 16 parent PAHs (Irvine et al., 2014; Ohiozebau et al., 2017). However, knowledge of the environmental concentrations of other PACs, including alkylated PAHs, which are more persistent and potentially more toxic to wildlife and humans, remains limited (Andersson and Achten, 2015; Baird et al., 2007; Lee et al., 2011; Uno et al., 2010). The majority of PACs present in oil sands (or bitumen) are in the form of alkylated PAHs, yet there is limited research considering this class of PACs in their risk assessment studies in the oil sands regions of Alberta (Irvine et al., 2014; Ohiozebau et al., 2017). For instance, alkylated PAHs constituted between 93% to 99% of the total PACs measured in sediment samples from the Athabasca deposit (Colavecchia et al., 2004). Similarly, alkylated PAHs accounted for 80% of the total dry and 60% of the total wet atmospheric deposition in the Athabasca oil sands regions (Zhang et al., 2015). Thus, evaluating concentrations of a broader suite of PACs, including the alkylated PAHs, in wildlife and humans situated proximate to the oil sands regions should be a research priority (Andersson and Achten, 2015; Colavecchia et al., 2004). Here, we carried out a community-led study in which the community members used traditional knowledge to select traditionally important plant and animal species (Baker, 2016) to address two main objectives: (1) to determine the levels of the 16 U.S. EPA priority PAHs (∑PAH), alkylated PAHs (∑alkyl-PAH), and DBTs (∑DBT) in traditional plant and animal foods of the Bigstone Cree living near the Athabasca oil sands, and; (2) to characterize the ring distribution profiles of the 16 U.S. EPA priority PAHs and alkylated PAHs in plant and animal species. Doing this indicated the dominant PAC compound classes, as well as congeners of PACs based on their ring numbers, in various samples consumed as traditional foods. It should be noted that this study was not designed to assess the risk of PACs through the consumption of traditional foods nor the source of exposure.

4.3. Materials and Methods

4.3.1. Study site and field sampling

The study site and sampling were described previously in Golzadeh et al. (2020). In brief, the Bigstone Cree Nation community is located in the boreal forest of north central Alberta—part of Treaty 8 agreement (http://www.treaty8.ca) (Government of Canada, 1899)—within the Athabasca region—the largest oil sands reserve in Alberta—and not far from the major oil sands operations in Fort McMurray (Figure 4.1; (Golzadeh et al., 2020)). In this participatory research project, traditional food samples consisted of various species of plants and muscle and liver tissues of animal species that the community members consume and refer to as foods. Frequently consumed foods in the Bigstone Cree Nation territory were collected by community members from June through September 2015, placed the samples in Ziplock bags (to follow the same sampling procedures in which traditional foods are collected by the community members). The majority of animal samples were sent to us after hunting and thus, were in the whole form with bones, fur, and/or feathers on. The samples were then frozen and sent to the Centre for Indigenous Peoples' Nutrition and Environment (CINE) at McGill University. There, samples were stored frozen at –20°C until further analysis. Following that, samples were sub-sampled (plants) or dissected (animal) for muscle and organ tissues.

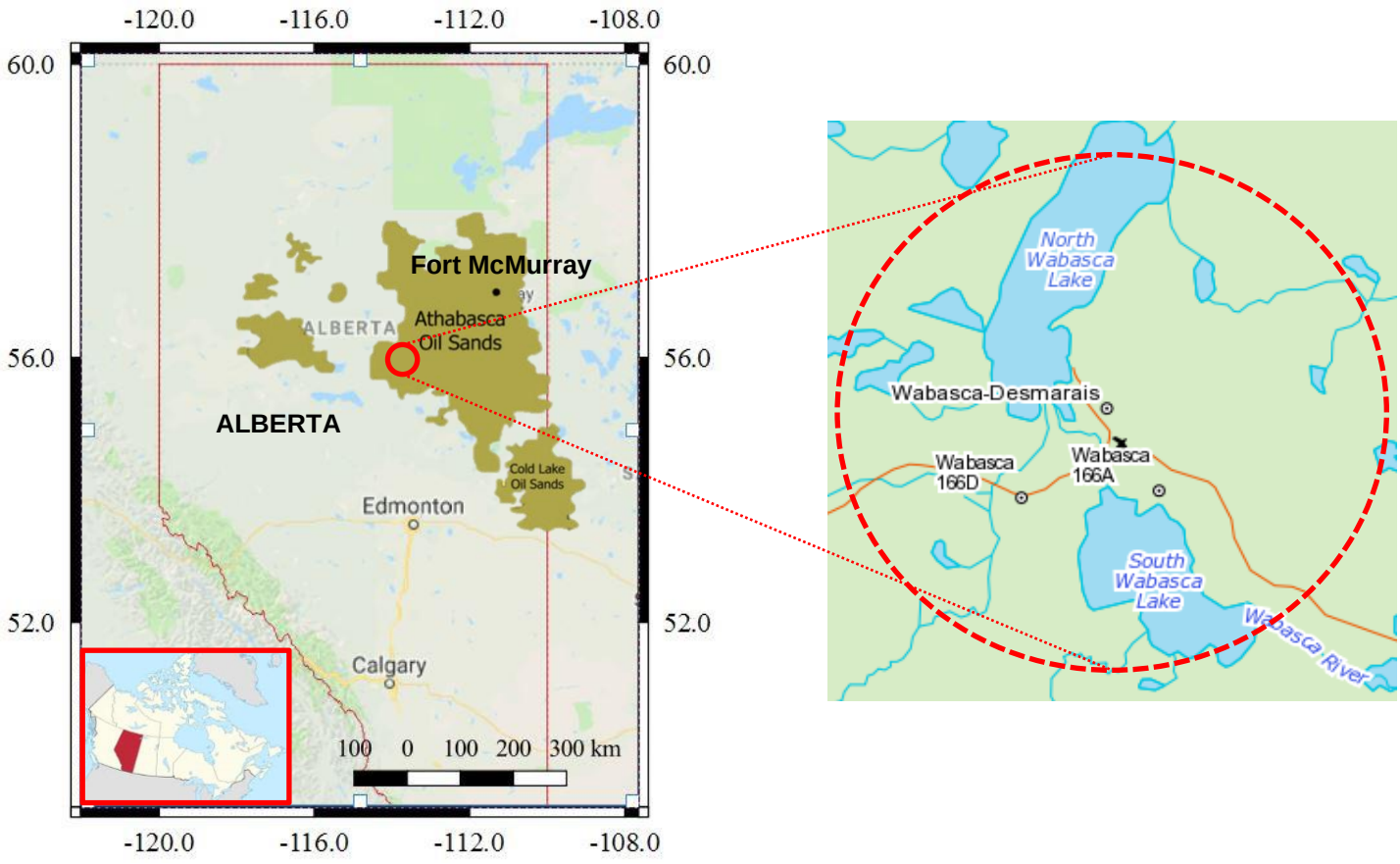

Figure 4.1. Map showing the centre of Bigstone Cree Nation territory and focus of this study (red dashed circle) in Alberta, Canada (Golzadeh et al., 2020). Bigstone Cree Nation has six reserves and a traditional territory that covers a significantly larger area.

For plant samples, different parts were subsampled (i.e., leaves, root, stems, fruits) from six aquatic and terrestrial species. The traditional plants included: water lily, Labrador tea, rat root, mountain ash, old man's beard (a type of lichen), and a mix of berry plants (fruit) that were grouped under "berry": Table 1). These plants are mostly used by the Bigstone Cree Nation as food and medicine, with little distinction between the two (Baker and Fort McKay Berry Group, 2019), both in raw and prepared (e.g., tea) form (Ayer, 1995; Baker, 2020; Uprety et al., 2012).

Table 4.1. Traditional plant samples of the Bigstone Cree Nation in Alberta, Canada, collected in 2015 (Adapted from Golzadeh et al. 2020).

	Plant samples	**Scientific name**	**Tissue**	**Sample size *(N)***
Aquatic	**Water lily**	*Nymphaeaceae* spp.	Roots	6
Terrestrial	**Labrador tea**	*Rhododendron groenlandicum*	Leaves	9
	Berry		Fruits	8
	Cranberry	*Vaccinium* spp.		
	Rosehip	*Rosa canina*		
	Highbush cranberry	*Viburnum trilobum*		
	Saskatoon berry	*Amelanchier alnifolia*		
	Rat root	*Acorus americanus*	Roots	10
	Mountain ash	*Sorbus aucuparia*	Stems	6
	Old man's beard	*Usnea* spp.	Whole tissue	3
	Total			**42**

Various species of animals, including fish, duck, grouse/hen, and hare (Table 2), were collected from both freshwater lakes and terrestrial environments and sent in whole form (i.e., skin/feathers on). Since the diets of ruffed grouse and spruce hen are similar, both were grouped as "grouse". Skin/feathers and bones were removed from these whole animals, and only their muscle and liver tissues were analyzed. For each species received in whole form, the livers of five individual animals per species were pooled to form a composite sample (due to low mass of liver samples to perform analysis). We also received muscle and traditionally smoked rib tissues from moose and muscle tissue from black bear (already dissected by the community members) (Table 2).

Table 4.2. Traditional animal samples of the Bigstone Cree Nation in Alberta, Canada, collected in 2015 (Adapted from Golzadeh et al. 2020).

	Animal samples	**Scientific name**	**Tissue**	**Sample size *(N)***
Aquatic	**Fish**		Muscle	6
	Whitefish	*Coregoninae clupeaformis*	Pooled liver	1
	Duck		Muscle	7
	Mallard	*Anas platyrhynchos*	Pooled liver	1
Terrestrial	**Grouse**		Muscle	10
	Ruffed grouse	*Bonasa umbellus*	Pooled liver	1
	Spruce hen	*Falcipennis canadensis*		
	Hare		Muscle	10
	Snowshoe hare	*Lepus americanus*	Pooled liver	1
	Moose		Muscle	3
	Moose	*Alces alces*	Rib-smoked	5
	Bear		Muscle	4
	American black bear	*Ursus americanus*		
	Total			**49**

4.3.2. PAC analysis

Samples were subsampled/dissected at CINE and then sent to AXYS Analytical Services Ltd. (Sidney, BC, Canada), where analytical determination of PACs were carried out following a standard operating procedures according to AXYS method MLA-021 (AXYS, 2013), and EPA methods 8270C,D and 1625B (EPA, 1984, 1998). PAC analysis monitored the 16 U.S. EPA priority PAHs, 49 alkylated PAHs, and 7 DBTs (Σ_{69} PACs). A total of 42 individual plant tissue samples, 40 individual animal muscle tissues, 5 individual animal ribs, and 4 pooled animal liver tissue samples were analyzed. Each individual food sample was kept in a semi-frozen state for the homogenization process, in which tissue was blended into a smooth paste, after which,

isotopically labeled standards were added. Then, approximately 10 g subsamples were Soxhlet extracted using dichloromethane, and all extracted samples were then chromatographically cleaned using column chromatography on silica combined with Bio-Beads (Bio-Rad, California, USA).

PAC analyses were conducted using gas chromatography- low resolution mass spectrometry (GC-LRMS) with an RTX-5 capillary gas chromatography column (30 m, 0.25 mm i.d., 0.25 μm film thickness (Restek, Pennsylvania, USA). Two ions were monitored for each PAH and alkylated PAH and their associated deuterated surrogate standard. The standard operation procedures used isotope dilution internal standard quantification to generate recovery-corrected results (Supplementary Table S4.1). A full analyte list, along with acquisition and quality control (QC) parameters are provided in Supplementary Tables S4.2 A, B, C, D. To perform the initial calibration for PAC quantification, a series of solutions including target analytes (parent and alkylated PACs), labelled surrogate and recovery standards were used. For calibration a five-point (20, 100, 500, 2000, 5000 ng/mL) standard calibration curved was used. Calibration verification was conducted at least once every 12 hrs using analysis of a mid-level calibration solution.

Quality control measures included method blanks and method spikes, which were analyzed along with the samples. Blank concentrations for all PACs ranged from 0.007 to 0.9 ng g^{-1} in 91 plant and animal samples. Method detection limits (calculated as 3×SD of blanks) ranged from 0.01 to 0.6 ng g^{-1} based on 10 g of wet weight samples. Sample specific detection limits (SDLs) were determined based on 3:1 signal-to-noise-ratio from multiple masses for every sample. The SDLs were used as reporting limits for sample concentrations and were generally < 0.5 ng g^{-1} for all plant and animal samples. Results were recovery-corrected, with the recoveries

(mean ± SD) calculated from all batches of samples (plants and animals) for the 16 surrogate compounds ranged from 20.0 ± 8.0% for naphthalene d-8 to 71.2 ± 13.3% for chrysene d-12. The rest of percent recovery rates are presented in Supplementary Table S4.3.

4.3.3. Data treatment and analysis

Total PACs ($\sum_{69}$ PACs) were reported as the sum of the 16 U.S. EPA priority PAHs (∑PAH), 49 alkylated-PAHs (∑alkyl-PAH), and 7 DBTs (∑DBT). For B[a]P, since it is a well-studied and known carcinogen, we also presented its concentrations in plants and animals separately. The concentrations of PAH4 (∑benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and B[a]P) were similarly presented as a broader marker of parent PAHs with an established guideline limit. It should be noted that not all of the individual congeners of PACs (i.e., the 16 U.S. EPA priority PAHs, 49 alkylated PAHs, and 7 DBTs) were detected in all plant and animal samples. That is, after blank-subtraction, for the parent PAHs between 9 to 16 congeners were detected in plants, while 3 to 15 congeners were detected in animal samples. For alkylated PAHs, between 29 to 44 congeners were detected in plants and 21 to 40 in animal samples. The number of individual DBTs detected in plants were between 1 to 6, whereas in animal samples the number of detected DBTs were between 2 to 5 congeners. All individual congeners were detected in at least one sample of plant and/or animal. The concentration of individual congeners of PAC are fully detailed in Supplementary Table S4.4 A, B.

Prior to the statistical analysis, data treatment was conducted as per Evans et al. (2019); that is, if the concentration of samples were below the detection limit, they were replaced by half of the value of the detection limit. The concentration data were blank corrected batch-by-batch and only those samples above the detection limit and that also met quantification criteria were

retained: for instance, any sample with one or more laboratory flags (i.e., NDR flag; peak detected but failed to meet quantification criteria) was deleted from the dataset. For animal samples, the lipid percentage was also provided by the AXYS Analytical Services Ltd. and ranged between 0.5 ± 0.0% in grouse muscle to 3.5 ± 0.8% in bear muscle. The pooled liver tissues had slightly higher lipid percentage ranged from 4.0% in pooled liver of hare to 12.7% in pooled liver of fish (Supplementary Table S4.5.). The PAC concentrations (ng g^{-1} w.w.) were plotted against percent lipid (Herbert and Keenleyside, 1995), indicating a weak positive correlation that was not significant ($\chi^2 = 0.13$, $P = 0.36$). Therefore, we did not lipid-correct the data.

Fitted models were checked for assumptions of normality of residuals and equal variances by visually checking their diagnostic plots. Since these assumptions were violated, dependent variables consisting of ∑PAH, ∑alkyl-PAH, and ∑DBT were $\log_{10}$-transformed, but this did not resolve model-fitting issues. After $\log_{10}$-transforming, diagnostic plots were checked to ensure no outliers were detected (Supplementary Table S4.6.). Thus, non-parametric Wilcoxon tests were used instead to compare the concentrations of various classes of PACs among species of animals or plants. For each dependent variable, one analysis (Mann-Whitney test) compared just the two food groups alone (i.e., plants versus animals) and two other analyses (Kruskal-Wallis test) compared the concentrations of PACs in animal and plant species, separately. For a significant effect of species, *post-hoc* pairwise comparisons were conducted with a Wilcoxon test (Wilcoxon sum-ranked). Since we only had one pooled liver sample for each species of animal ($n = 1$ pooled liver per species of fish, duck, grouse, and hare), the pooled liver samples were excluded from the statistical analysis. For presenting and interpreting our results, the aquatic and terrestrial samples were subsumed under their “animal” and “plant”

categories. Data were organized in Excel v16.25 (Microsoft, 2016) and all statistical analyses were conducted in JMP v14.1.0 (SAS Institute Inc., 2019). The *P* values lower than 0.05 ($P < 0.05$) were considered statistically significant. From here on, the concentration of various classes of PACs are reported as an arithmetic mean ± SE (ng g^{-1} w.w.) (Supplementary Table S4.7. A, B).

4.4. Results

4.4.1. PAC concentrations

Concentrations of the PACs varied across the sampled traditional foods of the Bigstone Cree Nation, with ∑PAC concentrations being significantly higher in plants than in animals (Mann-Whitney, food group, $\chi^2 = 19.65$, df = 1, $P < 0.001$). Significant differences were also found among the plant species (Kruskal-Wallis, $\chi^2 = 35.53$, df = 5, $P < 0.001$), with old man's beard showing the highest concentration of ∑PAC (808.7 ± 115.6 ng g^{-1} w.w.), whereas berry and water lily had the lowest concentrations at 6.8 ± 2.1 ng g^{-1} w.w. and 3.0 ± 1.1 ng g^{-1} w.w., respectively (Figure 4.2 A). Animal species also differed significantly in ∑PAC (Kruskal-Wallis, $\chi^2 = 33.5$, df = 6, $P < 0.001$), being highest in smoked moose rib and lowest in the muscles of fish, hare, grouse, and moose (Figure 4.2 B). Among the three classes of PACs, ∑alkyl-PAHs were predominant, accounted for 63.0% to 95.0% of the ∑PAC (percentage of PACs presented as %16 U.S. EPA priority PAHs, %alkylated PAHs, and %DBTs for plant and animal species shown in Supplementary Table S4.8.). The partial exception to this was that old man's beard, grouse liver, and hare liver, in which alkylated PAHs still predominated, showed higher concentrations of DBTs than parent PAHs by 1.2- to 3-fold.

Among various classes of PACs, the concentration of ∑PAH differed significantly between animal and plant samples (Mann-Whitney, food group, $\chi^2 = 8.47$, df = 1, $P < 0.003$), being higher in animals than in plants. Among plant species, ∑PAH concentrations were significantly higher (Kruskal-Wallis, $\chi^2 = 31.48$, df = 5, $P < 0.001$) in old man's beard (90.8 ± 12.9 ng g^{-1} w.w.) than in rat root, mountain ash, berry, and water lily, being 50- to 363-fold greater, with water lily being the lowest at 0.25 ± 0.14 ng g^{-1} w.w. (Figure 4.2 A). Similarly, ∑PAH concentrations differed significantly among various animal species/tissues (Kruskal-Wallis, animal species, $\chi^2 = 29.21$, df = 6, $P < 0.001$), with the highest concentration in smoked moose rib (168.5 ± 44.2 ng g^{-1} w.w.) and lowest in moose, grouse, and hare muscles (0.53 ± 0.16 ng g^{-1} w.w., 0.38 ± 0.08 ng g^{-1} w.w., and 0.18 ± 0.06 ng g^{-1} w.w., respectively) (Figure 4.2 B). Concentrations of ∑PAH in pooled livers of duck and fish were similar (3.9 and 3.3 ng g^{-1} w.w., respectively) and, at least qualitatively, higher than that of pooled livers of hare and grouse (1.04 and 0.55 ng g^{-1} w.w., respectively).

Among individual congeners of the 16 U.S. EPA priority PAHs with established guideline limits, the concentrations of B[a]P and ∑PAH4 varied among the traditional food samples. Concentrations of B[a]P were low or not detectable in most plant and animal samples. Among plants, all samples of old man's beard ($n = 3$) contained detectable B[a]P (0.86 ± 0.20 ng g^{-1} w.w.), but B[a]P was not detectable in other plants, except for in one individual sample each of rat root and Labrador tea (0.08 ng g^{-1} w.w. and 0.05 ng g^{-1} w.w., respectively). Considering animal samples, only smoked moose rib had detectable concentrations of B[a]P at 0.14 ± 0.05 ng g^{-1} w.w. The mean concentration of B[a]P in old man's beard was more than 6-fold higher than that in smoked moose rib. Similar to B[a]P, concentrations of ∑PAH4 were higher in plants compared with animals, with old man's beard having the highest ∑PAH4 concentrations at 14.6

± 2.3 ng g^{-1} w.w., nearly 10-fold higher than that of smoked moose rib. The rest of the plant samples showed relatively low ∑PAH4 concentrations compared with the old man's beard (means of 0.11± 0.06 to 1.4 ± 0.6 ng g^{-1} w.w.). Among animal samples, smoked moose rib had the highest ∑PAH4 concentrations at 1.51 ± 0.05 ng g^{-1} w.w. (detected in all individual samples), while the rest of non-smoked animal species showed mostly non-detectable concentrations of ∑PAH4 (Supplementary Table S4.9.).

Unlike for the parent PAHs, the concentrations of alkylated PAHs were higher in plant than in animal species (Mann-Whitney, food group, $\chi^2 = 21.27$, df = 1, $P < 0.001$), with the highest ∑alkyl-PAH concentrations among plants found for old man's beard at 605.5 ± 55.3 ng g^{-1} w.w., compared to the highest ∑alkyl-PAH concentrations among the animals being smoked moose rib at two-fold less (290.6 ± 75.2 ng g^{-1} w.w.). The remaining species of plants showed lower ∑alkyl-PAH concentrations than old man's beard (Kruskal-Wallis, $\chi^2 = 30.78$, df = 5, P <0.001), ranging from 2.7 ± 0.9 ng g^{-1} w.w. in water lily to 159.1 ± 24.9 ng g^{-1} w.w. in Labrador tea (Figure 1A). Concentrations of ∑alkyl-PAH among the rest of non-smoked animal samples were significantly lower than for the smoked moose rib (Kruskal-Wallis, $\chi^2 = 32.18$, df = 6, P <0.001), ranging from 1.26 ± 0.19 ng g^{-1} w.w. in grouse muscle to 6.7 ± 2.1 ng g^{-1} w.w. in duck muscle (Figure 4.2 B). The concentrations of alkylated PAHs were similar among pooled livers of duck, hare, grouse, and fish with corresponding concentrations of 12.2, 9.2, 7.7, and 7.6 ng g^{-1} w.w., respectively.

Similar to the alkylated PAHs, the concentrations of DBTs indicated higher variation in plant samples than in animals (Mann-Whitney, food group, $\chi^2 = 19.65$, df = 1, $P < 0.001$). In plant samples, the concentrations of the ∑DBTs ranged from 0.012 ± 0.009 ng g^{-1} w.w. in berries (with only two congeners—dibenzothiophene and C2-dibenzothiophenes— detected) to 112.3 ±

79.9 ng g^{-1} w.w. in old man's beard, which was significantly higher than for the rest of the plant species (Kruskal-Wallis, $\chi^2 = 34.81$, df = 5, $P < 0.001$). Among the animal samples, smoked moose rib (2.5 ± 0.5 ng g^{-1} w.w.) had significantly higher concentrations of ∑DBT compared to the non-smoked animal species (Kruskal-Wallis, $\chi^2 = 17.42$, df = 6, $P < 0.008$). Yet, pooled liver samples of hare, grouse, and fish had qualitatively similar ∑DBT concentrations to the smoked moose rib that ranged from 1.4 to 1.8 ng g^{-1} w.w., while pooled liver sample of duck had slightly higher ∑DBT concentration at 3.5 ng g^{-1} w.w.

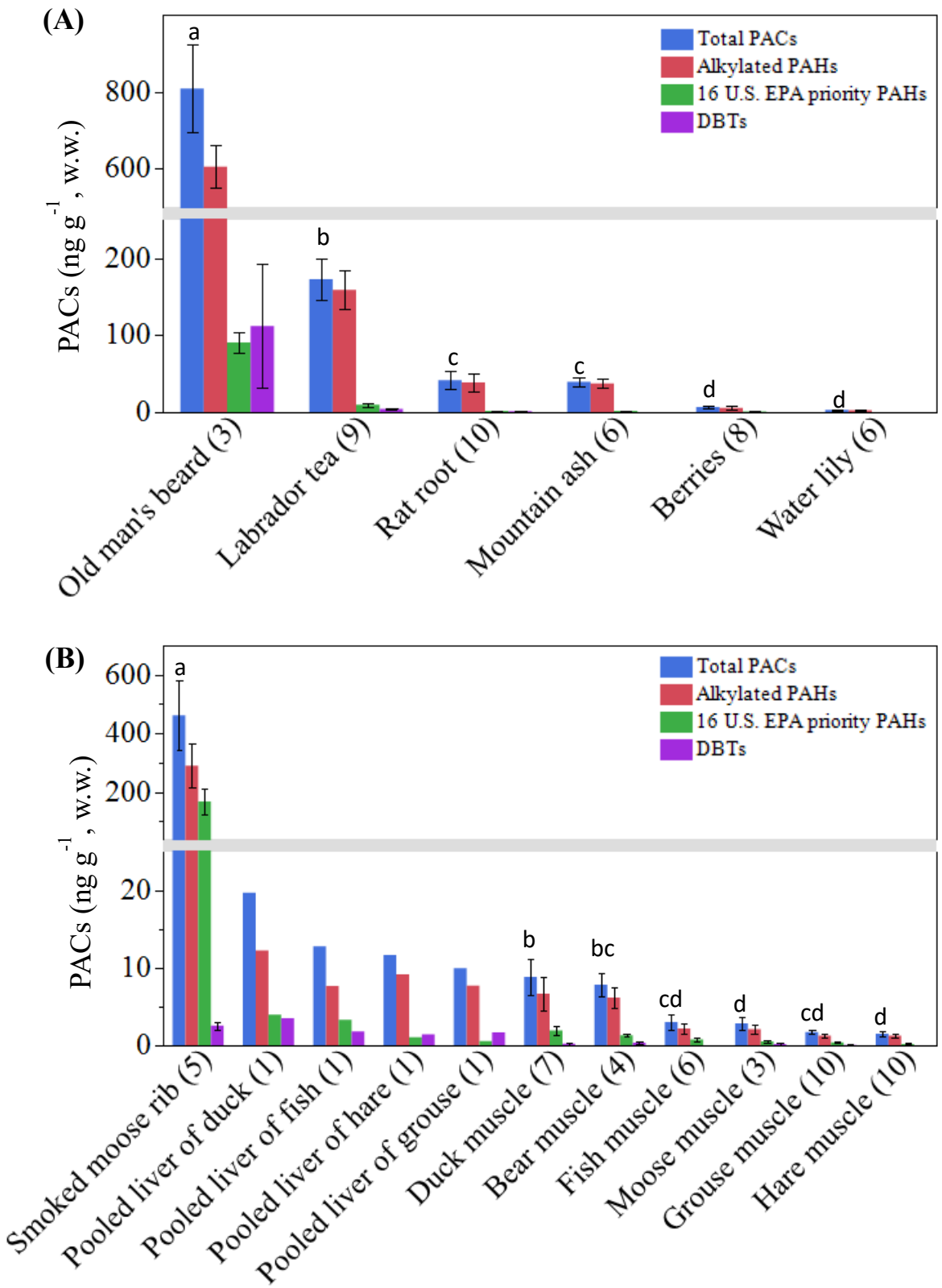
(A)
Total PACs
Alkylated PAHs
16 U.S. EPA priority PAHs
DBTs
PACs (ng g-1, w.w.)
800
600
200
100
0
a
b
c
c
d
d
Old man's beard (3)
Labrador tea (9)
Rat root (10)
Mountain ash (6)
Berries (8)
Water lily (6)
(B)
Total PACs
Alkylated PAHs
16 U.S. EPA priority PAHs
DBTs
PACs (ng g-1, w.w.)
600
400
200
20
10
0
a
b
bc
cd
d
cd
d
Smoked moose rib (5)
Pooled liver of duck (1)
Pooled liver of fish (1)
Pooled liver of hare (1)
Pooled liver of grouse (1)
Duck muscle (7)
Bear muscle (4)
Fish muscle (6)
Moose muscle (3)
Grouse muscle (10)
Hare muscle (10)

Figure 4.2. Mean (± SE) concentrations (ng g^{-1} w.w.) of the polycyclic aromatic compound (PAC) classes, parent polycyclic aromatic hydrocarbons (∑PAH), alkylated PAH (∑alkyl-PAH), and dibenzothiophenes (∑DBT), as well as total PACs (∑PAC), in (A) plant samples, (B) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada. Parenthetical numbers following the sample type denote sample size. Different lower-case letters indicate significantly different concentrations. Note the graphs differ in their broken y-axis scales. Statistical analyses were not performed for pooled livers due to low sample size (n = 1).

4.4.2. PAC patterns

To better understand the PAC congener distribution within the 16 U.S. EPA priority PAHs and alkylated PAHs, the proportion of each group separated according to aromatic ring number was also evaluated for both plant and animal samples separately. A similar analysis of the DBTs was not performed, since all seven monitored congeners were 3-ringed. For most plant samples, more than 80% of ∑PAH consisted of 2-, 3-, and 4-ring, except water lily that showed lower contribution of 2-ring PAHs and higher contribution of 5- and 6-ringed PAHs. For most animals, more than 60% of ∑PAH belonged to 2-ring PAHs. Naphthalene (2-ring PAH), in particular, was the predominant contributor to ∑PAH, except for fish muscle and smoked moose rib, which had higher contribution of 3-ringed PAHs (Figure 4.3 A, B). In general, the ∑5- and 6- ring PAHs accounted for lower proportion of the ∑PAH and were mostly only detected in plant species. Alkylated PAHs had similar ring distribution pattern as for the PAHs, wherein the Σ2- and 3-ring PAHs comprised around 70% or more of the ∑alkyl-PAH in all plant and animal samples (Figure 4.3 C, D). Several samples including berries, smoked moose rib, and old man's

beard showed that the ∑3-ring alkylated PAHs were more dominant compared with the ∑2-ring alkylated PAHs (60.2 %, 55.4%, and 46.1%, respectively). The ∑4-ring congeners were generally at a low proportion, ranging from 2.8% in pooled liver to 27% in old man's beard. The ∑5-ring alkylated PAHs were still lower in proportion, from 0.04% to 9.3%, while no 6-ring alkylated PAHs were detected in any plants or animal samples.

1

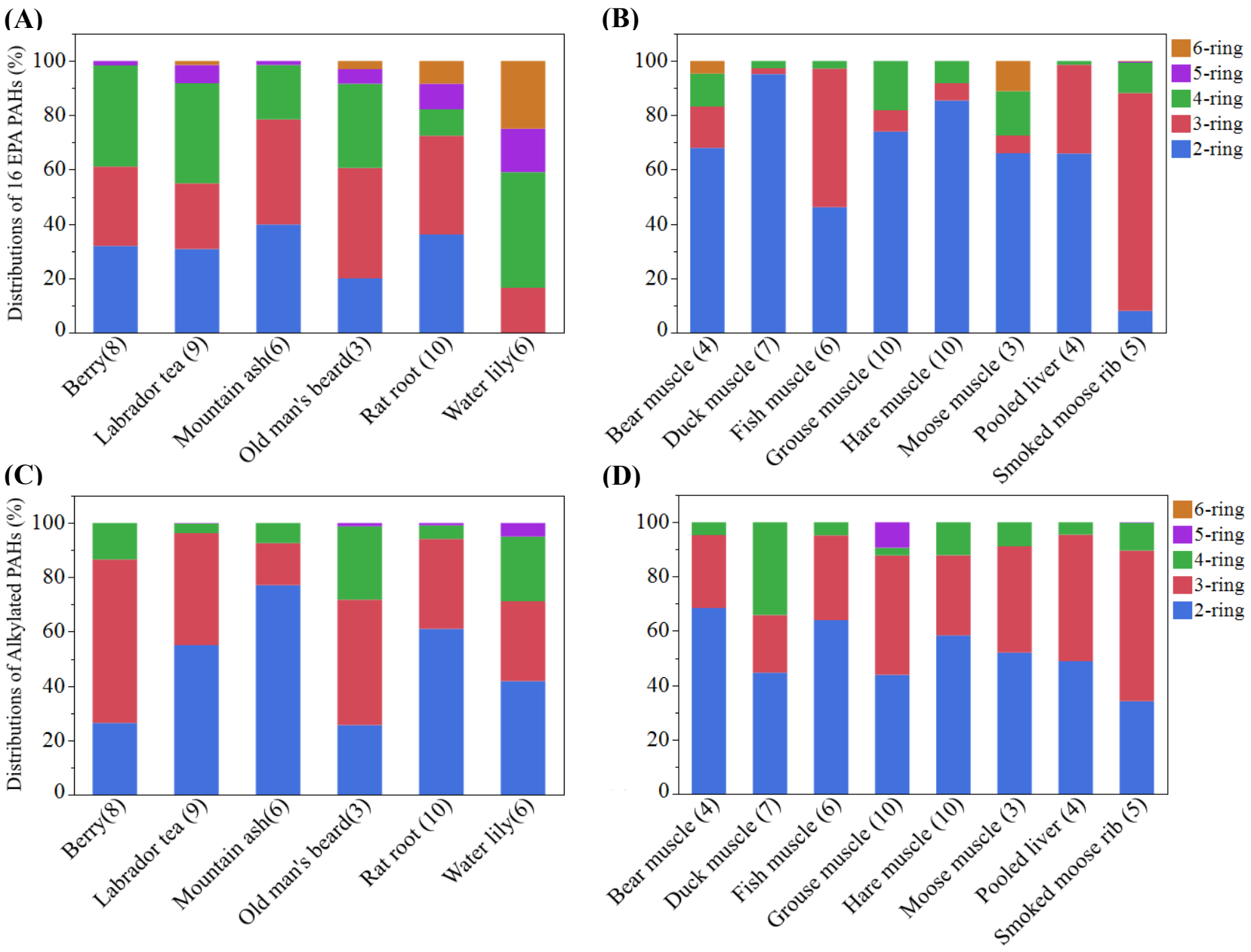
(A)
Distributions of 16 EPA PAHs (%)
0
20
40
60
80
100
Berry(8)
Labrador tea (9)
Mountain ash(6)
Old man's beard(3)
Rat root (10)
Water lily(6)
(B)
6-ring
5-ring
4-ring
3-ring
2-ring
Bear muscle (4)
Duck muscle (7)
Fish muscle (6)
Grouse muscle (10)
Hare muscle (10)
Moose muscle (3)
Pooled liver (4)
Smoked moose rib (5)
(C)
Distributions of Alkylated PAHs (%)
(D)

Figure 4.3. Ring distributions of the 16 U.S. EPA PAHs in (A) plants, (B) animals and that of the alkylated PAHs in (C) plants, (D) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada. Parenthetical numbers following the sample type denote respective sample size. Individual liver samples followed the same pattern in ring distributions; thus, they were pooled.

4.5. Discussion

Concentrations of ∑PAC, as well as ∑PAH, ∑alkyl-PAH, and ∑DBT, were higher in the lichen (old man's beard) than in the vascular plants and the animal samples consumed by the Bigstone Cree Nation community. Elevated PAC concentrations in old man's beard are likely related to lichens being able to sequester a great amount of atmospheric pollutants, including PACs, through wet and dry deposition processes (Augusto et al., 2010). This is due to their ecophysiology, specifically, they lack roots and their thalli do not have a cuticle, enabling them to accumulate nutrients and moisture, and incidentally, airborne pollutants, directly from air into their tissues (Conti and Cecchetti, 2001; Massimi et al., 2019), unlike for vascular plants (Fismes et al., 2002; Zhan et al., 2013). Consequently, the role of lichens as environmental bioindicators is well established (Blasco et al., 2011a; Van der Wat and Forbes, 2015). For old man's beard, PACs could be deposited on its surface due to surface and *in-situ* mining activities, emissions from mining equipment, and traffic (Harner et al., 2018). A recent study highlighted that fugitive dust sources including petroleum coke and raw oil dusts were the major contributor to PACs deposition (43.2 μg g^{-1} accounted for 63%) in the oil sands region in Alberta in which almost 90% of this 43.2 μg g^{-1} PACs was deposited with 25-km of the closest surface oil and production facility (Landis et al. 2019). Research in the oil sands region of Alberta indicated that the surface mining area had 9 times higher total (wet and dry) PAC deposition compared with more remote areas (Cheng et al., 2018a). That is, the total annual deposition fluxes (μg m^{-2} yr^{-1}) for alkylated

PAH within the mining surface area was reported 2.8 times that of PAH and 5.6 times that of DBT. For remote areas, the annual deposition of alkylated PAH was 1.6 and 7.9 times higher than that of PAH and DBT, respectively (Cheng et al., 2018a), qualitatively consistent with the PAC patterns we found in traditional foods. Concentrations of ∑PAC in various species of lichens reported in Canada and elsewhere ranged from 36 ng g^{-1} d.w. to 9080 ng g^{-1} w.w. (Augusto et al., 2013; Blasco et al., 2011b; Fernández et al., 2011; Guidotti et al., 2003; Studabaker et al., 2017). The ∑PAC concentrations in our lichen at 808.7 ± 115.6 ng g^{-1} w.w was within the range of most studies. Differences in the range of ∑PAC in lichen could be due to differences in the species that were included, different rate at which congeners of PAHs adsorb onto particulate matter in the atmosphere, and various uptake, penetration, and distribution rate of PAC on the surface of plants (i.e., leaf) (Abdel-Shafy and Mansour, 2016; Li et al., 2017). In comparing our results to other studies in Alberta, the concentrations of ∑PAH in the old man's beard from the Bigstone Cree Nation at 90.8 ± 12.9 ng g^{-1} w.w. was similar to that found in epiphytic lichens (97.0 ± 6.1 ng g^{-1} w.w.) collected within a 150-km radius of the main surface of oil sands mining in Alberta (Landis et al. 2019). Unlike old man's beard, the rest of the plant samples had significantly lower concentration of the ∑PAH that ranged from 0.26 ± 0.15 ng g^{-1} w.w. in water lily (aquatic plant) to 9.70 ± 2.40 ng g^{-1} w.w. in Labrador tea. This discrepancy could be due to different habitat of the plants (aquatic vs. terrestrial), uptake via roots, and possible dilution of some congeners of PAHs in water compared to terrestrial environment (Augusto et al., 2013).

Although lower than lichen, concentrations of ∑PAC were also elevated in smoked moose rib compared to the vascular plants and non-smoked animal samples. This finding is likely a consequence of food processing and preparation methods, as smoking, roasting, grilling, and barbecuing are known to generate and increase the concentrations of some PAC congeners (Chung et al., 2011; Garcia-Falcon and Simal-Gandara, 2005; Rose et al., 2015). The ∑PAH

concentrations in smoked moose rib of the Bigstone Cree Nation at 168.5 ± 44.2 ng g^{-1} w.w. was lower compared to partially or fully smoked moose muscle from the Tl'azt'en and Llheidli T'enneh First Nation Communities in British Columbia, Canada (400.9 ± 20.4 ng g^{-1} w.w. and 2127.8 ± 42.6 ng g^{-1} w.w., respectively) (Kitts et al., 2012). This difference is perhaps due to various methods used for smoking the rib among communities. The Bigstone Cree Nation members tend to use cold smoking methods, in which the meats are kept sufficiently far from the fire to avoid being cooked (J. Baker, personal communication). Another reason could be differences in PAC composition of tissue and type of meat (rib versus muscle), since the muscle has a bigger surface compare with ribs therefore, potentially higher quantities of PAHs could be deposited on its surface (Hokkanen et al., 2018). The wood type used for smoking could also affect the amount of PAHs generated, since various woods produce different congeners of PAHs when burned and, therefore, have an influence on the amount of PAHs present in smoked meat (Stumpe-Viksna et al., 2008). For instance, Stump-Viksna et al. (2008) concluded that samples that were smoked using apple and alder wood had lower concentrations of individual and ∑PAH; whereas samples smoked with spruce had higher concentrations of individual and ∑PAH, and in particular, B[a]P. Additionally, the generation and presence of various congeners of PACs in smoked meat will depend on many interacting factors, such as the temperature of smoking, humidity, flow rate and density of smoke, and the properties of meat being dried (Foster and Simpson, 1961; Foster et al., 1961). A study reported concentrations of PACs (range < 1 ng g^{-1} w.w. to 31 ng g^{-1} w.w.) in smoked meat products from grocery stores and restaurants from the Mississippi Gulf coast that were affected by the Deepwater Horizon Oil Spill Disaster (Xia et al., 2012). The ∑PAC concentrations in smoked moose rib of the Bigstone Cree Nation was higher than the store-bought smoked meat used in Xia et al. (2012) study. This could be due to higher congeners of PACs being analyzed in our study (69 versus 25) and different smoking process used in both studies. The rest of animal samples (non-smoked) of the Bigstone Cree showed

lower ∑PAC concentrations. Variation among these samples is most likely due to different accumulation pattern in various tissues including muscle and liver, which vary in biological functioning. For instance, liver acts as a detoxifying organ responsible for metabolizing PAHs and other contaminants to more water-soluble, and thus, excretable forms (Lehman-McKeeman, 2008). Additionally, fatty tissues such as liver tend to accumulate more PAHs due to lipophilic properties of PACs (Wu et al., 2012).

The concentrations of B[a]P and ∑PAH4 were assessed separately to provide information on these well-studied congeners relative to established guideline limits. Among the ∑PAH, benzo[a]pyrene (B[a]P), in particular, is known for its carcinogenic and mutagenic effects, being one of the most studied congeners; hence, there is sufficient toxicological evidence to draw a safety guideline for it. The European Commission guideline for human consumption for B[a]P is currently 5 ng g^{-1} wet weight (w.w.) for smoked fish and meat—since smoking and grilling are major sources of PAHs—and 2 ng g^{-1} w.w. for non-smoked food/products (European Commission, 2011). The European Commission has indicated that B[a]P alone may not be a sufficient indicator of occurrence of PAHs in food and, therefore, suggested a more comprehensive indicator such as ∑PAH4 (sum of benzo[a]anthracene, chrysene, benzo[b]fluoranthene, and B[a]P) with a guideline limit of 12 ng g^{-1} w.w. in smoked meat products (European Commission, 2015). Measurable concentrations of B[a]P were only detected in old man's beard and smoked moose rib. Concentrations in both were below of the European Commission guidelines of 5 ng g^{-1} w.w. for smoked fish and meat and 2 ng g^{-1} w.w. for non-smoked food/products (European Commission, 2011). The mean concentration of B[a]P found in our study for old man's beard was at 0.9 ± 0.2 ng g^{-1} w.w. In the aforementioned study of lichen in the region, *H. physodes* contained 9.3 ± 8.6 ng g^{-1} w.w. of B[a]P (Landis et al., 2019). In five species of lichens (*H. physodes , E.mesomorpha ,T. americana, B. furcellata, C. mitis*) at three different sites within a 100-km distance from the primary oil sands operations, concentrations of

B[a]P ranged from 0.2 ng g^{-1} w.w. to 6.0 ng g^{-1} w.w. (Graney et al., 2017). This discrepancy could be due to different species of lichen used among studies, or due to the distance from the oil sands developments where the samples were taken. For instance, the highest concentrations were found in those growing closer to surface oil and production facilities compared with those sampled at 25, 50, 100, and 150-km farther away (Graney et al., 2017; Landis et al., 2019; Studabaker et al., 2012). Concentrations of B[a]P for smoked moose rib averaged 0.14 ± 0.05 ng g^{-1} w.w., which was lower than mean concentrations of 1.4 ± 0.2 ng g^{-1} in fully smoked moose muscle and 3.6 ± 0.9 ng g^{-1} in fully smoked salmon muscle in the Tl'azt'en and Llheidli T'enneh First Nation Communities in British Columbia, used (Kitts et al., 2012). As stated previously, this could be mostly due to differences in the smoking process.

Similar to B[a]P, concentrations of ∑PAH4 were highest in old man's beard (14.6 ± 2.3 ng g^{-1} w.w.), followed by smoked moose rib (1.5 ± 0.5 ng g^{-1} w.w.). In comparing the concentrations of ∑PAH4 to the European Commission guideline limit of 12 ng g^{-1} w.w. (European Commission, 2015) for smoked meat, the smoked moose rib concentrations were well-below the guideline limit. Although a guideline level has not been established for ∑PAH4 in plants and non-smoked meat/animal products, nearly all plant and animal samples were below the guideline for smoked meat, except for old man's beard (14.6 ± 2.3 ng g^{-1} w.w.). Our ∑PAH4 concentrations in lichen were lower than the ∑PAH4 reported in the other study on epiphytic lichens (33.3 ± 8.6 ng g^{-1} w.w.) in the region (Landis et al., 2019) which could be due to various species of lichens being used in both studies and the distance from the oil sands developments. In a recent study in the Athabasca oil sands region of Alberta, Canada, concentrations of ∑PAH4 measured in forage fish ranged from 0.08 ± 0.04 ng g^{-1} w.w. to 2.71 ± 1.42 ng g^{-1} w.w. at different sites (Evans et al., 2019). Our results of the mean concentrations of ∑PAH4 for the animal samples ranging from 0.003 ng g^{-1} w.w. in fish muscle to 1.5 ± 0.5 ng g^{-1} w.w. in smoked moose rib were lower than in Evans et al. (2019). An interesting observation is that the

concentrations of ∑PAH4 in non-smoked forage fish from Evans et al. (2019) study was similar to the smoked moose rib from the Bigstone Cree Nation. The reason for this could be explained by the indirect smoking process of the moose rib by the Bigstone Cree Nation members, since research has shown significant reduction in the concentration of ∑PAH4 in fish and meat smoked over five meters of distance from the smoke source (Hokkanen et al., 2018).

Among all classes of PACs, the concentrations of ∑alkyl-PAH were predominant in all plant and animal samples (range: 63.0% to 95.0% of ∑PAC). Elevated contribution of ∑alkyl-PAH to ∑PAC is an indicator of petrogenic PACs, with ∑alkyl-PAH being ~2- to 7-fold higher than ∑PAH in old man's beard and moose rib, respectively. This may be due to emissions and deposition of PACs mostly in the form of alkylated PAHs— as major components of oil products— from the oil sands industry into the surrounding environment (Giesy et al., 2010; Kelly et al., 2009; Kurek et al., 2013; Parajulee and Wania, 2014; Schuster et al., 2015). Research in oil sands region has indicated that the levels of PAHs have increased since the 1960s, especially for the C1-C4-alkylated PAHs associated with industry (Kurek et al., 2013). The concentration of ∑alkyl-PAH in old man's beard in our study was 1.5 times higher that of the Landis et al. (2019) study (605.5 ± 55.4 ng g^{-1} w.w. versus 389.4 ± 28.5 ng g^{-1} w.w.). This difference may be due to various species of lichen used between the two studies or a lower number of alkylated PAHs congeners monitored in Landis et al. (2019) (13 congeners versus 49 in the current study). Not having a standardized alkyl-PAH congener list (like that for the EPA 16 PAHs) may preclude robust comparisons between studies because the sum of alkylated PAHs is usually reported, so including more congeners of PAHs may augment estimates of ∑PAC. As well, concentrations in plant samples may vary across studies, depending whether samples were washed before analysis (Vacha et al., 2010). This could be related to plants inadvertently capturing contaminants from the air on their leaf surfaces; in this respect, that we did not wash the plant samples before the analysis could be a reason for this accumulation. However, Landis et

al. (2019) did not wash their lichen samples either. Regardless, caution should be exercised when interpreting these data, since they could be affected by various experimental variables differing in magnitude across studies, such as sampling techniques, sample cleaning, and quality assurance procedures (Van der Wat and Forbes, 2015).

The concentrations of DBTs were minor contributors to the total PACs in the plant (range: < 1% to 13.9%) and animal (range: < 1% to 13.32%) samples. This is in line with Evans et al. (2019), who found that in general ∑DBTs accounted for less than that 10% of ∑PAC in forage fish from the Athabasca River in Alberta, Canada. These findings could be due to lower proportion of DBTs in oil products and rate of uptake from the environment, efficient elimination within species, and biotransformation of congeners of DBTs relative to other PACs (Evans et al., 2019; Yang et al., 2017). Although DBTs showed low abundance relative to the parent and alkylated PAHs, they still should be included in research as an important class of PACs. Research indicates that sulfur-containing PAC such as DBTs have relatively greater biotoxicity than non-sulfur-containing components with similar chemical structures (Cheng et al., 2018b).

In comparing the ring distribution profile of the PACs, our results indicated that in most of the plant and animal samples over 50% of PAHs and 65% of alkylated PAHs were dominated by the 2- and 3-ringed congeners. This is in line with other studies in the oil sands regions of Alberta, Canada (Evans et al., 2019; Ohiozebau et al., 2017). Among plant and animal samples, the unsubstituted and alkylated naphthalenes showed higher contributions in most animal samples than plants. However, water lily, the aquatic plant, did not contain the unsubstituted 2-ring PAHs (i.e., naphthalene), possibly due to the fact that the naphthalene biodegradation rate is higher in soil and sediments compared with water columns above the sediments (Herbes and Schwall, 1978) and as the root of water lily was used in our study. In contrast, ∑PAH in duck muscle was 95% naphthalene as ducks inhabit surface water and feed on small organisms in that

environment (Hoyo et al., 1992). Naphthalene is a volatile compound, and it has a short half-life of 71 hours on surface water, such that a small fraction of it has the ability to be associated with particulate matters on surface water (ATSDR, 2005). This could partially result in exposure of waterfowl (i.e., duck) to naphthalene through inhalation of its vapor on the surface water and ingesting water and their prey (ATSDR, 2005). The 4- and 5- ring PACs showed higher variation, notably in unsubstituted form, in plants than in animal samples. This could be due to atmospheric depositions of PACs from the oil sands activities on the surface of plants. That the unsubstituted 6-ring PACs were mostly presented in plant samples rather than in animals, was most likely due to oil sands mining operations and equipment or emissions from vehicle exhausts. However, none of the plant and animal samples contained alkylated 6-ring PAHs. This is mostly related to the temperature in the formation process of petrogenic versus pyrogenic PACs in which higher formation temperature is likely to produce PACs with fewer alkylated chains compared with PACs generated in lower temperature (Abdel-Shafy and Mansour, 2016). Additionally, research indicates that some higher molecular weight parent PAHs often have lower bioavailability, resulting in low (or negligible) concentrations in tissues including muscle after detoxification/elimination by the hepatobiliary system (Eickhoff et al., 2003; Hellou et al., 1995). Yet, toxicological research on individual congeners of PACs is limited, in particular alkylated PAHs, that their toxicity also depends on position of alkyl substituents and their chemical structures (Baird et al., 2007).

4.5.1. Conclusion

Our results provide timely insights for comparisons of the 16 U.S. EPA priority PAH, alkylated PAH, and DBT concentrations in traditional foods adjacent to Alberta's oil sands mining activities. By having different classes of PACs evaluated in a single study on plant and animal samples of traditional importance, we now have crucial baseline information on these

contaminants in wildlife and plants close to oil sands development. Our study showed that alkylated PAHs dominated the PAC signature, suggesting that only measuring the 16 U.S. EPA priority (parent) PAHs may substantially underestimate actual PAC levels in all of these food types. Given this finding, and as some alkylated PAHs tend to be more persistent and toxic than parent PAHs (Baird et al., 2007; Lee et al., 2011; Turcotte et al., 2011), we conclude that they should be included in subsequent studies to better gauge the exposure assessment of PACs in traditional foods.

A risk assessment was out of the scope of this study, thus, evaluation of food frequency questionnaire (i.e., frequency of consumption and food consumption preferences) along with lifestyle and habit survey (i.e., physical activity and smoking habits) could determine if the consumption of the traditional foods pose health risks to the community members. Given the cultural, social, nutritional values of traditional foods, consumption of these locally harvested wild plants and animals is more likely beneficial than consumption of store-bought foods (Gagné et al., 2012; Kuhnlein, 2015; Sheehy et al., 2015). Nonetheless, future studies should determine the source of PACs by including spatial, temporal, and seasonal variations of the occurrence and distribution of PACs in various abiotic and biotic matrices in the oil sands region. More research is needed to compare the toxicity of individual congeners of various classes of PACs to help better understand the full toxicological profile of this group of contaminants.

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Chapter 5. Summary and conclusion

Increasing global demand for energy, especially through consumption and use of fossil fuels, promotes large-scale extractive industries including the oil sands developments in northern Alberta, Canada. These massive developments are of major concern with regard to the elevated release of essential and non-essential trace elements—considered as PPE by the U.S. EPA— and a group of organic pollutants (including PACs) into the surrounding environment, where these contaminants can be taken up by plant and animal species and potentially cause negative health impacts on wildlife and humans (Tenenbaum, 2009). This issue is of importance to Indigenous communities, such as the Bigstone Cree Nation, inhabiting in close proximity to the largest oil sands region in Athabasca, Alberta, Canada.

This doctoral thesis was developed based on the request of the Bigstone Cree Nation regarding their concerns of levels of contaminants in traditional foods. Results of this thesis helped better understand the variation and distribution of PPE levels (including several essential and non-essential trace elements), and different classes of PACs, such as the 16 U.S. EPA PAHs, and the less studied classes comprising alkylated PAHs and DBTs in various aquatic and terrestrial plant and animal species consumed as important traditional food items. This was a community-led participatory project to provide results that are meaningful to the community members. The novelty of this research is based on providing important background data on key contaminants and nutrients (that can be toxic in elevated levels) of a wide variety of traditional foods in an area close to oil sands development in the boreal forest of Canada, which has received less attention compared to the northern regions (Arctic and near-Arctic). Most studies have been conducted on aquatic organisms and limited research has been performed on terrestrial plant and animal samples, and specifically animal organ tissues. Since the oil sands production is predicted to increase, future researchers could use this information to assess the changes in levels of contaminants in wild plants and animals relative to the release of the contaminants from the

oil sands industry. Additionally, the baseline concentrations data provided by this research could be used in comprehensive exposure/ risk assessment studies using food frequency questionnaires and personal habit surveys to better evaluate the risk of exposure through consumption of these traditional foods. This is in accordance with the holistic perspective ingrained in Indigenous communities regarding nutritional and cultural benefits of traditional foods.

5.1. Summary and Discussion of Results

In Chapter 2, I investigated THg, MeHg, Se, and Se:THg molar ratios in various plant and animal samples consumed as traditional foods by the Bigstone Cree Nation in Alberta, Canada. This comprehensive study filled an important knowledge gap by determining current levels of not only THg, but also MeHg and the micronutrient Se (thought to protect against Hg toxicity) in a wide variety of terrestrial plant and animal samples besides the aquatic species. The results of this chapter indicated that in general, animal samples had higher concentrations of THg compared to plant samples. Among the animal samples, the ones living in or near aquatic systems (i.e., fish and duck) showed the highest concentrations of THg. Additionally, all plants and animal samples had Se:THg molar ratios above 1 which might suggest there is potentially sufficient amount of Se to reduce the negative health consequences of Hg exposures through the consumption of these foods for the community members. This chapter filled an important knowledge gap on not only the levels of THg and MeHg on a variety of staple non-aquatic food items, but also highlighted the bigger picture in toxicology which clearly indicates the importance of conducting research on the potential associations between contaminants and nutrients (i.e., Hg and Se). Assessment based on single-contaminant exposure (i.e., Hg) may result in Indigenous communities reducing their consumption of traditional foods, yet remaining susceptible to other health issues (McAuley and Knopper, 2011). Thus, this chapter emphasised that only measuring concentrations of THg, without considering levels of MeHg and potential

associations with Se, may not result in a comprehensive understanding of levels of these elements in staple traditional food items. The result of this chapter will help better formulate traditional food consumption advisories, to have effective communication regarding the issue.

In Chapter 3, I compared the levels of nine out of thirteen elements considered as PPE by the U.S. EPA under the Clean Water Act (including As, Cd, Cr, Cu, Pb, Ni, Ag, Tl, and Zn) in plant and animal samples of the Bigstone Cree Nation. The result of this chapter indicated variation in the concentrations of PPE that depend on trace elements' characterization (essential versus non-essential) and species and tissues. In general, essential elements had higher concentrations compared to non-essential elements. For example, among the PPE in both plants and animals, Zn— an essential element— had significantly higher concentrations than other elements. There is currently limited research on the levels of PPE in traditional foods in boreal regions such as northern Alberta compared with northern (Arctic and near-Arctic) regions. Moreover, limited studies have been conducted on such a wide variety of terrestrial plants and animals as key species of traditional importance to communities residing close to the oil sands developments. This study filled an important knowledge gap which not only considered levels of contaminants, but also measured levels of nutrients (also can be toxic in excess amounts relative to an organism's requirements) in the traditional foods of the Bigstone Cree Nation. This is an important fact given the holistic approach adopted by Indigenous communities that highlights fundamental nutritional, sociocultural, spiritual, and economic values in traditional food system. In addition, many of these foods are consumed on a regular basis and have medicinal value to such communities. Given that the research on abiotic matrices indicated elevated levels of contaminants and nutrients in oil sands regions, thus, it is crucial to measure the concentrations of these trace elements in a comprehensive suite of traditional foods inhabiting close to the oil sands industry. The differences in PPE levels found in multiple species of aquatic and terrestrial plant and animal foods in this study may better elucidate levels of PPE in oil sands regions. The

result of this study could also be used as markers to identify baseline concentration levels in traditional foods (plants and animals) near the oil sands industry. In comparing the results of the Bigstone Cree Nation, I realized that limited guidelines of trace elements are available for medicinal plants and wild animals. Lack of guideline levels for each trace element in various species of plants and animals and their tissues such as muscle, kidney, liver, and brain prevent clear indication of potential harmful levels of PPE in these foods. This is an import issue regarding the interpretation of findings of this thesis because accumulation or target tissue/organ(s) for each trace element could be tissue-specific (i.e., primary target organ for Cd is kidney). Thus, comparing the levels of contaminants in liver or kidney with established guideline levels for muscle may not be pertinent.

In chapter 4, I evaluated and compared the concentrations of various classes of PACs including the 16 parent PAHs listed by U.S. EPA and alkylated PAHs, and DBTs in important traditional foods of the Bigstone Cree community adjacent to Alberta's oil sands mining activities. This study filled an important knowledge gap in regard to measuring concentrations of a less studied but potentially more toxic group of PACs to wildlife and humans, the alkylated PAHs. Research has pointed out that the health risks to wildlife and humans posed by the alkylated PAHs have been neglected due to limited data available on alkylated PAHs since most studies have focused on the 16 U.S. EPA priority PAHs (Andersson and Achten, 2015). By having different classes of PACs evaluated in a single study on plant and animal samples of traditional importance, we now have crucial baseline information on these contaminants in wildlife and plants close to oil sands development. This study showed that alkylated PAHs were the most dominant PAC signature; this suggests that only measuring the 16 U.S. EPA priority (parent) PAHs may significantly underestimate actual PAC levels in all of these food items. Thus, it is crucial to include a more persistent and toxic group of PACs than the parent PAHs in research to obtain comprehensive toxicological insights.

5.2. Conclusion

This doctoral thesis combined field information and laboratory studies to improve our understanding of the implications of elevated concentrations of infiltrating contaminants that have been reported in abiotic matrices proximate to the oil sands region in Alberta, Canada. Given that elevated concentrations of several trace elements and PACs have been found in the abiotic and biotic matrices, the results of this study will provide a better understanding of the occurrence and distribution of the levels of contaminants and nutrients in plants and animals consumed by a local Indigenous community. This thesis exemplified research as a combination of traditional ecological knowledge from the Indigenous community with science and showed how communities conceptualize framework of empirical observations of the environment can help science in developing better environmental/toxicological insights. This ties in to the considerable traditional ecological knowledge of Indigenous people as native people of the land who observe and gather empirical information of various species and their ecological interactions (Parlee et al., 2012). This thesis monitored the food items that the Bigstone community members considered worthy of studying according to their traditional ecological knowledge. A strong point of this thesis was inclusion of the community members in every aspects of the project that even created employment opportunities for the community members. Furthermore, I emphasised on reciprocity in conducting my research where the results of this study were presented to the community members. This study's findings on levels of contaminants and nutrients in various species of traditionally harvested plants and animals could better inform future discussions/decision-making by providing baseline concentrations on wildlife species, especially those living in close proximity to the oil sand industry. The findings of this study could also help others pursue exposure and risk assessments for a variety of traditional foods in Canada and elsewhere by having a better understanding of the PPE and PACs patterns/distributions among

various food species relative to dietary consumption through food frequency questionnaires. This research expanded upon pervious work that emphasises how critical it is to have reliable toxicological information in the form of clear guideline levels for all the nutrients and contaminants specific to each species of plant and animal, as well as the accepted levels in animal organ tissue, in a bid to improve the quality of life of the individuals of Bigstone Cree Nation, and other Indigenous communities facing a similar situation. Since the Bigstone Cree Nation members are living close to oil sands development activities where production is projected to increase (National Energy Board, 2018), we recommend on-going monitoring of PPE and PACs in traditional/wild foods and biota.

This thesis had several limitations that could be considered in future study designs; the Bigstone Cree Nation did not wish to share the locations of samples. This is an important factor in levels of contaminants since research in the oil sands regions in Alberta on lichens (used as bioindicator of air pollution) resulted in significant correlation between concentrations of PACs and trace elements and samples taken farther away from the main mining activities indicating that contaminant concentrations decreased with increasing distance (i.e., < 150 km) (Landis et al. 2019 ;Studabaker et al., 2012). Indicating source of exposure was outside the scope of this thesis, thus, distinction of whether these contaminants are released from the oil sands industry or long-range atmospheric transport should be made clear in future studies. Results of this thesis indicated that levels of trace elements and PACs were generally below the guideline levels, where available; meaning that their concentrations in the traditional foods of the Bigstone Cree Nation is not a public health concern at this time. However, future research should include conducting a risk assessment to identify if consumption of these traditional foods poses a health risk to the community members. Determining the safety of traditional food consumption in regard to the levels of contaminants is a complex matter that depends on numerous key factors including food consumption pattern/ habit and sensitivity of the consumers to the contaminants

(Chan et al., 1995). This thesis indicated that the levels of contaminants in these traditional foods is not a public health concern at this time and supports the notion that wholesome nutritional and sociocultural benefits of traditional foods may outweigh any drawbacks regarding levels of contaminants in traditional foods.

Supplementary Materials

6.1. Supplementary Materials for Chapter 2

Supplementary Table 2.1. Mean (± SD) moisture contents of (A) plants samples and (B) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

(A)

Plant Sample	**Scientific name**	***N***	**% Moisture content ± SD**
Labrador tea	*Rhododendron groenlandicum*	10	50 ± 16
Berry	lingonberry (*Vaccinium vitis-idaea*), cranberry (*Vaccinium* spp.), Rosehip (*Rosa canina*), highbush cranberry (*Viburnum trilobum*), bunchberry (*Cornus canadensis*), blueberry (*Cyanococcus* spp.), bog cranberry (*Vaccinium oxycoccos*), and Saskatoon berry (*Amelanchier alnifolia*)	16	40 ± 16
Water lily	*Nymphaeaceae* spp.	10	87 ± 4
Rat root	*Acorus americanous*	12	68 ± 6
Mountain Ash	*Sorbus aucuparia*	9	44 ± 7
Mint	*Mentha* spp.	3	37 ± 2
Old man's beard	*Usnea* spp.	5	30 ± 19

(B)

Animal Sample	Species	Scientific name	*N*	% Moisture content ± SD
Fish muscle	Whitefish	*Coregoninae clupeaformis*	6	74 ± 5
Fish liver			5	62 ± 11
Duck muscle	Mallard	*Anas platyrhynchos*	7	73 ± 3
Duck liver			6	72 ± 10
Duck brain			7	89 ± 4
Grouse muscle	Ruffed grouse and spruce hen	*Bonasa umbellus* and *Falcipennis Canadensis*	14	73 ± 3
Grouse liver			12	86 ± 4
Grouse brain			12	70 ± 13
Hare muscle	Snowshoe hare	*Lepus americanus*	10	65 ± 16
Hare liver			10	74 ± 6
Hare kidney			10	84 ± 8
Moose muscle	Moose	*Alces alces*	3	53 ± 36
Moose rib-smoked			5	72 ± 7
Bear muscle	American black bear	*Ursus americanus*	4	77 ± 14

Supplementary Table 2.2. Summary of (A) total mercury (THg) quality control measurements (% accuracy and % precision) within two mercury analyzers (DMA-80, Milestone and NIC MA-3000, Nippon Instruments, North America) for animal samples and plants collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada, including mean accuracy and standard deviation (SD), calculated as the percent recovery compared to certified value for standard reference materials for plants (NIST-1547 (peach leaves); National Institute of Standards and Technology) and for animal (DORM-4 (fish protein); National Research Council of Canada) , mean analytical precision, calculated as relative standard deviation (RSD), and duplicates for plant and animal samples, and (B) detection limits were calculated as theoretical method detection limit (TMDL) and practical method detection limit (PMDL) as follows: mean value of blank vessel samples + (3 × standard deviation (SD) of the mean) reported as TMDL and the mean value of blank vessel samples + (5 × standard deviation (SD) of the mean) reported as PMDL, expressed in nanograms (ng) of THg. The detection limits (DL) calculated from the mean concentration of blanks.

(A)

Instrument/ Samples	Number of Days	Number of samples	% Accuracy (SD)	% Precision (SD)
DMA-80				
SRM (NIST-1547)	4	23	116.00 (12.75)	11.00 (7.00)
DMA-80				
SRM (DORM-4)	6	24	90.20 (5.24)	3.49 (3.03)
NIC MA-3000SRM				
SRM (DORM-4)	1	2	91.93 (3.10)	3.10
Plant sample duplicates	4	13	NA	4.42 (3.12)
Animal sample duplicates	6	14	NA	5.68 (6.13)

(B)

Detection limit	Number of Days	Blank (DL) Mean μg g^{-1} ± SD	TMDL (ng) ± SD	PMDL (ng) ± SD
Plants				
DMA-80	4	0.0002 ± 0.0000	0.18 ± 0.02	0.20 ± 0.04 [1]
Animal				
DMA-80	6	0.0002 ± 0.0000	0.19 ± 0.03	0.22 ± 0.03[2]
NIC MA-3000	1	0.00002 ± 0.00003	0.04	0.06

1- All concentrations for the plant samples were above the DL, except for six berry samples that had values below the mean PMDL (0.20 ± 0.04 ng); however, all THg concentrations of the berry samples were above the detection limit (0.0002 ± 0.0000 μg g^{-1}) and, therefore, they were used in our analysis.

2- All concentrations in the animal samples were above the DL; however, two of grouse muscle, one of grouse brain, four of hare muscle, and one of moose muscle were below the mean PMDL of 0.06 ng. By contrast, the THg concentrations of all dried samples were above the detection limit of 0.00002 ± 0.00003 μg g^{-1} and, therefore, included in the data analysis.

Supplementary Table 2.3. Summary of (A) methylmercury (MeHg) quality control measurements (% accuracy and % precision) collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada, including mean accuracy and standard deviation (SD), calculated as the percent recovery compared to certified value for standard reference materials for animal (DOLT-5 (fish liver) and DORM-4 (fish protein), National Research Council of Canada), mean analytical precision, calculated as relative standard deviation (RSD), initial and ongoing precision and recovery (IPR and OPR) samples and (B) Detection limits were calculated as follows: mean value of reagent blank KOH samples + (3× SD of mean [TMDL]) and mean value of reagent blank KOH samples + (5× SD of mean [PMDL]); here, expressed as ng L^{-1} of MeHg. The detection limits from the KOH blank was calculated from mean concentration of the KOH blanks.

(A)

Sample	Number of Days	Number of Samples	% Accuracy (SD)	% Precision (SD)
IPR	3	4	98.23 (9.52)	9.70
OPR	3	16	98.21 (8.44)	8.60 (3.69)
SRM (DORM-4)	3	7	85.24 (4.70)	5.75 (5.11)
SRM (DOLT-5)	3	5	107.81 (6.04)	8.06 (9.79)
Sample duplicates	3	10	NA	16.50 (10.22)

(B)

Detection limit	Number of Days	Blank (DL) Mean ng L^{-1} ± SD	TMDL (ng L^{-1}) ± SD	PMDL (ng L^{-1}) ± SD
Animal samples	3	0.01 ± 0.00	0.02 ± 0.01	0.03± 0.01 [1]

1- All our analyzed dry-weight samples were greater than the DL (the mean concentrations of KOH blanks), except for three of the hare muscle and two of the hare kidney, which were thus omitted from further analysis.

Supplementary Table 2.4. Summary of Selenium (Se) quality control measurements (% accuracy and % precision) collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada, including (A) mean accuracy and standard deviation (SD), calculated as the percent recovery compared to certified value for standard reference materials for plants (NIST-1547 (peach leaves); National Institute of Standards and Technology) and for animal (DORM-4 (fish protein); National Research Council of Canada), mean analytical precision, calculated as relative standard deviation (RSD), and duplicates for plant and animal samples and (B) detection limits were calculated as the mean value of reagent blank samples + (3× SD of mean [TMDL]) and mean value of reagent blank samples + (5× SD of mean [PMDL]); and are reported as μg L^{-1} of Se. The detection limits were calculated as the mean value of reagent blank samples + (3× SD of mean [TMDL]) and mean value of reagent blank samples + (5× SD of mean [PMDL]); and are reported as μg L^{-1} of Se. The detection limits (DL) was calculated as mean concentrations of reagent blanks (μg L^{-1}).

(A)

Sample	Number of Days	Number of Samples	% Accuracy (SD)	% Precision (SD)
SRM (NIST-1547)	2	4	120.26 (9.38)	4.04 (1.96)
SRM (DORM-4)	2	8	95.40 (0.00)	2.90 (0.11)
Plant sample duplicates	2	5	NA	10.55 (5.63)
Animal sample duplicates	2	11	NA	11.62 (23.83)
Internal standard	3	14	NA	16.00 (5.32)

(B)

Detection limit	Number of Days	Blank (DL) Mean μg L^{-1} ± SD	TMDL (μg L^{-1}) ± SD	PMDL (μg L^{-1}) ± SD
Animal samples	3	0.006 ± 0.001	0.04 ± 0.01	0.07± 0.02 [1]

1- The Se concentrations were above the DL and TMDL for all samples.

Supplementary Table 2.5. Summary of significant effects in the mixed models, post hoc pairwise comparisons among factor levels using Tukey's HSD with least squares (LS) means in (A) plants (species) and (B) animal species (nested tissue/organs) collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

(A)

Response Variables		**Log THg**	**Log Se**	**Log Se:THg**
Species	**-Species**	**Prob>|t|**	**Prob>|t|**	**Prob>|t|**
Berry	Labrador tea	0.334	0.991	0.027
	Mint	0.382	0.903	0.955
	Mountain ash	0.985	0.357	0.024
	Old man's beard	<0.001	0.017	0.001
	Rat root	0.637	0.958	0.987
	Water lily	0.001	0.559	0.067
Labrador tea	Mint	0.995	0.706	0.949
	Mountain ash	0.908	0.863	1.000
	Old man's beard	<0.001	0.006	0.660
	Rat root	0.011	1.000	0.006
	Water lily	<0.001	0.961	<0.001
Mint	Mountain ash	0.774	0.197	0.928
	Old man's beard	0.023	0.827	0.333
	Rat root	0.049	0.602	0.788
	Water lily	0.000	0.293	0.103
Mountain ash	Old man's beard	<0.001	0.000	0.746
	Rat root	0.304	0.915	0.005
	Water lily	0.000	1.000	<0.001
Old man's beard	Rat root	<0.001	0.002	0.000
	Water lily	<0.001	0.000	<0.001
Rat root	Water lily	0.127	0.984	0.402

(B)

Response Variables		Log THg	Log MeHg	Log Se	Log Se:THg
Species	**-Species Organ**	**Prob>|t|**	**Prob>|t|**	**Prob>|t|**	**Prob>|t|**
Bear muscle	Grouse brain	1.000	1.000	0.920	0.643
	Grouse liver	0.841	0.876	1.000	0.152
	Grouse muscle	1.000	0.209	1.000	0.842
	Duck brain	0.969	0.001	1.000	0.980
	Duck liver	0.000	<0.001	0.004	0.957
	Duck muscle	0.063	<0.001	0.952	0.552
	Moose muscle	0.848	0.828	1.000	0.604
	Moose rib	0.994	1.000	1.000	0.993
	Hare kidney	0.001	1.000	0.294	0.280
	Hare liver	0.971	0.361	0.976	1.000
	Hare muscle	1.000	0.492	1.000	1.000
	Fish liver	0.000	<0.001	0.002	1.000
	Fish muscle	0.003	<0.001	1.000	0.002
Grouse brain	Grouse liver	0.194	0.005	0.945	0.963
	Grouse muscle	1.000	<0.001	0.968	1.000
	Duck brain	0.552	<0.001	0.936	0.003
	Duck liver	<0.001	<0.001	0.026	0.002
	Duck muscle	0.001	<0.001	1.000	<0.001
	Moose muscle	0.800	0.367	0.985	1.000
	Moose rib	0.994	1.000	0.745	1.000
	Hare kidney	<0.001	1.000	0.954	<0.001
	Hare liver	0.468	0.113	1.000	0.119
	Hare muscle	1.000	0.031	0.410	0.226
	Fish liver	<0.001	<0.001	0.011	0.044
	Fish muscle	<0.001	<0.001	0.999	<0.001
Grouse liver	Grouse muscle	0.610	0.565	1.000	0.635
	Duck brain	0.006	<0.001	1.000	<0.001
	Duck liver	<0.001	<0.001	0.001	<0.001
	Duck muscle	<0.001	<0.001	0.998	<0.001
	Moose muscle	1.000	1.000	1.000	1.000
	Moose rib	1.000	0.435	0.998	0.887
	Hare kidney	<0.001	0.279	0.289	<0.001
	Hare liver	0.002	<0.001	1.000	0.004
	Hare muscle	0.645	0.999	0.985	0.011
	Fish liver	<0.001	<0.001	0.000	0.003
	Fish muscle	<0.001	<0.001	1.000	<0.001
Grouse muscle	Duck brain	0.218	<0.001	1.000	0.007
	Duck liver	<0.001	<0.001	0.001	0.006
	Duck muscle	<0.001	<0.001	0.999	<0.001

	Moose muscle	0.947	1.000	1.000	0.999
	Moose rib	1.000	0.028	0.994	1.000
	Hare kidney	<0.001	0.006	0.327	<0.001
	Hare liver	0.143	<0.001	1.000	0.278
	Hare muscle	1.000	1.000	0.960	0.462
	Fish liver	<0.001	<0.001	0.001	0.102
	Fish muscle	<0.001	<0.001	1.000	<0.001
Duck brain	Duck liver	<0.001	<0.001	<0.001	1.000
	Duck muscle	0.114	0.008	0.810	0.981
	Moose muscle	0.062	<0.001	1.000	0.024
	Moose rib	0.188	0.002	1.000	0.212
	Hare kidney	0.013	0.000	0.220	0.955
	Hare liver	1.000	0.208	0.988	0.943
	Hare muscle	0.663	<0.001	1.000	0.847
	Fish liver	0.004	0.146	0.001	1.000
	Fish muscle	0.049	0.000	1.000	0.032
Duck liver	Duck muscle	0.112	0.137	0.005	0.998
	Moose muscle	<0.001	<0.001	0.017	0.019
	Moose rib	<0.001	<0.001	0.001	0.170
	Hare kidney	0.998	<0.001	0.551	0.991
	Hare liver	0.000	<0.001	0.020	0.890
	Hare muscle	<0.001	<0.001	<0.001	0.766
	Fish liver	1.000	0.964	1.000	1.000
	Fish muscle	0.999	1.000	0.008	0.072
Duck muscle	Moose muscle	0.000	<0.001	0.991	0.002
	Moose rib	0.000	<0.001	0.838	0.017
	Hare kidney	0.960	<0.001	0.989	1.000
	Hare liver	0.365	<0.001	1.000	0.269
	Hare muscle	0.002	<0.001	0.626	0.159
	Fish liver	0.617	1.000	0.037	0.973
	Fish muscle	0.987	0.472	0.999	0.354
Moose muscle	Moose rib	0.999	0.104	1.000	0.974
	Hare kidney	<0.001	0.449	0.544	0.000
	Hare liver	0.050	0.002	0.997	0.281
	Hare muscle	0.802	1.000	1.000	0.395
	Fish liver	<0.001	<0.001	0.008	0.105
	Fish muscle	<0.001	<0.001	1.000	<0.001
Moose rib	Hare kidney	<0.001	1.000	0.119	0.003
	Hare liver	0.153	0.576	0.890	0.922
	Hare muscle	0.994	0.140	1.000	0.974
	Fish liver	<0.001	<0.001	0.000	0.577
	Fish muscle	<0.001	<0.001	1.000	<0.001
Hare kidney	Hare liver	<0.001	0.008	0.585	0.004

	Hare muscle	<0.001	0.002	0.000	0.001
	Fish liver	0.999	<0.001	0.309	0.838
	Fish muscle	1.000	<0.001	0.585	0.439
Hare liver	Hare muscle	0.131	<0.001	0.247	1.000
	Fish liver	0.001	<0.001	0.008	0.999
	Fish muscle	0.016	<0.001	1.000	<0.001
Hare muscle	Fish liver	<0.001	<0.001	<0.001	0.995
	Fish muscle	<0.001	<0.001	0.998	<0.001
Fish liver	Fish muscle	0.992	0.382	<0.001	0.001

Supplementary Table 2.6. Summary of concentrations of total mercury (THg), methylmercury (MeHg) and selenium (Se) reported as arithmetic mean (μg g^{-1}, w.w.) ± SE, and Se:THg ratios (mean ± SE) in (A) plants and (B) animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

(A)

Plant samples	***N***	**THg** Mean (μg g^{-1}, w.w.) ± SE	**Se** Mean (μg g^{-1}, w.w.) ± SE	**Se:THg molar ratios** Mean ± SE
Berry	16	0.005±0.001	0.030±0.008	18.46±5.01
Labrador Tea	10	0.010±0.001	0.017±0.004	3.80±0.45
Mint	3	0.014±0.003	0.033±0.009	6.96±2.91
Mountain Ash	9	0.007±0.002	0.009±0.002	4.27±0.98
Old Man's Beard	5	0.114±0.025	0.076±0.011	1.84±0.16
Rat Root	12	0.003±0.000	0.013±0.001	12.26±0.85
Water lily	10	0.001±0.000	0.009±0.001	25.11±4.08

(B)

Animal species	***N***	**THg** Mean (μg g^{-1}, w.w.) ± SE	**MeHg** Mean (μg g^{-1}, w.w.) ± SE	**Se** Mean (μg g-1, w.w.) ± SE	**Se:THg molar ratios** Mean ± SE
Bear Muscle	4	0.008±0.002	0.001±0.000	0.142±0.043	46.21±1.40
Duck Brain	7	0.018±0.008	0.011±0.005	0.127±0.021	32.78±8.22
Duck Liver	6	0.113±0.036	0.066±0.022	0.820±0.121	27.97±7.72
Duck Muscle	7	0.044±0.015	0.032±0.012	0.229±0.044	20.09±3.96
Fish Liver	5	0.094±0.035	0.027±0.007	1.115±0.268	38.08±7.63
Fish Muscle	6	0.068±0.021	0.071±0.023	0.152±0.032	10.00±3.05
Grouse Brain	12	0.006±0.001	0.001±0.001	0.211±0.011	120.12±17.99
Grouse Liver	12	0.003±0.000	0.0003±0.0000	0.149±0.014	154.02±11.72
Grouse Muscle	14	0.004±0.001	0.0002±0.0000	0.175±0.029	118.62±21.71
Hare Kidney	10	0.093±0.029	0.001±0.000	0.509±0.120	17.98±3.26
Hare Liver	10	0.015±0.005	0.002±0.000	0.275±0.072	53.97±11.12
Hare Muscle	10	0.006±0.001	0.0002±0.000	0.132±0.038	57.76±10.68
Moose Muscle	3	0.003±0.001	0.0004±0.0001	0.159±0.088	159.41±57.52
Moose Rib	5	0.003±0.001	0.001±0.001	0.094±0.011	96.11±34.92

6.2. Supplementary Materials for Chapter 3

Supplementary Table 3.1. Sample types and sample size *N* of plant foods of the Bigstone Cree collected by community members in 2015 (Adapted from Golzadeh et al. 2020).

	Plant Samples	**Scientific name**	**Tissue**	***N***	**% Moisture content ± SD**
Aquatic	Water lily	*Nymphaeaceae* spp.	Roots	10	87 ± 4
Terrestrial	Labrador tea	*Rhododendron groenlandicum*	Leaves	10	50 ± 16
Terrestrial	Berry[a]		Fruits	16	40 ± 16
Terrestrial	Rat root	*Acorus americanus*	Roots	12	68 ± 6
Terrestrial	Mountain ash	*Sorbus aucuparia*	Stems	9	44 ± 7
Terrestrial	Mint	*Mentha* spp.	Leaves and stem	3	37 ± 2
Terrestrial	Old man's beard	*Usnea* spp.	Whole tissue	5	30 ± 19
Total				**65**	

[a]Comprised of 3 lingonberry (*Vaccinium vitis-idaea*), 3 cranberry (*Vaccinium spp.*), 3 rosehip (*Rosa canina*), 3 highbush cranberry (*Viburnum trilobum*), 3 bunchberry (*Cornus canadensis*), 1 blueberry (*Cyanococcus spp.*), 1 bog cranberry (*Vaccinium oxycoccos*), and 1 Saskatoon berry (*Amelanchier alnifolia*).

Supplementary Table 3.2. Sample types and sample size *N* of animal foods of the Bigstone Cree collected by community members in 2015 (Adapted from Golzadeh et al. 2020).

	Animal Samples	**Scientific name**	**Tissue**	***N***	**% Moisture content ± SD**
Aquatic	Fish (Whitefish)	*Coregoninae clupeaformis*	Muscle	6	74 ± 5
			Liver	5	62 ± 11
Aquatic	Duck (Mallard)	*Anas platyrhynchos*	Muscle	7	73 ± 3
			Liver	6	72 ± 10
			Brain	7	89 ± 4
Terrestrial	Grouse (Ruffed grouse Spruce hen)	*Bonasa umbellus, Falcipennis canadensis*	Muscle	14	73 ± 3
			Liver	12	86 ± 4
			Brain	12	70 ± 13
Terrestrial	Hare (Snowshoe hare)	*Lepus americanus*	Muscle	10	65 ± 16
			Liver	10	74 ± 6
Terrestrial	Moose	*Alces alces*	Kidney	10	84 ± 8
			Muscle	3	53 ± 36
			Rib-smoked	5	72 ± 7
Terrestrial	Bear (American black bear)	*Ursus americanus*	Muscle	4	77 ± 14
Total				**111**	

Supplementary Table 3.3. List of (A) plant and (B) animal samples in which several non-essential trace elements had concentrations below the detection limit (BDL). The samples were collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

(A)

Plant samples (sample size *N* not-detected/ total samples size *N*)		
Silver (Ag)	**Arsenic (As)**	**Thallium (Tl)**
Berries (1/16)	Berries (3/16)	Labrador tea (1/10)
	Mountain ash (2/9)	Berries (14/16)
		Mountain ash (8/9)
		Water lily (8/10)

(B)

Animal samples (sample size *N* not-detected/ total samples size *N*)		
Silver (Ag)	**Arsenic (As)**	**Thallium (Tl)**
Fish muscle (6/6)	Duck brain (2/7)	Fish muscle (6/6)
Fish liver (1/5)	Grouse muscle (6/14)	Duck muscle (7/7)
Duck muscle (2/5)	Grouse brain (7/12)	Duck liver (6/6)
Grouse muscle (12/14)	Hare muscle (7/10)	Duck brain (7/7)
Grouse liver (11/12)	Hare liver (7/10)	Grouse muscle (14/14)
Grouse brain (3/12)	Hare kidney (8/10)	Grouse liver (12/12)
Hare muscle (7/10)	Moose muscle (3/3)	Grouse brain (12/12)
Moose muscle (3/3)	Moose rib (5/5)	Hare muscle (8/10)
Moose rib (5/5)	Bear muscle (4/4)	Hare Kidney (8/10)
Bear muscle (4/4)		Moose muscle (3/3)
		Moose rib (5/5)
		Bear muscle (4/4)

Supplementary Table 3.4. List of outlier samples in lead (Pb) concentration in animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

Lead (Pb) outliers in animal samples (sample size *N*)
Grouse muscle (1)
Grouse liver (1)
Grouse brain (2)
Moose rib (1)

Supplementary Table 3.5. Mean ± SE concentrations (μg g^{-1} w.w.) of nickel (Ni), cupper (Cu), zinc (Zn), chromium (Cr) in the plant and animal samples of the Bigstone Cree Nation in Alberta, Canada.

Sample	***N***	**Essential Elements** Mean (μg g^{-1} w.w.) ± SE			
		Ni	**Cu**	**Zn**	**Cr**
Berry	16	0.48 ± 0.06^{b}	2.32 ± 0.37^{b}	8.77 ± 1.64^{b}	0.07 ± 0.02^{b}
Labrador tea	10	0.57 ± 0.14^{b}	1.77 ± 0.22^{b}	15.42 ± 3.86^{ab}	0.72 ± 0.37^{a}
Mint	3	1.98 ± 0.80^{a}	8.18 ± 1.68^{a}	36.03 ± 5.42^{a}	0.39 ± 0.09^{a}
Mountain ash	9	1.27 ± 0.23^{a}	2.26 ± 0.32^{b}	41.56 ± 12.45^{a}	0.03 ± 0.01^{b}
Old man's beard	5	0.84 ± 0.11^{ab}	1.96 ± 0.34^{b}	25.30 ± 3.56^{a}	0.62 ± 0.09^{a}
Rat root	12	0.30 ± 0.03^{b}	1.39 ± 0.30^{b}	5.98 ± 0.69^{b}	0.06 ± 0.01^{b}
Water lily	10	0.06 ± 0.02^{c}	0.82 ± 0.68^{c}	1.13 ± 0.25^{c}	0.08 ± 0.03^{b}
Bear muscle	4	0.015 ± 0.008^{bc}	1.675 ± 0.631^{cde}	43.477 ± 16.920^{abc}	0.027 ± 0.008^{bc}
Duck brain	9	0.032 ± 0.009^{bc}	1.248 ± 0.172^{de}	6.030 ± 0.804^{de}	0.055 ± 0.032^{bc}
Duck liver	8	0.011 ± 0.002^{bc}	12.854 ± 2.391^{a}	31.190 ± 3.992^{ab}	0.030 ± 0.003^{abc}
Duck muscle	9	0.008 ± 0.001^{c}	5.331 ± 1.061^{ab}	11.510 ± 1.345^{cde}	0.030 ± 0.003^{abc}
Fish liver	6	0.021 ± 0.005^{bc}	5.278 ± 1.848^{abc}	35.448 ± 6.658^{abc}	0.045 ± 0.012^{abc}
Fish muscle	6	0.030 ± 0.020^{bc}	0.196 ± 0.016^{f}	4.269 ± 0.392^{e}	0.028 ± 0.007^{bc}
Grouse brain	12	0.123 ± 0.026^{a}	4.352 ± 0.387^{b}	18.868 ± 2.054^{bc}	0.088 ± 0.013^{a}
Grouse liver	12	0.018 ± 0.002^{bc}	1.608 ± 0.192^{cd}	13.448 ± 1.452^{bcd}	0.015 ± 0.002^{c}
Grouse muscle	14	0.040 ± 0.013^{b}	0.648 ± 0.069^{e}	5.771 ± 0.596^{e}	0.052 ± 0.013^{ab}
Hare kidney	10	0.057 ± 0.015^{ab}	1.999 ± 0.334^{cd}	17.285 ± 2.859^{bcd}	0.017 ± 0.003^{c}
Hare liver	10	0.028 ± 0.011^{bc}	3.453 ± 0.297^{bc}	30.730 ± 3.976^{ab}	0.028 ± 0.004^{bc}
Hare muscle	10	0.017 ± 0.004^{bc}	3.014 ± 0.428^{bcd}	16.875 ± 2.913^{bc}	0.045 ± 0.008^{abc}
Moose muscle	3	0.028 ± 0.011^{abc}	2.605 ± 1.163^{bcde}	89.878 ± 38.100^{a}	0.044 ± 0.015^{abc}
Moose rib	5	0.048 ± 0.005^{ab}	1.556 ± 0.220^{bcde}	70.572 ± 13.180^{a}	0.033 ± 0.004^{abc}

N represents the number of individual samples. Different lower-case letters within columns indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other.

Supplementary Table 3.6. Mean ± SE concentrations (μg g^{-1} w.w.) of non-essential elements including silver (Ag), cadmium (Cd), thallium (Tl), lead (Pb), and arsenic (As) in the plant and animal samples of the Bigstone Cree Nation in Albert, Canada.

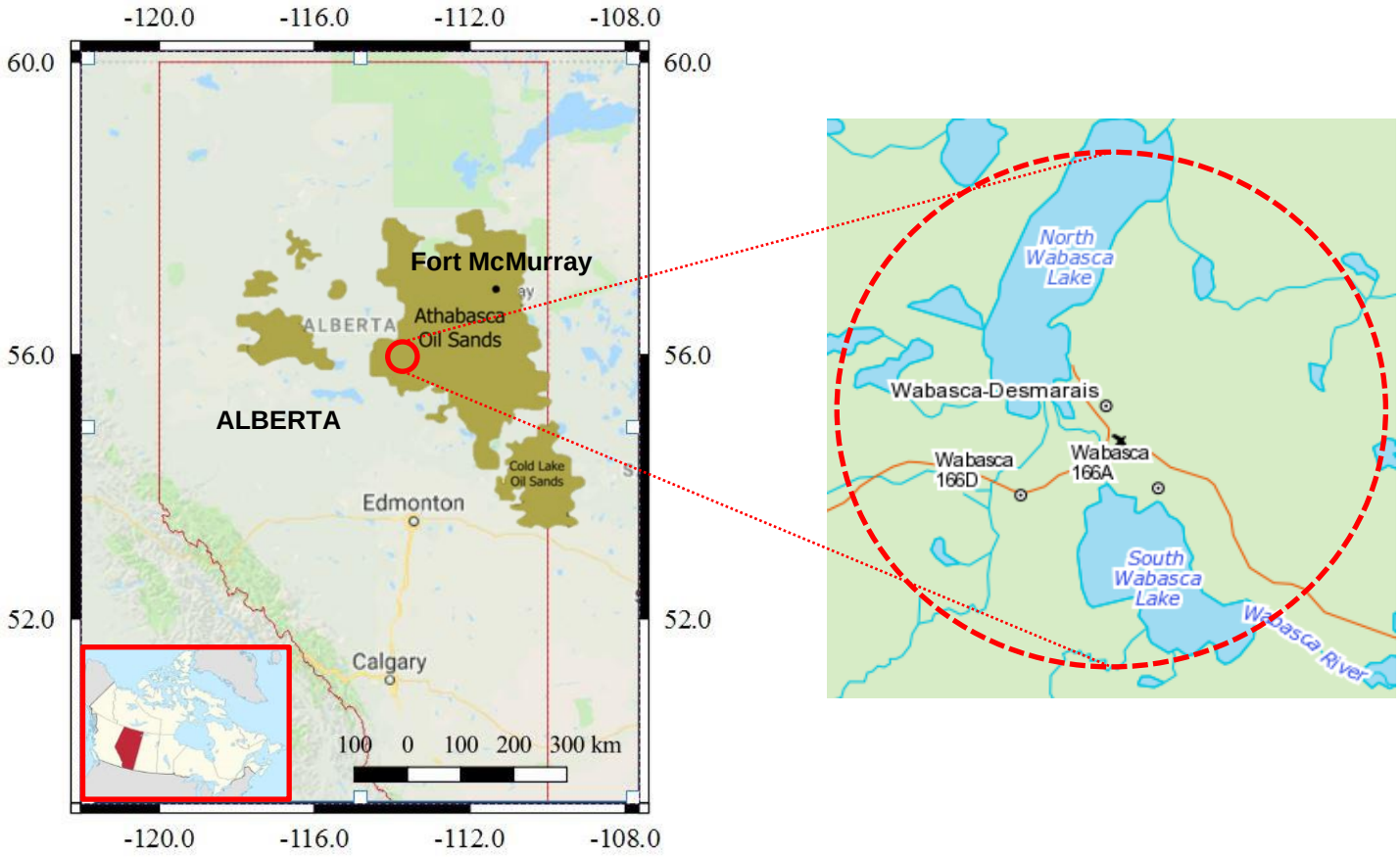
Sample	***N***	**Non-essential Elements** Mean (μg g^{-1} w.w.) ± SE				
		Ag	**Cd**	**Tl**	**Pb**	**As**
Berry	16	0.002 ± 0.000^{bcd}	0.01 ± 0.00^{bc}	BDL	0.043 ± 0.013^{cd}	0.02 ± 0.01^{cd}
Labrador tea	10	0.006 ± 0.001^{ab}	0.02 ± 0.01^{bc}	0.008 ± 0.003^{a}	0.157 ± 0.059^{bc}	0.15 ± 0.06^{ab}
Mint	3	0.006 ± 0.002^{abc}	0.04 ± 0.03^{abc}	0.002 ± 0.000^{a}	0.806 ± 0.543^{ab}	0.02 ± 0.00^{ab}
Mountain ash	9	0.022 ± 0.047^{bc}	0.27 ± 0.05^{a}	BDL	0.029 ± 0.006^{cd}	0.03 ± 0.02^{d}
Old man's beard	5	0.014 ± 0.003^{a}	0.07 ± 0.01^{ab}	0.007 ± 0.002^{a}	1.262 ± 0.293^{a}	0.18 ± 0.06^{a}
Rat root	12	0.001 ± 0.000^{cd}	0.004 ± 0.001^{c}	0.005 ± 0.000^{a}	0.043 ± 0.008^{cd}	0.08 ± 0.02^{a}
Water lily	10	0.001 ± 0.000^{d}	0.002 ± 0.001^{c}	BDL	0.028 ± 0.014^{d}	0.01 ± 0.00^{bc}
Bear muscle	4	BDL	0.006 ± 0.002^{c}	BDL	0.005 ± 0.002^{a}	BDL
Duck brain	9	0.007 ± 0.002*	0.001 ± 0.000^{c}	BDL	0.055 ± 0.039^{a}	0.007 ± 0.001^{bcd}
Duck liver	8	0.020 ± 0.004*	0.022 ± 0.008^{c}	BDL	0.041 ± 0.024^{a}	0.033 ± 0.008^{ab}
Duck muscle	9	0.003 ± 0.001*	0.001 ± 0.000^{c}	BDL	0.035 ± 0.030^{a}	0.014 ± 0.005^{abc}
Fish liver	6	0.032 ± 0.019*	0.030 ± 0.015^{c}	BDL	0.008 ± 0.002^{a}	0.075 ± 0.021^{a}
Fish muscle	6	BDL	0.001 ± 0.000^{c}	BDL	0.009 ± 0.004^{a}	0.043 ± 0.007^{ab}
Grouse brain	12	0.010 ± 0.003*	0.007 ± 0.001^{c}	BDL	0.013 ± 0.003^{a}	0.067 ± 0.044^{cd}
Grouse liver	12	0.000 ± 0.000*	0.452 ± 0.075^{b}	BDL	0.081 ± 0.048^{a}	0.057 ± 0.047^{abc}
Grouse muscle	14	BDL	0.008 ± 0.002^{c}	BDL	0.032 ± 0.013^{a}	0.005 ± 0.001^{d}
Hare kidney	10	BDL	3.772 ± 1.500^{a}	BDL	0.010 ± 0.005^{a}	BDL
Hare liver	10	BDL	0.249 ± 0.067^{b}	BDL	0.024 ± 0.011^{a}	BDL
Hare muscle	10	BDL	0.011 ± 0.004^{c}	BDL	0.007 ± 0.002^{a}	BDL
Moose muscle	3	BDL	0.006 ± 0.001^{c}	BDL	0.008 ± 0.003^{a}	BDL
Moose rib	5	BDL	0.004 ± 0.001^{c}	BDL	0.008 ± 0.004^{a}	BDL

N represents the number of individual samples. Different lower-case letters within columns indicate significantly different mean values based on *post-hoc* Tukey HSD pairwise comparisons. Levels not sharing the same letter are considered significantly different from each other.

NA: Not applicable since the data did not meet the QA/QC quantifications.

BDL: Below detection limit.

*: No robust statistical analysis was possible due to significant portion of samples being below the detection limit.



Supplementary Figure 3.1. Map showing the location of the Bigstone Cree territory (red dashed circle) in Alberta, Canada (Golzadeh et al., 2020).

6.3. Supplementary Materials for Chapter 4

Supplementary Table 4.1. Summary of key attributes of methods AXYS MLA-021, U.S. EPA 8270C, 8270D and 1625B (AXYS method MLA-021, 2013).

Analysis by GC/LRMS, Key Attributes of AXYS MLA-021, EPA 8270C/D and EPA 1625B				
	MLA-021	**EPA 8270C**	**EPA 8270D**	**EPA 1625B**
MS acquisition mode	SIM[1]	Full Scan or SIM[1]	Full Scan or SIM[1]	Full Scan[1]
Qualitative Identification Criteria	Retention time & ratio of 2 ions	Retention time & ratio of 3 [2] ions	Retention time & ratio of 3 [2] ions	Retention time & ratio of characteristic ions
MS Ion Ratio Criteria	20 %	30 %	30 %	-50 % to +200 %
MS Tuning Type and Check Frequency	PTFBA, daily	DFTTP[1], 12 hrs	DFTTP[1], 12 hrs	DFTTP[1], 8 hrs
Quantification References	Isotopically labeled standards added prior to extraction	Internal standards added prior to instrumental analysis	Internal standards added prior to instrumental analysis	Isotopically labeled standards added prior to extraction
Recovery correction of results	YES	NO	NO	YES
Initial Calibration, # levels	5	5	5	5
Initial Calibration Limit (% RSD)	20 % (35 % if no labeled analog)	15 %	20 %	20 % (35 % if no labeled analog)
Calibration Verification Frequency	12 hrs	12 hrs	12 hrs	8 hrs
Calibration Verification Relative Response Limit (% diff.)	< 25 % of I-CAL	< 20 % of I-CAL	< 20 % of I-CAL	Various; most stringent is -20% to +25% of I-CAL
Calibration Verification IS area (% of I-CAL midpoint)	50-200 %	50-200 %	50-200 %	n.a.
Calibration verification IS RT (diff. from I-CAL midpoint)	n.a.	30 sec.	30 sec.	n.a.
Extraction	DCM (L/L (aqueous) DCM, Soxhlet (solids)	Options specified externally	Options specified externally	DCM, L/L (aqueous), pH>11 or pH other [3]

Note:

1. SIM (Selected Ion Monitoring) acquisition protocol is permitted by EPA8270 and Federal Register Vol.77 Iss. 97 (May 18, 2012) Part 136
2. Based on availability, use of fewer ions is permitted
3. Modifications are permitted under Federal Register Vol.77 Iss.97 (May 18, 2012) Part 136.6

Supplementary Table 4.2A. Analyte Ions Monitored, Surrogates Used and relative response factors (RRF) Determination for PAC (AXYS method MLA-021, 2013).

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
Naphthalene	128	102	0.064	d_8-Naphthalene	6.84	Naphthalene
Acenaphthylene	152	151	0.222	d_8-Acenaphthylene	10.83	Acenaphthylene
Acenaphthene	154	153	1.18	d_8-Acenaphthylene	11.33	Acenaphthene
Fluorene	166	165	1.01	d_{10}-Phenanthrene	12.63	Fluorene
Phenanthrene	178	176	0.202	d_{10}-Phenanthrene	15.04	Phenanthrene
Anthracene	178	176	0.196	d_{10}-Phenanthrene	15.15	Anthracene
Fluoranthene	202	200	0.214	d_{10}-Fluoranthene	18.06	Fluoranthene
Pyrene	202	200	0.219	d_{10}-Fluoranthene	18.60	Pyrene
Benz[a]anthracene[6]	228	226	0.281	d_{12}-Benz[a]anthracene	21.68	Benz[a]anthracene
Chrysene[1]	228	226	0.312	d_{12}-Chrysene	21.79	Chrysene
Benzo[b]fluoranthene	252	253	0.218	d_{12}-Benzo[b]fluoranthene	25.21	Benzo[b]fluoranthene
Benzo[j,k]fluoranthenes	252	253	0.215	d_{12}-Benzo[k]fluoranthene	25.30	Benzo[k]fluoranthene
Benzo[e]pyrene	252	253	0.213	d_{12}-Benzo[a]pyrene	26.36	Benzo[e]pyrene
Benzo[a]pyrene	252	253	0.217	d_{12}-Benzo[a]pyrene	26.58	Benzo[a]pyrene
Perylene	252	253	0.212	d_{12}-Perylene	27.00	Perylene
Dibenzo[ah]anthracene[2]	278	139	0.144	d_{14}-Dibenzo[ah]anthracene	31.86	Dibenz[ah]anthracene
Indeno[1,2,3-cd]pyrene	276	138	0.179	d_{12}-Indeno[1,2,3,cd]pyrene	31.71	Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene	276	138	0.194	d_{12}-Benzo[ghi]perylene	32.53	Benzo[ghi]perylene
Biphenyl[3]	154	152	0.304	d_{10}- Biphenyl	9.81	Biphenyl
Dibenzothiophene[3]	184	152	0.073	d_8-Dibenzothiophene	14.72	Dibenzothiophene
1-Methylnaphthalene[3]	142	141	0.962	d_{10}-2-Methylnaphthalene	8.81	1-Methylnaphthalene
2-Methylnaphthalene[3]	142	141	0.930	d_{10}-2-Methylnaphthalene	8.55	2-Methylnaphthalene
1-Naphthalenes[3]	142	[4]	[4]	d_{10}-2-Methylnaphthalene	[5]	1- & 2-Methylnaphthalene
2,6-Dimethylnaphthalene[3]	156	141	0.666	d_{12}-2,6 Dimethylnaphthalene	10.17	2,6-Dimethylnaphthalene
1,2-Dimethylnaphthalene	156	141	1.26	d_{12}-2,6 Dimethylnaphthalene	10.90	1,2-Dimethylnaphthalene
C2-Naphthalenes[3]	156	[4]	[4]	d_{12}-2,6 Dimethylnaphthalene	[5]	2,6- & 1,2-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene[3]	170	155	0.873	d_{12}-2,6 Dimethylnaphthalene	12.35	2,3,5- Trimethylnaphthalene
2,3,6-Trimethylnaphthalene	170	155	0.876	d_{12}-2,6 Dimethylnaphthalene	12.17	2,3,6- Trimethylnaphthalene

C3-Naphthalenes[3]	170			d_{12}-2,6 Dimethylnaphthalene	[5]	2,3,5- & 2,3,6-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene	184	139	0.027	d_{12}-2,6 Dimethylnaphthalene	13.89	1,4,6,7-Tetramethylnaphthalene

1- Coelutes with Triphenylene
2- Coelutes with Dibenz[ac]anthracene
3- These compounds are in addition to the regular suite of analytes, and are analyzed by client request only.
4- Secondary ion confirmation procedures do not apply
5- RRT ranges apply to alkylated PAH Totals
6- Benz(a)anthracene coelutes with cyclopenta(cd)pyrene, which may contribute response in the second ion to cause a failing ion abundance ratio. Therefore quantification of benz(a)anthracene should use response from the first ion only.

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
C4-Naphthalene		[4]	[4]	d_{12}-2,6 Dimethylnaphthalene	[5]	1,4,6,7-Tetramethylnaphthalene
2-Methylanthracene	192	191	0.531	d_{10}-Phenanthrene	16.45	2-Methylanthracene
3-Methylphenanthrene	192	191	0.608	d_{10}-Phenanthrene	16.27	1- & 2-Methylphenanthrene & 2-Methylanthracene
2-Methylphenanthrene	192	191	0.608	d_{10}-Phenanthrene	16.36	2-Methylphenanthrene
9/4-Methylphenanthrenes	192	191	0.634	d_{10}-Phenanthrene	16.59	1- & 2-Methylphenanthrene & 2-Methylanthracene
1-Methylphenanthrene[3]	192	191	0.634	d_{10}-Phenanthrene	16.64	1-Methylphenanthrene
C1-Phenanthrenes/Anthracenes[3]	192	[4]	[4]	d_{10}-Phenanthrene	[5]	1- & 2-Methylphenanthrene & 2-Methylanthracene
3,6-Dimethylphenanthrene[3]	206	191	0.342	d_{10}-Fluoranthrene	17.46	3,6-Dimethylphenanthrene
2,6-Dimethylphenanthrene	206	191	0.342	d_{10}-Fluoranthrene	17.54	3,6- & 1,7-Dimethylphenanthrenes
1,7-Dimethylphenanthrene	206	191	0.332	d_{10}-Fluoranthrene	17.89	1,7-Dimethylphenanthrene
1,8-Dimethylphenanthrene	206	191	0.332	d_{10}-Fluoranthrene	18.13	3,6- & 1,7-Dimethylphenanthrenes
C2-Phenanthrenes/Anthracenes[3]	206	[4]	[4]	d_{10}-Fluoranthrene	[5]	3,6- & 1,7-Dimethylphenanthrenes

1,2,6-Trimethylphenanthrene	220	205	0.581	d_{10}-Fluoranthrene	19.41	1,2,6-Trimethylphenanthrene
C3-Phenanthrenes/Anthracenes				d_{10}-Fluoranthrene	[5]	1,2,6-Trimethylphenanthrene
Retene[3]	234	219	1.63	d_{10}-Fluoranthene	19.53	Retene
C4-Phenanthrenes/Anthracenes	234	[4]	[4]	d_{10}-Fluoranthrene	[5]	Retene
C1-Biphenyls	168	[4]	[4]	d_{10}- Biphenyl	[5]	Biphenyl
C2-Biphenyls	182	[4]	[4]	d_{10}- Biphenyl	[5]	Biphenyl
C1-Acenaphthenes	168	[4]	[4]	d_8-Acenaphthylene	[5]	Acenaphthene
2-Methylfluorene	180	165	1.23	d_{10}-Phenanthrene	14.06	2-Methylfluorene
C1-Fluorenes	180	[4]	[4]	d_{10}-Phenanthrene	[5]	2-Methylfluorene
1,7-Dimethylfluorene	194	177	0.092	d_{10}-Phenanthrene	15.49	1,7-Dimethylfluorene
C2-Fluorenes	194	[4]	[4]	d_{10}-Phenanthrene	[5]	1,7-Dimethylfluorene
C3-Fluorenes	208	[4]	[4]	d_{10}-Phenanthrene	[5]	1,7-Dimethylfluorene
2/3-Methyldibenzothiophenes	198	197	0.738	d_8-Dibenzothiophene	16.07	2/3-Methyldibenzothiophenes
C1-Dibenzothiophenes	198	[4]	[4]	d_8-Dibenzothiophene	[5]	2/3-Methyldibenzothiophenes
2,4-Dimethyldibenzothiophene	212	197	0.514	d_8-Dibenzothiophene	17.08	2,4-Dimethyldibenzothiophene
C2-Dibenzothiophenes	212	[4]	[4]	d_8-Dibenzothiophene	[5]	2,4-Dimethyldibenzothiophene
C3-Dibenzothiophenes	226	[4]	[4]	d_8-Dibenzothiophene	[5]	2,4-Dimethyldibenzothiophene
C4-Dibenzothiophenes	240	[4]	[4]	d_8-Dibenzothiophene	[5]	2,4-Dimethyldibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene	216	215	0.880	d_{10}-Fluoranthrene	19.53	3-Methylfluoranthene
C1-Fluoranthenes/Pyrenes	216	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C2-Fluoranthenes/Pyrenes	230	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C3-Fluoranthenes/Pyrenes	244	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C4-Fluoranthenes/Pyrenes	258	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
5/6-Methylchrysenes	242	[4]	[4]	d_{12}-Chrysene	23.15	6-Methylchrysene
1-Methylchrysene	242	[4]	[4]	d_{12}-Chrysene	23.32	1-Methylchrysene
C1-Benz(a)anthracenes/Chrysenes	242	[4]	[4]	d_{12}-Chrysene	[5]	1- & 6-Methylchrysenes
5,9-Dimethylchrysene	256	[4]	[4]	d_{12}-Chrysene	24.49	5,9-Dimethylchrysene
C2-Benz(a)anthracenes/Chrysenes	256	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
C3-Benz(a)anthracenes/Chrysenes	270	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
C4-Benz(a)anthracenes/Chrysenes	284	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
7-Methylbenzo(a)pyrene	266	[4]	[4]	d_{12}-Benzo[a]pyrene	29.35	7-Methylbenzo(a)pyrene
C1-Benzofluoranthenes/Benzopyrenes	266	[4]	[4]	d_{12}-Benzo[a]pyrene	[5]	7-Methylbenzo(a)pyrene
C2-Benzofluoranthenes/Benzopyrenes	280	[4]	[4]	d_{12}-Benzo[a]pyrene	[5]	7-Methylbenzo(a)pyrene
LABELLED SURROGATE STANDARDS	**Quantification Ion (m/z)**	**Confirmation Ions (m/z)**		**RECOVERY CALCULATED AGAINST**		
d_8-Naphthalene	136	134	0.095	d_{10}-Acenaphthene	6.80	
d_{10}-2-Methylnaphthalene	152	151	0.195	d_{10}-Acenaphthene	8.47	
d_{10}-Biphenyl	164	[4]	[4]	d_{10}-Acenaphthene	9.75	
d_{12}-2,6-Dimethylnaphthalene	168	150	0.747	d_{10}-Acenaphthene	10.07	
d_8-Acenaphthylene	160	158	0.159	d_{10}-Acenaphthene	10.80	
d_8-Dibenzothiophene	192	160	0.085	d_{10}-Pyrene	14.67	
d_{10}-Phenanthrene	188	184	0.143	d_{10}-Pyrene	14.97	
d_{10}-Fluoranthene	212	208	0.173	d_{10}-Pyrene	18.02	
d_{12}-Benz[a]anthracene	240	236	0.250	d_{10}-Pyrene	21.63	
d_{12}-Chrysene	240	236	0.278	d_{10}-Pyrene	21.73	

d_{12}-Benzo[b]fluoranthene	264	260	0.216	d_{12}-Benzo[e]pyrene	25.11
d_{12}-Benzo[k]fluoranthene	264	260	0.208	d_{12}-Benzo[e]pyrene	25.23
d_{12}-Benzo[a]pyrene	264	260	0.216	d_{12}-Benzo[e]pyrene	26.47
d_{12}-Perylene	264	260	0.256	d_{12}-Benzo[e]pyrene	26.88
d_{12}-Indeno[1,2,3,cd]pyrene	288	284	0.192	d_{12}-Benzo[e]pyrene	31.63
d_{14}-Dibenzo[ah]anthracene	292	288	0.260	d_{12}-Benzo[e]pyrene	31.75
d_{12}-Benzo[ghi]perylene	288	284	0.205	d_{12}-Benzo[e]pyrene	32.45
LABELLED RECOVERY STANDARDS	**Quantification Ion (m/z)**	**Confirmation Ions (m/z)**			
d_{10}-Acenaphthene	164	160	0.464		11.24
d_{10}-Pyrene	212	208	0.176		18.56
d_{12}-Benzo[e]pyrene	264	260	0.269		26.25

Supplementary Table 4.2B. Concentration of PAHs/Alkylated PAHs Calibration Standard Solutions (AXYS method MLA-021, 2013).

TARGET ANALYTE	Level A (Sens. Std) (ng/mL)	Concentration of Calibration Standard Solutions (ng/mL)					Conc. of Native Std (Low Level) (ng/mL)	Conc. of Native Std (High Level) (ng/mL)
		Level B	Level C	Level D	Level E (Mid-level)	Level F		
Acenaphthene	10	50	100	500	2000	5000	2000	20 000
Acenaphthylene	10	50	100	500	2000	5000	2000	20 000
Anthracene	10	50	100	500	2000	5000	2000	20 000
Benz[a]anthracene	10	50	100	500	2000	5000	2000	20 000
Benzo[b]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[k]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[ghi]perylene	10	50	100	500	2000	5000	2000	20 000
Benzo[a]pyrene	10	50	100	500	2000	5000	2000	20 000
Benzo[e]pyrene	10	50	100	500	2000	5000	2000	20 000
Biphenyl	10	50	100	500	2000	5000	2000	20 000
Chrysene	10	50	100	500	2000	5000	2000	20 000
Dibenzo[ah]anthracene	10	50	100	500	2000	5000	2000	20 000
2,6-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Fluoranthene	10	50	100	500	2000	5000	2000	20 000
Fluorene	10	50	100	500	2000	5000	2000	20 000
Indeno[1,2,3-cd]pyrene	10	50	100	500	2000	5000	2000	20 000
1-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
1-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Naphthalene	10	50	100	500	2000	5000	2000	20 000
Perylene	10	50	100	500	2000	5000	2000	20 000
Phenanthrene	10	50	100	500	2000	5000	2000	20 000
Pyrene	10	50	100	500	2000	5000	2000	20 000
2,3,5-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Dibenzothiophene	10	50	100	500	2000	5000	2000	20 000
3,6-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Retene	10	50	100	500	2000	5000	2000	20 000
2-Methylanthracene	10	50	100	500	2000	5000	2000	20 000
1,2-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,2,6-Trimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
2,3,6-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000

1,7-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,4,6,7-Tetramethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylfluorene	10	50	100	500	2000	5000	2000	20 000
1,7-Dimethylfluorene	10	50	100	500	2000	5000	2000	20 000
2-Methyldibenzothiophene	10	50	100	500	2000	5000	2000	20 000
2,4-Dimethyldibenzothiophene	10	50	100	500	2000	5000	2000	20 000
5,9-Dimethylchrysene	10	50	100	500	2000	5000	2000	20 000
7-Methylbenzo(a)pyrene	10	50	100	500	2000	5000	2000	20 000
3-Methylfluoranthene	10	50	100	500	2000	5000	2000	20 000
6-Methylchrysene	10	50	100	500	2000	5000	2000	20 000
1-Methylchrysene	10	50	100	500	2000	5000	2000	20 000

LABELLED SURROGATE STANDARDS	**Level A (Sens. Std) (ng/mL)**	**Concentration of Calibration Standard Solutions**					**Conc. of Surrogate Std (Low Level) (ng/mL)**	**Conc. of Surrogate Std (High Level) (ng/mL)**
		Level B	**Level C**	**Level D**	**Level E**	**Level F**		
d_8-Naphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-2-Methylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_8-Acenaphthylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Phenanthrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benz[a]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Chrysene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-2,6-Dimethylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[b]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[k]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[a]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Indeno[1,2,3-cd]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{14}-Dibenzo[ah]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[ghi]perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Biphenyl	2000	2000	2000	2000	2000	2000	2000	20 000
d_8-Dibenzothiophene	2000	2000	2000	2000	2000	2000	2000	20 000
LABELLED RECOVERY STANDARDS							**Conc. of Recovery Std (ng/mL)**	
d_{10}-Acenaphthene	2000	2000	2000	2000	2000	2000	20 000	
d_{10}-Pyrene	2000	2000	2000	2000	2000	2000	20 000	
d_{12}-Benzo[e]pyrene	2000	2000	2000	2000	2000	2000	20 000	

Supplementary Table 4.2C. Surrogate Standards Recovery ranges% (AXYS method MLA-021, 2013).

SURROGATE STANDARD RECOVERIES:	**% RECOVERY RANGES ALL MATRICES**
d_8-naphthalene	15 – 130
d_8-acenaphthylene	20 – 130
d_{10}-phenanthrene	30 – 130
d_{10}-fluoranthene *	30 – 130
d_{12}-benz[a]anthracene	30 – 130
d_{12}-chrysene	30 – 130
d_{12}-benzo[b]fluoranthene	30 – 130
d_{12}-benzo[k]fluoranthene	30 – 130
d_{12}-benzo[a]pyrene	30 – 130
d_{12}-perylene	30 – 130
d_{14}-dibenz[ah]anthracene *	30 – 130
d_{12}-indeno[1,2,3-cd]pyrene	30 – 130
d_{12}-benzo[ghi]perylene	30 – 130
d_{10}-2-methylnaphthalene	20 – 130
d_{12}-2,6-dimethylnaphthalene	20 – 130
d_{10}-biphenyl	15 – 130
d_8-dibenzothiophene	30 – 130

Supplementary Table 4.2D. QC Specification Table: Instrumental Analysis, and Analyte Quantification (AXYS method MLA-021, 2013).

Parameter	Acceptance Specification
Procedural Blank	Refer to Table "QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples" above, or 5 times lower than analogous analyte value detected in the samples.
Analysis Duplicate	Duplicates must fall within ±20% of the mean (applicable to concentrations >10 times the DL) These are guidelines – departures based on professional judgement allowed. (Note that ±20% of the mean is equivalent to 40 relative percent difference)
Instrument Sensitivity	S/N 3:1 for 10 pg of acenaphthene, dibenzo(a,h)anthracene.
Instrument Resolution	Calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220, Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present and all labelled compounds, ≤35% for targets with no labelled analog present.
Continuing Cal Ver	Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within ±25% of expected values for all targets. Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%
Bracketing Cal (optional)	RRFs for the opening and closing calibrations over a 12 hour period must agree to within ±20% of the mean (i.e., ≤40 RPD between RRFs and for the opening and closing calibrations, which is equivalent to ≤28.3 % RSD).
GC Resolution	Benzo[b] & [k]fluoranthene valley height must be ≤75% for equal concentrations. Phenanthrene/anthracene valley height must be ≤30% for equal concentrations.
Chromatogram Quality	Maximum peak width must be ≤15 seconds for benzo[ghi]perylene peak at 10% peak height.
Retention Time Window for Target Compounds	RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). A second requirement is that an authentic elute after its labelled analog.
Ion Abundance Ratios	CAL VER: Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL All other native analytes and labelled surrogates must be within ±20% of the mid-point of the I-CAL Samples: Ion ratios for authentic and labelled dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the 12 hour CAL VER (or bracketing) calibration standard. All other native analytes and labelled surrogates must be within ±20% of the 12 hour CAL VER (or bracketing) calibration standard.

Supplementary Table 4.3. Percentage recoveries (%Mean ± SD) calculated from all batches of samples (plants and animals) for the 16 surrogate compounds used in PACs concentrations analyses in food samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada.

Surrogate	**%Recovery (mean ± SD)**
Naphthalene d-8	20.0 ± 8.0
2-Methylnaphthalene d-10	28.9 ± 11.0
2,6-Dimethylnaphthalene d-12	35.4 ± 13.3
Acenaphthylene d-8	35.2 ± 14.3
Dibenzothiophene d-8	37.8 ± 11.0
Phenanthrene d-10	51.7 ± 12.2
Fluoranthene d-10	61.3 ± 10.3
Benzo[a]anthracene d-12	65.6 ± 12.1
Chrysene d-12	71.2 ± 13.3
Benzo[b]fluoranthene d-12	60.0 ± 9.6
Benzo[k]fluoranthene d-12	61.5 ± 9.7
Benzo[a]pyrene d-12	54.6 ± 9.6
Perylene d-12	53.3 ± 9.4
Dibenzo[a,h]anthracene d-14	52.0 ± 11.0
Indeno[1,2,3-cd]pyrene d-12	52.6 ± 11.0
Benzo[ghi]perylene d-12	56.6 ± 11.0

Supplementary Table 4.4. Mean (± SE) concentrations of individual PACs compounds (16 U.S. EPA priority PAHs, 49 alkylated PAHs, 7 dibenzothiophenes (DBTs)) presented in ng g^{-1}, wet weight (w.w.) in **(A)** plant samples and **(B)** animal samples (muscle and rib tissues), collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada.

(A)

PACs compounds Mean ± SE (ng g^{-1} w.w.)	**Ring number**	**PAHs type**	**Labrador tea (9)**	**Berry (8)**	**Water lily (6)**	**Mountain ash (6)**	**Rat root (10)**	**Old man's beard (3)**
Naphthalene	2	parent	4.44±0.37	0.43±0.10	ND	0.70±0.14	1.11±0.20	18.19±2.98
Acenaphthylene	3	parent	0.27±0.16	0.03±0.01	NDR	NDR	0.07±0.01	0.91±0.21
Acenaphthene	3	parent	0.36	0.05±0.00	0.00	0.05±0.01	0.03±0.01	0.81±0.18
2-Methylfluorene	3	alkylated	0.19	NDR	ND	ND	0.05	1.15±0.18
C2 Phenanthrenes/Anthracenes	3	alkylated	3.09±0.93	0.28±0.11	0.10±0.08	0.45±0.09	0.19±0.04	21.22±1.99
Fluorene	3	parent	0.33±0.01	0.07	0.05±0.01	0.13±0.02	0.94±0.30	3.55±0.26
Phenanthrene	3	parent	2.51±0.70	0.20±0.05	0.03	0.51±0.08	0.05±0.02	31.07±4.06
Anthracene	3	parent	NDR	0.05±0.01	NDR	NDR	0.03	0.67±0.17
C1 Phenanthrenes/Anthracenes	3	alkylated	1.62±0.36	0.21±0.06	0.18	0.31±0.07	0.12±0.07	31.45±5.37
Fluoranthene	4	parent	3.18±2.68	0.15±0.05	0.08±0.04	0.12±0.03	0.09±0.02	12.14±1.28
Pyrene	4	parent	0.92±0.51	0.12±0.04	0.05±0.03	0.06±0.01	0.06±0.02	5.24±1.01
Benz[a]anthracene	4	parent	NDR	0.09	0.04	0.01	0.03±0.01	NDR
Chrysene	4	parent	1.20±0.54	0.14±0.05	0.06±0.02	0.16±0.03	0.11±0.03	10.83±1.51
Benzo[b]fluoranthene	5	parent	0.23±0.04	0.02±0.01	0.09±0.05	0.03±0.01	0.12±0.04	2.91±0.61
Benzo[j,k]fluoranthenes	5	parent	0.68	NDR	NDR	NDR	0.09±0.04	1.05±0.26
Benzo[a]pyrene	5	parent	0.05	ND	NDR	NDR	0.08	0.86±0.20
Dibenz[a,h]anthracene	6	parent	ND	ND	NDR	ND	0.04±0.01	0.44±0.02
Indeno[1,2,3-cd]pyrene	6	parent	NDR	NDR	NDR	NDR	0.12±0.05	0.87±0.21
Benzo[ghi]perylene	6	parent	0.21	NDR	0.14	NDR	0.10±0.02	1.47±0.31
2-Methylnaphthalene	2	alkylated	1.90±0.29	0.21±0.06	0.33±0.23	0.41±0.04	0.61±0.11	16.40±3.03
1-Methylnaphthalene	2	alkylated	1.01±0.18	0.10±0.04	0.12±0.07	0.27±0.03	0.32±0.05	9.26±1.64
C1-Naphthalenes	2	alkylated	2.91±0.47	0.30±0.10	0.39±0.27	0.68±0.07	0.93±0.16	25.66±4.67
C2-Naphthalenes	2	alkylated	13.48±2.13	0.48±0.26	0.50±0.43	26.46±4.55	4.91±1.40	40.45±6.71
1,2-Dimethylnaphthalene	2	alkylated	0.37±0.24	NDR	NDR	ND	0.21±0.11	1.81±0.37
2,6-Dimethylnaphthalene	2	alkylated	0.81±0.21	0.12±0.02	0.13±0.11	0.20	0.17	8.66±1.76
C3-Naphthalenes	2	alkylated	68.41±16.86	0.25±0.09	0.17±0.16	0.45±0.07	8.77±3.07	28.51±3.79
2,3,6-Trimethylnaphthalene	2	alkylated	0.43±0.08	0.03±0.01	0.04±0.02	0.15±0.03	0.11±0.05	6.49±1.11
2,3,5-Trimethylnaphthalene	2	alkylated	1.85±0.26	0.07	0.03±0.01	0.10±0.01	1.73	5.63±0.41
C4-Naphthalenes	2	alkylated	26.06±3.42	0.14±0.03	ND	0.87±0.14	8.27±2.32	18.60 ±3.41
C1-Acenaphthenes	3	alkylated	55.80	ND	ND	0.06±0.01	0.98±0.25	0.05

C1-Fluorenes	3	alkylated	0.77±0.14	0.07±0.02	0.08±0.02	0.29±0.04	8.87±4.50	6.95±0.86
1,7-Dimethylfluorene	3	alkylated	NDR	ND	ND	ND	NDR	0.78±0.02
C2-Fluorenes	3	alkylated	2.56±0.42	0.06±0.01	0.06±0.03	0.19±0.03	0.92±0.19	8.81±1.01
C3-Fluorenes	3	alkylated	3.23±0.44	0.09	0.01	0.28	0.33±0.05	12.62±2.60
Dibenzothiophene	3	DBT	NDR	0.02	NDR	NDR	NDR	1.55
C1-Dibenzothiophenes	3	DBT	0.17	ND	ND	0.05±0.01	0.10±0.04	3.29±0.73
2/3-Methyldibenzothiophenes	3	DBT	NDR	ND	ND	NDR	0.14	1.65±0.02
C2-Dibenzothiophenes	3	DBT	2.17±0.33	0.08	ND	0.11±0.06	0.82±0.18	17.36±5.96
2,4-Dimethyldibenzothiophene	3	DBT	0.32±0.08	ND	ND	ND	NDR	NDR
C3-Dibenzothiophenes	3	DBT	0.77±0.18	ND	0.14	0.16±0.07	0.27±0.04	5.84±0.49
C4-Dibenzothiophenes	3	DBT	1.28±0.37	0.02±0.00	ND	ND	0.19±0.05	84.26±75.90
3-Methylphenanthrene	3	alkylated	0.35±0.06	0.05±0.01	0.01	NDR	0.05±0.02	5.42±0.91
2-Methylphenanthrene	3	alkylated	0.62±0.08	0.07±0.02	0.01	0.10±0.03	NDR	11.31±2.14
2-Methylanthracene	3	alkylated	0.24	NDR	0.02	ND	0.04	1.10
9/4-Methylphenanthrene	3	alkylated	0.28±0.06	0.04±0.00	0.02±0.02	0.06±0.01	0.06±0.03	4.78±0.85
1-Methylphenanthrene	3	alkylated	0.93±0.30	0.08±0.03	0.03±0.02	0.20±0.04	0.04±0.02	9.58±1.44
3,6-Dimethylphenanthrene	3	alkylated	NDR	NDR	NDR	NDR	NDR	NDR
2,6-Dimethylphenanthrene	3	alkylated	0.14±0.04	0.03±0.00	0.01	0.01	0.02±0.01	1.92±0.27
1,7-Dimethylphenanthrene	3	alkylated	1.59±0.59	0.20±0.09	NDR	0.22±0.05	0.04±0.02	11.39
1,8-Dimethylphenanthrene	3	alkylated	0.14±0.11	NDR	NDR	NDR	0.02	0.66±0.01
C3-Phenanthrenes/Anthracenes	3	alkylated	2.27±0.62	0.30±0.12	0.10±0.04	0.42±0.07	0.20±0.03	27.33±4.79
1,2,6-Trimethylphenanthrene	3	alkylated	0.17±0.06	0.05±0.02	0.02	0.03	0.03	1.44±0.32
C4-Phenanthrenes/Anthracenes	3	alkylated	13.92±3.80	2.37±1.03	0.57±0.22	3.33±0.49	2.15±0.58	133.54±27.33
C1-Fluoranthenes/Pyrenes	4	alkylated	3.62±1.25	0.39±0.14	0.15±0.07	1.82±0.44	0.50±0.10	98.04±70.53
3-Methylfluoranthene/Benzo[a]fluorene	4	alkylated	NDR	0.16±0.07	0.06±0.03	0.09±0.04	0.15±0.04	11.75±1.35
C2-Fluoranthenes/Pyrenes	4	alkylated	1.99±0.37	0.17±0.08	0.24±0.11	0.49±0.06	0.33±0.08	30.25±7.95
C3-Fluoranthenes/Pyrenes	4	alkylated	0.45±0.12	0.04	0.16±0.10	0.17±0.03	0.22±0.05	11.97±1.69
C4-Fluoranthenes/Pyrenes	4	alkylated	0.16	ND	0.08±0.05	0.10	0.16±0.04	3.00±0.65
C1-Benzo[a]anthracenes/Chrysenes	4	alkylated	0.42±0.12	0.07±0.05	0.08±0.04	0.08±0.02	0.11±0.04	7.13±0.96
5/6-Methylchrysene	4	alkylated	0.05±0.01	ND	0.01±0.01	ND	0.03±0.02	0.61±0.07
1-Methylchrysene	4	alkylated	0.09±0.03	0.03	0.02±0.01	0.01±0.00	0.03±0.01	1.04±0.10
C2-Benzo[a]anthracenes/Chrysenes	4	alkylated	0.18±0.07	ND	0.09±0.05	0.04±0.01	0.13±0.05	4.50±0.97
5,9-Dimethylchrysene	4	alkylated	0.06±0.02	ND	0.03	ND	0.03±0.01	0.91±0.17
C3-Benzo[a]anthracenes/Chrysenes	4	alkylated	0.14	ND	0.04	0.02±0.00	0.11±0.03	1.09±0.44
C4-Benzo[a]anthracenes/Chrysenes	4	alkylated	0.24±0.14	ND	ND	ND	0.33	0.23
C1-Benzofluoranthenes/Benzopyrenes	5	alkylated	0.44±0.21	ND	0.17±0.12	ND	0.22±0.14	4.85±0.91
7-Methylbenzo[a]pyrene	5	alkylated	ND	ND	ND	ND	ND	0.22±0.02
C2-Benzofluoranthenes/Benzopyrenes	5	alkylated	ND	ND	0.03±0.02	0.02	0.14	2.38±0.44
1,4,6,7-Tetramethylnaphthalene	2	alkylated	NDR	ND	NDR	NDR	NDR	0.45

ND: not detected

NDR: peak detected but failed to meet quantification criteria

(B)

PACs compounds Mean ± SE (ng g^{-1} w.w.)	Ring number	PAHs type	Duck muscle (7)	Grouse muscle (10)	Fish muscle (6)	Moose muscle (3)	Moose rib (5)	Bear muscle (4)	Hare muscle (10)
Naphthalene	2	parent	3.12±0.99	0.43±0.07	0.46±0.08	0.46±0.10	10.47±4.01	0.99±0.13	0.25±0.08
Acenaphthylene	3	parent	NDR	NDR	0.12	NDR	17.67±7.22	0.03	ND
Acenaphthene	3	parent	0.07±0.01	0.03	0.02±0.01	0.03±0.01	2.09±0.83	0.04	ND
2-Methylfluorene	3	alkylated	NDR	ND	0.03	NDR	6.78±2.12	0.04	NDR
C2 Phenanthrenes/Anthracenes	3	alkylated	0.14±0.11	0.03±0.02	0.01±0.01	0.08±0.01	14.05±3.66	0.15±0.05	0.01±0.01
Fluorene	3	parent	0.00	NDR	0.10±0.06	0.01±0.01	9.65±3.44	0.00±0.00	0.02±0.00
Phenanthrene	3	parent	ND	ND	0.24±0.17	ND	67.60±26.90	0.13±0.09	ND
Anthracene	3	parent	NDR	0.02±0.01	0.04±0.01	0.01	13.23±3.90	0.02±0.01	NDR
C1 Phenanthrenes/Anthracenes	3	alkylated	ND	ND	0.04	ND	35.33±12.50	0.30±0.13	ND
Fluoranthene	4	parent	ND	0.02±0.02	0.03	0.01	24.85±12.38	0.03±0.01	NDR
Pyrene	4	parent	0.07±0.06	0.08±0.07	ND	0.09	10.88±2.68	0.15±0.05	NDR
Benz[a]anthracene	4	parent	NDR	NDR	NDR	NDR	35.773	NDR	NDR
Chrysene	4	parent	0.01±0.00	ND	NDR	0.02	3.27±2.05	ND	0.02
Benzo[b]fluoranthene	5	parent	ND	ND	ND	ND	1.96±1.75	ND	ND
Benzo[j,k]fluoranthenes	5	parent	ND	ND	ND	ND	0.14±0.04	ND	ND
Benzo[a]pyrene	5	parent	ND	ND	NDR	ND	0.14±0.05	ND	ND
Dibenz[a,h]anthracene	6	parent	ND	ND	ND	ND	0.03±0.01	ND	NDR
Indeno[1,2,3-cd]pyrene	6	parent	NDR	NDR	NDR	NDR	0.15±0.03	NDR	NDR
Benzo[ghi]perylene	6	parent	NDR	NDR	NDR	0.08	0.15±0.04	0.07±0.01	NDR
2-Methylnaphthalene	2	alkylated	1.65±0.49	0.10±0.03	0.17±0.06	0.16±0.06	5.94±2.32	0.90±0.25	0.17±0.07
1-Methylnaphthalene	2	alkylated	0.74±0.23	0.08±0.02	0.13±0.05	0.10±0.03	6.96±2.20	0.40±0.10	0.05±0.03
C1-Naphthalenes	2	alkylated	2.39±0.72	0.17±0.04	0.30±0.10	0.26±0.09	11.55±4.51	1.30±0.35	0.23±0.10
C2-Naphthalenes	2	alkylated	0.40±0.13	0.08±0.03	0.26±0.22	0.22±0.08	19.74±6.22	0.72±0.15	0.22±0.02
1,2-Dimethylnaphthalene	2	alkylated	0.08	ND	NDR	NDR	2.16±0.70	0.09	ND
2,6-Dimethylnaphthalene	2	alkylated	0.08±0.03	0.03	0.07±0.02	0.03±0.02	3.31±1.03	0.17±0.06	0.10
C3-Naphthalenes	2	alkylated	0.19±0.03	0.15±0.04	0.29±0.05	0.21±0.02	23.99±6.50	0.45±0.06	0.60
2,3,6-Trimethylnaphthalene	2	alkylated	0.05±0.02	0.03±0.01	0.05±0.01	0.03±0.01	3.16±0.89	0.09±0.02	0.07±0.00
2,3,5-Trimethylnaphthalene	2	alkylated	0.04±0.01	0.04±0.02	0.08±0.02	0.03±0.00	2.986	0.10±0.01	0.08
C4-Naphthalenes	2	alkylated	0.30±0.06	0.17±0.06	0.21±0.05	0.20±0.06	18.06±4.43	0.27±0.04	0.13±0.01
C1-Acenaphthenes	3	alkylated	ND	ND	ND	ND	1.00±0.69	ND	ND
C1-Fluorenes	3	alkylated	0.09±0.03	0.06±0.01	0.14±0.03	0.11±0.02	18.37±6.13	0.23±0.08	0.09±0.01
1,7-Dimethylfluorene	3	alkylated	ND	ND	ND	ND	4.40±3.36	ND	ND
C2-Fluorenes	3	alkylated	0.21±0.05	0.34±0.04	0.13±0.05	0.33±0.13	21.27±8.45	0.23±0.05	0.42±0.07
C3-Fluorenes	3	alkylated	1.56±0.75	0.33±0.04	0.21±0.06	0.20±0.01	12.70±3.15	0.18±0.04	0.19±0.04
Dibenzothiophene	3	DBT	NDR	NDR	NDR	NDR	0	NDR	NDR
C1-Dibenzothiophenes	3	DBT	ND	ND	ND	ND	10.47±4.01	0.07	ND
2/3-Methyldibenzothiophenes	3	DBT	ND	ND	ND	ND	10.47±4.01	0.03	ND
C2-Dibenzothiophenes	3	DBT	0.08±0.03	0.01±0.01	0.03±0.00	0.05±0.02	10.47±4.01	0.25±0.03	0.08±0.03
2,4-Dimethyldibenzothiophene	3	DBT	NDR	ND	ND	ND	0	NDR	ND

C3-Dibenzothiophenes	3	DBT	0.15±0.08	0.13±0.03	0.04±0.00	0.15±0.04	10.47±4.01	0.16±0.05	0.08±0.05
C4-Dibenzothiophenes	3	DBT	0.49	ND	0.00	0.10±0.07	10.47±4.01	0.04±0.03	ND
3-Methylphenanthrene	3	alkylated	ND	0.01	ND	ND	8.85±2.98	0.09±0.04	ND
2-Methylphenanthrene	3	alkylated	NDR	ND	NDR	NDR	13.31±4.49	0.11±0.05	NDR
2-Methylanthracene	3	alkylated	ND	NDR	ND	ND	3.91±1.37	ND	ND
9/4-Methylphenanthrene	3	alkylated	ND	NDR	0.03±0.01	0.03	7.46±1.95	0.05±0.01	0.02±0.00
1-Methylphenanthrene	3	alkylated	ND	ND	0.00	ND	8.67±2.20	0.04±0.03	ND
3,6-Dimethylphenanthrene	3	alkylated	NDR	ND	ND	NDR	3.33	0.04	ND
2,6-Dimethylphenanthrene	3	alkylated	0.05	ND	ND	0.00	2.89±1.14	0.03	ND
1,7-Dimethylphenanthrene	3	alkylated	0.04	0.00	NDR	0.01	3.18±1.15	NDR	ND
1,8-Dimethylphenanthrene	3	alkylated	ND	ND	ND	0.03±0.00	0.89±0.03	NDR	NDR
C3-Phenanthrenes/Anthracenes	3	alkylated	0.40±0.37	0.04±0.02	0.06±0.04	0.06±0.02	3.17±1.11	0.12±0.04	0.02±0.01
1,2,6-Trimethylphenanthrene	3	alkylated	0.15	ND	ND	ND	0.82±0.32	ND	ND
C4-Phenanthrenes/Anthracenes	3	alkylated	0.45±0.34	0.05±0.01	0.11±0.03	0.08±0.05	2.54±0.70	0.16±0.03	0.07±0.01
C1-Fluoranthenes/Pyrenes	4	alkylated	1.05±1.02	0.04	0.04	0.07±0.07	11.75±4.71	0.19±0.01	0.04±0.00
3-Methylfluoranthene/Benzo[a]fluorene	4	alkylated	0.43	ND	ND	0.02	5.45±1.80	0.02±0.01	ND
C2-Fluoranthenes/Pyrenes	4	alkylated	0.41±0.38	ND	ND	0.08±0.05	4.73±1.77	0.07±0.03	0.10
C3-Fluoranthenes/Pyrenes	4	alkylated	0.09	ND	ND	ND	4.24±2.55	0.02	ND
C4-Fluoranthenes/Pyrenes	4	alkylated	ND	ND	ND	ND	1.62±1.04	ND	ND
C1-Benzo[a]anthracenes/Chrysenes	4	alkylated	ND	ND	ND	0.03	1.68±0.78	0.02±0.01	0.11
5/6-Methylchrysene	4	alkylated	ND	ND	ND	ND	0.17±0.10	ND	0.02
1-Methylchrysene	4	alkylated	ND	ND	ND	ND	0.28±0.11	ND	0.01
C2-Benzo[a]anthracenes/Chrysenes	4	alkylated	0.03±0.01	0.02	0.07±0.02	ND	0.75±0.46	ND	0.04±0.02
5,9-Dimethylchrysene	4	alkylated	ND	ND	ND	ND	0.17±0.13	ND	0.03
C3-Benzo[a]anthracenes/Chrysenes	4	alkylated	ND	ND	ND	ND	0.18±0.09	ND	ND
C4-Benzo[a]anthracenes/Chrysenes	4	alkylated	ND	ND	0.03±0.01	ND	0.18±0.11	ND	ND
C1-Benzofluoranthenes/Benzopyrenes	5	alkylated	ND	0.09	ND	ND	0.28±0.20	ND	ND
7-Methylbenzo[a]pyrene	5	alkylated	ND	ND	ND	ND	0.03±0.01	ND	ND
C2-Benzofluoranthenes/Benzopyrenes	5	alkylated	ND	0.10	ND	ND	0.15±0.12	ND	ND
1,4,6,7-Tetramethylnaphthalene	2	alkylated	0.03	NDR	NDR	NDR	0.0432	NDR	ND

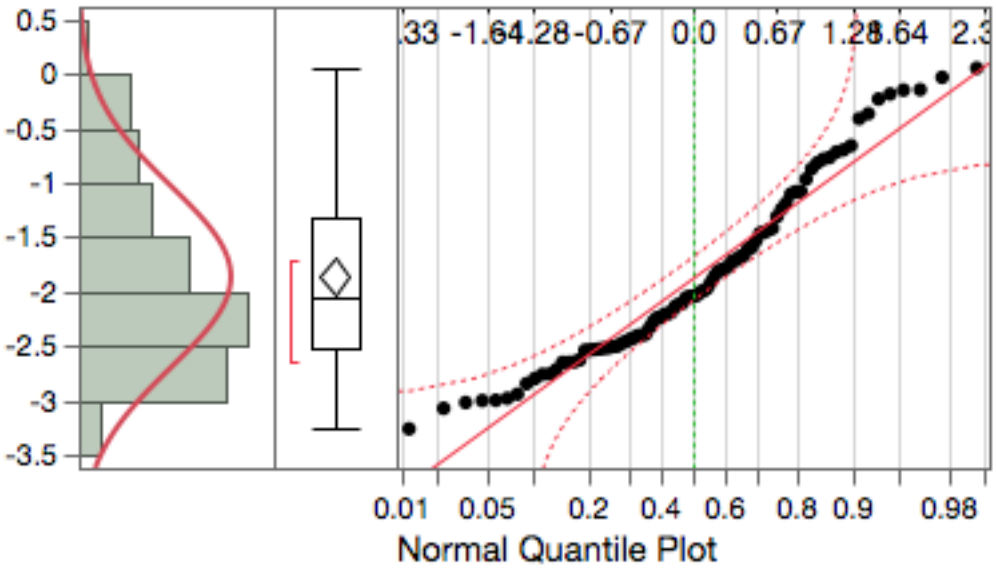
ND: not detected

NDR: peak detected but failed to meet quantification criteria

Supplementary Table 4.5. Mean lipid content (± SE) presented in percentage (%) in animal samples (muscle, rib, and pooled liver tissues), collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation in Alberta, Canada.

Animal samples (*n*)	Lipid %
Duck muscle (7)	2.72 ± 0.17
Grouse muscle (10)	0.52 ± 0.04
Fish muscle (6)	2.28 ± 0.79
Moose muscle (3)	2.20 ± 0.27
Smoked moose rib (5)	3.02 ± 0.29
Bear muscle (4)	3.52 ± 0.82
Hare muscle (10)	1.61 ± 0.10
Pooled liver of grouse (1)	5.59
Pooled liver of fish (1)	12.70
Pooled liver of duck (1)	5.53
Pooled liver of hare (1)	4.00

Supplementary Table 4.6. Log_{10}-transformed diagnostic (residual) plot for total PACs.



Supplementary Table 4.7. Mean (± SE) and median of concentrations of various classes of PACs compounds (16 U.S. EPA priority PAHs, 49 alkylated PAHs, 7 dibenzothiophenes (DBTs)) presented in ng g^{-1}, wet weight (w.w.) in **(A)** plant samples and **(B)** animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada.

(A)

	Benzo(a)pyrene		**16 U.S. EPA PAHs**		**Alkylated PAHs**		**Dibenzothiophenes**		**Total PACs**	
Sample name (*n*)	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**
Berries (8)	ND	NA	1.14±0.25	0.97	5.72±1.92	4.00	0.01±0.01	0.00	6.88±2.13	4.98
Labrador tea (9)	0.05	NA	9.70±2.40	7.66	159.14±24.98	151.35	4.30±0.53	4.02	173.15±26.75	163.19
Mountain ash (6)	ND	NA	1.68±0.30	1.84	37.58±5.48	32.49	0.22±0.10	0.10	39.49±5.80	34.20
Old man's beard (3)	0.86±0.20	0.20	90.85±12.98	99.16	605.49±55.37	641.76	112.37±79.95	46.66	808.71±115.61	796.42
Rat root (10)	0.08	NA	1.83±0.46	1.69	38.66±11.37	24.66	1.26±0.24	1.31	41.76±11.34	29.99
Water lily (6)	ND	NA	0.26±0.15	0.09	2.74±1.0	1.86	0.02±0.02	0.00	3.02±1.09	2.01

ND: not detected
NA: not applicable

(B)

	Benzo(a)pyrene		16 U.S. EPA PAHs		Alkylated PAHs		Dibenzothiophenes		Total PACs	
Sample name (*n*)	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**	**Mean ± SE (ng g^{-1}ww)**	**Median**
Bear muscle (4)	ND	NA	1.32±0.23	1.40	6.18±1.27	5.49	0.33±0.16	0.31	7.84±1.53	6.97
Duck muscle (7)	ND	NA	1.94±0.62	1.61	6.69±2.13	3.82	0.21±0.15	0.07	8.84±2.28	7.37
Fish muscle (6)	ND	NA	0.76±0.28	0.58	2.20±0.67	1.62	0.04±0.02	0.03	3.00±0.95	2.24
Grouse muscle (10)	ND	NA	0.38±0.08	0.40	1.26±0.19	1.09	0.08±0.03	0.07	1.73±0.25	1.55
Hare muscle (10)	ND	NA	0.19±0.06	0.09	1.27±0.89	1.02	0.04±0.02	0.00	1.50±0.31	1.12
Moose muscle (3)	ND	NA	0.53±0.16	0.37	2.11±0.61	2.29	0.20±0.12	0.16	2.84±0.86	2.82
Smoked moose rib (5)	0.14±0.05	0.13	168.48±44.23	196.27	290.66±75.22	366.07	2.54±0.48	3.00	416.69±119.75	565.56
Pooled liver of grouse (1)	ND	NA	0.55	NA	7.75	NA	1.67	NA	9.96	NA
Pooled liver of duck (1)	ND	NA	3.90	NA	12.25	NA	3.53	NA	19.74	NA
Pooled liver of fish (1)	ND	NA	3.32	NA	7.70	NA	1.81	NA	12.83	NA
Pooled liver of hare (1)	ND	NA	1.05	NA	9.20	NA	1.44	NA	11.69	NA

ND: not detected

NA: not applicable

Supplementary Table 4.8. Percentage of PACs presented as %16 U.S. EPA priority PAHs, %alkylated PAHs, and %dibenzothiophenes (DBTs) in **(A)** plant samples and **(B)** animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada.

(A)

Plant samples (*n*)	Labrador tea (9)	Berries (8)	Water Lily (6)	Mountain Ash (6)	Rat root (10)	Old man's beard (3)
% 16 U.S. EPA PAHs	5.60	16.57	8.28	4.25	4.38	11.23
% Alkylated PAHs	91.91	83.14	90.73	95.16	92.58	74.87
% DBTs	2.48	0.17	0.73	0.56	3.02	13.89

(B)

Animal samples (*n*)	Duck Muscle (7)	Grouse Muscle (10)	Pooled liver (4)	Fish muscle (6)	Moose muscle (3)	Moose rib (5)	Bear muscle (4)	Hare muscle (10)
% 16 U.S. EPA PAHs	21.49	21.97	19.61	25.28	18.66	36.49	16.86	12.08
% Alkylated PAHs	75.68	73.41	67.07	73.19	74.30	62.95	78.93	85.23
% DBTs	2.38	4.05	13.32	1.30	6.69	0.56	4.21	2.68

Supplementary Table 4.9. Mean (± SE) concentrations of PAH4 (sum of benzo[a] anthracene, chrysene, benzo[b]fluoranthene, and benzo[a]pyrene) presented in ng g^{-1}, wet weight (w.w.) in plant samples and animal samples collected in 2015 and representing traditional foods consumed by the Bigstone Cree Nation community in Alberta, Canada.

Plant samples (*n*)	**PAH4** **Mean ± SE (ng g^{-1}ww)**
Berries (8)	0.17 ± 0.06
Labrador tea (9)	1.41 ± 0.60
Mountain ash (6)	0.18± 0.03
Old man's beard (3)	14.60 ± 2.30
Rat root (10)	0.20 ± 0.07
Water lily (6)	0.11 ± 0.06
Animal samples (*n*)	
Bear muscle (4)	0.002 ± 0.001
Duck muscle (7)	ND
Fish muscle (6)	0.003
Grouse muscle (10)	0.004
Hare muscle (10)	0.024
Moose muscle (3)	0.002 ± 0.001
Moose rib (5)	1.51 ± 0.50
Pooled liver of grouse (1)	ND
Pooled liver of duck (1)	ND
Pooled liver of fish (1)	ND
Pooled liver of hare (1)	ND

ND: not detected

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