

Organic carbon, mercury and climate change:
Towards a better understanding of
biotic contamination in the Canadian Arctic

by

Jesse D. Carrie

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Department of Environment & Geography
University of Manitoba
Winnipeg, Canada

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Abstract

Mercury (Hg) is a known neurotoxin that is often found in concentrations exceeding safe consumption guidelines in aquatic biota. This is especially evident in northern Canada, where northerners typically consume significant amounts of edible tissues of animals such as beluga, seals and burbot. In the Mackenzie River Basin, recent increases in Hg concentration in many of these animals over the past 25 years have been observed, although no definite reasons for this have been ascertained: atmospheric Hg levels have remained stable or slightly decreasing, and other factors (e.g., age, trophic level) do not always explain the higher biotic Hg concentrations. The warming climate, and with it, the changing carbon cycle, are hypothesised in this thesis to play a role in the increases, with increasing amounts of labile, algal-derived organic matter (OM) able to scavenge water column Hg, thus rendering it more bioavailable. Within the context of the two major zones (mountainous and peatland), with distinct geomorphology, hydrology and geology, traditional fossil fuel exploration methods (Rock-Eval pyrolysis, organic petrography) have been employed in a novel manner on recent sediments to qualify and quantify the OM and several geochemical analyses (Hg, dissolved organic carbon (DOC), SO_4^{2-} , Cl^- , sequential extractions) have been used to determine the geochemical sources of Hg. The mountainous zone is composed mostly of refractory OM, primarily from forest fire char and heavily reworked OM. It also contains, and fluxes, most of the Hg, which derives from oxidative weathering and erosion of widespread sulfide minerals. However, Hg from this zone is in chemical forms that are of limited bioavailability. The peatland zone has a greater proportion of labile OM, with higher concentrations of DOC

and algal-derived OM. Lake-fed tributaries in this zone contain even higher proportions of labile OM. Indeed, significant correlation exists between Hg and labile OM at these sites, suggesting a correspondingly higher bioavailability. At one of these sites (Hare Indian Lake), the sediment core record shows that Hg has been increasingly associated with labile OM over time, due to increasing primary productivity, accelerated by climate change, and is resulting in an increase in scavenged Hg. The temporal trend in algal-bound Hg in the sediment record matches very well with the temporal trend of Hg in burbot sampled from the area, providing one of the first and strongest lines of evidence for the climatic impact on Hg bioaccumulation in Arctic ecosystems.

Manuscript claims

Chapter 2:

Carrie, J, Sanei, H, Goodarzi, F, Stern, G, Wang, F. 2009. Characterisation of organic matter in surface sediments of the Mackenzie River Basin, Canada. *International Journal of Coal Geology* 77: 416-423.

I collected and analysed the samples and wrote most of the paper.

Chapter 3:

Carrie, J, Wang, F, Sanei, H, Stern, G, Macdonald, R. 2009. Biogeochemical controls of mercury in the Mackenzie River Basin. Submitted to *Chemical Geology*. July 10, 2009. 28p.

I collected and analysed the samples and wrote most of the paper.

Chapter 4:

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I collected and analysed the sediment core, interpreted the climate and fish data and wrote most of the paper.

Chapter 1: Introduction

1.1 Rationale and hypothesis

Mercury (Hg) is a toxic, bioaccumulative and biomagnifiable element. Horrific examples of Hg poisoning have been seen in Minamata, Japan (Harada, 1978), which gave its name to Hg poisoning (Minamata disease), as well as in Iraq (Bakir et al., 1973), with the most pressing problem being damage to the nervous system, perhaps most memorably personified in the character of the Mad Hatter in Lewis Carroll's *Alice in Wonderland*. Recently, several studies have been focussing on changes to the endocrine system (Tan et al., 2009).

The ubiquitous presence of Hg is a cause for concern virtually everywhere on the planet. However, it is in aquatic environments that its negative effects are most strongly felt, as Hg is transformed into the more toxic and bioaccumulative form, monomethyl Hg (MeHg). Conditions favouring production of MeHg are relatively high dissolved organic carbon (DOC) concentrations, a redox transition zone, and sufficiently high SO_4^{2-} concentrations, which acts as oxidant for sulfate-reducing bacteria (SRB), the most prominent Hg methylators (Fitzgerald et al., 2007). Any region satisfying the requirements of sufficient DOC, redox conditions and SO_4^{2-} , such as a river, lake or basin, is also likely to contain significant concentrations of MeHg and bioavailable Hg (Gorski et al., 2008; Liu et al., 2009, Garcia et al., 2007; Mitchell and Gilmour, 2008). As most societies live adjacent to some body of water and consume fish and other aquatic

biota, this is of great concern, especially for those who rely heavily upon such creatures for sustenance, as they do in the Canadian north.

In the Canadian Arctic, several aquatic species (e.g., beluga, burbot, ringed seals) have Hg concentrations exceeding the safe consumption guideline for fish of Health Canada of 0.2 µg/g (wet wt.) as well as the commercial limit of 0.5 µg/g (wet wt.) (Lockhart et al., 2005; Evans et al., 2005; Gaden et al., 2009; Stern and Tomy, 2008). There has also been a noticeable increasing temporal trend in biotic Hg burdens among burbot and for most years in beluga (Stern and Tomy, 2008; Lockhart et al., 2005). Several hypotheses have been put forward to explain these high and increasing Hg levels. Foremost among these is the high trophic level of most analysed species (Lockhart et al., 2005; Evans et al., 2005), which, following the definition of biomagnification for Hg, should contain the highest concentrations of Hg. While a valid and useful observation, this does not explain how Hg entered the system in the first place, and does not always explain Hg contamination within a single species (see Chapter 4). Second, another hypothesis relates to the age of the biota (Evans et al., 2005), as Hg is bioaccumulative, hence older biota should contain higher concentrations of Hg. As will be discussed later (Chapter 4), this is not always the case. Third among the hypotheses is an increase in anthropogenic loading of Hg to the atmosphere (Muir et al., 2009), which then enters the watershed, leading to increases seen in biota. In the Canadian Arctic, there are no significant sources of atmospheric Hg (e.g., coal-burning power plants, heavy industry) that can impact the local and/or regional location (e.g., Donahue et al., 2006). Furthermore, several researchers have noticed stable or decreasing atmospheric Hg levels over the recent past where increases in biota Hg were reported (Steffen et al., 2005; Li et

al., 2009). This leads us to the hypothesis that changes in the carbon (C) cycle affect how Hg cycles in the environment.

Grosso modo, it is our hypothesis that a warming climate entails greater primary productivity (i.e., algae, phytoplankton), and with it, larger amounts of labile organic matter (OM) and a greater tendency for the primary producers to scavenge water column Hg (Outridge et al., 2007), rendering it more bioavailable, which in turns end up accumulating in the foodweb, either directly in the pelagic zone, or indirectly via transformation in the benthic zone. We have chosen the Mackenzie River Basin as an ecosystem in which to test this hypothesis, both spatially and temporally, as several of the above-mentioned studies on biota are within its boundaries.

The objective of this thesis is thus to test whether a link between labile OM and Hg exists, and how a changing climate affects the cycling of each, and ultimately, the biota that live in the Mackenzie River Basin ecosystem, including the humans who consume them.

1.2 Study Area

The Mackenzie River Basin (MRB) is a very large watershed ($1.78 \times 10^6 \text{ km}^2$; Leitch et al., 2007) situated in northwestern Canada (Figure 1.1). The Mackenzie River has the largest water discharge of all Canadian rivers, and second largest after the Mississippi in North America (Millot et al., 2003). It is also the largest source of sediment and OM to the Arctic Ocean, and thus has a large impact on the biogeochemistry of Hg, especially in the Beaufort Sea. Several different sub-ecosystems

exist within the MRB. We have chosen to group these sub-ecosystems into two main groups (mountainous and peatland zones) based upon major differences in mineralogy (Figures 1.1 and 1.2), hydrology and geomorphology. The mountainous zone is situated to the west of the Mackenzie River, from the Liard River in the south to the Mackenzie delta in the north, and contains numerous sedimentary exhalative (SEDEX) and Mississippi-Valley Type (MVT) deposits, along with abundant sulfide minerals, found as base metal (mostly lead and zinc, (Zn and Pb), as sphalerite (ZnS) and galena (PbS)) and iron sulfides (mostly pyrite (FeS₂)), all of which are known geological sources of Hg (Yudovich and Ketris, 2005a; Ryall, 1981; Ozerova et al., 1975). The mountainous terrain receives the greatest amount of precipitation in the basin (Louie et al., 2002), experiences flash floods during the summer months (Brooks, 2000), and high runoff and suspended sediment from erosion (Carson et al., 1998). The peatland zone has no major mineral deposits that significantly affect the hydrogeochemistry of the Mackenzie River, as the large number of lakes and low topography act as sediment and water sinks. As the name suggests, peat, in the form of bogs and fens, is abundant in this zone. All of the above-mentioned characteristics influence the C and Hg cycles in distinguishable ways and will be discussed in Chapters 2 and 3.

1.3 Methods in Organic Matter Characterisation

Chapter 2 describes the spatial variability of OM present in the sediment of rivers in the MRB, and serves as a foundation for the subsequent chapters. This is the first study detailing the quality and quantity of OM throughout the MRB. The qualitative and

quantitative characterisation of OM allows us to determine the location of the highest concentrations of labile OM, and by extension, where Hg is most likely to be bioavailable. In other words, this chapter aims to highlight “hotspots” worthy of more in-depth studies. We have applied traditional fossil fuel exploration techniques (Rock-Eval pyrolysis and organic petrography) in a novel manner to recent sediments. Rock-Eval pyrolysis is a more detailed analysis of the OM that is present in a sample, and gives several other, operationally defined, fractions (e.g., S1, S2, S3, PC, RC), in addition to the common total organic carbon (TOC). The pyrolysable carbon (PC) is composed of the S1, S2 and S3 fractions. The dried sediment sample is placed into a pyrolysis chamber under inert, oxygen-free atmosphere (either helium or nitrogen) and heated from 300-650°C, evolving a number of compounds (Figure 1.3). S1 and S2 are analysed by flame-ionisation detection (FID) and measured as mgHC/g (HC = hydrocarbons). S3 (and S3CO) is measured by Infrared (IR) detection, and looks at the carbon dioxide (CO₂) (or monoxide (CO)) emitted, and is measured as mgCO₂/g (or mgCO/g), denoting the amount of C present measured as CO₂ (or CO). S1 is generally made up of pigments, “free” hydrocarbons and other labile compounds such as short chain lipids (Figure 1.4). S2 is composed of more refractory compounds, such as algal and plant cell walls, long-chain fats, waxes, etc. (Figure 1.5). S3 derives from oxygenated compounds, such as sugars, although mineral sources of CO and CO₂ can complicate the interpretation. Due to the difficulty in attributing definite sources to S3, it has not been used in any research thus far, nor in this study. Refractory C (RC) is analysed by combustion in an oxic atmosphere from 400-850°C, immediately following the pyrolysis stage. It is composed mostly of highly resistant OM, such as lignins and cellulosic materials from higher

plants, and remnants of fires (char). It is measured by IR. TOC is summed from the total pyrolysed and combusted C (Lafargue et al., 1998; Behar et al., 2001).

Organic petrography is the visual examination of a sample with a microscope under white or fluorescent light, each yielding different information. There are three main groups of macerals (organic “minerals”) upon which organic petrography is based (Taylor et al., 1998): vitrinite/huminite (e.g., coal and precursor forms of C such as peat), liptinite (e.g., plant resin, known as resinite, and algae, known as alginite), and inertinite (e.g., heavily reworked and oxidised OM, usually char from fires). Point counting is used to determine the relative proportion of each major group on the overall OM content. Under white light, measurements of reflectance (%R_o) on standardised (i.e., “identical”) types of OM in the vitrinite group (Figure 1.6A) allow qualification of the rank, or how far along in diagenesis and/or catagenesis, of the OM. The brighter or higher the reflectance, the more mature the OM. This may be used to trace fragments of OM back to their original sources, such as the amount of coal that has been eroded into the river from an outcrop (see Chapter 3). Inertinite is also measured under white light (Figure 1.6B). Larger proportions of inertinite indicate either the impact of a recent/nearby forest fire or OM that has undergone significant oxidation. Liptinite is measured under ultraviolet or blue light, with characteristic fluorescence for most macerals. For example, red fluorescence is almost invariably due to chlorophyll from diatoms (Figure 1.6C), while fresh plant materials may fluoresce in varying shades of blue and green (Figure 1.6D).

1.4 Mercury, Organic Matter, and Bioavailability

Chapter 3 demonstrates the major sources of Hg to the MRB, links between the various types of OM presented in Chapter 2, and what the relative bioavailability is of each major source. Much of Chapter 3 builds on previous research from Leitch et al. (2007), with new interpretations on the high Hg concentrations seen in the middle reaches of the Mackenzie River. Further, this is the first study to use traditional petroleum research techniques (i.e., Rock-Eval pyrolysis, organic petrography) to understand the relationship of OM and Hg speciation in a riverine environment. As less than 1% of all OM is ultimately preserved in the sedimentary record (Hedges and Keil, 1995), this means that at some given point, it is used as fuel by something. Clearly, forms of C that are inherently labile (DOC, S1, S2) will be consumed first, and any metals associated with them are likely to be consumed/absorbed simultaneously. Moreover, certain forms of OM are more likely to bond Hg than others. According to the hard-soft/acid-base theory (Ayers et al., 2006), Hg ions are considered soft acids, and bonds most strongly with soft bases, such as reduced sulfur (S), thus any system with abundant reduced S is also likely to contain significant quantities of bound Hg. Reduced S is commonly found in anoxic systems, such as sediments in a low hydrodynamic setting, such as in lakes (Mitchell and Gilmour, 2008). It is also found among biota, especially mobile, aquatic biota, as cysteine- or methionine-based biochemicals (e.g., proteins, metallothioneins), which explains the high concentrations seen in fish muscle. Contrariwise, reduced S is infrequently found in oxic settings, such as terrestrial systems, as the oxygen in the atmosphere easily oxidises it. Furthermore, higher plants, such as trees, require protection against atmospheric oxidation, and are composed of resistant cellulosic

materials, which have little ability to bind Hg. Several studies (Friedli et al., 2003; Mailman and Bodaly, 2005; St. Louis et al., 2001) have shown that the bulk of Hg is found in the organic horizon of soil (with abundant microbes), often exceeding by an order of magnitude concentrations seen in foliage (Hg in soil organic layer: 200-600 ng/g; in foliage: 20-50 ng/g). Refractory OM, and any that has undergone a significant degree of diagenesis, is unlikely to bind Hg, as most of the functional groups able to bind metals (e.g., -SH, -OH, -COOH, -NH₂) have been removed, leaving higher proportions of aromatic groups (Taylor et al., 1998; Vanderbroucke and Largeau, 2007). Additionally, higher plants are prone to the natural fire cycle, which has been shown to release >95% of the Hg, most of which is originally found in the organic layer of the soil (Friedli et al., 2003). Systems dominated by terrestrial OM, and inertinite in particular, are thus expected to have minimal OM-bound Hg. In sum, if a system is dominated by labile, autochthonous (i.e., aquatic) OM, the probability of Hg being bound to OM, and thus of greater bioavailability, is high.

As Hg in several aquatic species in the MRB is above the human consumption threshold, bioavailability is clearly important, as is how this bioavailability has changed over time: species such as burbot have seen significant increases in Hg over the past 25 years (Stern and Tomy, 2008). As mentioned above, labile, autochthonous OM is more likely to both bind Hg and be more bioavailable. With warming temperatures, and longer ice-free seasons, more sunlight is able to penetrate the water column, as there is less high-albedo ice to reflect incident sunlight. As primary producers require the energy derived from sunlight for photosynthesis, increased exposure to sunlight can lead to greater primary production. However, longer ice-free periods may also contribute to more

sediment-laden water from runoff and erosion, which can limit light penetration. The longer ice-free seasons are also able to create more productivity when winds recycle nutrients such as phosphate and nitrate/nitrite (Lavoie et al., 2009). As much of the primary produced OM contains proteins, and thus reduced S, it can thus scavenge water column Hg. Furthermore, scavenging of Hg by particles such as primary producers decreases the partial pressure of Hg (the amount of dissolved gaseous Hg) in the water column. This decrease then leads to a re-establishment of equilibrium between gaseous (atmospheric) and dissolved Hg, thereby increasing drawdown of Hg into the water column. Clearly, when constant warming results in a continual increase of primary productivity, we should see corresponding increases in the amount of scavenged Hg (Outridge et al., 2007). Chapter 4 examines how Hg has been cycling over time in a lake singled out among the five lake-fed tributary sites described in Chapter 3, with respect to the effects of a warming climate. Chapter 4 tests whether the hypothesis put forth in Outridge et al. (2007) is applicable to a warmer, sub-Arctic, and more complex lacustrine system (e.g., more complex vegetation, mineralogy, and hydrology). Finally, trends between OM and Hg in the lake core are then related to the increasing concentrations of Hg seen in burbot. This is the first to show a link between climate-induced cycling of Hg and increasing Hg concentrations in aquatic biota.

1.5 Organisation of the Thesis

The thesis is organized in 5 chapters essentially composed of three published or submitted manuscripts. Chapter 1 (this chapter) provides a general introduction to the

research hypothesis, background and methodology. Chapter 2 (Paper 1, published in the International Journal of Coal Geology) describes the OM in the basin. Chapter 3 (Paper 2, submitted to Chemical Geology) depicts the sources of Hg and their (possible) relation to varying types of OM. Chapter 4 (submitted to Environmental Science and Technology) illustrates the effect of OM on Hg cycling over time in a lake, coupled with the effects of a warming temperature on productivity and Hg burdens in the freshwater fish, burbot. Chapter 5 summarises the findings in this thesis, and presents new venues of research based on unanswered questions borne from this study.

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1.7 Figures

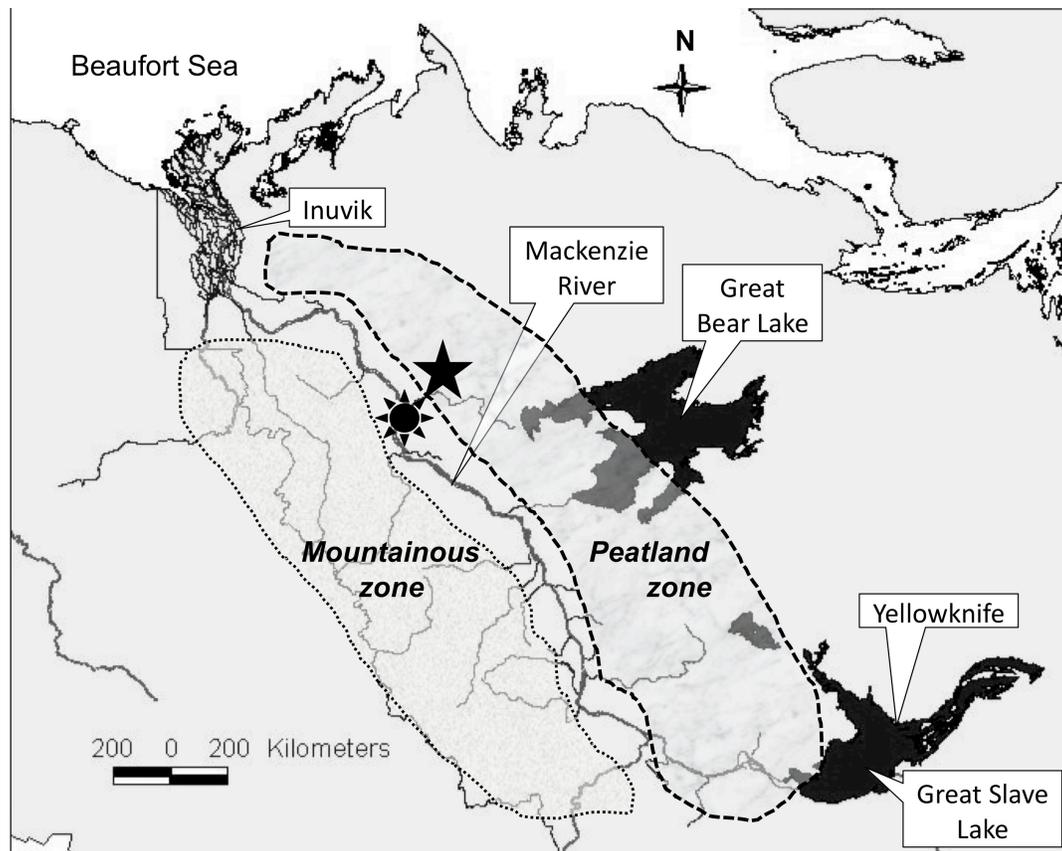


Figure 1.1: Map of the lower Mackenzie River Basin (MRB) and its two main zones (mountainous, peatland) discussed in this thesis. The lake core detailed in Chapter 4 is marked with a star, and the burbot sampling site is marked with a sun.

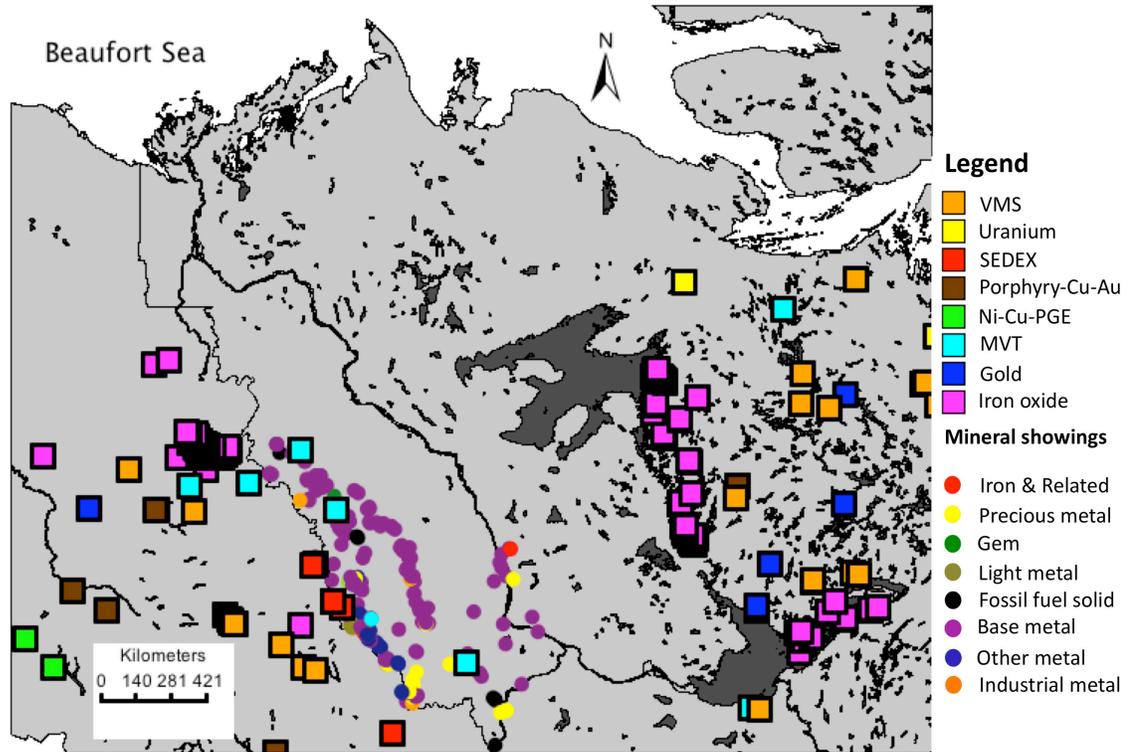


Figure 1.2: Map showing the various mineral deposits in the MRB. The mountainous zone contains substantial sulfide deposits (i.e., SEDEX, MVT, base metal), while the peatland zone to the east has few deposits that influence the geochemistry of the Mackenzie River. Data modified from GSC Open File 5344 and Goodfellow, 2007.

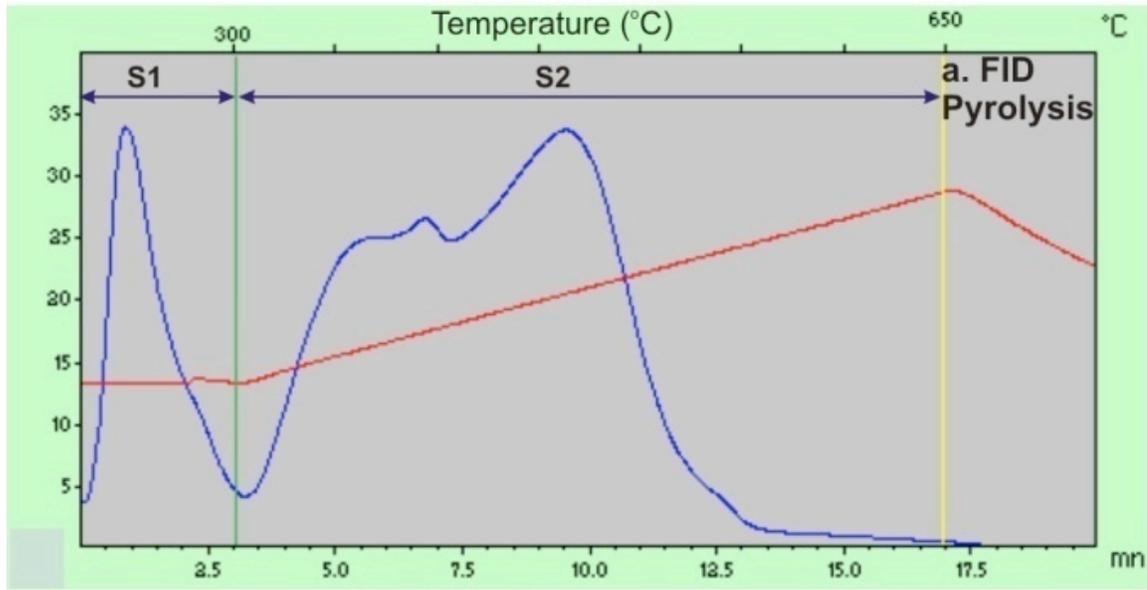


Figure 1.3: Typical pyrogram from Rock-Eval pyrolysis showing the S1 and S2 peaks (blue lines). The red line is the temperature.

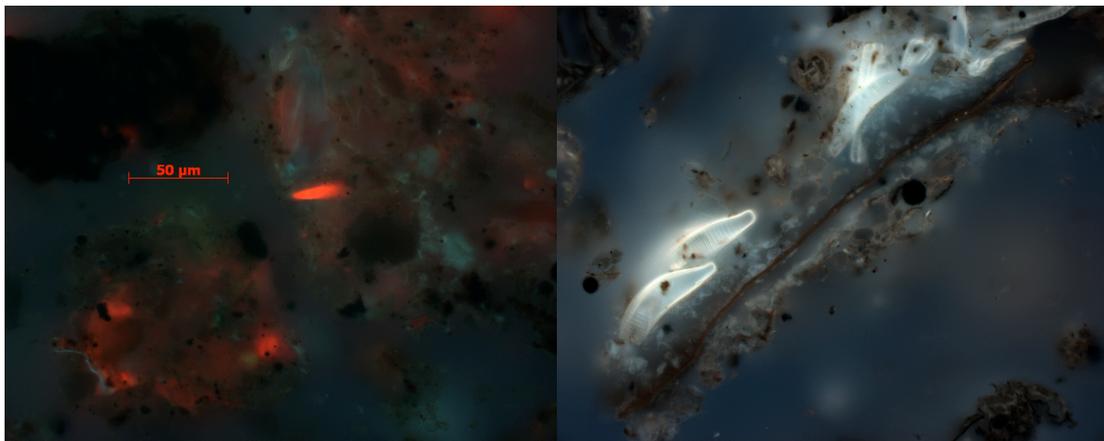


Figure 1.4: Representative photomicrographs of typical algal sedimentary OM (red-fluorescing diatom) prior to pyrolysis in (A); after S1 (up to 300°C) showing loss of chlorophyll in (B). Photomicrograph taken under fluorescent light.

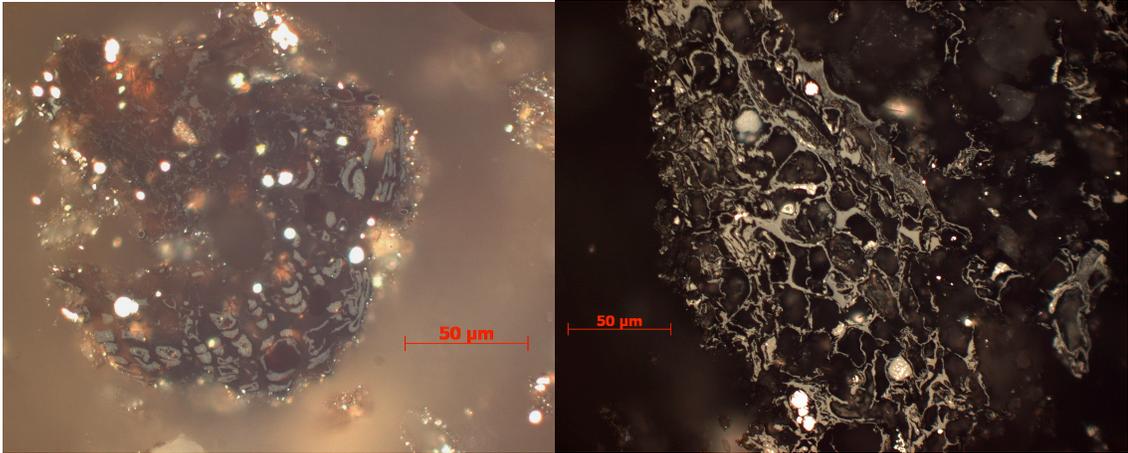


Figure 1.5: Representative photomicrograph of plant cells after loss of S1 material (A) and after loss of S2 compounds (B). Only the resistant cellulosic structure remains clearly visible. Photomicrograph in reflected white light.

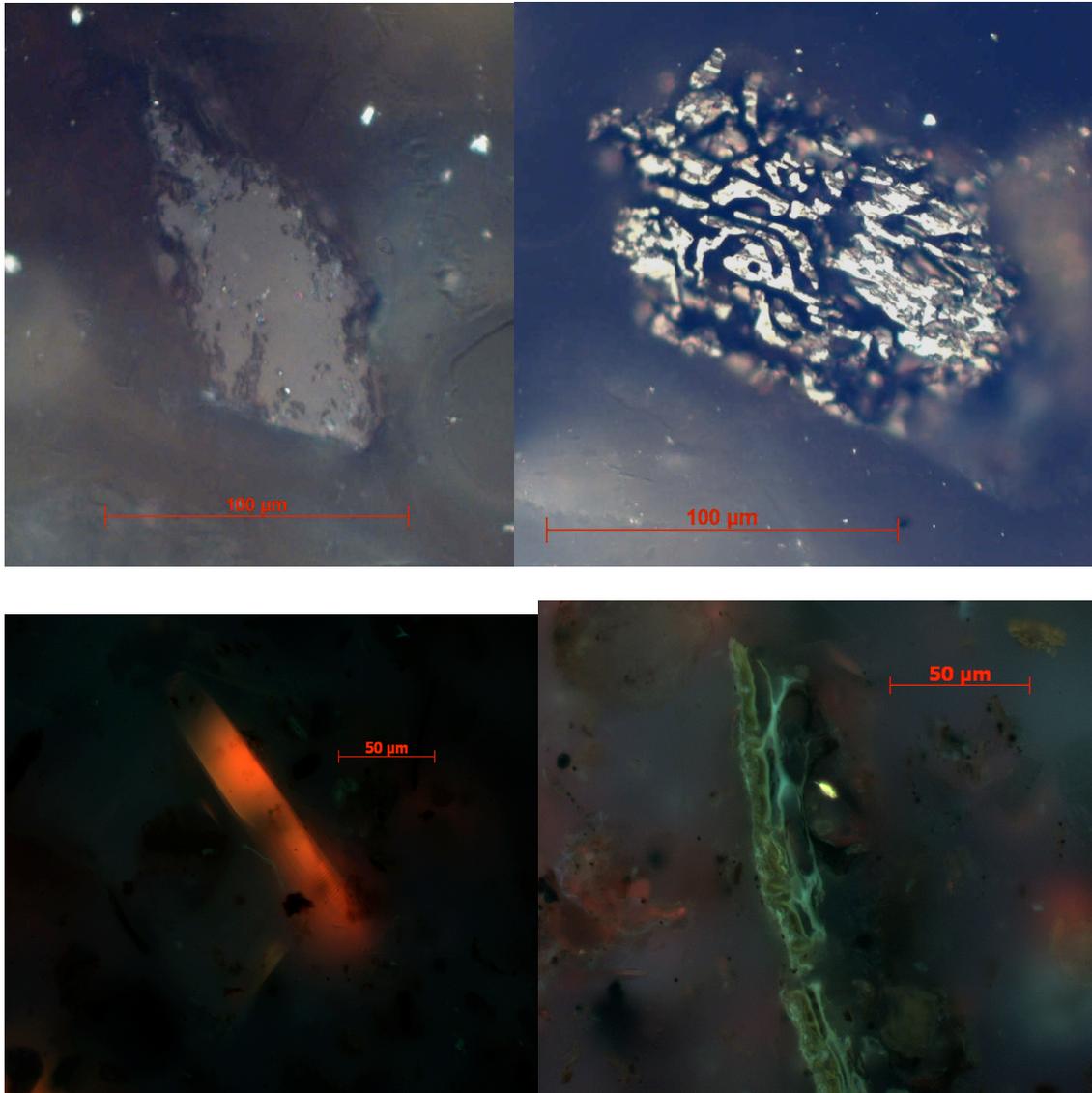


Figure 1.6: Representative photomicrographs of the various maceral groups. (A, top left) Vitritinite/huminite, derived from coal/peaty materials. (B, top right) Inertinite, derived from fire char. (C, bottom left) Liptinite (alginite): Red fluorescing diatom. (D, bottom right) Blue and green fluorescing plant fragment.

Chapter 2:

Characterization of Organic Matter in Surface Sediments of the Mackenzie River Basin, Canada

2.1 Abstract

The Mackenzie River Basin (MRB) is a largely unstudied and complex basin. Organic matter (OM) studies in the basin have been mainly limited to the fossil fuel deposits in the middle of the basin, and to various biomarkers found in the offshore region of the Arctic Ocean. Here we report a detailed description of the composition of the OM present throughout the basin, including ancient and modern OM, and aquatic and terrestrial sources of OM. The particulate OM in $< 63 \mu\text{m}$ surface sediments from the Mackenzie River and its main tributaries was studied using Rock-Eval pyrolysis and organic petrology. The organic matter in the sediments is dominated by refractory residual organic carbon (RC) of mainly terrigenous nature, as indicated by abundant inertinite, vitrinite, and type III kerogen. Sediments from the tributaries contained significantly more algal-derived organic matter than from the main channel of the river, highlighting the importance of low-energy system dynamics in the tributaries, which allows modest algal production, more accumulation, and better preservation of autochthonous organic matter. This is particularly true for tributaries fed by lacustrine systems, which showed the highest S1 and S2 fractions, and consequently higher total particulate organic carbon (POC) in the basin. Organic petrology of the sediment samples confirms abundant liptinitic materials (i.e., fat-rich structured algae, spores and pollen, cuticles, and resins). Forest fire and coal deposits are also confirmed to contribute to the

basin. Assuming that suspended and fine surficial sediments have a similar OC composition, the Mackenzie River is estimated to deliver a total POC flux of 1.1 Mt C/yr to its delta, of which 85% is residual carbon with liptinitic OC (S1+S2) and S3 accounting for another 9% and 6%, respectively.

Keywords: Mackenzie River, organic carbon, Rock-Eval pyrolysis, organic petrology, recent sediments, Arctic Ocean.

2.2 Introduction

The Mackenzie River is the largest source of suspended sediments to the Arctic Ocean, the second largest in dissolved matter, and the fourth in water discharge (Milot et al., 2003). The Mackenzie River is also a major source of terrigenous organic carbon (defined here as organic matter from terrestrial sources) to the Arctic Ocean, delivering a total of 2.1 Mt C/yr to its delta and 1.2 Mt C/yr to the Beaufort Sea, which accounts for more than 16% of the total terrigenous organic carbon influx to the Arctic Ocean (Macdonald et al., 1998; Stein and Macdonald, 2004). While many studies have focused on the organic carbon geochemistry in the Mackenzie delta and shelf (Drenzek et al., 2007; Goni et al., 2000, 2005; Macdonald et al., 1998; O'Brien et al., 2006; Yunker et al., 2005), few data are available on the sources, speciation, and distribution of organic carbon in the Mackenzie River Basin itself (Feinstein et al., 1988, 1991a,b).

The Mackenzie River Basin (MRB) comprises the Mackenzie River valley from Great Slave Lake to the delta, and encompasses various types of terrain including Arctic

tundra, boreal forest, peatland, and mountainous cordillera (Dyke and Brooks, 2000). The tundra is virtually devoid of higher vegetation and is expected to make relatively small contribution to the total organic matter content of the MRB due to its secluded geographical location. The boreal forest is distributed along the entire length of the river with margins close to the river, mainly in the southwestern part. The boreal forest is likely an important source of terrigenous organic matter of mainly higher-plant origin such as tree barks, needles, leaves, pollen, and char from the frequent forest fires (Reyes et al., 2006). This terrigenous organic matter enters the MRB through the watershed runoff and/or aerial deposition. Peatland is spread throughout much of the basin, though predominantly on the eastern side of the MRB. To the west are the Mackenzie Mountains, with elevations ranging from 700 to 2500 m a.s.l. (Larter, 2004). The mountainous regions are sparsely vegetated in most areas (Wright et al., 2003). However, the tributaries from these mountains contribute the vast majority of suspended sediment to the Mackenzie River, particularly the Liard River, which adds approximately 40% of the total sediment load of the river (Carson et al., 1998).

Diverse geological formations in the MRB include organic-rich rocks, such as shale and coal, which may provide significant input of organic matter into the MRB and the Beaufort Sea. The coal deposits are most notably located near the small community of Tulita (63-65°N; 120°-127°W) and consist of thermally immature coal, mostly lignite with some sub-bituminous coal (Sweet et al., 1989). These coal deposits and associated strata are exposed to the river and often subject to natural combustion as seen by frequent smoking events. The northern reaches of the river are underlain by organic-rich shale (Feinstein et al., 1988).

Furthermore, the Mackenzie River is the drainage basin for several lakes, including the Great Slave and Great Bear Lakes, which may discharge organic matter (OM) into the MRB through their outlets. Lakes are loci for production of autochthonous OM (e.g., algae), which is often labile in quality, and sinks for allochthonous OM (e.g., soil OM, plant materials) that enters via runoff.

Based on organic geochemical analysis and organic petrology, here we report the distribution, characterization, and flux of organic matter in the MRB. The distribution of organic matter in the sediments of the Mackenzie River and its tributaries may provide important information related to the carbon cycle, source identification and apportionment in the MRB and consequently in the Beaufort Sea and Arctic Ocean. The nature of organic matter in the sediments is also expected to influence the transport, cycling, speciation and bioavailability of organic and trace metal contaminants.

2.3 Materials and Methods

Surface sediment samples were collected at intervals along the entire length (1 738 km) of the Mackenzie River in the summers of 2003 and 2004, including its main tributaries (Fig. 2.1). The sediment was retrieved using an Ekman or Ponar dredge onboard a river boat. The samples were collected from the top 2 cm below the sediment-water interface using a plastic spoon; the outer layer of the sediment that had contact with the dredge was removed prior to the sample collection. Samples were placed in Ziploc bags and immediately frozen at -20°C until analysis. After freeze-drying, they were sieved to $<63\ \mu\text{m}$ to standardise the grain size (Horowitz and Elrick, 1988). Coal samples

were collected from various locations in the Brackett Basin (64°-65°N, 120°-127°W; see the squared area in Fig. 2.1) in 1984, 1985 and 1987 and were pulverised prior to analysis.

The pulverised samples were analysed on a Rock-Eval 6 analyser (Vinci Technologies, France), with a FID detector for measuring hydrocarbon gases and an on-line infrared cell for CO and CO₂ generated during the pyrolysis (Lafargue et al., 1998). The samples were first pyrolysed in an inert atmosphere (He) from 100 to 650°C, at a rate of 25°C/min, to separate and determine the contents of the labile, mainly algal-derived fractions of organic matter (S1, S2; mg HC/g sample). The amounts of CO₂ (S3; mg CO₂/g sample) and CO (S3CO; mg CO/g sample) produced during pyrolysis were also measured. Samples were then automatically transferred to an oxidation oven, and were heated from 400 to 850°C to incinerate all the residual carbon (RC; wt %). The total particulate organic carbon (POC; in this paper “TOC” is reserved for the total organic carbon in the aquatic system which is the sum of POC and dissolved organic carbon - DOC) was calculated from the sum of the pyrolysable carbon (PC; 100-650°C) and RC (400-850°C). An internal shale standard (9107, Geological Survey of Canada - Calgary) was used for the QA/QC purpose, with precision (as relative standard deviation) greater than 4% (n=6) and accuracy better than 4%, based on recovery.

For the imaging study, sediment samples were pelletised in 3-cm diameter Teflon moulds using a mixture of EPOTECH® epoxy-resin mixture, and after curing were sequentially polished under increasingly finer grit material (carborundum grit, 0.5 µm alumina on Pelon®, and 0.03 µm alumina on a silk lap). They were then examined under a Zeiss Axioplan II microscope in white and blue light under oil immersion. Digital

images were captured using the Zeiss Axiocam[®] and Axiovision[®] software. Counting statistics were used to quantify the particles of inertinite, vitrinite (huminite) and liptinite (exinite and alginite), with a minimum of 300 counts per sample.

The statistic analysis was done with the statistical package SPSS (version 15; SPSS Inc., Chicago, IL). Because of the relatively small sample size of the lake-fed sediment samples (n=5), the non-parametric Mann-Whitney Test was used to compare the differences among the three groups: sediments from the main-channel Mackenzie River, from the lake-fed tributaries, and from the other tributaries/delta. The Mann-Whitney Test does not require that sample populations be normally distributed, and data were used as is. The null hypothesis (H_0) is that there is no difference between the groups. Significant difference between the groups is inferred when $p < 0.05$ (the p-value is the probability of committing a Type I error, i.e., when a true H_0 is rejected (stating there is a difference between two populations when one does not exist), or, contrariwise, a Type II error, i.e., when a false H_0 is accepted (stating there is no difference between two populations when one does exist)).

2.4 Results and Discussion

2.4.1 Overall Results

The results of the Rock-Eval analyses are shown in Table 2.1 and Fig. 2.2. Maceral analysis results are shown in Table 2.2. The POC in the sediments from the lake-fed tributaries (1.14 ± 0.66 %; mean \pm 1 s.d., n=5) was significantly higher ($p=0.026$,

d.f.=18) than that in the main-channel Mackenzie River (0.46 ± 0.23 %, $n=13$). It was also higher than that from the non-lake fed tributaries (0.65 ± 0.29 , $n=13$), but the difference is not statistically significant ($p=0.12$, d.f.=18). The sediments from the lake-fed tributaries also contain the highest amount of S1 ($p=0.001$ and 0.002 respectively) and S2 ($p=0.007$ and 0.01 , respectively) when compared to those from the main-channel Mackenzie River and other non-lake fed tributaries. While non-algal OM is known to contribute to S1 and S2 in sedimentary rocks, such as shale and coal, in which humification occurs, S1 and S2 in recent sediments are mainly contributed from algal-derived OM (Sanei and Goodarzi, 2006; Sanei et al., 2005). This is confirmed by the maceral analysis which shows the dominance of alginite and exinite in the sediments from the lake-fed tributaries (Table 2.2).

The organic matter in the MRB sediments is predominantly type III kerogen as characterised by their low hydrogen indices ($HI = 100 - 200$ mg HC/g POC) and high oxygen indexes ($OI = 150-300$ mg CO_2 /g POC) in the van Krevelen diagram (Fig. 2.2a). The Type III kerogen is attributed to terrigenous and reworked organic matter, which is typical of riverine and deltaic systems. The lake-fed tributary sediments contain slightly higher HI ($p = 0.002$ and 0.001 compared to the main-channel and non-lake fed tributaries, respectively) and hence fall within the border of Type II and Type III kerogens (Figs. 2.2a,b), indicating the influence of lacustrine input of predominantly algal-derived organic matter.

The spatial distributions of POC, S1, HI and OI in the MRB are shown in Figs. 2.3a-d. Since S1 and S2 are significantly correlated ($r=0.969$, $p < 0.001$), the distribution of S2 is very similar to that of S1 (Fig. 2.3b).

The results of the Rock-Eval pyrolysis and organic petrology of the sediments suggest that the following major processes largely control the distribution of various types of organic matter in the MRB.

2.4.2 Hydrodynamic energy level of the system

The energy level of the river channel is mainly controlled by the topography and other hydrodynamic factors, such as the size, depth, and form (straight or bent) of the channel, as well as the existence of any physical obstruction in the channel (aquatic vegetation, such as macrophytes and trees). For the purposes of this paper, we have used annual discharge of suspended sediment as a measure of energy (cf. Carson et al., 1998): the greater the discharge of suspended sediment, the higher the energy present in the system. In that study, the largest sources of suspended sediment were the mountainous tributaries in the west of the MRB. Fine sediments tend to accumulate in the channels with lower energy, such as tributaries in topographically flat areas of the MRB. The low energy level of these tributaries allow for fine suspended sediments/particulates to settle due to relatively longer water residence time as compared to the fast-flowing main river channel. In addition, the energy level of the channels may also play an important role in the distribution of sediment grain size and consequently the type and quantity of associated organic matter, and is discussed below.

The strong relationship between organic matter and grain size is due to two main facts: (1) The individual organic particulates behave hydrodynamically similar to finer-grained sediments due to their overall lower density (Peters et al., 2007). Therefore

organic particulates tend to accumulate in the same places as fine-grained sediments (Mayer et al., 1985; Suess, 1973; Tanoue and Handa, 1979; Weiler and Mills, 1965). (2) The greater surface area of finer-grained sediments allow for greater adsorptive (surface-coating) accumulation of organic matter by these fractions (Premuzic et al., 1982; Tyson, 1995). The more labile fraction of predominantly algal-derived-origin tends to participate in the surface-coating form and hence accumulate with fine-grained sediments. The S1 (and in some extent S2) measurements from Rock-Eval analyses are shown to be a very good indicator of the surface-coating fraction of organic matter in recent sediments (Keil et al., 1994; Sanei and Goodarzi, 2006; Sanei et al., 2005).

The results of this study show that there is a direct relationship between the type and quantity of the sedimentary organic matter in the MRB and the energy level of the channels where the samples are obtained as observed by the water current. Most tributaries from the Mackenzie Mountains in the west have high energy dynamics. For example, the Liard and North Nahanni Rivers, which have energy dynamics greater than the Mackenzie River, have substantially lower concentrations of POC (Fig. 2.3a) and lipitinitic OC (Fig. 2.3b) than virtually all of the rest of the sites. In contrast, the increased concentrations of S1 and S2 in other tributaries are related to the lower energy in these systems (Fig. 2.3b).

2.4.3 Lacustrine input of autochthonous, algal-derived organic matter

The five lake-fed tributaries all have significantly higher concentrations of predominantly algal-derived OM compared to all other sites (Tables 2.1 and 2.2, Fig. 2.3b). The concentration of S1 and S2 in the sediments averaged 0.31 and 2.13 mg HC/g

from the lake-fed tributaries, 0.08 and 0.62 mg HC/g from non-lake fed tributaries and deltaic regions, and 0.07 and 0.48 mg HC/g from the main-channel Mackenzie River, respectively. S1 is approximately four times higher in the lake-fed tributaries compared to the other groups ($p < 0.002$, d.f.=18); S2 is also much higher in the lake-fed tributaries compared to both groups ($p < 0.01$, d.f.=18) (Table 2.1). This is in agreement with the maceral analysis (Table 2), which shows that the sediments from the lake-fed tributaries contains much higher lipitinite ($72.6 \pm 20.7\%$) than those from the main channel (20.5 ± 14.6) or non-lake fed tributaries ($16.9 \pm 12.5\%$), suggesting a greater production and/or preservation of mainly algal-derived OM in lake-fed tributaries. Examples of lipitinite macerals in lake-fed tributaries are shown in Fig. 2.4a-e.

Hydrogen index (HI; Fig. 2.3c) supports the trend seen in the S1 data (Fig. 2.3b) ($r = 0.85$, $p < 0.001$, $n=31$), which corresponds mainly to the higher algal productivity of the associated lacustrine environments. The lake-fed tributaries all have higher HI than the rest of the MRB (182 versus 97 and 90 mg HC/g POC for the main channel and tributaries/delta, respectively; $p < 0.002$, d.f.=18), suggesting that primary productivity from the lakes influences the distribution of organic matter in the basin. The HI for the main channel and non-lake fed tributaries do not differ significantly ($p = 0.225$, d.f.=26). This is in agreement with the result from Carson et al. (1998), which stated that effectively all of the sediment in the Mackenzie Delta derived from the higher energy tributaries flowing from the Mackenzie Mountains. It is also evident that the region near the Mackenzie Mountains (higher energy systems) contains much lower HI values (Fig. 2.3c), indicative of little lacustrine primary productivity. Petrographical analysis of these sites shows that lipitinitic macerals (i.e., alginite) are scarce, corroborating the HI

evidence of little primary productivity. To further highlight this, the values on the west side closest to the mountains have lower HI than those on the opposite side of the Mackenzie (Fig. 2.3c). The higher HI values in some of the main channel sediments are likely due to hysteresis-like effects from the nearby lacustrine tributaries, where the higher labile OM concentrations of the lakes appear to impact a limited region of the main channel downstream.

It is thus clear that lakes in the MRB act as an important source of mostly autochthonous, predominantly algal-derived organic matter formed due to primary productivity within the lacustrine water body, and then contribute these OM into the river through their permanent and intermittent outlets. Additionally, lakes could also trap the organic carbon from the rivers upstream.

2.4.4 Terrigenous input of organic matter

Oxygen index (OI) is effectively a measure of terrigenous OM. Given the extent of the boreal forest in the MRB, the most likely source of terrigenous OM is trees, particularly conifers. Fig. 2.3d shows the distribution of OI throughout the MRB. Higher OI values are found in the higher energy tributaries and the main channel sediments (averages of 222 and 259 mg CO₂/g POC, respectively); the differences between the tributaries and the main channel are not statistically significant ($p = 0.50$, d.f.=26), despite one very high OI value in the main channel dataset (the Mackenzie below the Liard, OI = 733 mg CO₂/g POC) (Table 2.1). This is further evidence that shows the same components of the higher energy tributaries in the main channel

sediments, and that both systems are more heavily impacted by terrigenous OM than lacustrine OM. The lowest OI values are found in lake-fed tributaries (average 165 mg CO₂/g POC) and the delta sites (average 174 mg CO₂/g POC for Sites 2 and 3) which are composed of several lakes (Fig. 2.1), suggesting that lacustrine-derived OM is more prevalent at these sites (Table 2.1). The higher energy systems (the Liard River and tributaries of the Mackenzie Mountains) all show the highest OI, concordant with the primarily terrigenous OM. The higher OI values in the higher energy sites (mountainous tributaries and main channel) may also be due to more degraded OM relative to the low energy sites (peatlands and lake-fed sites). Specific biomarker studies, such as lignin analysis (e.g., Goni et al., 2000), could be used to determine the relative importance of degradation on the OM in the MRB. Terrigenous OM is more recalcitrant than algal-derived OM, and can thus be preserved, as is shown in these sediments. The petrology of the sediments makes it evident that forest fires have had a notable impact on the distribution of OM in the MRB, as inertinitic particles of char origin were widespread (Table 2.2, Figs. 2.5a,b).

Refractory carbon (RC), which likely corresponds to remnants of ancient carbon (e.g., coal) (Yunker et al., 1995, 2002; Guo et al., 2007) and/or highly degraded OM (e.g., char from forest fires), is the lowest in the main channel of the Mackenzie River and highest in the tributaries (Table 2.1). This can be noted in the difference in the main-channel sediments ($0.37 \pm 0.20\%$, n=13), non-lake fed tributaries ($0.54 \pm 0.24\%$, n=13), and the lake-fed tributaries ($0.84 \pm 0.46\%$, n=5). Higher RC content in tributaries appear to be correlated with the availability of more labile liptinitic OM in these sediments. Aerobic bacterial degradation as well as the oxidation of OM in the aerated water current would

leave a greater portion of RC from the initial organic content of the sediments. Additionally, the prevalence of forest fires may also contribute to the increased RC values in these sediments. The lower energy tributaries are also more likely to preserve whatever RC enters into them. The increased RC values in the delta are evidence that the delta acts as a filter or repository of OM from the MRB.

On the contrary, higher energy tributaries such as the Liard and North Nahanni rivers have some of the lowest RC values, similar to the main channel of the Mackenzie River. Guo et al. (2007) recently reported that the suspended and sedimentary POC from the Mackenzie River at the Arctic Red River is ancient POC (6000-7800 yr BP) derived from permafrost thawing and riverbank erosion.

2.4.5 Geogenic input of organic matter

Terrigenous input of organic-rich sedimentary rocks, such as coal and shale, may include a significant portion of OM in the MRB. The coal in the Brackett Basin is situated along the Mackenzie River (Fig. 2.1), where it is subject to erosion. These thermally immature shales and coals have POC content ranging from 17.4 to 63.0 wt.%, 14.1 to 54.0 wt.% of which consist of refractory residual carbon (Sweet et al., 1989). The geogenic contribution of coal to the organic matter in the MRB is confirmed by the petrologic analysis, and select biomarkers (Yunker et al., 1995, 2002). The largest particles of vitrinitic material were concentrated near the coal outcrops (Fig. 2.1, Table 2.2); examples are shown in Fig. 2.5c.

2.4.6 Particulate Organic Carbon Fluxes

Although the sediment samples collected in this study were not suspended sediments in the water column, their composition likely mimics the composition of suspended sediments, as the samples were taken from the surface layer (< 2-cm below the sediment-water interface) and were further sieved to < 63 μm for the analysis. Various studies suggested that the < 63 μm fraction of surface sediments show similar trace elements (Horowitz and Elrick et al., 1988) and organic carbon (Guo et al., 2007) composition as suspended sediments in rivers. With the suspended particulate matter (SPM) flux reported by Carson et al. (1998), this allows us to estimate the flux of POC to the Mackenzie River and to its delta region. The results are shown in Table 2.3.

In total the Mackenzie River delivers about 1.1 Mt (as C)/yr of POC to its delta region. This value is in good agreement with Macdonald et al. (1998) who estimated the flux to the delta to be 2.1 Mt/yr for TOC, 1.3 Mt/yr for dissolved organic carbon (DOC), and 0.8 Mt/yr for POC. As can be seen from Table 2.3, most of the POC originates from tributaries on the western, mountainous side of the MRB, particularly from the Peel and Liard Rivers due to their greater SPM flux. The total POC load of the Mackenzie River is dominated by residual carbon (85%), with about 9 % in the form of more labile OC (S1+S2), and 6% in the form of other pyrolysable carbon (S3).

It should be noted, however, that the flux calculated above is from the Mackenzie River to its delta region only; not all of this flux reaches the Beaufort Sea. As shown by Stein and Macdonald (2004), a significant amount of organic carbon could be deposited in the delta region and only ~57% of the TOC from the Mackenzie River is discharged into the Beaufort Shelf.

2.5 Conclusions

The Rock-Eval pyrolysis and organic petrology allowed the examination of the speciation and spatial distribution of organic matter in surface sediments from the vast MRB. While the organic carbon in the sediments is dominated by refractory residual organic matter, the sediments from the tributaries, particularly from the lake-fed tributaries, are found to contain higher fraction of more labile, predominantly algal-derived organic matter (S1 and S2), suggesting the role of the primary productivity and hydrodynamic energy of the system in the production and accumulation of autochthonous organic matter in the river system. Forest fire and coal deposits are also confirmed to contribute directly to the organic matter input of the basin.

Although only 9% of the total POC flux to the delta is in the form of labile, predominantly liptinitic OC (S1+S2), this fraction of the POC is expected to play a major role in the biogeochemistry of organic carbon and associated contaminants due to its higher lability and reactivity. For instance, Outridge et al. (2007) recently reported a strong correlation of Hg and algal-derived OC in sediment cores taken from 2 high Arctic lakes, due to the effective scavenge of Hg by the labile OC. They further suggested that the 20th Century increases in sedimentary mercury in high altitude Arctic lakes are largely driven by increases in autochthonous primary productivity (source of S1 and S2). The relative importance of such a process in the MRB and in the Beaufort Sea warrants further studies.

2.6 Acknowledgments

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2.8 Tables and Figures

Table 2.1: Rock-Eval analysis of organic matter in the sediments from the MRB

Sample ID	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO ₂ /g)	S3CO (mg CO/g)	Algal OC (S1+S2; %)	PC (%)	RC (%)	POC (%)	HI (S2/POC, %)	OI (S3/POC, %)	Location
Main Channel											
8	0.05	0.67	1.83	0.13	0.07	0.12	0.71	0.83	81	220	Downstream from the Arctic Red R.
10	0.08	0.50	1.26	0.14	0.06	0.10	0.49	0.59	85	214	at the Travaillant R
13	0.09	0.50	0.85	0.16	0.06	0.09	0.33	0.42	119	202	Upstream from the Ontaritue R.
19	0.10	0.58	0.91	0.53	0.07	0.12	0.38	0.50	116	182	Upstream from the Mountain R.
25	0.11	0.49	0.86	0.04	0.06	0.08	0.32	0.40	122	215	Downstream from the Great Bear R.
24	0.01	0.03	0.29	0.07	0.00	0.02	0.05	0.07	43	414	Upstream from Norman Wells
30	0.09	0.47	0.71	0.05	0.06	0.07	0.33	0.40	118	178	Upstream from the Keele R.
31	0.06	0.29	0.50	0.05	0.04	0.05	0.22	0.27	107	185	Downstream from the Redstone R.
33	0.04	0.40	1.12	0.03	0.04	0.07	0.44	0.51	78	220	Upstream from the Redstone R.
34	0.09	0.59	1.09	0.26	0.07	0.11	0.42	0.53	111	206	Downstream from the Dahadinni R.
36	0.13	1.01	1.54	0.12	0.11	0.15	0.56	0.71	142	217	Between the Blackwater and Dahadinni R.
44	0.10	0.67	1.18	0.28	0.08	0.12	0.54	0.66	102	179	Upstream of the Wrigley R.
51	0.00	0.01	0.22	0.47	0.00	0.03	0.00	0.03	33	733	Downstream from the

Liard R.

	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO₂/g)	S3CO (mg CO/g)	Algal OC (S1+S2; %)	PC (%)	RC (%)	POC (%)	HI (S2/POC, %)	OI (S3/POC, %)	Location
<i>Median</i>	0.09	0.50	0.91	0.13	0.06	0.09	0.38	0.50	107	214	
<i>Average</i>	0.07	0.48	0.95	0.18	0.06	0.09	0.37	0.46	97	259	
<i>SD</i>	0.04	0.26	0.46	0.16	0.03	0.04	0.20	0.23	32	155	

Tributaries/Delta**Lake-
fed**

15	0.16	1.42	3.15	0.65	0.16	0.27	0.87	1.14	125	276	Hare Indian River
18	0.39	2.65	1.02	0.07	0.30	0.29	0.79	1.08	245	94	Mountain River
26	0.25	1.47	1.93	0.83	0.17	0.25	0.77	1.02	144	189	Great Bear River
60	0.60	4.53	3.65	1.64	0.51	0.62	1.54	2.16	210	169	Horn River
61	0.16	0.57	0.30	0.02	0.07	0.07	0.24	0.31	184	97	South Channel
<i>Median</i>	0.25	1.47	1.93	0.65	0.17	0.27	0.79	1.08	184	169	
<i>Average</i>	0.31	2.13	2.01	0.64	0.24	0.30	0.84	1.14	182	165	
<i>SD</i>	0.19	1.53	1.41	0.66	0.17	0.20	0.46	0.66	49	75	

Others

02	0.14	0.89	1.72	0.75	0.10	0.18	0.71	0.89	100	193	Delta region (Inuvik)
03	0.13	0.77	1.08	0.02	0.09	0.11	0.55	0.66	117	164	Delta region
05	0.17	1.28	1.88	0.42	0.15	0.20	0.94	1.14	112	165	Peel R.
29	0.03	0.17	0.67	0.29	0.02	0.06	0.27	0.33	52	203	Keele R.
32	0.06	0.49	1.12	0.13	0.06	0.09	0.51	0.60	82	187	Redstone R.
35	0.11	0.97	1.82	0.14	0.11	0.16	0.76	0.92	105	198	Dahadinni R.
37	0.07	0.65	1.45	0.27	0.07	0.12	0.49	0.61	107	238	Blackwater R.
40	0.05	0.31	0.94	0.50	0.04	0.09	0.25	0.34	91	276	White Sands Creek
41	0.08	0.72	1.86	0.37	0.08	0.14	0.60	0.74	97	251	Ochre R.
43	0.05	0.55	1.62	0.32	0.06	0.12	0.58	0.70	79	231	Wrigley R.
46	0.10	1.23	2.65	0.12	0.13	0.20	0.95	1.15	107	230	Willowlake R.

<i>Others</i>	S1 (mg HC/g)	S2 (mg HC/g)	S3 (mg CO ₂ /g)	S3CO (mg CO/g)	Algal OC (S1+S2; %)	PC (%)	RC (%)	POC (%)	HI (S2/POC, %)	OI (S3/POC, %)	Location
47	0.04	0.48	1.91	0.55	0.05	0.13	0.58	0.71	68	269	Root R.
49	0.05	0.21	0.68	0.05	0.03	0.05	0.24	0.29	72	234	North Nahanni R.
52	0.05	0.24	0.76	0.24	0.03	0.06	0.25	0.31	77	245	Liard R.
<i>Median</i>	<i>0.06</i>	<i>0.55</i>	<i>1.45</i>	<i>0.27</i>	<i>0.06</i>	<i>0.12</i>	<i>0.55</i>	<i>0.66</i>	<i>91</i>	<i>231</i>	
<i>Average</i>	<i>0.08</i>	<i>0.62</i>	<i>1.42</i>	<i>0.26</i>	<i>0.07</i>	<i>0.12</i>	<i>0.54</i>	<i>0.65</i>	<i>90</i>	<i>222</i>	
<i>SD</i>	<i>0.04</i>	<i>0.37</i>	<i>0.60</i>	<i>0.17</i>	<i>0.04</i>	<i>0.05</i>	<i>0.24</i>	<i>0.29</i>	<i>20</i>	<i>36</i>	

Entire Mackenzie River Basin

<i>Median</i>	<i>0.11</i>	<i>0.80</i>	<i>1.32</i>	<i>0.29</i>	<i>0.09</i>	<i>0.13</i>	<i>0.52</i>	<i>0.65</i>	<i>107</i>	<i>228</i>
<i>Average</i>	<i>0.09</i>	<i>0.56</i>	<i>1.11</i>	<i>0.15</i>	<i>0.06</i>	<i>0.11</i>	<i>0.49</i>	<i>0.60</i>	<i>107</i>	<i>210</i>
<i>SD</i>	<i>0.12</i>	<i>0.87</i>	<i>0.80</i>	<i>0.33</i>	<i>0.10</i>	<i>0.11</i>	<i>0.31</i>	<i>0.41</i>	<i>44</i>	<i>109</i>

Table 2.2: Composition of macerals in the sediment samples

Sample ID	% Liptinite			% Vitrinite (Huminite)	% Inertinite
	% Exinite	% Alginite	% Total Liptinite		
Main Channel					
10	7.1	5.4	12.5	32.1	55.4
13	9.4	7.5	17.0	30.2	52.8
19	4.8	27.4	32.3	24.2	43.5
24	10.3	24.1	34.5	25.3	40.2
25	23.4	14.3	37.7	11.7	50.6
30	6.3	6.3	12.5	38.8	48.8
33	6.9	5.7	12.6	39.1	48.3
36	4.5	3.0	7.6	34.8	57.6
44	10.5	7.0	17.5	29.8	52.6
<i>Median</i>	<i>7.1</i>	<i>7.0</i>	<i>14.2</i>	<i>30.2</i>	<i>50.6</i>
<i>Average</i>	<i>9.3</i>	<i>11.2</i>	<i>20.5</i>	<i>29.6</i>	<i>50.0</i>
<i>SD</i>	<i>5.7</i>	<i>8.8</i>	<i>14.6</i>	<i>8.5</i>	<i>5.5</i>
Tributaries/Delta					
<i>Lake-fed</i>					
15	36.6	27.6	64.2	19.4	16.4
18	29.2	36.9	66.2	10.8	23.1
26	29.0	49.5	78.5	14.0	7.5
60	37.3	42.9	80.2	3.2	16.7
61	52.4	21.7	74.1	11.2	14.7
<i>Median</i>	<i>36.6</i>	<i>36.9</i>	<i>73.5</i>	<i>11.2</i>	<i>16.4</i>
<i>Average</i>	<i>36.9</i>	<i>35.7</i>	<i>72.6</i>	<i>11.7</i>	<i>15.7</i>
<i>SD</i>	<i>9.5</i>	<i>11.2</i>	<i>20.7</i>	<i>5.9</i>	<i>5.6</i>
<i>Others</i>					
5	24.4	14.5	38.9	31.3	29.8
29	3.3	20.0	23.3	23.3	53.3
32	10.4	6.3	16.7	29.2	54.2
37	11.8	7.8	19.6	33.3	47.1
41	16.3	4.7	20.9	30.2	48.8
46	19.3	13.6	33.0	35.2	31.8
47	7.1	2.4	9.5	38.1	52.4
49	4.9	0.0	4.9	34.1	61.0
52	7.5	0.0	7.5	37.5	55.0
<i>Median</i>	<i>9.0</i>	<i>5.5</i>	<i>14.4</i>	<i>33.7</i>	<i>52.9</i>
<i>Average</i>	<i>10.1</i>	<i>6.8</i>	<i>16.9</i>	<i>32.6</i>	<i>50.4</i>
<i>SD</i>	<i>5.5</i>	<i>7.0</i>	<i>12.5</i>	<i>4.9</i>	<i>8.6</i>

Table 2.3: Organic carbon flux to the Mackenzie River and the delta as determined from the surface sediments

River	Suspended Particulate Matter (SPM) (10 ⁶ t/yr) ^a	POC (10 ³ t C/yr)					Total POC	DOC	TOC
		S1	S2	S3	RC	(10 ³ t C/yr)		(10 ³ t C/yr)	
The Upper Mackenzie	5 ^b	1.8	11.8	2.7	44	62			
Western tributaries									
Peel River	20	3.1	23.6	10.3	188	228			
Mountain R.	5 ^b	1.8	12.2	1.4	40	54			
Keele R.	10	0.3	1.6	1.8	27	33			
Redstone R.	10	0.6	4.5	3.1	51	60			
Root R.	5 ^b	0.2	2.2	2.6	29	36			
N. Nahanni R.	5 ^b	0.2	1.0	0.9	12	14			
Liard R.	40	1.8	8.9	8.3	100	124			
<i>Sub-total</i>	<i>95</i>	<i>8.0</i>	<i>54.0</i>	<i>28.4</i>	<i>446</i>	<i>549</i>			
Eastern tributaries - Total	5 ^b	2.3	19.6	11.8	146	192			
The Mackenzie to its delta	120	7.8	85.5	60.2	898	1058			
The Mackenzie to the Arctic Ocean						800 ^c	1300 ^c	2100 ^c 1200 ^c	

^aAverage data from Carson et al. (1998).

^bUpper limit from Carson et al. (1998).

^cMacdonald et al. (1998), Stein and Macdonald (2004)

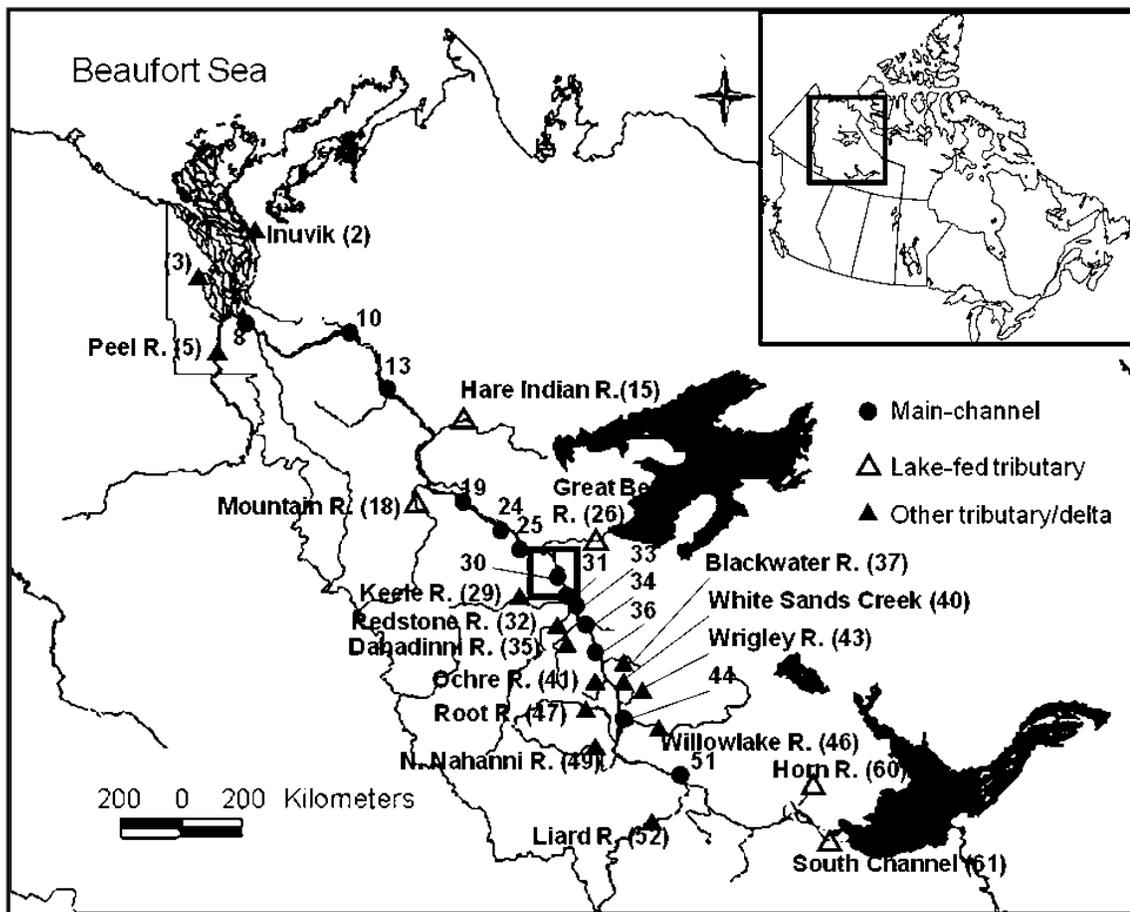


Figure 2.1: Map of the Mackenzie River Basin showing the sampling locations for sediments. The square in the middle shows the sampling region for coal.

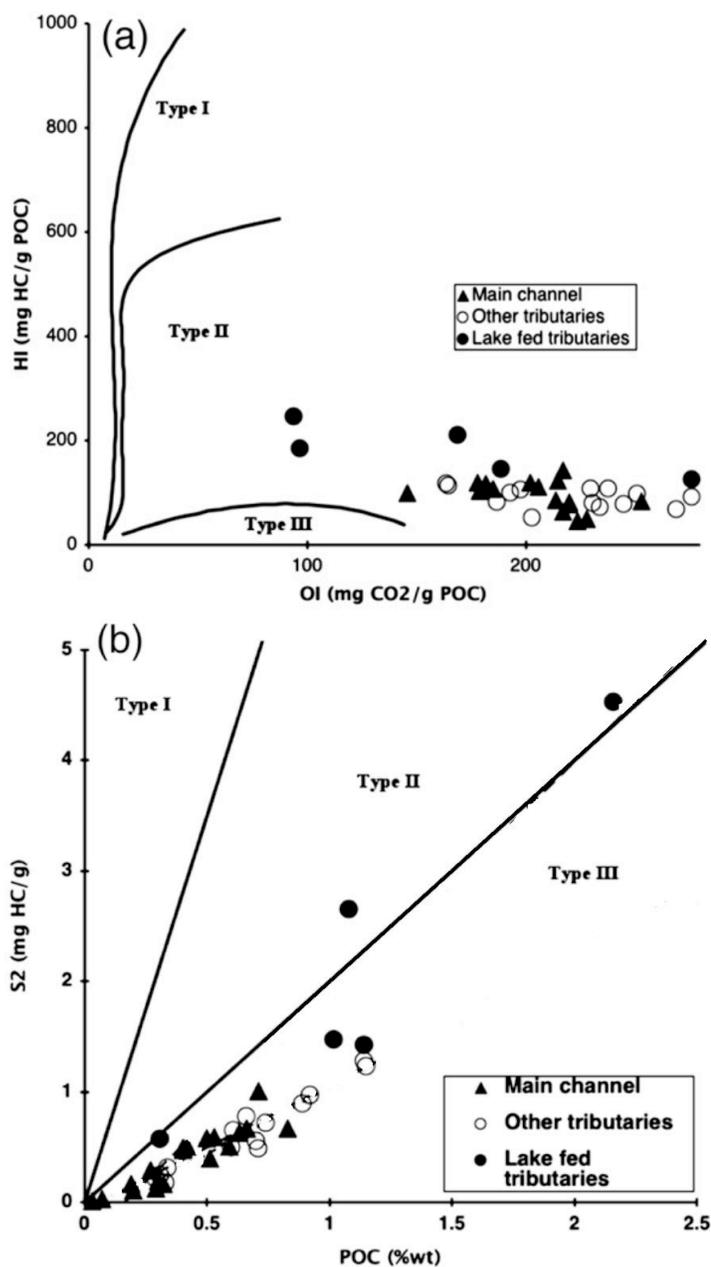


Figure 2.2: Type of organic matter (kerogen) in recent sediments from the Mackenzie River Basin as determined by (a): hydrogen index (HI) vs. oxygen index (OI) plot, and (b): S₂ vs. POC plot. The solid curves in (a) and solid lines in (b) define the boundaries of Type I, II, and III kerogens (Peters et al., 2005 and references therein).

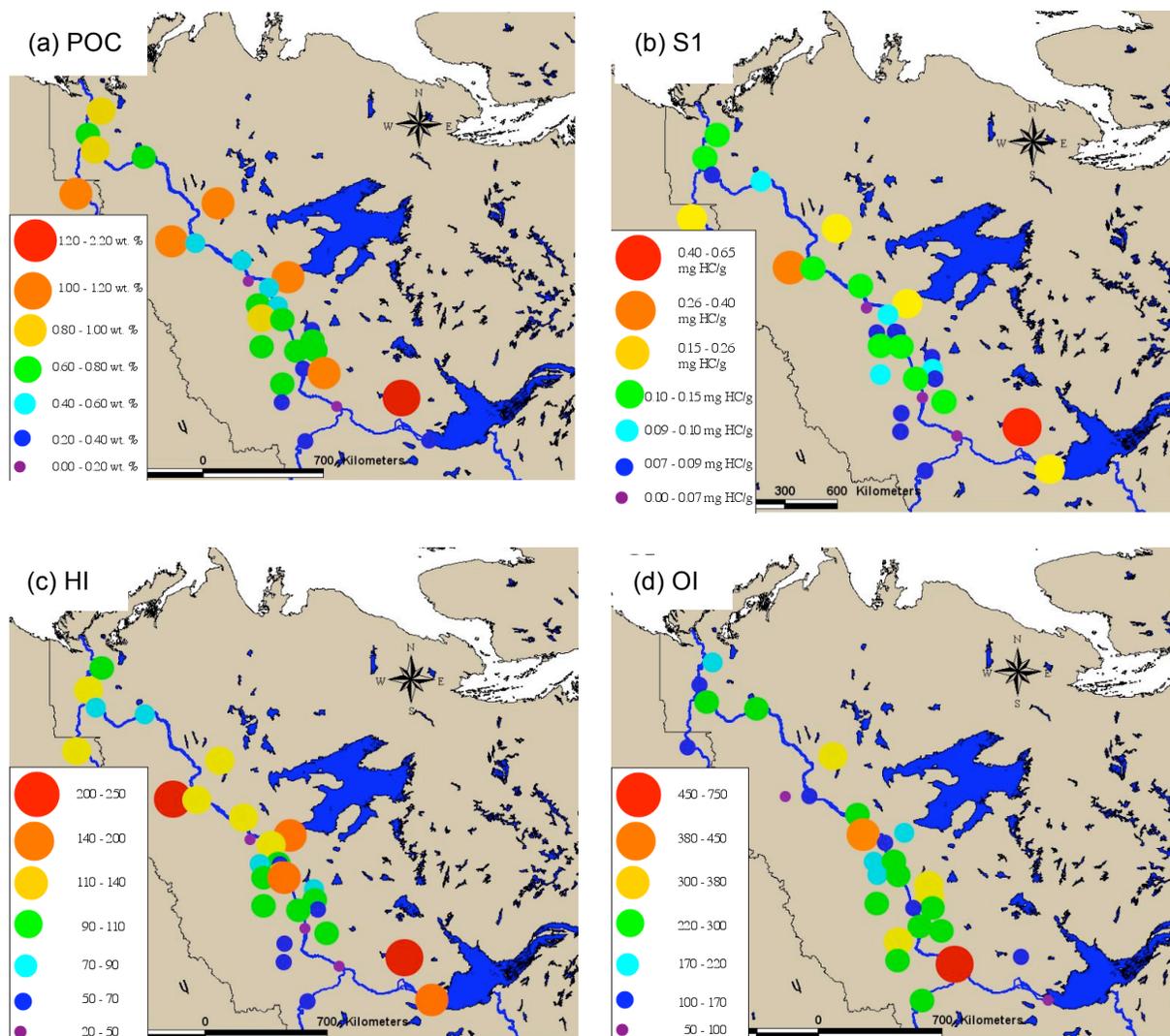


Figure 2.3: Spatial distribution of (a): POC (%), (b): S1 (mg HC/g sediment), (c): the hydrogen index (HI; mg HC/g POC) and (d): the oxygen index (OI; mg CO₂/g POC) in the surface sediments of the Mackenzie River Basin.

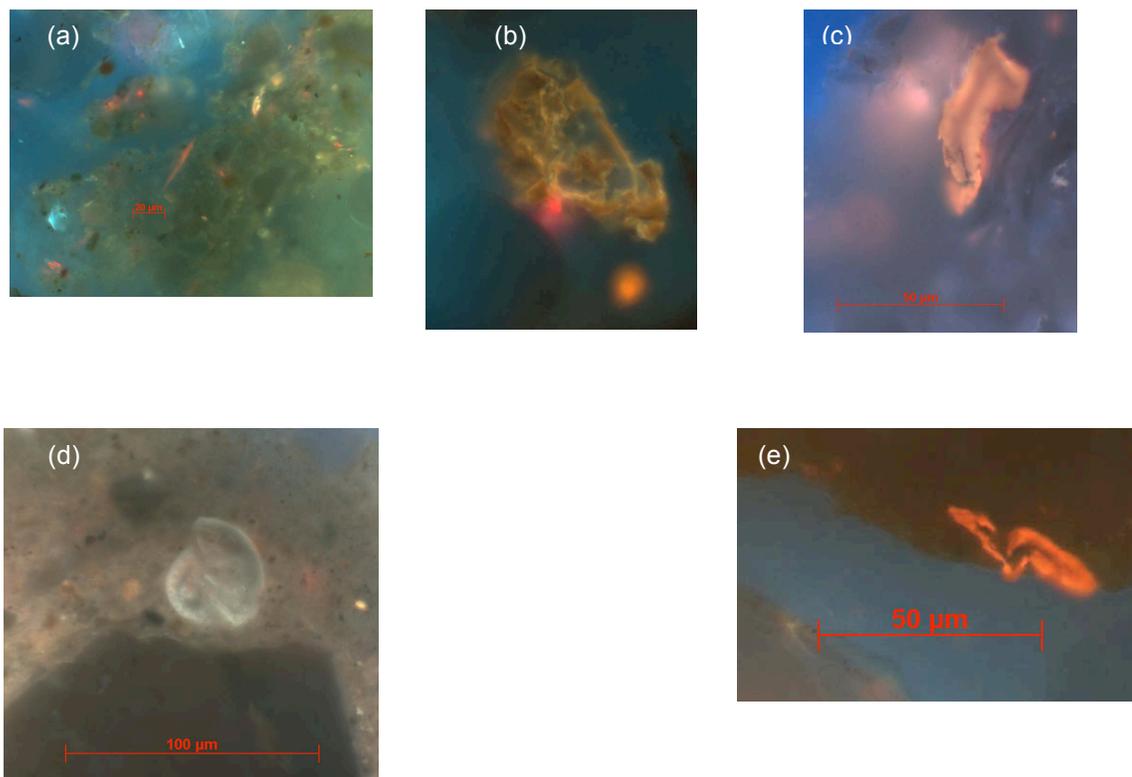


Figure 2.4: Blue-light fluorescence photomicrographs showing examples of the significant biological activity and the presence of algal-derived organic carbon in the form of fluorescent liptinitic macerals in sediments from the lake-fed tributaries. (a-b): Siliceous diatom frustules showing the remnants of entrapped pigment-derived and other lipidic material (Sample MK26 from the Great Bear R.). (c): Recent algal matter (Sample MK18 from the Mountain R.). (d): Eolian pollen grain (Sample MK60 from the Horn R.). (e): Sporinite (Sample MK26 from the Great Bear R.).

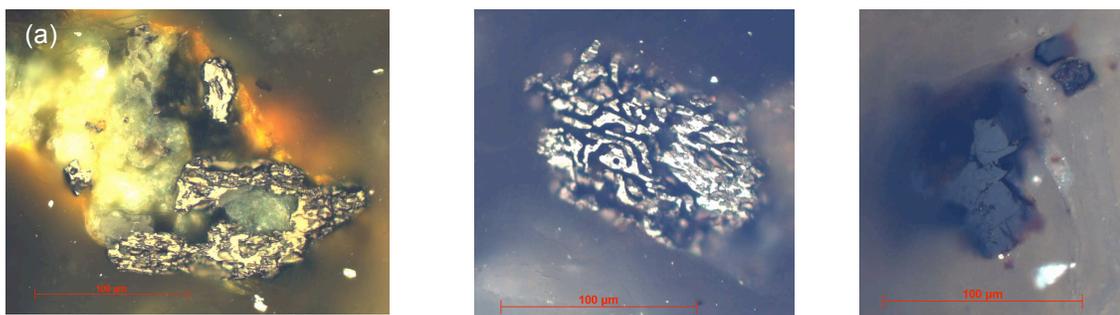


Figure 2.5: (a): Inertinitic fragment (under white-light oil immersion) which was the most common maceral found among the sediments from the main channel of the Mackenzie River. (b): Inertinitic fragment showing clear resemblance to char from forest fires. (c): A coal-derived huminitic/vitrinitic particle from sediment near the coal deposits.

Chapter 3:

Biogeochemical controls of mercury in the Mackenzie River Basin

3.1 Abstract

The Mackenzie River Basin (MRB) in northwest Canada is one of the least human-impacted large watersheds in the world. The western and eastern sub-basins of the MRB are also marked by contrasting geology, geomorphology, hydrology, and biology. These remarkable differences in a remote river basin provide a unique opportunity to probe the biogeochemical processes governing the sources, transport, and bioavailability of mercury (Hg) at the terrestrial-marine interface and ultimately in the Arctic Ocean. Based on a large dataset of the concentration and speciation of Hg and organic matter in the surface sediments across the MRB, we constructed a source-apportioned budget for Hg in the MRB. Here we report that the Hg flux in the basin is originated primarily (74%) from the oxidation of sulfide minerals in the western mountainous sub-basin, followed by the erosion of coal deposits along the mainstream of the Mackenzie River which accounts for 17% of the total. Although the Hg flux from the eastern peatland sub-basin only accounts for about 9% of the total riverine Hg flux, it is this fraction of Hg that shows correlation with algal-derived labile organic matter, particularly in those tributaries that are fed from headwater lakes, and is expected to be more bioavailable. The overall riverine Hg flux to the Arctic Ocean will likely further increase under a warming climate due to increased weathering of the Hg-containing geological materials in the basin and increased primary productivity due to longer ice-free periods.

Keywords: Mackenzie River; Arctic Ocean; Trace metals; Weathering; Coal; Primary productivity; Climate change

3.2 Introduction

The high concentration of mercury (Hg) in marine mammals in the Arctic Ocean and its widespread temporal and spatial variations have received major scientific attentions in recent years (AMAP, 2005; Leitch et al., 2007; Lockhart et al., 2005; Loseto et al., 2008; Macdonald et al., 2000; Macdonald et al., 2008; Outridge et al., 2008). While the net contribution of the atmospherically transported Hg continues to be a subject of debate (Outridge et al., 2008), evidence is emerging that biogeochemical processes in Arctic marine ecosystems and at the land-ocean interface have become increasingly important drivers for the recent Hg trend in Arctic marine mammals (Macdonald et al., 2005; Macdonald et al., 2008; Outridge et al., 2008). The land-ocean interface processes are of particular significance in the Beaufort Sea area which is heavily influenced by the Mackenzie River (Carson et al., 1998; Leitch et al., 2007; Macdonald et al., 1998; Raymond et al., 2007); the marine mammal population from this region is also among the most contaminated by Hg (Lockhart et al., 2005). We have recently shown that the Mackenzie River transports on average 2.2 t/yr of total Hg and 15 kg/yr of methylmercury (MeHg) to the Delta region, and that the riverine Hg and MeHg fluxes are highly dependent on the water discharge of the river (Leitch et al., 2007). The significance of this large and variable riverine source for Hg bioaccumulation in the Arctic Ocean remains to be understood.

A major finding from (Leitch et al., 2007) is that the bulk of the riverine Hg flux to the Mackenzie Delta derives from the western tributaries that drain the Mackenzie and Selwyn Mountains (Figure 3.1). The majority (73-87%) of the Hg is bound to the particulate phase, with higher levels occurring during higher water flow events (e.g., during the spring melt and/or intense summer rain events), suggesting weathering and erosion of the local geology may play a major role in the speciation and flux of Hg in the river. The Mackenzie River Basin (MRB), here defined as the watershed flowing from the Great Slave Lake to the Mackenzie Delta (approximately 61-69°N, 128-134°W; Figure 3.1), is minimally impacted by human activity, as human settlements are sparse with virtually no industrial activity except small oil extraction operations in Norman Wells, Northwest Territories, Canada. The basin includes two large lakes (Great Slave and Great Bear), in addition to a myriad of smaller lakes which dot the landscape, particularly to the east on the Interior Platform. The Mackenzie and Selwyn Mountains, and their fast flowing tributaries, dominate the western side of the basin, while the eastern half of the basin is virtually all peatlands of the Interior Platform.

The contrasting geology, geomorphology, hydrology, and biological productivity in the western and eastern sub-basins of the remote MRB provide a unique opportunity to probe the abiotic and biotic processes governing the speciation and transport of riverine Hg to the Arctic Ocean under a changing climate. This is important as atmospherically transported Hg may not be impinging on the Arctic marine ecosystems as strongly as was once thought (Outridge et al., 2008). Building upon our recent characterization of Hg (Leitch et al., 2007) and organic matter (OM) (Carrie et al., 2009) in the MRB, here we

report the relative importance of various biogeochemical controls on the Hg dynamics in the MRB and their implications under a changing climate.

3.3 Materials and Methods

3.3.1 Sampling

The sampling areas of the MRB are shown in Figure 3.1. Detailed sampling locations can be found in (Carrie et al., 2009; Leitch et al., 2007) (see Table A1 in Appendix A). Briefly, surface water and sediment samples were collected onboard the Canadian Coast Guard Ships Dumit and Eckaloo during the summers of 2003-2005 along the Mackenzie River and its tributaries. Both raw water samples and dissolved water samples (filtered through 0.45µm cellulose acetate filters (Millipore)) were taken in the field, following the “clean hand, dirty hand” ultraclean sampling techniques (Fitzgerald, 1999). The surface sediment samples were retrieved using an Ekman or Ponar dredge from the top 2 cm below the sediment-water interface. Coal samples from the Brackett Basin near Tulita (64.87°N, 125.18°W) were supplied by the Geological Survey of Canada-Calgary.

3.3.2 Sample Analysis

The water samples were analyzed for dissolved Hg (Hg_D), particulate Hg (Hg_P), total Hg (Hg_w), dissolved methylmercury ($MeHg_D$), SO_4^{2-} and Cl^- . The sediment samples

were freeze-dried and analyzed for total Hg (Hgs), total organic carbon, pyrolyzable carbon (PC) (which consists of the S1, S2, S3 fractions), refractory carbon (RC), oxygen index (OI), and hydrogen index (HI). Briefly, S1 and S2 typically derive from algal-derived materials. S1 contains more labile compounds such as pigments and small chain hydrocarbons that are pyrolyzed up to 300°C, whereas S2 contains less labile materials pyrolyzed up to 650°C, often as cell wall materials (Sanei et al., 2005). RC is composed of numerous sources of OM, including char from fires, heavily reworked plant and bacterial OM, as well as coal particles that have been released upstream and deposited at a given site. The detailed analytical procedures and the data were reported in (Carrie et al., 2009; Leitch et al., 2007) and Table A1 in Appendix A. All chemicals used were ACS reagent grade or better. Deionized ultrapure water from a Milli-Q Element system (Millipore, Billerica, MA) was used as the laboratory water.

A subset of the freeze-dried sediment samples (n=6) draining the Mackenzie Mountains (Figure 3.1) were further analyzed for Hg speciation. One gram of sediment was placed in a clean, 50 mL polypropylene centrifuge tube, and was subject to a four-step sequential extraction procedure modified from (Sanei et al., 2001; Tessier et al., 1979). The exchangeable Hg (F1) was extracted by 1M MgCl₂ at pH 7. The carbonates-bound Hg (F2) was extracted with 1M NaOAc at pH 5. The Fe/Mn oxides-bound Hg (F3) was extracted with 0.04M NH₂OH•HCl in acetic acid, and the sulfides and organic matter-bound Hg (F4) was extracted by concentrated HNO₃. The detailed sequential extraction procedures are given in Appendix A, and comprise a composite of several methods used for Hg analysis, with the intent of elucidating the mineralogical association of Hg. The diluted extractants from each step were analyzed for Hg by cold vapor atomic

fluorescence spectroscopy (CVAFS) on a Tekran 2600 Mercury Analyzer following USEPA Method 1631 (U.S.EPA, 2002). The sum from the sequential extractions gave 95-115% of the total Hg concentrations reported earlier (Leitch et al., 2007). Procedural blanks were run through the entire extraction process to determine any possible contamination of Hg.

Coal samples were ground to fine powders followed by closed-vessel microwave digestion on MARS V (CEM, Matthews, NC). Briefly, 0.1g of each sample was added into a PTFE vessel, followed by the addition of 5mL of concentrated HNO₃ and 1mL of 30% H₂O₂ (Wang et al., 2006). The temperature was ramped to 220°C for 20 min., and then held for 20 min. The digestant was diluted and analyzed for Hg on a Tekran 2600 as described above. The certified reference material NIST1632c (bituminous coal; National Institute of Standards and Technology, USA) was digested and analyzed followed the same procedure and the results were found within 10% of the certified value of 93.8 ng/g.

3.4. Results and Discussion

3.4.1 Oxidative Weathering of Pyrites as a Mercury Source

Despite the widespread presence of carbonates in the Mackenzie Mountains, sequential extraction results (Figure 3.2) suggests that the carbonate fraction (F2) of Hg is very low (0-2%) in the sediments from this region. This is not surprising as carbonate minerals in general are known to be poor in Hg (Yudovich and Ketris, 2005) (Table A2 in Appendix A). The concentrations of exchangeable Hg (F1; <1%) and Fe/Mn oxides-bound Hg (F3; <5%) are also very low to negligible in the sediments from the

mountainous sites (Figure 3.2). In contrast, the Hg association in these sediments is dominated by the sulfide fraction (F4; 95-99.9%; Figure 3.2), suggesting much of the Hg is bound to sulfides and OM in the sediments. While the sequential extraction used in this study does not discriminate between sulfide- and OM-bound Hg, the low TOC levels and predominance of char (Carrie et al., 2009), which would have released all of its Hg (Friedli et al., 2003), indicate that this Hg is mainly bound to sulfides. It should be emphasised here that the sequential extraction method is operationally defined, and may be subject to artefacts such as re-adsorption (Gomez-Ariza et al., 1999). However, due to the low concentrations of Hg in most environmental samples, the use of definitive mineralogical identification methods, such as SEM-EDS, are precluded. Sequential extractions nevertheless offer a first-order estimate on the mineralogical association of Hg, and remain one of the best tools currently available for this endeavour.

Black shales, which are known to contain higher Hg than most other sedimentary rocks (Yudovich and Ketris, 2005), are widespread in the MRB, especially in the Mackenzie Mountains on the western side of the basin (Reichenbach, 1993). Furthermore, numerous sedimentary exhalative and Mississippi-Valley Type deposits exist throughout the Mackenzie and Selwyn Mountains (Goodfellow, 1987; Paradis, 2007). These deposits contain PbS, ZnS, FeS₂, and to a lesser extent CuFeS₂, all of which are known to co-precipitate Hg, generally in the form of cinnabar (Feng and Hong, 1999). Comprehensive geochemical surveying by the Geological Survey of Canada (Day et al., 2005) has shown that stream sediments in the Sekwi and Mackenzie Mountains have Hg concentrations ranging from <5 to 8300 ng/g (n=668) with a median value of 35 ng/g, similar to the median of 32 ng/g for the mountainous tributary sites (Figure 3.2), with

18% of the sites having concentrations greater than 89 ng/g, the maximum concentration found in our samples (at the Arctic Red River). These Hg-enriched sites have higher Hg than all values observed near the mouths of rivers emptying into the Mackenzie River, and may result from the oxidative weathering of sulfide minerals and subsequent dilution by runoff. This is supported by the positive spatial correlations of S and Hg in the sediments, and their negative correlations with the pH of the stream waters (Day et al., 2005).

To further assess the relative importance of the oxidation of sulfide minerals as a source of Hg in the Mackenzie, we calculated the molar ratios of SO_4^{2-} to Cl^- in the river water. Various studies have shown that oxidative weathering of pyrite (OWP), where pyrite is defined as any major sulfide mineral (e.g., FeS_2 , PbS , ZnS , CuFeS_2), is the predominant source of SO_4^{2-} in the Mackenzie River (Calmels et al., 2007; Hitchon and Krouse, 1972), followed by dissolution of gypsum (Calmels et al., 2007). The Cl^- in the Mackenzie river water originates primarily from groundwater sources and weathering of evaporates (mainly CaSO_4 , MgSO_4 , and NaCl) (Millot et al., 2003). Atmospheric SO_2 is not a significant source of SO_4^{2-} in the Mackenzie basin due to the long distance from major industrial sources, decreasing SO_2 emissions from North American and European sources (Berglen et al., 2004), short atmospheric lifetime of SO_2 (~1 day; (Berglen et al., 2004)), and meteorology specific to the Arctic; it has been estimated that <7% of Eurasian S reaches the Arctic (Pacyna, 1995). The contribution of SO_4^{2-} and Cl^- from seasalt aerosols to the Mackenzie Basin is minimal due to the limited atmosphere-ocean interaction because of ice cover and low precipitation in the region (Millot et al., 2003;

Pacyna, 1995). Therefore, lower $\text{SO}_4^{2-}/\text{Cl}^-$ ratios are indicative of evaporite dissolution (Huh et al., 2004), while higher values are indicative of OWP in the Mackenzie Basin.

As shown in Table A1 and Figure 3.3d, the $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratio in the MRB varies over a wide range from 0.1 to 57, with an average value of 6.5. Mountainous sites have significantly higher $\text{SO}_4^{2-}/\text{Cl}^-$ than the main stem ($p = 0.01$) or peatland sites ($p = 0.03$), whereas there is no significant difference in the $\text{SO}_4^{2-}/\text{Cl}^-$ ratios between the peatland sites and the main stem sites ($p=0.65$). One peatland site, the Hare Indian River, stands out with a very high SO_4/Cl (90.9). Isotopic studies have shown that this site is affected by OWP (Hitchon and Krouse, 1972), and a small lake that flows into the Hare Indian River near the Mackenzie River has abundant pyrite grains in the bottom sediments (J. Carrie, unpublished results). It is thus appropriate to group the Hare Indian River with the “High OWP” mountainous sites, which leads to an even more significant difference in $\text{SO}_4^{2-}/\text{Cl}^-$ between the “High OWP” sites and the remainder of the sites ($p < 0.0001$).

The High OWP sites (i.e., the mountainous sites and the Hare Indian River) are characterized with significantly higher particulate ($p = 0.02$) and total Hg ($p=0.001$) in surface waters than peatland sites (excluding the Hare Indian River). These values, coupled with the data on geological materials in Table A2 in Appendix A, suggest that OWP is the dominant geochemical source for high Hg concentrations in surface waters of the mountainous tributaries and the Hare Indian River. A strong correlation exists between fluxes of total Hg and dissolved SO_4^{2-} (see Figure 3.6). Carson et al. (1998) showed a strong dependence of sediment flux on water discharge, while others (Calmels et al., 2007) demonstrated strong links between physical erosion rates and sulfide

oxidation rates. There are thus two possible, synergistic mechanisms contributing to this increased Hg. First, the high percentage of particulate Hg found in the river combined with the sequential extraction data showing mainly sulfide-bound Hg demonstrates that sulfide oxidation greatly enhances erosion of the lithosphere, and that small particles of cinnabar or Hg-bearing minerals could be eroded into the river, contributing to the high particulate Hg seen in the mountainous sites. Our previous study (Leitch et al., 2007) showing strong links between water discharge (and hence erosion) and Hg concentrations corroborates this. Second, the high acidity produced from sulfide oxidation can leach Hg from its mineral matrix, and release it in the dissolved form.

3.4.2 Carbonaceous Rocks as a Mercury Source

The MRB is rich in carbonaceous reserves. Two major coal outcrops are located in the Brackett Basin coals (2000 Mt) near Tulita and the Bonnet Plume Basin (2800 Mt) which drains into the Peel River that joins into the western Mackenzie Delta. Smaller and distinct (based on low vitrinite reflectance (Cameron and Beaton, 2000) coal outcrops also exist in other parts of the basin. Those coal outcrops are subject to the effects of ice-jamming during spring breakup and the strong scouring effects of the heavily sediment-laden Mackenzie River (Carson et al., 1998; Macdonald et al., 1998). Analysis of coal samples from the Brackett Basin shows that the Hg concentration ranges from 36.1 to 2420 ng/g (n=25; Figure 3.4, Table A2), with a median value of 173 ng/g and average value of 490 ng/g). Two of the carbonaceous samples of coaly origin from the Brackett Basin have Hg concentrations exceeding 2000 ng/g, which are among the highest known

in the world (Yudovich and Ketris, 2005). Since coaly particles are found in the sediments of the Mackenzie River all the way into the delta (Carrie et al., 2009), they contribute to the Hg loading to the Mackenzie sediments, but the mobility of the coal particles and bioavailability of Hg they contain may be less than other Hg-containing sediment phases.

3.4.3 Recent Organic Matter as a Mercury Source

A recent study in Arctic lakes has shown that the Hg concentration in surface sediments could be significantly affected by the changes in autochthonous organic matter (OM) in the lakes (Outridge et al., 2007). No significant correlation is however found between Hg and any of the Rock-Eval OM parameters representing the labile autochthonous OM ($r^2 = 0.03$ for S1, and 0.07 for S2) in the Mackenzie Basin as a whole (Figure 3.6). This is not surprising as the OM in the MRB is mainly terrigenous and petrogenic (Goni et al., 2005; Macdonald et al., 1998; Outridge et al., 2007), with refractory OM constituting greater than 80% of OM at most sites (Carrie et al., 2009). Isotopic studies ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) have shown that particulate organic carbon (POC) in the Mackenzie River is old (6,000 – 8000 years BP) compared to DOC (400 – 1400 years BP), suggesting that POC has undergone greater oxidative and/or diagenetic alteration before entering the river (Guo et al., 2007). The reworked, refractory organic carbon, derived mainly from terrestrial/higher plant remains, is poor at binding Hg. Also the selective degradation of labile organic matter removes the Hg-complexing functional

groups (e.g., -SH, -OH, -COOH, -NH₂) during diagenesis (Hedges and Keil, 1995; Stach, 1982).

Some sites, however, differ from this general trend. In particular, tributaries with a strong lacustrine influence show much higher labile carbon (i.e., S1 and S2 fractions) in their sediments (Figure 3.5 and Table A1). This labile carbon, derived primarily from algal matter, has been shown to be able to bind Hg (Outridge et al., 2007; Sanei and Goodarzi, 2006), likely via reduced S bonds derived from proteinaceous materials, as well as to other cysteine- and methionine-based biomolecules. Mercury may be bound to labile carbon at these sites due to scavenging of atmospherically deposited Hg by algae, which then sink upon death (Outridge et al., 2007; Sanei and Goodarzi, 2006). A moderate though statistically not significant correlation is found between Hg and S1 concentrations in the sediment from these lake-fed sites ($r^2 = 0.51$, $n = 5$; Figure 3.5). This small sample size precludes any definitive statements on Hg cycling. However, as several lakes in the Arctic and sub-Arctic show strong correlation between Hg and the labile OM fraction S2, including one in this basin (Carrie et al., 2009; Stern et al., 2009; Outridge et al., 2007), and that these lakes produce OM at much higher levels than those seen in the river tributaries presented here, it is likely that OM-bound Hg produced in the lakes enters the tributaries. Although there is no significant difference in the sedimentary Hg concentration between the lake-fed sites and the rest of the MRB, the correlation between Hg and S1 at the lake-fed sites suggest that the Hg at the lake-fed sites is bound to a large degree to algal matter and thus has a higher bioavailability, since less than 1% of labile OM produced is preserved in sediments (Hedges and Keil, 1995). It is important to note that three of these sites (the Hare Indian, Horn and Great Bear Rivers) are home to

communities (Fort Good Hope, Fort Providence and Tulita, respectively; Figure 3.1) that subsist upon fishing.

3.5 Fluxes and Bioavailability of Mercury

We have recently shown that the Mackenzie River transports on average 2.2 t/yr of total Hg to the Delta region (Leitch et al., 2007). The additional data from the present study allow us to further apportion the total Hg flux to various sources. The contribution of OWP to the total Hg flux is estimated from a regression analysis between the fluxes of total Hg and the OWP-derived SO_4^{2-} in the tributaries of the Mackenzie River. As indicated by the r^2 value (Figure 3.6), the SO_4^{2-} flux explained 93% of the variance in the total Hg flux. Furthermore, isotopic studies (Calmels et al., 2007; Hitchon and Krouse, 1972) have shown that OWP accounts for about 85% of the SO_4^{2-} found dissolved in Mackenzie River waters. Therefore, we estimate that OWP contributes ~ 1.7 t/yr of Hg to the riverine Hg flux to the Mackenzie Delta. Note that this value is likely an underestimate, as sulfidic minerals in the Mackenzie and Selwyn Mountains dominate the SO_4^{2-} supply for the Mackenzie River (e.g., ((Calmels et al., 2007; Carson et al., 1998)), yet the dataset from (Calmels et al., 2007) only included a few tributaries draining from this region (the Peel and Liard Rivers).

To estimate the relative importance of coal as a source of Hg in the MRB, we based our calculations on the estimated POC flux of 2.1 Mt/yr (Macdonald et al., 1998) and assumed 40% of the POC is vitrinitic (i.e., coal-derived) (Carrie et al., 2009). By

using an average Hg concentration in the coal of 490 ng/g of Hg (Figure 3.4), we estimate that the erosion and weathering of coal yields 0.4 t/yr of Hg.

We recently estimated that a total of 7800 t/yr of S1 fraction of OM is transported from the Mackenzie River to its delta (Carrie et al., 2009). However, the total amount of S1 produced is 11250 t/yr, leaving 3450 t/yr, or approximately 30% of the total produced S1 OM removed by sedimentation. Conversely, approximately 70% of the total S1 produced reaches the delta. S1 fluxes from lake-fed sites are approximately 24% of the total S1 fluxed (Carrie et al., 2009). Based upon the S1 sediment transport efficiency (70%) and proportion of S1 derived from lake-fed sites, we calculate that 17% of the total S1 reaching the delta is due to lake-fed tributaries. Combining this with the moderate correlation of S1 and Hg in lake-fed sites ($r^2 = 0.51$, Figure 3.6), we derive upper limits of 0.2 t/yr due to labile OM-bound Hg.

This results in a total Hg flux of 2.3 t/yr which agrees very well with the flux estimated by (Leitch et al., 2007), with OWP, coal and S1 OM accounting for 74%, 17% and 9% of the total Hg flux respectively. The dominance of sulfide minerals as a Hg source in the Mackenzie River suggests that most of the Hg in the basin is of low bioavailability (Bloom et al., 2003). While the S1 fraction of the OM only accounts for <10% of the total Hg reaching the delta, it is this Hg flux that is of most significance with respect to bioavailability. When spatially segregating the MeHg data, peatland sites appear to contain higher concentrations of dissolved MeHg (0.020-0.175 ng/L with a median value of 0.089 ng/L) than mountainous sites (0.025-0.098 ng/L; median: 0.047 ng/L), though the difference is not statistically significant ($p = 0.10$). The higher OM, warmer water temperatures, and lower hydrodynamic energies of the peatland tributaries

(Carrie et al., 2009; Leitch et al., 2007) likely permit greater concentrations of MeHg to form (Fitzgerald et al., 2007).

3.6 Implications for Future Climate Change

Climatic models show two general trends for the MRB: increasing air temperatures, and increasing precipitation (Szeto, 2008). Over the last 30 years, the MRB has been warming faster than the global average, at a rate of 1°C per decade (Woo and Thorne, 2003). Warmer temperatures and increased precipitation will increase coastal erosion and permafrost melting, thus increasing the load of sediment and associated Hg to the Mackenzie River and the Beaufort Sea (Leitch et al., 2007). As OWP is the major source of Hg in the MRB, an increasing rate of weathering and erosion due to warmer temperature and increased precipitation (Berner, 2003; Millot et al., 2003) will further increase the release of sulfides-associated Hg. This is likely to be exacerbated by industrial activities in the upstream of the MRB. The rapid development in the oil sand industry in Northern Alberta has resulted in significant decrease in water discharge from upstream rivers such as the Athabasca and Slave Rivers (Schindler and Donahue, 2006), increasing the relative importance of the Mackenzie Mountain tributaries, in particular the Liard River, as source water to the Mackenzie River. This will increase the amount of suspended solids in the river and is expected to increase the concentration of Hg, as most of the Hg in the system is in the particulate phase (Leitch et al., 2007). The overall result will be an increase in the total riverine Hg flux to the Beaufort Sea and the Arctic Ocean (Outridge et al., 2008).

Of particular significance is the Hg biogeochemistry at peatland sites under a warming climate. Warmer temperatures are likely to increase primary productivity due to longer ice-free periods, especially in lakes that feed the Mackenzie River. An increased primary productivity could increase the scavenging of Hg from the atmosphere and hence in algal organic matter-associated Hg (Outridge et al., 2007) that is more bioavailable than the sulfides-bound Hg (Fitzgerald et al., 2007). It is however also possible that increased primary productivity could result in increased volatilization of Hg back to the atmosphere (Poullain et al., 2004). Warming temperatures and increased DOC concentrations are also expected to increase Hg methylation rates (Fitzgerald et al., 2007), resulting in higher MeHg production. The peatland zone will see the greatest increases in MeHg, as abundant lakes and wetlands are present, which are known net sources of MeHg (Mitchell et al., 2008). Permafrost slumping triggered by warming (Jorgenson and Osterkamp, 2005) will also be most strongly felt in the peatland zone, creating new and/or larger wetlands, with consequent increases in MeHg production. If trends seen elsewhere (Outridge et al., 2007; Sanei and Goodarzi, 2006) apply to the MRB, the Hg burden of fish stocks is likely going to increase. Monitoring data at Fort Good Hope have indeed shown increasing Hg concentrations in burbot (Stern and Tomy, 2008). The dependence of local communities on these fish stocks thus warrants further attention.

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3.8 Supplementary Content Notice (Appendix A, pp.126-136)

Detailed sequential extraction procedures for determining Hg speciation in the sediments and two tables. Table A1 shows the raw data for Hg, organic carbon, and ancillary parameters for the water and surface sediments samples collected from the Mackenzie River Basin. Table A2 shows the Hg concentrations in various types of surface and geological materials.

3.9 References

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3.10 Figures

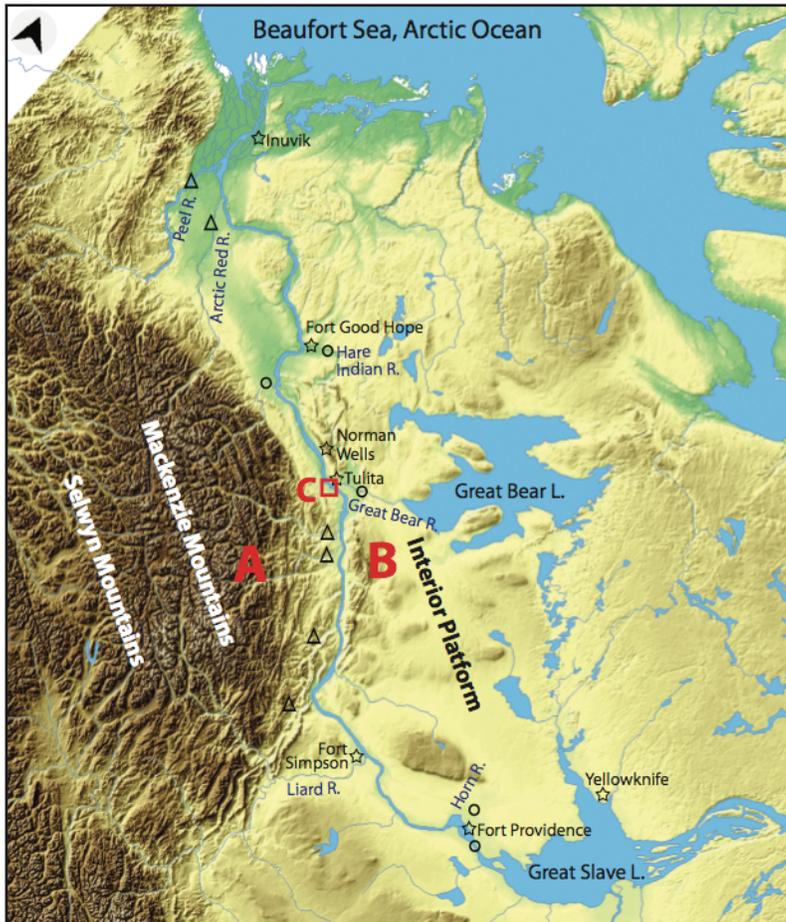


Figure 3.1: A topographic map showing the Mackenzie River Basin. The detailed sediment and water sampling locations in the western mountainous (A) and eastern peatland (B) areas are given elsewhere (Carrie et al., 2009; Leitch et al., 2007). The red rectangular area C shows the coal sampling location, the open circles indicate the sediment sampling sites on the lake-fed tributaries, and the open triangles indicate the mountainous sites where sediment samples were analyzed further by the sequential extraction procedures as detailed in the text. The stars indicate locations of major cities and communities. The topographic basemap was produced using the online tools from the National Topographic System (NTS) of Natural Resources Canada

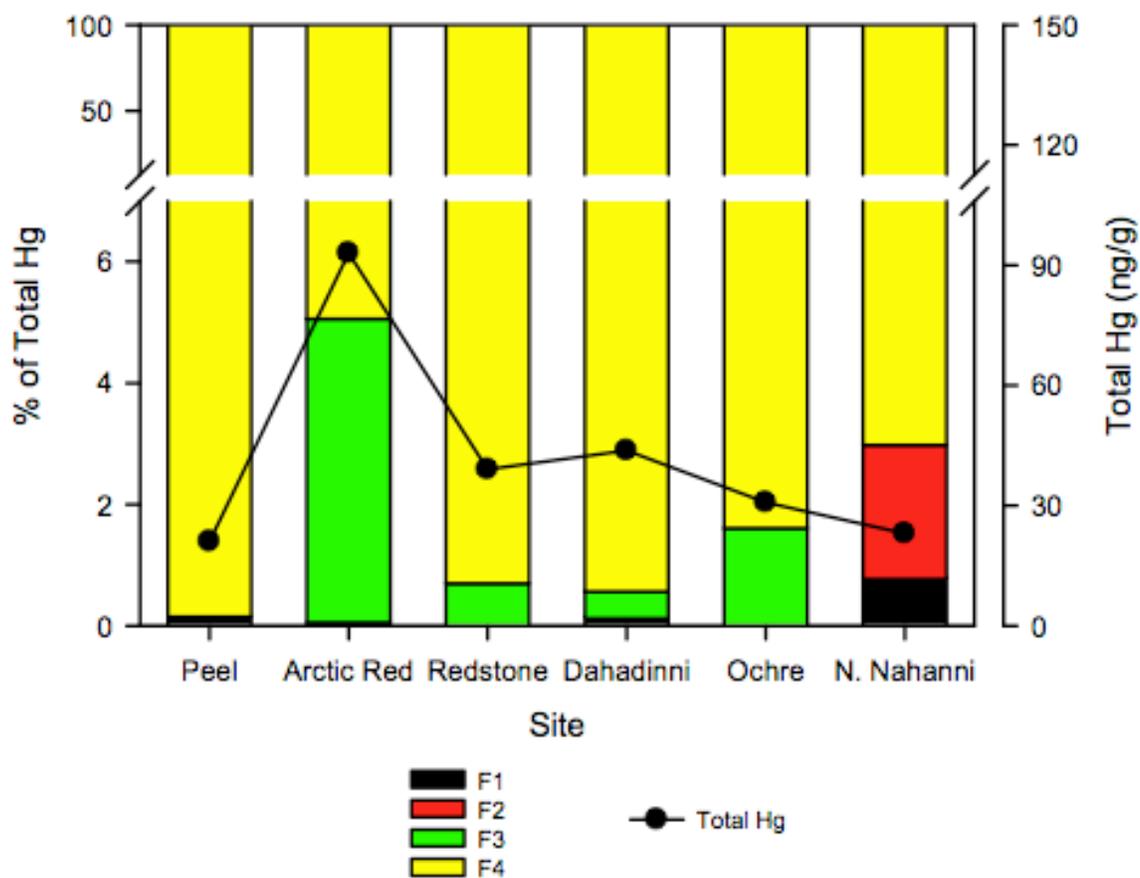


Figure 3.2: Speciation of Hg in the sediment samples from six mountainous sites (those marked by open triangles in Figure 1). F1: exchangeable Hg; F2: Carbonates-bound Hg; F3: Fe/Mn oxides-bound Hg; F4: Sulfide- and organic-bound Hg.

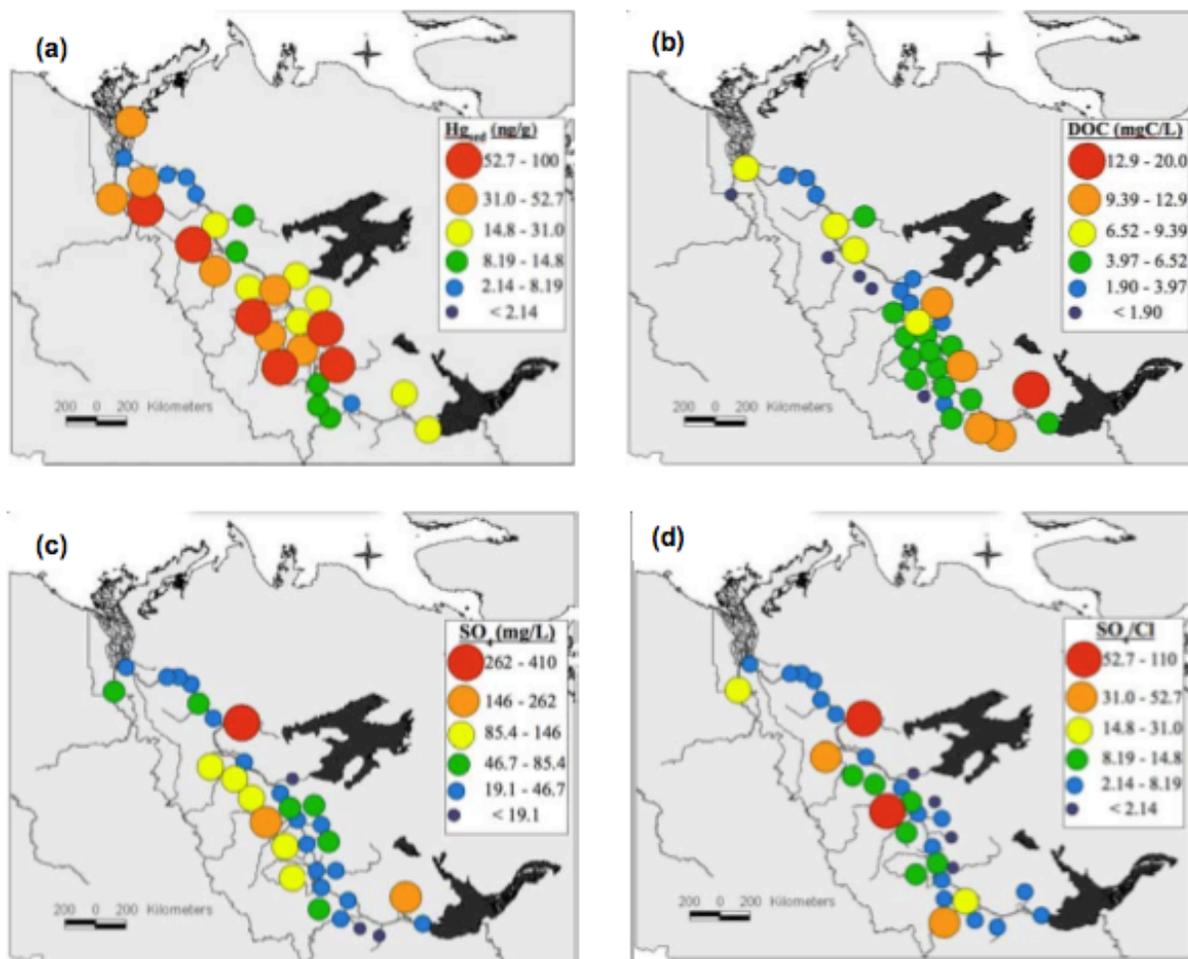


Figure 3.3: Distribution of (a) Hg, (b) DOC, (c) Dissolved SO₄²⁻ and (d) SO₄²⁻/Cl⁻ ratio in the Mackenzie River Basin.

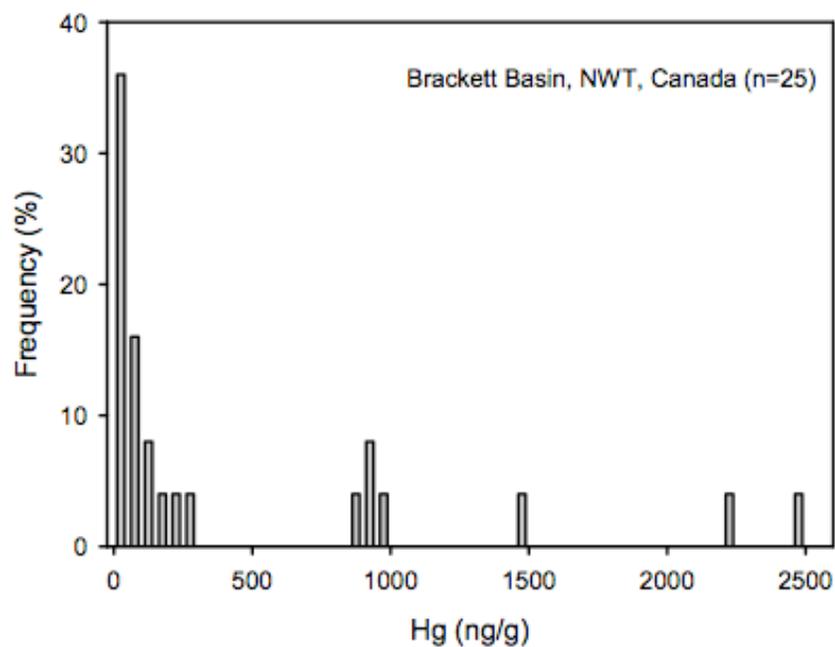


Figure 3.4: The frequency distribution of the Hg concentration in coal samples taken from the Brackett Basin.

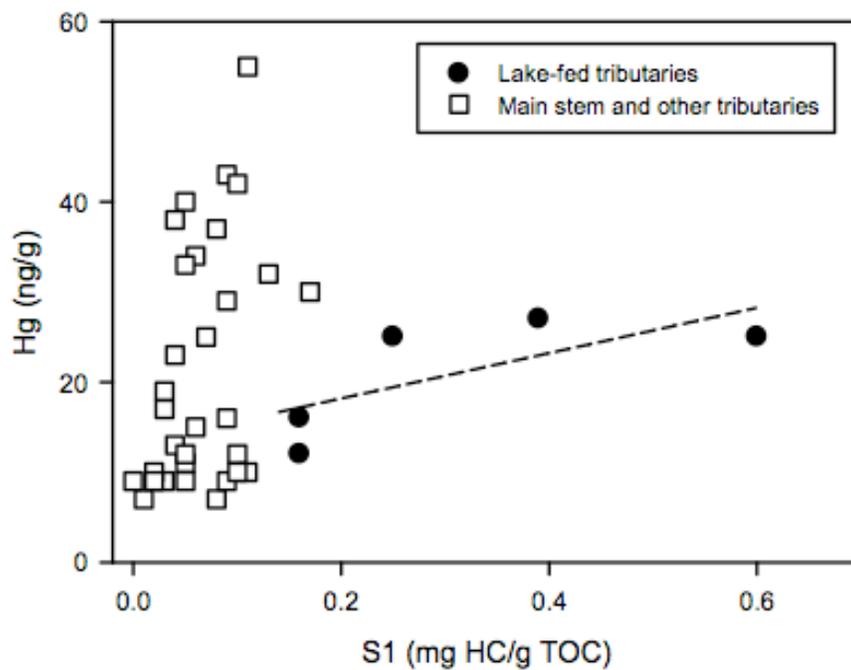


Figure 3.5: Relationship between Hg and S1 organic matter in surface sediments in the Mackenzie River Basin.

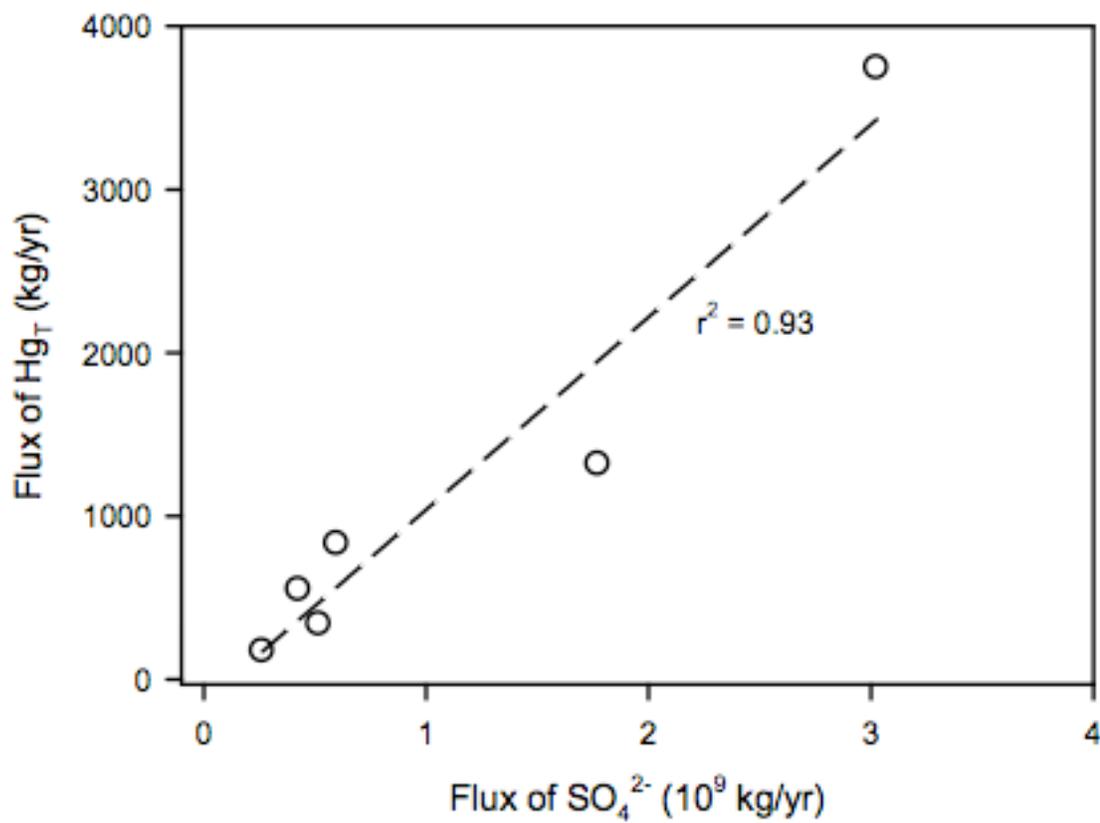


Figure 3.6: Relationship between the fluxes of total Hg and dissolved SO₄²⁻ in the tributaries of the Mackenzie River.

Chapter 4:

Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate

4.1 Abstract

High and increasing concentrations of mercury (Hg), polychlorinated biphenyls (PCBs) and other contaminants in Arctic aquatic biota are usually attributed to atmospheric sources. However, climate variability and change is proposed as another means to alter contaminant fate and bioavailability. We show here that the concentrations of Hg and PCBs in Mackenzie River burbot (*Lota lota*), a top predator fish and important staple for northern Canadian communities, have increased significantly over the last 25 years despite falling or stable atmospheric concentrations, suggesting that environmental processes subsequent to atmospheric transport are responsible. Using a dated sediment core from a tributary lake near the Mackenzie River sampling site, we show that variations in Hg concentrations down-core are strongly associated with labile, algal-derived organic matter (OM). This is the first study to show that strong temporal correlations between increasing primary productivity and biotic Hg and PCBs as reflected by burbot suggest that warming temperatures and/or reduced ice cover are leading to increased exposure to these contaminants in high trophic level Arctic biota.

Keywords: Burbot, mercury, PCBs, Mackenzie River, lake sediments, carbon, climate change

4.2 Introduction

Contaminant concentrations in Arctic freshwater and marine biota have been monitored fairly consistently since the late 1980s (e.g., Braune et al., 2005, and references therein; Lockhart et al., 2005). The prevailing paradigm attributes changes in Arctic biotic contaminant concentrations to global contaminant emissions and usage patterns, and to processes such as long-range atmospheric transport or food web structures and length (AMAP 1998; 2004a, b).

There is no doubt that the global banning and restricted usage of contaminants such as DDT, Toxaphene, and polychlorinated biphenyls (PCBs) and stricter emissions regulations for mercury (Hg) during the late 20th century have resulted in a subsequent downturn in their trends in temperate marine and freshwater biota (e.g., Levinton and Pochron, 2008). However, since the mid-1990s, the concentrations of these contaminants in many species of Arctic marine and fresh water biota and sediments have not declined and in some cases have even increased (Braune et al., 2005; Stern et al. 2005; Outridge et al. 2007; Michelutti et al. 2009). Atmospheric concentrations of these contaminants over the same time period, have remained unchanged or have slightly declined (Steffen, 2007; Li et al., 2009; Hung et al., 2009).

Based on regional Hg budgets, Outridge et al. (2008) and Hare et al. (2008) concluded that the Hg exchanges in the Arctic Ocean and Hudson Bay, respectively, were near steady-state. Furthermore, the large reservoir size and long residence time (~10 years) of Hg in surface waters implied that inter-annual variations in Hg concentrations in marine biota were unlikely to be due to changes in ambient seawater Hg concentrations

brought on by altered deposition but, rather, reflect dynamic ecological and geochemical processes within the ocean. Indeed, Loseto et al. in a series of papers (2006, 2008a, 2008b) postulated that the dramatic increases in liver Hg concentrations measured in Beaufort Sea beluga since the early 1990s (Lockhart et al. 2005) could be attributed to changes in sea ice regimes in the open water season, sexual segregation, and associated feeding behaviour. In a study on western Arctic ringed seals, while no significant temporal trend in Hg was observed over a 30-year period in their muscle tissue, a strong correlation was observed with length of the ice-free season (Gaden et al, 2009). Higher ringed seal Hg concentrations followed relatively short ice-free seasons due to consumption of older, more highly contaminated Arctic cod cohorts. Conversely, relatively long ice-free seasons increased survival and abundance of Arctic cod with the overall result of more fish consumption and thus Hg accumulation. McKinney et al. (2009) reported that increasing contaminant concentration in Hudson Bay polar bears could be, at least in part, attributed to differences in timing of the annual sea ice break-up and the resulting increase in consumption of open water-associated seal species in years of earlier ice break-up.

Arctic lake and marine sediment cores have been widely used as proxies to infer historical rates of atmospheric contaminant deposition (Muir et al., 1995, 1996, 2009) and consequently how change in deposition may have affected biota. In the case of Hg, an approximate 2-fold increase in deposition since pre-industrial times has been observed (Lockhart et al., 1995, 1998; Muir et al., 2009). However, Outridge et al. (2005, 2007) and Stern et al. (2005) raised serious questions concerning the conventional interpretation of sedimentary records as reliable historical archives for atmospheric deposition of Hg

and other contaminants in northern lakes whose limnology is profoundly affected by climate warming. These authors argued that recent climate-induced increases in algal productivity within high Arctic lakes could result in a substantial overestimation of historical rates of atmospheric Hg deposition when derived from sediment fluxes. Furthermore, Macdonald et al. (2005) pointed out that enhanced fluxes of Hg to sediments supported by enhanced particle flux consequent to increased algal production could lead to the non-intuitive result of reduced exposure of Hg to higher trophic levels due to bloom dilution. PCBs and organochlorine pesticides are known to preferentially sorb onto organic matter particles and colloids because of their hydrophobic behaviour, with the amount of sorption possibly influenced by the degree of compound chlorination (Mackay et al. 1992; Skoglund et al. 1999; Moon et al. 2004). Stern et al. (2005) reported that the post-1950 fluxes of PCBs and a range of pesticides in Lake DV-09 sediments on Devon Island were strongly correlated to changes in diatom numbers, which was taken as possible evidence of a climate-driven effect on the sedimentary accumulation of these compounds.

The Mackenzie River Basin (MRB) has been experiencing one of the most noticeable climate warming trends in North America (Woo and Thorne, 2003). Several new reports on Hg in the MRB, delta and estuary and the delivery of Hg *via* the Mackenzie River to the Beaufort Sea have emerged (Leitch et al. 2007; Graydon et al. 2009; Carrie et al. 2009 and Lockhart et al. 2005), showing the importance of the environmental and climatic conditions on the biogeochemical cycling of Hg. Here we report temporal trend results for Hg and selected PCBs in Mackenzie River burbot collected over a 24-year period from 1985 to 2008 and a 21-year period from 1988 to

2008, respectively. We then examine the relationship between the trends of Hg in these fish and those in a dated sediment core collected from a nearby lake which feeds directly into a tributary along the Mackenzie River where these fish are thought to feed.

4.3 Materials and Methods

4.3.1 Burbot

Since 1985, burbot (*Lota lota*) have been collected in winter (December-January) from the Rampart Rapids by residents of the nearby community of Fort Good Hope (66.3°N, 128.6°W, Figure 4.1), with fish being collected annually over the past 10 years. A minimum of 10 fish have been collected each year, with 20-40 fish collected annually since 1999. After collection, the whole fish was sealed in plastic bags, frozen and shipped to the Freshwater Institute in Winnipeg for aging (*via* otoliths), sexing, morphometric measurements and tissue analysis ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, total Hg (HgT) and PCBs; see below).

HgT analysis of muscle and liver tissue was conducted using Cold Vapour Atomic Absorption Spectrometry (CVAAS; Lockhart et al., 2005b). The limit of detection was 0.005 $\mu\text{g/g}$ wet weight. Replicates, blanks, and certified reference materials (DORM-3, TORT-2, CRM 2976; NRC-Canada) were used for QA/QC for the Hg in the fish. Accuracy, based on recovery, was within 4%, 7% and 10%, and precision (as relative standard deviation) was better than 2%, 7% and 1%, respectively.

PCB analysis was conducted as per Stewart et al. (2003). Briefly, liver samples were extracted using a ball mill and combined with anhydrous sodium sulphate and extracted in an accelerated solvent extractor (ASE 200, Dionex Canada, Oakville, ON). PCB 30 and octachloronaphthalene (OCN) were used as recovery. Florisil® fractions were analysed by high-resolution gas chromatography with electron capture detection (HR-GC-ECD), using a 60m DB-5 capillary column (0.25mm ID, 0.25 Am film thickness, J&W Scientific). Chemicals were quantified by comparing peak areas (identified by retention time) to those of commercially available standards of known concentration.

Dried, homogenised sub-samples of burbot muscle tissue were analysed for stable isotopes of carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) following the method described by Loseto et al. (2008). In brief, analysis was conducted by Continuous Flow Ion Ratio Mass Spectrometry (CFIR-MS) at the University of Winnipeg Stable Isotope Laboratory. Isotopic data are presented in units of per mil (‰), with δ notation. Here, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are derived from

$$\delta_{\text{sample}}\text{‰} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] * 1000$$

where R is the ratio of heavy to light isotope ($^{15}\text{N}/^{14}\text{N}$ or $^{13}\text{C}/^{12}\text{C}$) in the sample and standard.

4.3.2 Sediments

A sediment core was collected from Hare Indian Lake (66.3°N, 128.5°W, Figure 4.1), a small, shallow lake (0.28 km², maximum depth 2m) that drains into the Hare Indian River near Fort Good Hope, Northwest Territories, Canada, before flowing into the Mackenzie River approximately 10 km down stream. The core was sliced into 0.5cm intervals for the first 10cm down core, followed by 1cm intervals for the 10-20cm section, 2cm intervals for 20-40cm, and every 5cm for the remainder of the core (total depth 74cm). Samples were collected using a polycarbonate 5.5cm ID plastic corer, and a diver was used to minimise compression of the core. Samples were immediately placed in plastic bags, sealed, and stored at ambient temperatures (5-10°C) until reaching the sampling base, where they were frozen and brought to the Freshwater Institute in Winnipeg. All samples were freeze-dried, and stored in the dark at 4°C until further analysis. Geochemical data and visual observations show Hare Indian Lake sediments to be under reducing conditions.

Pb-210 and Cs-137 were used to date the core. Sedimentation rates were calculated using the linear and constant rate of supply (CRS) models (Appleby and Oldfield, 1978; Robbins, 1978). Precision of the CRS dates and sedimentation rates were calculated using the method of Wilkinson and Simpson (2003) and was better than 4%. Cs-137 activity (from atmospheric fallout of nuclear weapons, peaking in 1963) was measured to confirm Pb-210 dates. See appendix B (Figure B.1).

Each slice of the sediment core was analysed by ICP-MS for a suite of 53 elements after aqua regia digestion, including As, Se, Fe, Mn and S. Analysis was

conducted at ACME Analytical Laboratories, Ltd., in Vancouver, Canada. Recoveries for all elements were within 10% of established values (internal standard DS7), except for Au and Nb. Precision was better than 10%, except for La, Nb and Y. HgT was analysed by CVAAS at the Freshwater Institute, using certified reference materials (MESS-2 and PACS-2, National Research Council of Canada) for quality control. HgT was accurate within 10% of established values, and precision better than 5%.

Sediment was also analysed by Rock-Eval pyrolysis (Lafargue et al., 1998). This method quantifies and qualifies the OM in the sample based on the degree of thermal degradation and evolution of various organic compounds. Bulk sediment is first heated in an inert, O₂-free atmosphere up to 650°C, followed by combustion in an oxidation oven up to 850°C. The first stage (pyrolysis) releases two major groups of hydrocarbons (HC), defined as S1 and S2, which are detected by flame ionisation (FID). S1 and S2 (mg HC/g) represent mostly algal-derived kerogen. Simultaneously, infrared (IR) detection of CO and CO₂ yields the S3 peak (mg CO-CO₂/g), representing mostly oxygen-bearing OM. The second stage (combustion) burns the remaining OM, yielding the refractory carbon (RC, wt.%) peak. Total organic carbon (TOC; wt.%) is derived from the sum of OM from the pyrolysis and combustion steps. Accuracy and precision were measured using Geological Survey of Canada internal standard 9107 (shale). Accuracy was within 4% of established values, and precision better than 4%.

A bulk surface sediment grab, collected from the same lake for organic petrology, was analysed using white/fluorescence, incident light microscopy. Organic components were identified and classified into major maceral groups (vitrinite, liptinite/alginite, and inertinite). Relative volumetric quantities of the macerals were assigned using point

counting ($n > 300$) to determine the relative proportion of terrestrial (vitrinite and inertinite) and aquatic (alginite) organic matter following methods in Taylor et al. (1998).

4.3.3 Climate

Meteorological data for Norman Wells (1943-2008, approximately 120km south of Fort Good Hope with similar meteorology) were obtained from the Meteorological Service of Canada (Environment Canada 2009). Monthly temperature data was averaged to give mean annual temperatures. End of month snow cover was also used for March and April.

4.3.4 Statistics

Isotopic data ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were used to detect changes in diet in the burbot over time. Data are available for 1995 and 1999-2005. Data were normally distributed ($n=10$ per year) and the variances between years were also not significantly different based upon a F-test analysis of variance. T-tests were used to compare whether there were any significant differences between years.

4.4 Results and Discussion

4.4.1 Mercury, PCB and DDT Temporal Trends in Fort Good Hope Burbot

HgT temporal trend data from Fort Good Hope burbot tissues span 13 time points over the 24-year period from 1985 to 2008 (Figures 4.2A and 4.2B). Over this period, concentrations have increased approximately 2-fold and cannot be explained by differing physiological characteristics or changes in feeding behaviour. There is no significant change in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ data over the years 1995-2005 ($\delta^{15}\text{N}$: $r^2=0.002$, $p>0.10$; $\delta^{13}\text{C}$: $r^2=0.026$, $p>0.10$), implying that burbot have not been feeding differently; nor are there significant differences for $\delta^{15}\text{N}$ (t-test, $p=0.82$, $n_1=n_2=10$) or $\delta^{13}\text{C}$ (t-test, $p=0.31$, $n_1=n_2=10$) between years of lower Hg concentrations (1999: $0.24 \pm 0.06 \mu\text{g/g}$; mean ± 1 s.d.) and higher Hg concentrations (2004: $0.40 \pm 0.09 \mu\text{g/g}$; mean ± 1 s.d.). Additionally, no correlation was noted between muscle HgT and $\delta^{15}\text{N}$ ($r^2=0.0004$, $p>0.10$, $n=80$) nor $\delta^{13}\text{C}$ ($r^2=0.017$, $p>0.10$, $n=80$). There is also no correlation between HgT and fish size (weight or length), with the exception of a weak, though statistically significant, correlation with age ($r^2=0.14$, $p<0.01$, $n=276$). This last finding is contrary to observations of other fish species (e.g., Gantner et al., 2009; Evans et al., 2005) and may be attributed to a relatively short half-life of HgT in burbot muscle and liver: Under natural conditions a HgT half-life of 90 days was observed in liver of yellow perch (Van Walleggem et al, 2007). Further, the HgT half-life in muscle was reported to be significantly longer due to Hg redistribution from other tissues. The lack of relationship between HgT in the collected burbot muscle and morphometrics suggests that this transfer mechanism may not be significant in these fishes.

Concern over the impact of PCBs on the environment led to a North American ban on manufacturing and importing of PCBs in 1977. Worldwide PCB production is thought to have ended when Russia ceased production of Sovol in 1993 (Stern et al. 2005). As a result, PCB concentrations have in general significantly declined in Canadian Arctic biota from the 1970s to the late 1990s, and today are generally less than half the levels of the 1970s (Braune et al. 2005). Despite this general decline in Arctic marine biota since the 1970s, significant increases in the more highly chlorinated PCBs have been observed since the early 1990s in the liver of the Mackenzie River burbot measured as part of this study. Figure 4.2C and D show the lipid-corrected concentrations over the period from 1988 to 2008 for Σ Hexa-PCB and Σ Hepta-PCB homologue groups and CB153, respectively. While not shown, Σ DDT levels have also increased by approximately 3-fold over the same time period. This increase is driven primarily by *pp'*-DDE which also implies old or recycled DDT rather than new applications. There are no known local major PCB or DDT sources that could contribute to the burbot's increasing loads. The increasing trends in burbot, which oppose the decreasing trends in the atmosphere, rule out atmospheric concentration as a dominant driver of fish PCB and DDT concentrations over recent decades, and other mechanisms must be considered.

4.4.2 Sedimentary Record of Organic Matter and Mercury

Both S1 and S2 carbon, measures of labile, algal-derived OM (Sanei et al., 2006; Sanei and Goodarzi, 2006), increase markedly from the 1980s onwards (Table 4.1, Figure 4.3A). The nearly constant S2/RC down core denotes that there have been no significant

changes in the type of OM input to the sediments; the large increases near the surface are thus due to increased input of algal OM (Table 4.1; see Appendix B; also Outridge et al., 2007). Microscopic investigation establishes the OM as predominantly algal-derived (63% alginate, 81% of which were diatoms; 10% vitrinite; 14% plant liptinite; 12% char/inertinite), corroborating the Rock-Eval data. Pyrolysable carbon (PC, sum of S1, S2 and S3) forms a substantial portion of the total organic carbon (TOC) (33-41%, average 35%) (Table 4.1), higher than other surface sediments throughout the MRB (10-28%, average 19%) (Carrie et al., 2009), showing that younger, more labile OM derived mostly from algal OM is present at this site. With all OM fractions found to be highly correlated (e.g., S1 and S2; S2 and TOC; $r^2=0.96$, $p<0.01$), accelerated algal production is thus the most likely source of increases in sedimentary OM.

Climate warming and resultant physical change is clearly evident in the MRB. The mean annual air temperature for Norman Wells has seen a statistically significant increase ($r^2=0.18$, $p<0.01$) of $\sim 1.9^\circ\text{C}$ since the early 1970s (Figure 4.3B). This region has also seen a significant decrease in snow cover (March: $r^2=0.28$, $p<0.01$; April: $r^2=0.27$, $p<0.01$) over the same time period, losing approximately 1cm/yr for the end of March snow cover, and being devoid of snow at the end of April for most years since 1975 (see Appendix B). Reduction in ice-season length, and consequent improvement in the light regime for algal growth, is thus a plausible explanation for the coincidence between rising air temperature, algal productivity (Smol et al. 2005) and increasing HgT in northern lake sediment (see Outridge et al. 2007) since the early 1970s.

HgT concentrations increased in the upper slices of the Hare Indian Lake core with an approximate 1.5-fold increase over the last 30 years (Table 4.1). Similar increases

have been measured in sediment cores collected in many sub- and high Arctic lakes (Lockhart et al 1998; Outridge et al. 2007; Muir et al. 2009). These decadal increases seem to be occurring despite the fact that atmospheric mercury concentrations in the Arctic have not changed since at least the mid-1990s (Steffen et al. 2005) and have possibly even declined since the mid-1970s (Li et al. 2009).

Hare Indian Lake is situated in what can be described as the Mackenzie River floodplain (Maidment, 1993; Peters and Prowse, 2006); during spring ice break-up in some years, flooding of the lake by the sediment-rich Mackenzie River may occur, leading to an increase in coarser-grained sediment, which dilutes the OM present while adding trace amounts of inorganic Hg. Springtime flooding is suggested by the significant decreases in labile OM (S1 and S2) at the same depths as the highest measured sedimentation rates (e.g., near 5cm downcore, Table 4.1). To correct for potential geogenic inputs of inorganic Hg to the core sediments, HgT in each core slice was normalized against the conservative lithogenic element, Ti (Meyers et al., 2001; White, 2003; Sageman and Lyons, 2003). The almost perfect point-by-point match between HgT/Ti and S2, and the strong positive correlation ($r^2=0.77$, $p<0.01$; Figs. 4.3A and 4.3C), suggest that Hg inputs to sediments are strongly related to algal-derived organic matter from the water column, as proposed by Outridge et al. (2005, 2007) for other northern lakes.

4.4.3 The Link Between Algal Contaminant Scavenging and Increasing Contaminant Concentrations in Burbot

Striking temporal similarities are observed when HgT concentrations in burbot muscle and in Hare Indian Lake sediment core slices are plotted against year of collection and median year of deposition, respectively (Figure 4.4A). In addition, for years in which the median year of sediment deposition and year of burbot collections coincide, a moderately strong positive correlation between HgT in the burbot muscle and sediment is observed ($r^2=0.67$, $p<0.02$, Figure 4.4B). Algal blooms are efficient scavengers, concentrators, and possibly producers, of MeHg from and to the water column and hence sources of bioaccumulative Hg to larger biota (Balogh et al., 2002; Pickhardt et al., 2002; Luengen and Flegal, 2009). Although several studies (e.g., Pickhardt et al., 2002; Luengen and Flegal, 2009) show that algal blooms dilute the overall MeHg exposure to larger biota, our results suggest that this dilution is not as important in this environment and/or larger predators of all trophic levels are simply consuming more prey. We thus posit that the algal-derived OM-bound Hg is in some way impacting the HgT burdens in burbot.

The Hare Indian River, which drains Hare Indian Lake, was one of five tributaries in the MRB with higher levels of labile OM in sediments and showed a significant correlation between the sedimentary S1 and S2 fractions and HgT (Carrie et al., 2009; submitted). Hare Indian Lake is a likely source of this labile OM, as sedimentary OM concentrations there are significantly higher than those found in either the Hare Indian River or the Mackenzie River near its confluence with the Hare Indian River (S1: 2.70,

0.16 and 0.09 mg HCg⁻¹, respectively; S2: 11.75, 1.42 and 0.50 mg HCg⁻¹, respectively; and TOC: 4.25, 1.14 and 0.42 wt.%, respectively). Similarly, HgT concentrations were the highest in the Hare Indian Lake surface sediments (0.039 µg g⁻¹; Table 4.1) followed by the sediments from the Hare Indian River and Mackenzie River tributary and just upstream of the tributary along the Mackenzie (0.020 and 0.017 µg g⁻¹; Leitch et al. 2007), respectively. In addition, HgT concentrations and the percentage of dissolved vs. particulate HgT in the surface water were higher in the tributary (6.20 ng L⁻¹; 99%) relative to the Mackenzie River (5.56 ng L⁻¹; 39%). Clearly, the lake is substantially more productive than either river, and because it drains into the Mackenzie River the lake is probably an important source of OM-bound Hg to local aquatic biota such as burbot.

In the Pacific Ocean, microbial processing of algal OM has been shown to act on the associated inorganic Hg to produce methyl-mercury (MeHg) (Sunderland et al. 2009). The possible link between algal-bound Hg from Hare Indian Lake and MeHg production is demonstrated by the co-occurrence in lake sediments of sulphate-reducing bacteria and diatoms (Figure 4.5). Because MeHg production by sulfate-reducing bacteria is known to depend on the supply of labile organic matter (Kainz et al. 2003), climate-driven variations in lake algal productivity could easily support similar variations in production of MeHg. Thus climate variation leading to variation in algal productivity supports both the sedimentary pathway for HgT and the methylation process, which leads to potential increases in fish exposure. Inorganic Hg bound in algal OM exported from the lake may itself also be more bioavailable than dissolved or mineral-bound Hg forms.

While tagging data on MRB burbot are scarce, the results of a study conducted in Aklavik (450 km away in the Mackenzie Delta) found that 93% of burbot (n=98) stayed

within 15 km of their tagging point (Stein et al., 1973). Also, Hare Indian Lake is characteristic of burbot feeding habitat (McPhail and Lindsey, 1970; Scott and Crossman, 1973). Thus, it is very probable that the Mackenzie River burbot analysed in this study feed in the more biologically productive organic carbon and Hg-rich Hare Indian River tributary which is located only a few kilometres from where they were captured (see Figure 4.1).

While PCB concentrations in the Hare Indian Lake sediment core were not measured (due to lack of material available), other studies of Arctic lake sediment cores (Krummel et al., 2009; Muir et al., 1996; Stern et al., 2005) have noted surface enrichments of PCBs, which run counter to well-documented recent declines in global production, usage and atmospheric cycling (Breivik et al. 2002). In particular, Stern et al. (2005) reported that the post-1950 fluxes of PCBs and a range of pesticides in Lake DV-09 sediments on Devon Island were strongly correlated to changes in diatom numbers, which was taken as possible evidence of a climate-driven effect on the sedimentary accumulation of these compounds. If similar processes apply in Hare Indian Lake and its surrounding region, it would suggest that the observed increase in burbot liver PCB (and DDT) concentrations could also be linked to climate warming and the resulting increase in primary productivity. A significant correlation between CB-153 and HgT in burbot liver ($r^2=0.72$, $p<0.01$) was also observed.

Many studies on Arctic contaminants suggest that rate of atmospheric deposition, supported by vapour and particulate concentrations in the atmosphere, is the primary driver behind the continued accumulation of contaminants in Arctic marine and freshwater biota (Braune et al., 2005). Yet, the large recent increases in biotic burdens of

contaminants such as Hg and PCBs, simply do not match the concurrent decreasing or stable atmospheric concentrations: other environmental processes must be operating. We have shown that under a general warming trend, with concomitant decreases in the ice-cover season, that large increases in primary productivity, such as in Hare Indian Lake, has occurred since about the early 1980s. This result suggests that the significant rise in HgT (and possibly PCB) content recorded in the sediments since this time may be strongly influenced by increased concentrations of algal-derived OM in the water-column. This, in turn, likely increases the scavenging rate of “available” Hg and PCBs from the water column, potentially enhances MeHg production, and likely increases bioavailability.

4.5 Acknowledgements

Funding and support for the burbot collections and analysis was provided by the Canadian Departments of Fisheries and Oceans (Winnipeg, Hay River) and Indian and Northern Affairs (the Northern Contaminants Program). This study would not have been possible if not for the community of Fort Good Hope, NWT. Whole fish samples were both collected and shipped to FWI by the community residents as part of an ongoing community monitoring program. The authors would also like to thank George Low, Rob Smith and Fred Taptuna (DFO, Hay River) for their help with the organization of the burbot collections and for acting as a liaison between ourselves and the resident of Fort Good Hope. The collection and analysis of the sediment core from Hare Indian Lake was

made possible through funding from ArcticNet, the Polar Continental Shelf Project (PCSP) and the Geological Survey of Canada (Calgary).

4.6 Supplementary Content Notice (Appendix B, pp. 137-143)

A detailed discussion on the redox processes in the sediment core are presented in Appendix B. Information on radiometric dating of the core (Pb-210, Cs-137) is in Table B.1 and Figure B.1. Figure B.2 shows plots of selected redox sensitive elements down core. A plot of S₂/RC down core, which shows stable values suggesting similar sources of organic matter over time, is given in Figure B.3. Finally, end of month snow depth (for March and April) for Norman Wells for 1946-2008, a community close to Fort Good Hope which acts as a proxy for climate in Fort Good Hope, is shown in Figure B.4.

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4.8 Tables and Figures

Table 4.1: Concentrations values for HgT, and S1 and S2 carbon and percent weight residual, pyrolysable and total organic carbon in the Hare Indian Lake sediment core.

Depth (cm)	Year ¹	Sed Rate ² (g m ⁻² yr ⁻¹)	[HgT] (µg g ⁻¹ , dw)	[Ti] (µg g ⁻¹)	[S1] (mg HCg ⁻¹ , dw)	[S2] (mg HCg ⁻¹ , dw)	RC (wt.%)	PC (wt.%)	TOC (wt.%)
0.25	2008	459	0.0396	43.93	3.80	15.1	2.94	2.07	5.01
0.75	2005	358	0.0390	47.93	4.02	15.0	3.03	2.06	5.09
1.25	2002	303	0.0403	42.67	4.27	15.8	3.20	2.16	5.36
1.75	2000	322	0.0430	43.91	3.08	12.9	2.83	1.78	4.61
2.25	1997	330	0.0318	41.99	2.85	13.0	2.93	1.76	4.69
2.75	1994	387	0.0280	42.82	2.33	10.5	2.37	1.45	3.82
3.25	1992	440	0.0306	46.13	2.22	10.2	2.47	1.40	3.87
3.75	1990	434	0.0424	55.29	1.97	9.60	2.35	1.33	3.68
4.25	1987	438	0.0306	53.56	1.43	8.52	2.21	1.16	3.37
4.75	1984	686	0.0292	56.17	1.06	6.85	2.05	0.93	2.98
5.25	1982	1099	0.0258	55.65	0.82	5.84	1.47	0.80	2.27
5.75	1979	531	0.0251	53.82	1.01	7.18	1.53	0.93	2.46
6.25	1977	522	0.0256	56.97	1.13	7.61	1.59	0.96	2.55
6.75	1973	551	0.0353	58.06	1.02	7.18	1.93	0.92	2.85
7.25	1970	388	0.0380	57.06	1.38	8.52	2.17	1.10	3.27
7.75	1967	500	0.0333	59.49	1.42	8.32	2.21	1.08	3.29
8.25	1963	416	0.0334	57.10	0.99	7.24	1.66	0.87	2.53
8.75	1958	263	0.0329	56.07	1.49	9.40	2.39	1.23	3.62
9.25	1953	342	0.0293	52.02	1.52	9.10	1.74	1.14	2.88
9.75	1949	320	0.0272	54.50	1.32	8.03	1.53	0.93	2.46
10.5	1944	446	0.0251	51.70	0.88	6.66	1.51	0.87	2.38

Depth (cm)	Year ¹	Sed Rate ² (g m ⁻² yr ⁻¹)	[HgT] (µg g ⁻¹ , dw)	[Ti] (µg g ⁻¹)	[S1] (mg HCg ⁻¹ , dw)	[S2] (mg HCg ⁻¹ , dw)	RC (wt.%)	PC (wt.%)	TOC (wt.%)
11.5	1935	399	0.0222	46.59	0.79	5.90	1.63	0.81	2.44
12.5	1927	515	0.0235	57.32	0.77	6.26	1.42	0.85	2.27
13.5	1916	250	0.0293	55.44	0.75	6.09	1.44	0.84	2.28
14.5	1897	163	0.0300	46.51	0.84	6.38	1.44	0.84	2.28
15.5	1864	89	0.0274	54.53	0.56	4.84	1.18	0.65	1.83

¹Median year of deposition; ²Sedimentation rates were calculated using CRS model (Wilkinson and Simpson, 2003).

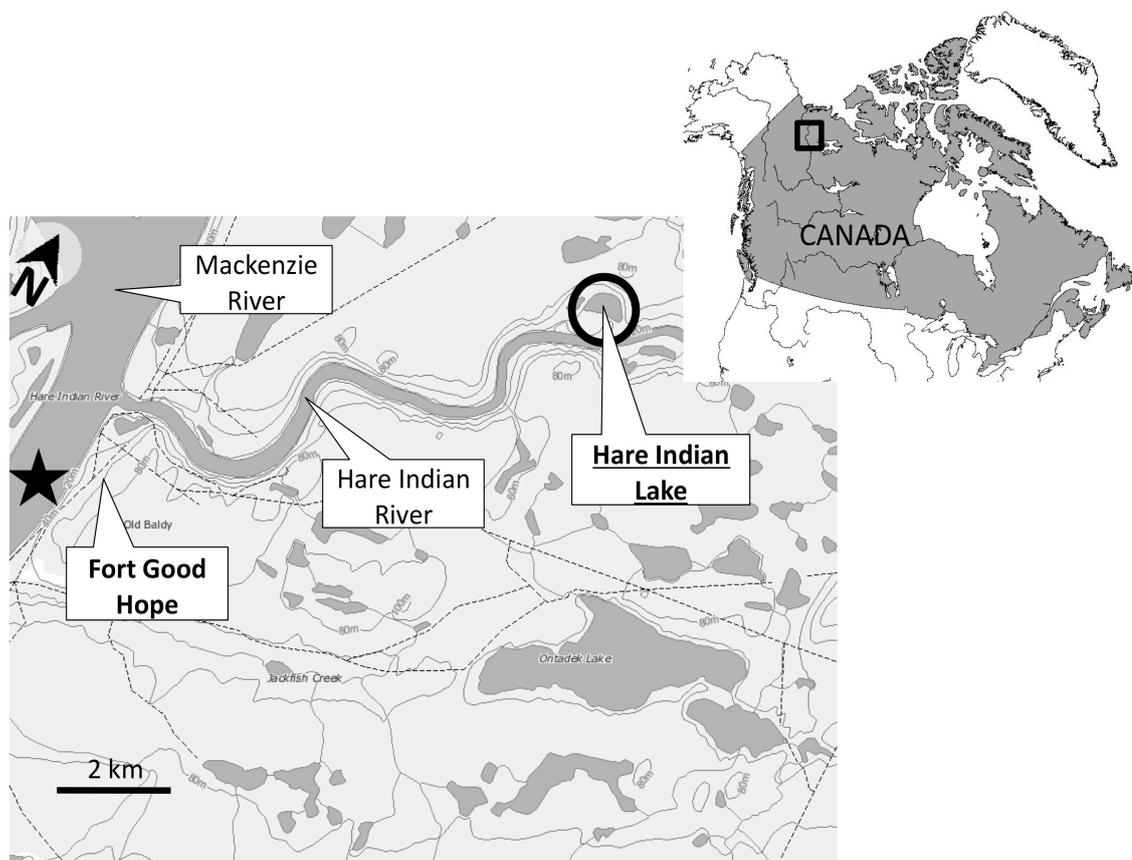


Figure 4.1: Map of Fort Good Hope region, showing fish collection site (star) and lake sediment core (circle, Hare Indian Lake).

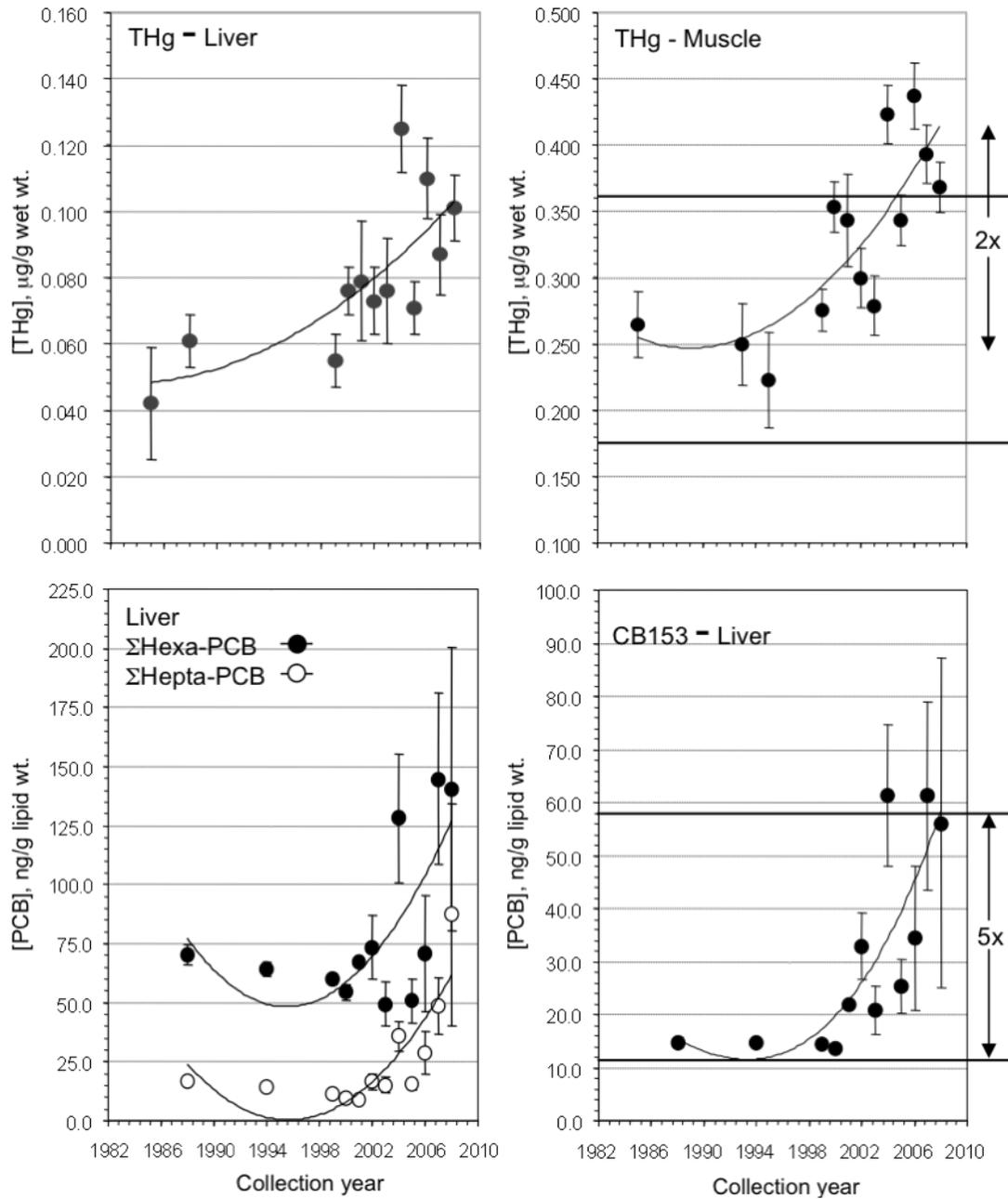


Figure 4.2: Mean (± 1 SE) contaminant concentrations in Mackenzie River Burbot.

(A) Liver HgT, (B) Muscle HgT, (C) Sum of Hexa and Hepta PCB congeners, (D) CB

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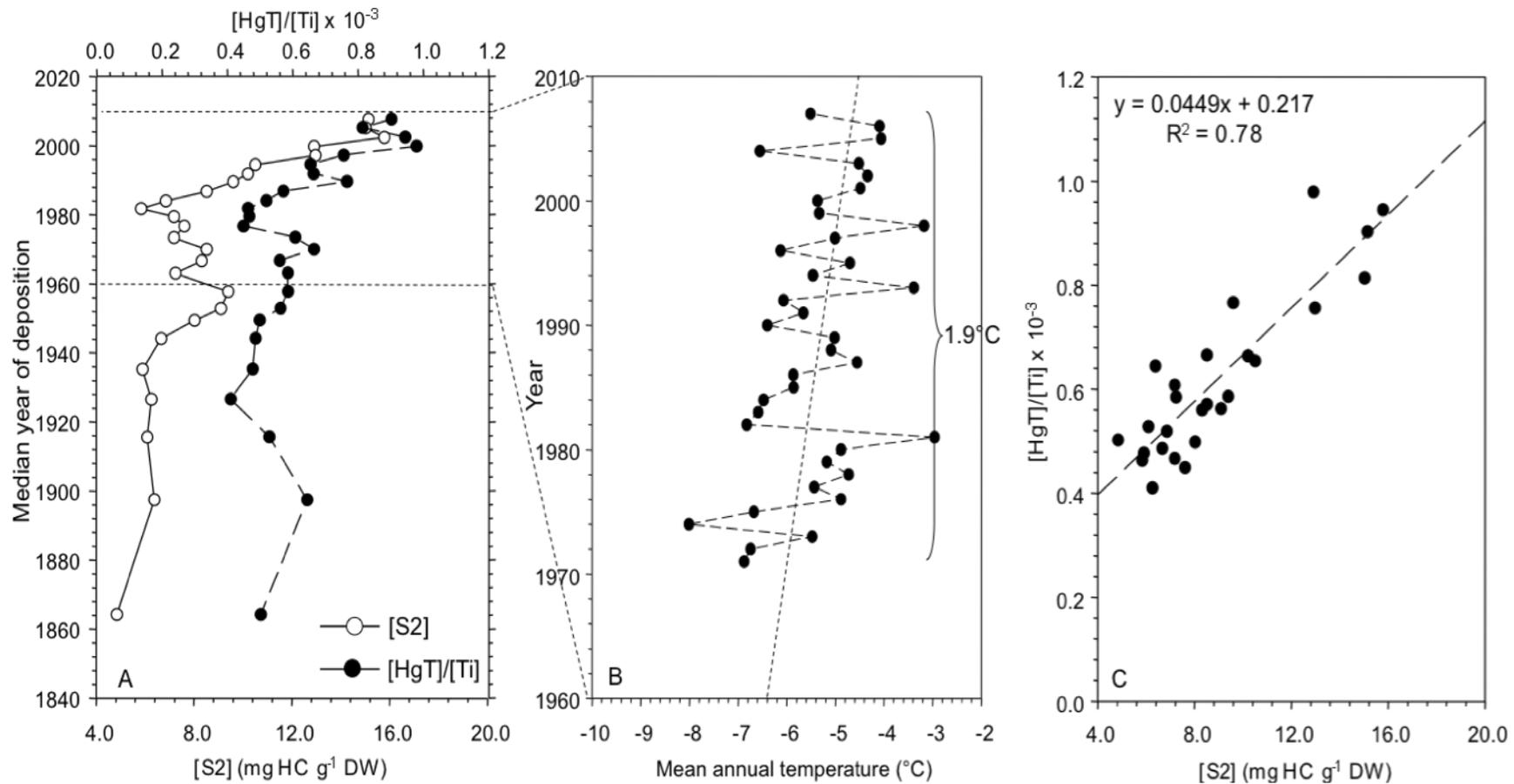


Figure 4.3: (A) Point by point comparison between [THg]/[Ti] and S2 carbon concentrations in the Hare Indian lake sediment core, (B) mean annual air temperatures at Norman Wells, NWT and (C) regression line for correlation between [HgT]/[Ti] and [S2] (C).

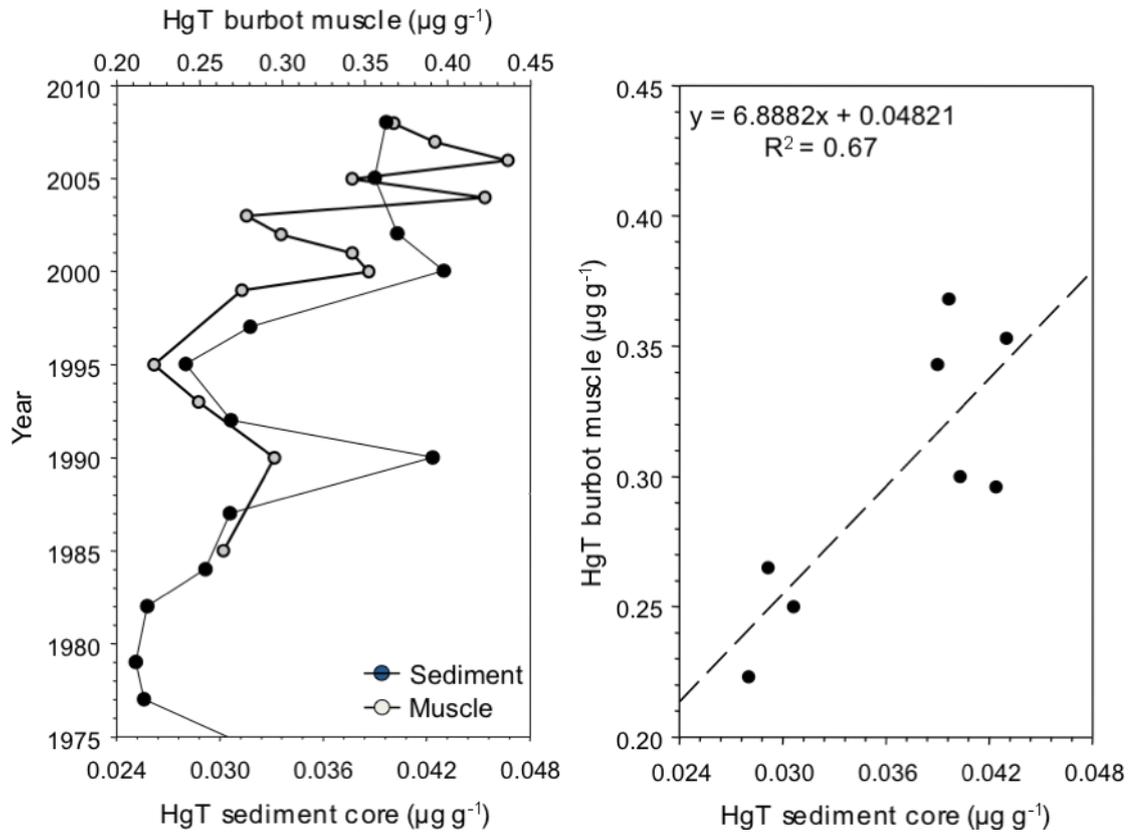


Figure 4.4: Chronological variations (1977-2008) of HgT concentrations in Hare Indian Lake sediment core and in Mackenzie River burbot (left) and regression line showing the good correlation between HgT in burbot muscle and sediment core slices (median year of deposition) in corresponding years (right).

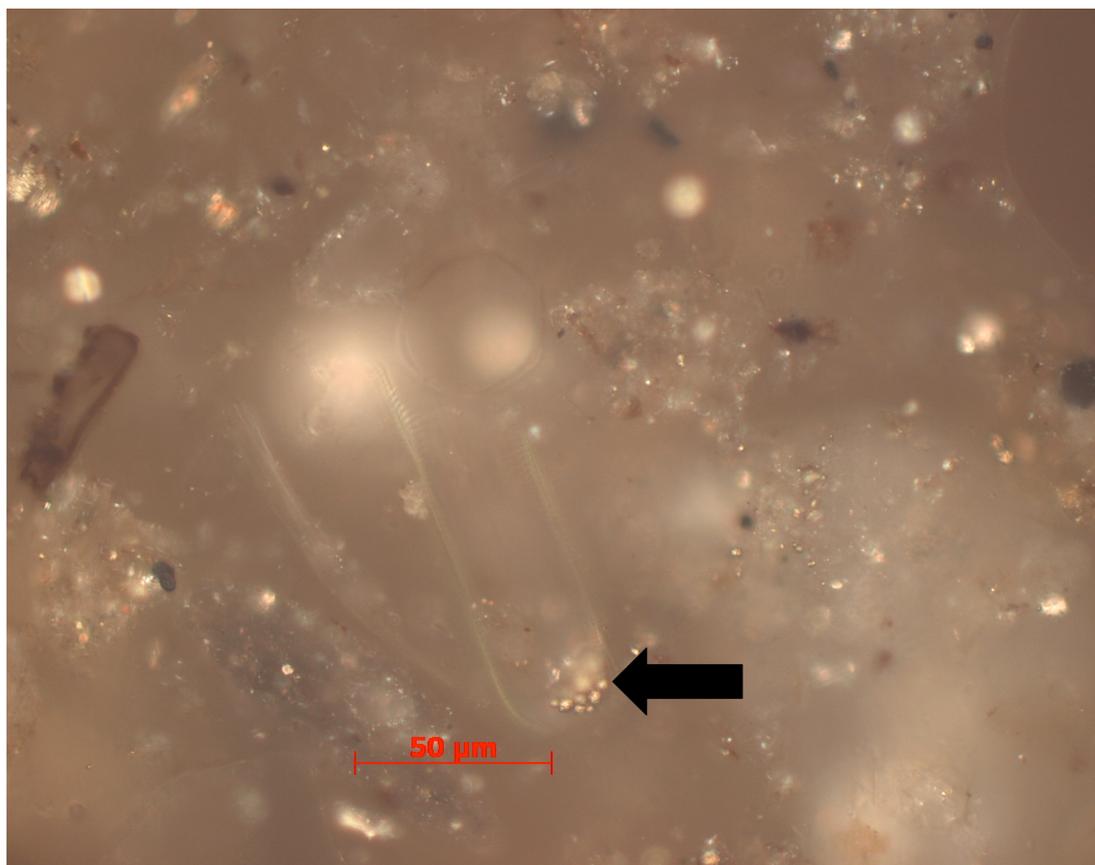


Figure 4.5: White light photomicrograph of a sulfate-reducing bacteria (framboidal pyrite grains, black arrow), known mercury methylators, inside a diatom.

Chapter 5: Conclusion

5.1 Conclusion

The overarching premise of this study was to determine the links between labile organic matter and Hg, and how this affects Hg in biota in the Mackenzie River Basin. First, it is important to note that the Mackenzie River itself acts as a source of Hg. Strong erosion of its banks is driven by the strong water discharge and the scouring effect of ice during spring breakup. This is particularly evident in the case of the large coal outcrop in the middle reaches of the river, which is the source of approximately one-sixth of the total Hg reaching the Mackenzie Delta. While no studies on the mode of occurrence of Hg in these coals has been done to date, Hg is frequently found to be bound to pyrite (FeS_2) (Finkelman, 1999), which is of low bioavailability, and is not likely to contaminate biota.

Clearly, the Mackenzie River Basin is a complex system, but one that may be partitioned into two main geographical regions with distinct hydrological, geological and biogeochemical characteristics which play into OM and Hg cycling: the mountainous zone to the west of the Mackenzie River, and the peatland zone, situated mostly to the east and south of the Mackenzie River.

The overall trend for the mountainous zone is an area subject to the effects of forest fires, and low productivity. Maceral analysis showed that inertinite was the most common maceral, with very little algal matter present. Rock-Eval analysis showed that this region was dominated by refractory C, which the petrography showed was predominantly char. Previous studies on forest fires and OM diagenesis

have proved that this type of OM is not likely to contain significant OM-bound Hg, nor is it likely to be bioavailable.

Of the two zones, the mountainous zone dominates the water, sediment and Hg flux to the Beaufort Sea. Abundant sulfide minerals are present in the form of base metal, SEDEX and MVT deposits, all of which are known to be enriched in Hg. Consequently, sedimentary Hg concentrations in this zone are several-fold higher than those seen in the tributaries as they enter the Mackenzie River. The majority of the mountainous zone Hg is particulate bound, derived from sulfide oxidation and weathering, and thus of low bioavailability.

The peatland zone has a lesser impact on the overall hydrogeochemical and physical characteristics of the Mackenzie River and has no significant Hg-bearing minerals. It is mainly petrogenic, and, as the name of the zone suggests, contains abundant peat, which is the precursor to coal. Notably, peats are known accumulators of Hg (Cortizas et al., 2007). However, what is more important is that this zone contains substantial quantities of labile OM (all but one of the sites with the highest amount of labile OM are present). This has strong implications for Hg cycling and bioavailability, as labile OM is an efficient transporter of metals such as Hg, and is readily consumed by biota. Furthermore, in the sites with the highest S1 concentrations, significant correlation was noted with S1 and Hg, suggesting that Hg is preferentially bound to the labile OM and thus of greater bioavailability. What this study shows is that this is especially so in lakes and lake-fed tributaries which are abundant in this zone.

Most fish, such as the burbot studied here, spend part or all of their life history in lakes, and are thus greatly affected by any changes that occur in these lakes. We have shown that a lake near Fort Good Hope, Northwest Territories- which has

experienced significant warming over the last 40 years- has seen notable increases in primary productivity. Concurrent trends in Hg were also apparent. A multi-faceted approach has shown that Hg cycling in lake sediment is governed to a large degree by OM production. The strength of this approach was even more evident when taking into account detrital inputs of sediment from the flooding by the heavily sediment-laden Mackenzie River which dilute the OM-Hg link. The warming temperatures have thus brought on longer ice-free periods, engendering more primary producers that are able to remove Hg from the water column, demonstrating that the Hg scavenging hypothesis is correct in a sub- and High Arctic context. Furthermore, strong correlations between sedimentary Hg and Hg in burbot over the last 25 years were shown, proving that a change in the C cycle, derived from a warming climate, is just as or even more important than increases to atmospheric Hg loadings to the concentrations found in aquatic biota.

5.2 Remaining Questions and Future Work

5.2.1 Organic Matter

The strong dependence on seasonality and discharge on OM characteristics in Arctic systems (Raymond et al., 2007), delivers new questions on the cumulative analysis of OM in this study. For example, younger OM is typically found in the early spring during high discharge events, likely as the extensive flooding removes fresher OM from soils (Raymond et al., 2007). This more labile OM is more likely to bind metals such as Hg. Linking the two temporally is thus of great importance, especially in the light of the link of labile OM to fish Hg levels. Furthermore, what is

the spatial distribution of this OM? No measures of the age of the particulate and dissolved OM were taken in this study, nor were measures of lability in the DOC. While the logistical difficulties of sampling in the basin are tremendous, a cruise similar to the ones undertaken during the summers of 2003-05 could be used to collect water samples for DOC, and analysis of lability could be done with excitation-emission fluorescence measurements (Wilson and Xenopoulos, 2009).

5.2.2 Natural Springs

The impact of natural springs in the mountainous zone on Hg and MeHg concentrations remains unknown. Natural springs are present virtually everywhere in the mountainous zone, and have all of the characteristics of acid mine drainage, unless sufficient carbonates are present to buffer the acidity (Caron, 2007). While nearby stream sediments were analysed for Hg- in some cases reaching as high as 8334 ng/g or over 250 times the average concentration seen in the sediments analysed in this study- water samples were not taken for Hg. Winch et al. (2008) and Boyd et al. (2009) have demonstrated that MeHg may form in these high SO_4^{2-} waters and be taken up by bacteria and microbial mats. Given the range in pH of these springs and the high runoff of this area, these sites thus present an excellent opportunity in which to test Hg methylation rates *in situ* and the impact they may have on concentrations seen farther downstream.

5.2.3 Forest Fires

Several studies on the effects of wildfires on Hg have been published (e.g., Turetsky et al., 2006; Friedli et al., 2003; Friedli et al., 2007). The low population density in the Mackenzie River Basin translates to a natural cause for most fires, with the result that most fires are allowed to follow their natural course. Consequently, most of the fires in the MRB are rather large, and burn large tracts of land, especially abundant Hg- and OM-rich peat, and thus have the possibility of greatly affecting the Hg cycle. However, no concrete data exists on Hg or OM in the Northwest Territories. Nonetheless, extrapolations using the area burned per year and data from elsewhere in Canada (Friedli et al., 2003; Turetsky et al., 2006) could be used to determine the approximate amount of Hg released per year in the MRB.

5.2.4 The Big One: the Mackenzie Delta

There is very little data (Graydon et al., 2009) on the processes governing Hg cycling in the Mackenzie Delta before the abundant OM and Hg is released to the Arctic Ocean. What is known is that total Hg concentrations drop, while MeHg concentrations stay approximately stable through the delta (Graydon et al., 2009). Further, according to Macdonald et al. (1998), much of the OM exiting the delta has likely been resuspended, meaning it has undergone some sort of change during its tenure there. The varying lake-sill heights (Marsh and Hey, 1989) also affect the Hg and OM cycles (Graydon et al., 2009). Most importantly, most studies of biota in the Beaufort Sea (Gaden et al., 2009; Lockhart et al., 2005; Loseto et al., 2008), which is greatly affected by the Mackenzie River, show high Hg concentrations, and processes

involving the Hg and OM (largely from the Mackenzie) within the delta and shelf are likely drivers of these high concentrations. A more detailed analysis of the delta, and its myriad lakes, is thus warranted.

5.3 Summary and Closing Statement

This is the first study on the composition of sedimentary OM throughout the MRB; it also fills in the numerous knowledge gaps with respect to sources of Hg to the MRB initially presented in Leitch et al. (2007). This thesis also shows that the hypothesis of Outridge et al. (2007) is applicable to more complex sub-Arctic environments, and is the first to show that climate variation may be affecting aquatic biota via changes to the biogeochemical cycling of Hg.

In sum, this thesis demonstrates how a warming climate can significantly alter the C cycle, even over a short time period, and how this affects the Hg cycle and the biota that consume it, quickly reaching the highest echelons of the foodweb in short order. This is also the first study to prove a direct link between climate-change induced increases in primary produced C and Hg exposure in upper trophic level biota (burbot). Further, this study shows that the algal-scavenging hypothesis likely holds true for other atmospherically transported contaminants such as polychlorinated biphenyls (PCBs). PCB levels in the atmosphere have been stagnant or decreasing over the last 25-30 years, yet levels of highly chlorinated PCBs in biota like burbot continue to rise. Indeed, as has been seen in Chapter 4, PCBs have also dramatically increased in the liver of the Fott Good Hope burbot, and, like Hg, this increase is almost certainly associated with the increasing labile OM found in Hare Indian Lake.

Clearly, we must take a detailed view of the C cycle into consideration when looking at contaminants in aquatic biota and long-term trend evidence from sediment cores.

5.4 References

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Appendix A:

Supplementary Information for Chapter 3:

Biogeochemical controls of mercury in the Mackenzie River Basin

A.1 Sequential extraction procedures for determining Hg speciation in sediments

A subset of the freeze-dried sediment samples (n=6) draining the Mackenzie Mountains (Figure 3.2, see Chapter 3) were further analyzed for Hg speciation. One gram of sediment was placed in a clean, 50 mL polypropylene centrifuge tube, and was subject to a four-step sequential extraction procedure modified from (Tessier et al., 1979; Sanei et al., 2001). The first fraction (F1), defined as exchangeable (Tessier et al., 1979), was extracted by the addition of 8 mL 1M MgCl₂ adjusted to pH 7. The sample was agitated for 1 hr, centrifuged at 3000 rpm for 20 min, and 1 mL of the supernatant was extracted by pipette and diluted to 50 mL in ultrapure water. The remainder of the supernatant was decanted, and 10 mL of ultrapure water was added to the tube, centrifuged at 3000 rpm for 20 min, and decanted. The second fraction (F2), defines the carbonates-bound Hg (Tessier et al., 1979), was extracted with 8 mL of 1M NaOAc adjusted to pH 5 with acetic acid and agitated for 5 hr at room temperature. The sample was centrifuged, 1 mL was extracted by pipette and diluted to 50 mL, and decanted as above. The third fraction (F3), defined as bound to Fe-Mn oxides (Tessier et al., 1979), was extracted with 20 mL of 0.04M NH₂OH•HCl in 25% (v/v) acetic acid. Samples were heated at 96°C for 6 hr on a Digi-Prep block heater (SCP Science, Champlain, NY). Samples were diluted 1:100 with ultrapure water. The final extraction step (F4), defined as bound to sulfides and organic matter, involved the addition of 10 mL of concentrated HNO₃, and the vials were left in a fumehood overnight. The supernatant was diluted 1:500 with ultrapure water. The diluted extractants from each step were analyzed for Hg by cold vapor atomic fluorescence

spectroscopy (CVAFS) on a Tekran 2600 Mercury Analyzer following USEPA Method 1631 (USEPA, 2002). The sum from the sequential extractions gave 95-115% of the total Hg concentrations reported earlier (Leitch et al., 2007). Accuracy based on BCR-079 was better than 5% using an external calibration curve, and precision (as relative standard deviation) was better than 7%. Procedural blanks were run through the entire extraction process to determine any possible contamination of Hg.

A.2 Tables

Table A1: Mercury, organic matter and other characteristics of the surface water and surface sediments from the Mackenzie Basin. Hg_D, Hg_P, Hg_T: dissolved, particulate and total Hg in surface water; MeHg: methylmercury; DOC: dissolved organic carbon; Hg_S: total Hg in sediments; S1, S2, S3, RC: Rock-Eval fractions of organic matter; TOC: total organic carbon; HI: hydrogen index; OI: oxygen index.

Sample	Surface water							Surface sediments							
	Hg _D (ng/L)	Hg _P (ng/L)	Hg _T (ng/L)	MeHg (ng/L)	DOC (mgC/L)	SO ₄ ²⁻ (mg/L)	Cl (mg/L)	Hg _S (mg/kg)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	RC (wt.%)	TOC (wt.%)	HI	OI
Mainstream sites:															
At Point Separation	1.53	6.64	8.79	0.128	3.44	40.2	9.87	-	-	-	-	-	-	-	-
Below Arctic Red R.	1.67	2.48	4.29	0.062	8.50	29.5	9.00	0.040	0.05	0.67	1.83	0.71	0.83	81.0	220
At Travaillant R.	7.49	2.94	11.0	0.099	3.59	38.2	9.86	0.007	0.08	0.50	1.26	0.49	0.59	85.0	214
Below Ontaritue R.	6.31	2.46	8.77	0.020	2.98	44.1	11.3	0.009	0.03	0.16	0.48	0.15	0.19	84.0	253
Above Ontaritue R.	6.31	2.46	8.77	0.020	3.79	37.5	9.73	0.009	0.09	0.50	0.85	0.33	0.42	119	202

Sample	Hg _D (ng/ L)	Hg _P (ng/ L)	Hg _T (ng/ L)	MeHg (ng/L)	DOC (mgC /L)	SO ₄ ²⁻ (mg/ L)	Cl (mg/L)	Hg _S (mg/kg)	S1 (mgHC /g)	S2 (mgHC /g)	S3 (mgCO ₂ / g)	RC (wt. %)	TOC (wt. %)	HI	OI
Above Hare Indian R.	2.16	3.40	6.44	0.071	-	-	-	0.017	0.03	0.16	0.73	0.28	0.32	50. 0	228
Below Mountain R.	9.47	5.73	19.8	0.020	-	-	-	0.043	0.09	0.63	0.92	0.52	0.63	100	146
Above Mountain R.	5.51	8.15	16.3	0.048	-	-	-	0.012	0.10	0.58	0.91	0.38	0.50	116	182
Below Great Bear R.	4.89	6.10	10.9	0.060	-	-	-	0.010	0.11	0.49	0.86	0.32	0.40	122	215
Above Norman Wells	3.01	3.22	6.08	0.039	3.71	30.4	7.25	0.007	0.01	0.03	0.29	0.05	0.07	43. 0	414
Above Great Bear R.	4.16	5.47	9.63	0.041	-	-	-	0.013	0.04	0.19	0.65	0.25	0.30	63. 0	217
Above Keele R. Below Redstone R.	5.67	5.02	10.7	0.115	3.31	43.4	7.30	0.029	0.09	0.47	0.71	0.33	0.40	118	178
Above Redstone R.	1.50	4.86	6.35	0.049	2.30	77.8	8.26	0.015	0.06	0.29	0.50	0.22	0.27	107	185
Below Dahadinni R.	3.80	3.60	7.39	0.097	4.30	30.2	10.0	0.023	0.04	0.40	1.12	0.44	0.51	78. 0	220
Below Blackwater R.	1.43	4.26	5.69	0.086	-	-	-	0.016	0.09	0.59	1.09	0.42	0.53	111	206
Below Wrigley R.	1.03	2.24	3.27	0.076	4.51	31.1	13.8	0.032	0.13	1.01	1.54	0.56	0.71	142	217
Above Wrigley R.	-	-	-	-	-	-	-	0.010	0.02	0.11	0.67	0.17	0.20	55. 0	335
Below Willowlake R.	1.65	14.2	15.9	0.187	4.28	36.8	3.71	0.010	0.10	0.67	1.18	0.54	0.66	102	179
	1.15	1.94	3.32	0.035	4.38	26.1	8.29	0.009	0.02	0.13	0.65	0.26	0.29	45. 0	224

Sample	Hg _D (ng/L)	Hg _P (ng/L)	Hg _T (ng/L)	MeHg (ng/L)	DOC (mgC/L)	SO ₄ ²⁻ (mg/L)	Cl (mg/L)	Hg _s (mg/kg)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	RC (wt.%)	TOC (wt.%)	HI	OI
Below Liard R.	2.55	4.47	7.02	0.053	5.08	36.2	1.47	0.009	0.00	0.01	0.22	0.00	0.03	33.	733
<i>Mean</i>	<i>3.75</i>	<i>4.72</i>	<i>8.96</i>	<i>0.069</i>	<i>4.17</i>	<i>38.6</i>	<i>8.45</i>	<i>0.017</i>	<i>0.06</i>	<i>0.40</i>	<i>0.87</i>	<i>0.34</i>	<i>0.41</i>	87.	251
<i>Median</i>	<i>3.01</i>	<i>4.26</i>	<i>8.77</i>	<i>0.060</i>	<i>3.79</i>	<i>36.8</i>	<i>9.00</i>	<i>0.012</i>	<i>0.06</i>	<i>0.47</i>	<i>0.85</i>	<i>0.33</i>	<i>0.40</i>	85.	217
<i>SD</i>	<i>2.48</i>	<i>2.86</i>	<i>4.44</i>	<i>0.043</i>	<i>1.49</i>	<i>13.0</i>	<i>3.15</i>	<i>0.011</i>	<i>0.04</i>	<i>0.27</i>	<i>0.41</i>	<i>0.18</i>	<i>0.22</i>	31.	131
Peel R.	1.71	3.58	6.72	0.042	0.78	80.6	2.75	0.030	0.17	1.28	1.88	0.94	1.14	8	165
Arctic Red R.	1.96	5.06	7.02	0.098	1.31	128	0.83	0.089	-	-	-	-	-	-	-
Mountain R.**	2.07	6.46	9.44	0.041	1.38	113	2.58	0.027	0.39	2.65	1.02	0.79	1.08	94.	245
Keele R.	1.41	2.42	3.83	0.045	1.61	113	7.95	0.019	0.03	0.17	0.67	0.27	0.33	52.	203
Redstone R.	1.88	5.09	6.97	0.049	1.69	92.9	8.09	0.034	0.06	0.49	1.12	0.51	0.60	82.	187
Dahadinni R.	2.51	6.26	7.25	0.025	6.06	191	1.76	0.055	0.11	0.97	1.82	0.76	0.92	105	198
Ochre R.	8.62	1.00	13.7	0.054	4.51	99.0	9.61	0.037	0.08	0.72	1.86	0.60	0.74	97.	251
Root R.	0.99	3.86	5.50	0.075	1.75	85.4	6.64	0.038	0.04	0.48	1.91	0.58	0.71	68.	269
N. Nahanni R.	2.44	4.42	7.94	0.028	2.09	79.4	15.4	0.011	0.05	0.21	0.68	0.24	0.29	72.	234
Liard R.	3.13	4.87	8.00	0.081	4.63	38.8	0.85	0.012	0.05	0.24	0.76	0.25	0.31	77.	245
<i>Mean</i>	<i>2.67</i>	<i>4.30</i>	<i>7.63</i>	<i>0.054</i>	<i>2.58</i>	<i>102</i>	<i>5.65</i>	<i>0.035</i>	<i>0.11</i>	<i>0.80</i>	<i>1.30</i>	<i>0.55</i>	<i>0.68</i>	101	205

Sample	Hg _D (ng/ L)	Hg _P (ng/ L)	Hg _T (ng/ L)	MeHg (ng/L)	DOC (mgC /L)	SO ₄ ²⁻ (mg/ L)	Cl (mg/L)	Hg _s (mg/kg)	S1 (mgHC /g)	S2 (mgHC /g)	S3 (mgCO ₂ / g)	RC (wt. %)	TOC (wt. %)	HI 82.	OI 203
<i>Median</i>	2.02	4.65	7.14	0.047	1.72	96.0	4.70	0.032	0.06	0.49	1.12	0.58	0.71	0	203
<i>SD</i>	2.17	1.67	2.60	0.024	1.79	39.7	4.74	0.023	0.11	0.79	0.56	0.26	0.33	57.	53.
Ontaritue R.	5.29	1.89	7.17	0.138	3.53	43.5	11.8	0.057	-	-	-	-	-	-	-
Hare Indian R.**	6.11	0.09	9.07	0.094	4.82	408	4.49	0.012	0.16	1.42	3.15	0.87	1.14	125	276
Stinky Creek	-	-	-	-	16.2	147	46.9	-	-	-	-	-	-	-	-
Great Bear R.**	2.16	0.61	3.71	0.032	1.94	11.3	5.03	0.025	0.25	1.47	1.93	0.77	1.02	144	189
Big Smith Creek	0.98	0.11	1.46	0.020	5.46	461	226	0.035	-	-	-	-	-	-	-
Blackwater R.	1.35	0.17	1.98	0.089	10.2	65.6	48.8	0.025	0.07	0.65	1.45	0.49	0.61	107	238
White Sands Creek	-	-	-	-	3.90	34.4	6.53	0.009	0.05	0.31	0.94	0.25	0.34	91.	276
Wrigley R.	0.95	8.27	8.10	0.084	5.29	69.0	95.9	0.033	0.05	0.55	1.62	0.58	0.70	79.	231
River Between Two Mountains	1.45	0.99	3.34	0.042	9.79	18.6	6.61	-	-	-	-	-	-	-	-
Willowlake R.	2.73	1.14	4.95	0.103	11.6	33.6	100	0.042	0.10	1.23	2.65	0.95	1.15	107	230
Jean Marie R.	2.85	1.68	4.59	0.133	12.5	12.1	2.83	0.015	-	-	-	-	-	-	-
Trout R.	2.59	0.80	4.51	0.175	11.5	8.0	1.06	0.019	-	-	-	-	-	-	-
Horn R.**	1.05	1.46	3.21	0.020	19.9	258	59.4	0.025	0.60	4.53	3.65	1.54	2.16	210	169
South Channel**	1.48	0.68	2.65	0.069	4.28	24.8	9.39	0.016	0.16	0.57	0.30	0.24	0.31	184	0
<i>Mean</i>	2.42	1.49	4.56	0.083	8.64	114	44.6	0.023	0.18	1.34	1.96	0.71	0.93	131	213
<i>Median</i>	1.82	0.90	4.11	0.087	7.63	39.0	10.6	0.025	0.13	0.94	1.78	0.68	0.86	116	231
<i>SD</i>	1.69	2.22	2.41	0.050	5.32	152	62.6	0.010	0.18	1.36	1.13	0.43	0.60	45.	59.

Sample	Hg _D (ng/L)	Hg _P (ng/L)	Hg _T (ng/L)	MeHg (ng/L)	DOC (mgC/L)	SO ₄ ²⁻ (mg/L)	Cl (mg/L)	Hg _S (mg/kg)	S1 (mgHC/g)	S2 (mgHC/g)	S3 (mgCO ₂ /g)	RC (wt.%)	TOC (wt.%)	8	9
														HI	OI
<u>Basin-wide</u>															
Mean	3.10	3.67	7.35	0.069	5.43	84.2	21.4	0.024	0.10	0.71	1.22	0.47	0.59	100	231
Median	2.16	3.40	7.02	0.060	4.28	43.4	8.26	0.019	0.08	0.50	0.98	0.43	0.52	5	217
SD	2.24	2.77	3.94	0.042	4.31	99.8	42.0	0.017	0.11	0.83	0.78	0.30	0.41	44.	103
<u>All tributaries</u>															
Mean	2.53	2.77	5.96	0.070	6.11	109	28.4	0.030	0.14	1.06	1.61	0.63	0.80	115	209
Median	2.02	1.79	6.11	0.062	4.57	80.0	7.30	0.026	0.08	0.65	1.62	0.58	0.71	105	230
SD	1.88	2.41	2.90	0.042	5.15	117	51.0	0.019	0.15	1.09	0.91	0.35	0.48	52.	55
<u>Lake-fed sites</u>															
Mean	2.57	1.86	5.62	0.051	6.47	163	16.2	0.021	0.31	2.13	2.01	0.84	1.14	182	165
Median	2.07	0.68	3.71	0.041	4.28	113	5.03	0.025	0.25	1.47	1.93	0.79	1.08	184	169
SD	2.03	2.62	3.35	0.030	7.66	168	24.3	0.007	0.19	1.53	1.41	0.46	0.66	49	75

Table A2: Mercury in surface sediments in the Mackenzie River Basin as compared with geological materials from various regions in the world

Matrix	Region	Hg (ng/g) mean (range)	Reference
Surface sediments	Mackenzie River – mountainous tributaries	29 (11-89)	This study
	Mackenzie River – peatland tributaries	25 (15-57)	This study
	Mackenzie River - entire basin	21 (7-89)	(Leitch et al., 2007)
	Mackenzie Mountain streams	68 (<5 - 8300)	(Day et al., 2005)
	Arctic Ocean	34-116	(Gobeil et al., 1999)
	Hudson Bay	30 (8-54)	(Hare et al., 2008)
Black shales	Mackenzie Mountains	50	(Goodfellow, 1987)
	US	2200; 4400	(Huyck, 1990; Kane et al., 1990)
	Eastern Finland	840 (<5 - 7470)	(Loukola-Ruskeeniemi et al., 2003)
	World	230	(Yudovich and Ketris, 2005)
Sulfide minerals	Australia	5030 (450-70000)	(Ryall, 1981)
	World	100-100000	(Ozerova et al., 1975)
SEDEX deposits	World	32000	(Schwartz, 1997)
Sedimentary rocks	World	30-60	(Yudovich and Ketris, 2005)
Igneous and metamorphic rocks	World	6	(Ashley et al., 2002)
Coal	Brackett Basin, NWT, Canada	490 (36-2400)	This study
	World	100 (5-5600)	(Yudovich and Ketris, 2005)
Petroleum	World	10 (1-29600)	(Rytuba, 2005)

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Appendix B:

Supplemental Information for Chapter 4:

Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate

B.1: Redox Processes in Hare Indian Lake Sediment Core:

Several indicators of redox conditions point to a reducing environment. Sediment was mostly black, with a noticeable hydrogen sulfide odour when the sediment was disturbed. Evidence of widespread framboidal pyrite, which only occurs under reducing conditions, and the moderately strong correlation between Fe and S ($r=0.77$, $p<0.01$) indicate reducing conditions. The S and P profiles indicate that there is a redox boundary of sorts around 5cm downcore, with reducing conditions present below that point, as S decreases near the surface and P becomes enriched. A depletion in As occurs near the surface starting around 20cm, indicating mobilisation of As via OM (Sullivan and Aller, 1996). None of the geochemical elements show significant correlation with Hg, with the exception of U, P, Na and Mo. U is often found bound to organic matter ($r=0.83$, $p<0.01$ with TOC; Schoner et al., 2009), again suggesting that Hg is bound mostly to organic matter. Surprisingly, Hg shows a weak negative correlation with S ($r=-0.28$, $p<0.05$). The reasons for this are still unclear.

B.2 Radiometric dating of the core

Raw data for the sediment core taken from Hare Indian Lake are presented in Table B.1. Excess Pb-210 was calculated by taking the average Pb-210 activity of the

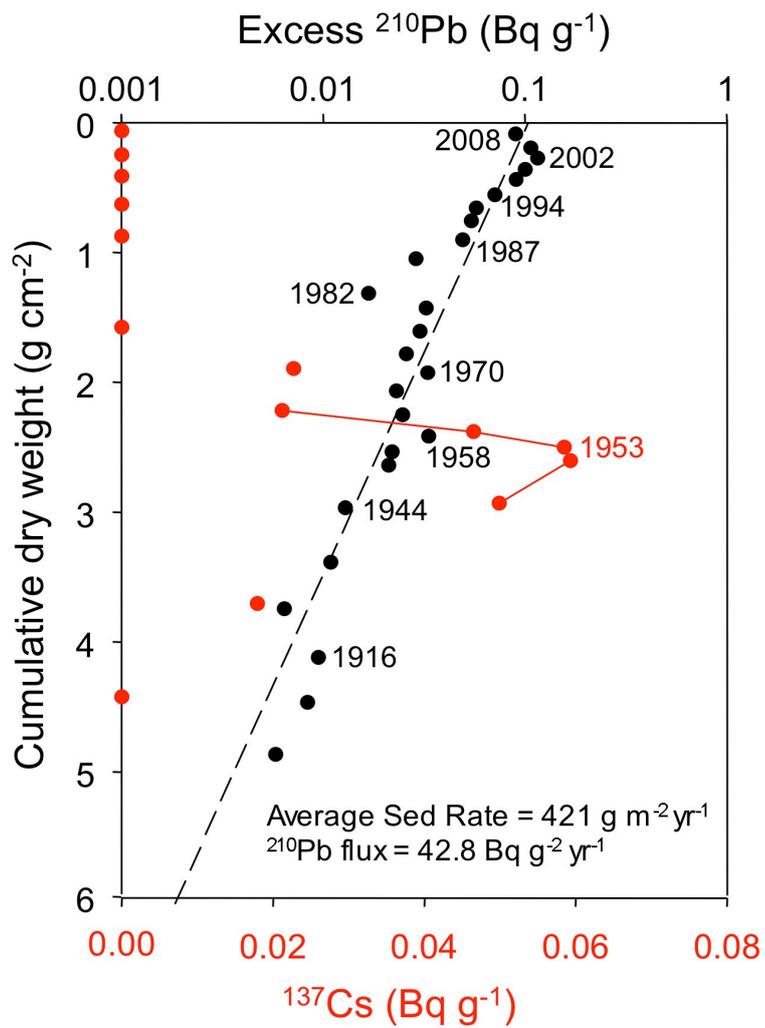
vertical section of the slope of Pb-210 activity (approx. 0.028 Bq/g), and subtracting this average from the value at shallower depths (i.e., closer to the surface, with higher activities). Porosity was calculated using the difference between wet and dry weight of the sample. A plot of excess Pb-210 versus accumulated dry weight (Figure B1) shows a mostly linear slope, suggesting very little mixing throughout the core. However, the slight decrease in activity near the top (from approx. 1.5cm to the surface) suggests some degree of mixing. Cs-137 was used to corroborate the dates, as Cs-137 should have a maximum in the core *c.* 1963, due to atmospheric fallout of nuclear bomb testing (which peaked that year). While the date established in this study is slightly less than 1963, several studies have shown that Cs-137 may be mobilised post-deposition (e.g., Appleby et al., 1991). Another study in the region (Marsh et al., 1999) showed that numerous lake sediment cores (n=68) in the Mackenzie Delta showed very little mixing due to wind or erosion from influxes of the Mackenzie River.

B.3 Tables

Table B1: Physical data and activity of sediment core

Depth (cm)	Accumulated dry weight (g/cm ²)	Porosity	Dry bulk density (g/cm ³)	Pb-210 activity (Bq/g)	Pb-210 activity error (+/- 2 s.d.)	Excess Pb-210 activity (Bq/g)	Estimated year (CRS)	Sed'n rate (g/m ² /yr)
-0.25	0.0881	0.94	0.0236	0.1180698	0.0072431	0.0900698	2008	459.2
-0.75	0.1951	0.91	0.0830	0.1350454	0.0080136	0.1070454	2005	358.0
-1.25	0.2731	0.93	0.1553	0.1438411	0.0092892	0.1158411	2002	303.4
-1.75	0.3612	0.93	0.1938	0.1285350	0.0076470	0.1005350	2000	321.9
-2.25	0.4396	0.93	0.2604	0.1184581	0.0064135	0.0904581	1997	330.3
-2.75	0.5568	0.91	0.2693	0.0990029	0.0056614	0.0710029	1994	387.0
-3.25	0.6572	0.91	0.3941	0.0854666	0.0050414	0.0574666	1992	440.1
-3.75	0.7560	0.92	0.3979	0.0822459	0.0055122	0.0542459	1990	434.3
-4.25	0.9022	0.89	0.4084	0.0772665	0.0056184	0.0492665	1987	438.3
-4.75	1.0494	0.85	0.6203	0.0568845	0.0047672	0.0288845	1984	686.3
-5.25	1.3153	0.81	0.4775	0.0447943	0.0039104	0.0167943	1982	1099.4
-5.75	1.4279	0.90	0.6810	0.0603984	0.0039822	0.0323984	1979	531.0
-6.25	1.6067	0.86	0.6366	0.0582304	0.0039519	0.0302304	1977	522.1
-6.75	1.7820	0.87	0.6486	0.0538363	0.0037126	0.0258363	1973	551.2
-7.25	1.9266	0.87	0.8392	0.0609442	0.0037878	0.0329442	1970	388.3
-7.75	2.0672	0.88	0.8581	0.0511130	0.0035500	0.0231130	1967	499.7
-8.25	2.2511	0.85	0.8575	0.0528174	0.0037001	0.0248174	1963	416.0
-8.75	2.4152	0.88	0.8252	0.0612793	0.0042861	0.0332793	1958	263.0
-9.25	2.5354	0.87	1.2732	0.0499671	0.0037168	0.0219671	1953	342.0
-9.75	2.6393	0.92	0.9196	0.0491044	0.0034788	0.0211044	1949	320.4
-10.5	2.9674	0.85	0.6291	0.0408807	0.0027918	0.0128807	1944	445.8
-11.5	3.3861	0.84	0.5742	0.0389273	0.0027739	0.0109273	1935	398.8
-12.5	3.7443	0.84	0.7317	0.0344287	0.0027638	0.0064287	1927	515.3
-13.5	4.1177	0.84	0.7473	0.0374779	0.0027897	0.0094779	1916	250.5
-14.5	4.4651	0.85	0.8392	0.0363805	0.0026064	0.0083805	1897	162.5
-15.5	4.8650	0.83	0.8675	0.0338068	0.0023595	0.0058068	1864	88.7
-16.5	5.4585	0.73	0.6899	0.0259230	0.0018975			
-17.5	6.1870	0.68	0.8276	0.0234837	0.0023538			
-18.5	6.8161	0.73	0.6837	0.0257223	0.0022407			
-19.5	7.3520	0.78	0.5700	0.0276191	0.0023345			
-21	7.9536	0.85	0.3856	0.0362299	0.0026190			
-23	8.6363	0.85	0.3900	0.0324534	0.0026579			
-25	9.4875	0.81	0.4808	0.0296368	0.0021426			
-27	10.3953	0.80	0.5216	0.0297269	0.0023282			
-29	11.3851	0.78	0.5720	0.0270592	0.0021546			
-31	12.4916	0.74	0.6545	0.0246763	0.0018515			
-33	13.5925	0.74	0.6590	0.0270998	0.0020067			
-35	14.7005	0.75	0.6440	0.0267579	0.0018855			
-37	15.8579	0.74	0.6689	0.0293748	0.0019891			
-39	16.8502	0.78	0.5605	0.0292774	0.0018217			
-42.5	19.7723	0.73	0.7006	0.0256763	0.0016569			
-47.5	22.4508	0.71	0.7337	0.0276774	0.0017400			

B.4: Figures



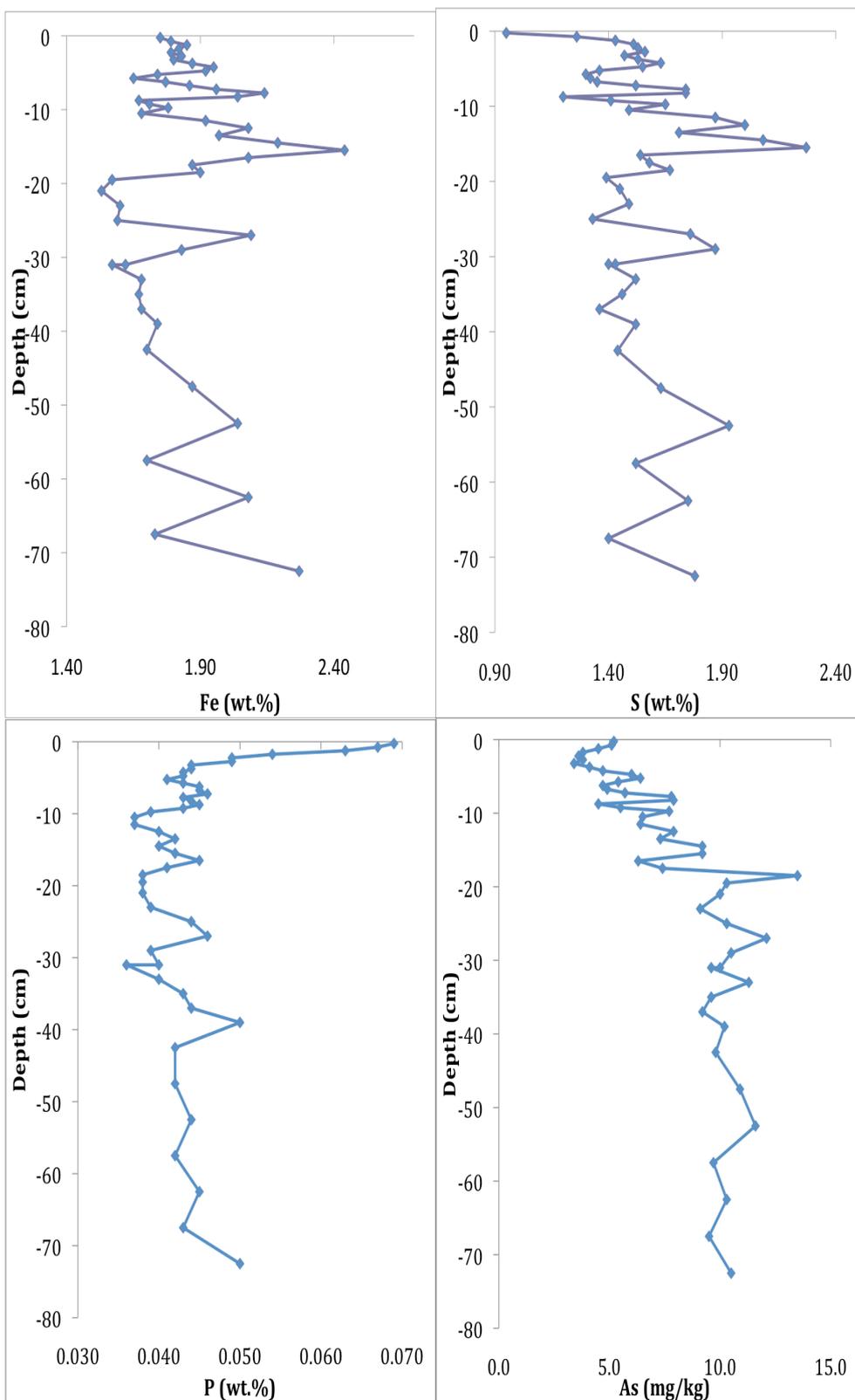


Figure B2: Plot of selected geochemical redox markers (Fe, S, P, As) in Hare Indian Lake sediment core.

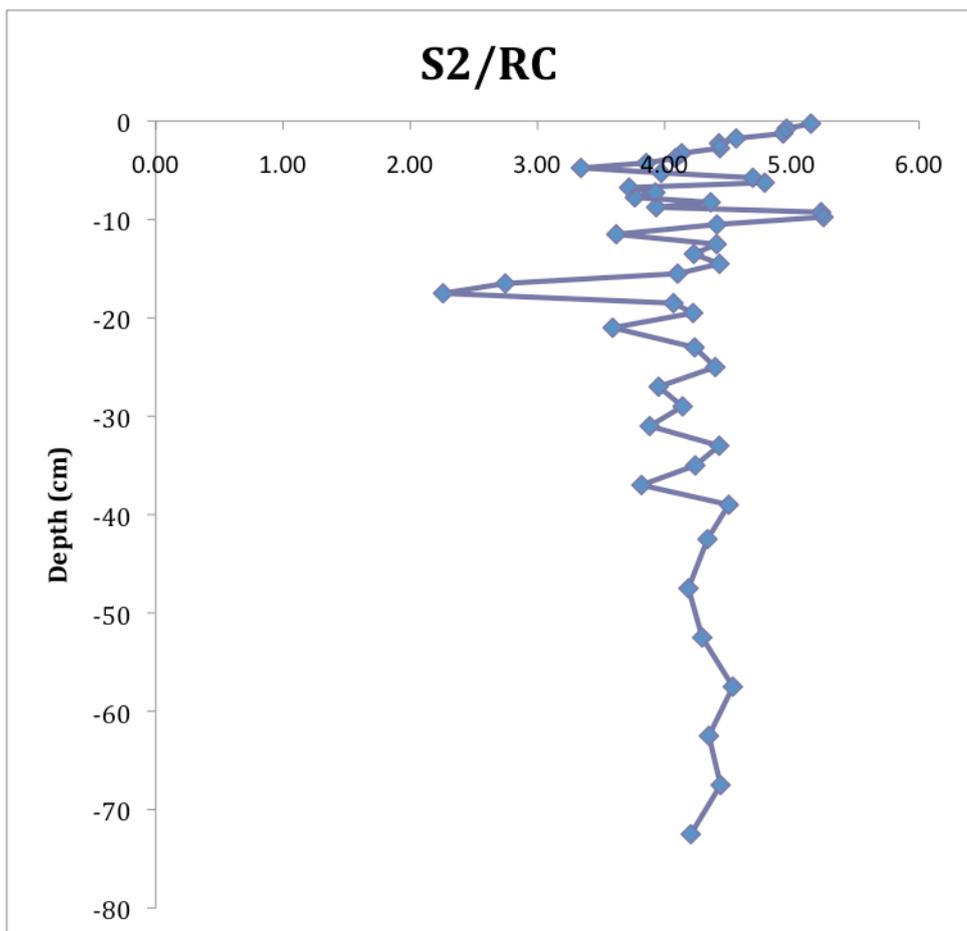


Figure B3: Plot S2/RC in the Hare Indian Lake sediment core. The nearly constant ratio suggests that the source of OM to the sediments has not changed significantly over time (Outridge et al., 2007).

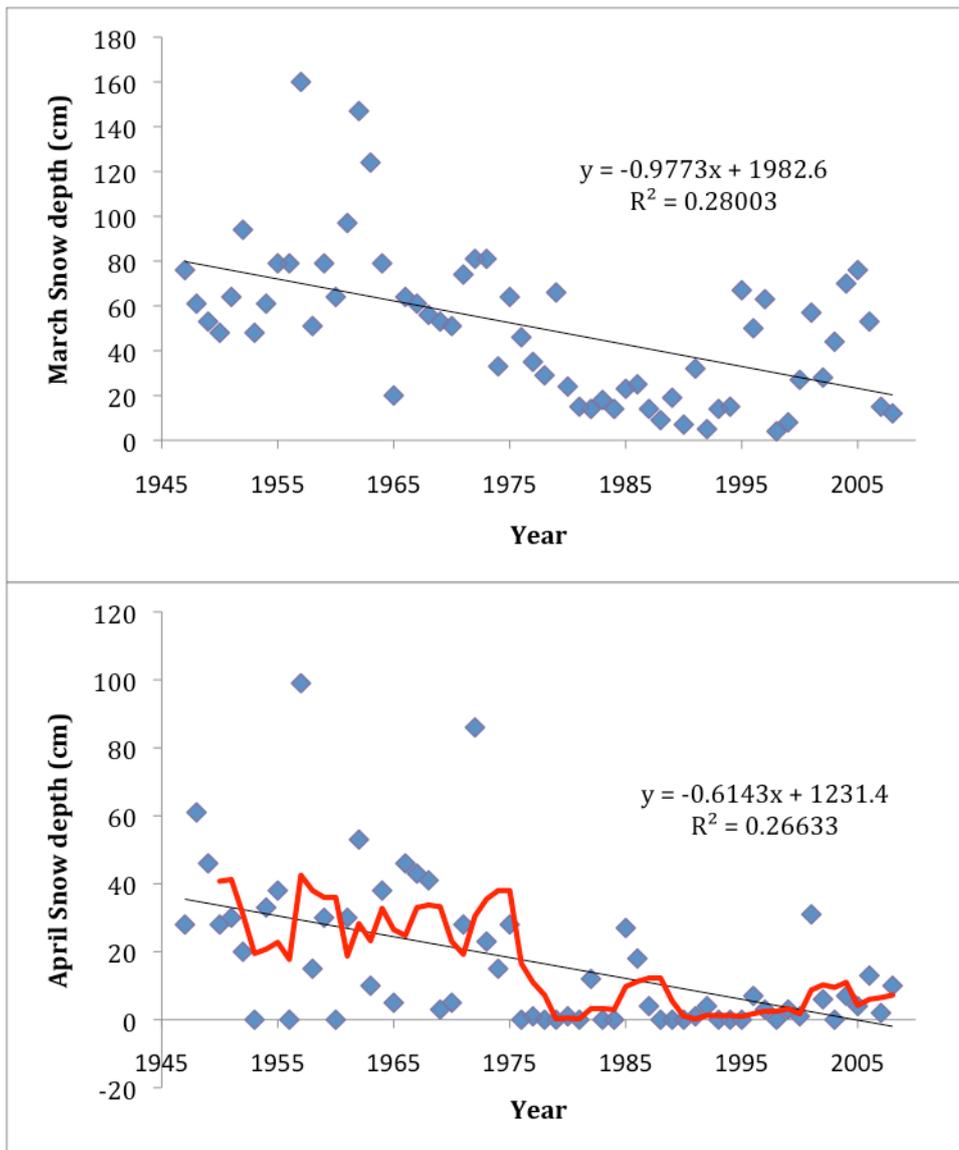


Figure B4: Decreasing snow-cover depth at Norman Wells, NWT for the years 1946-2008 in end of March (top) and April (bottom). The red line in (b) is a 4-year moving average. Data accessed from http://climate.weatheroffice.ec.gc.ca/climateData/monthlydata_e.html.

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