

Mercury distribution in water and permafrost of the lower Mackenzie Basin, their contribution to the mercury contamination in the Beaufort Sea marine ecosystem, and potential effects of climate variation

By

Daniel Ryan Leitch

Submitted to
The University of Manitoba
In partial fulfillment of the requirements for the degree

MASTER OF SCIENCE

Department of Environment and Geography
University of Manitoba
Winnipeg, Manitoba

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THE UNIVERSITY OF MANITOBA
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**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree**

OF

MASTER OF SCIENCE

Daniel Ryan Leitch © 2006

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Abstract

High levels of mercury (Hg) have recently been found in marine mammals in the Beaufort Sea, causing concerns over the health of the marine ecosystem and of indigenous people who consume marine mammals as part of their traditional diet. As part of a long-term research program aiming to probe the causes of such high Hg contamination, this thesis investigates the distribution and speciation of Hg in water of the lower Mackenzie River and in permafrost along the southern Beaufort Sea, their contribution as Hg sources to the Beaufort Sea, and their potential response to climate warming in the region.

The Mackenzie River is the largest water and sediment source to the Beaufort Sea. Five sampling campaigns were carried out between 2003 and 2005 throughout the lower Mackenzie Basin. Large seasonal and annual variations of Hg were observed, with higher water levels resulting in higher Hg levels. This suggests additional Hg sources at high water levels. For the period of 2003-2005, the Mackenzie River discharged an average of 2.2 ± 0.9 tonnes of Hg/year, of which approximately 15 kg was in the form of methylmercury (MeHg). The fact that approximately half of the annual Hg discharge occurs during the spring freshet is of concern to marine mammals, as this is the time of the year when marine mammals grow rapidly after a long winter, and hence would bioaccumulate more Hg in doing so. Higher fluxes of Hg and MeHg are expected from the Mackenzie River with projected climate warming in the area.

Rates of permafrost melt and coastal erosion along the southern Beaufort Sea coast are high, and likely to increase with climate change. Several permafrost cores were sampled along the Canadian portion of the Beaufort Sea coast showing two distinct types of profiles. Using published estimates of permafrost melt and coastal erosion, it was estimated that approximately 610 kg of Hg are degraded into the Beaufort Sea annually. As increases in temperature, open water season, storms, large waves, and sea level are predicted, it is very likely that permafrost degradation will increase.

Acknowledgments

I would like to thank my co-supervisors, Dr. Feiyue Wang and Dr. Gary Stern, for their guidance, support, patience and teachings throughout the duration of this project. Thank you to Dr. Mike Paterson and Dr. Mark Hanson for being on my advisory committee, and to Dr. Robie Macdonald and Dr. David Lean for their contributions. I am grateful to everyone around the lab for all their help. Special thanks go to Bryan Page and Marcos Lemes for always being there for support and help. I also extend my thanks to Joanne Delaronde, Gail Boila, Debbie Armstrong, and Bob Flett for their help in the lab. I am grateful to the Captains and crews of the Canadian Coast Guard Ships Dumit and Eckaloo. Captains Les Wylie and Ken Burrows were especially helpful and accommodating. Thanks to the Aurora Research Institute for providing the necessary support for our field program. Many thanks to Dr. Wayne Pollard's group of McGill University (especially Nicole Couture) for their help along the Yukon Coast. Thanks to Dr. Terry Dick and Colin Gallagher for their help in sampling in the summer of 2003, to Scott Coughtrey for all his help throughout the summer of 2004, and to Jesse Carrie for all his help in 2005. I am also grateful for all the support from friends and family including Meghan Duncan, Colin Gilmore, Mariah Mailman, Colleen Wilson, and of course my parents Gordon and Cathy Leitch who have instilled upon me a keen interest in the natural world.

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My role in papers

This thesis is organized as a “sandwich thesis” where chapters 2 and 3 are papers that are submitted or being submitted for publication. Therefore, each of these 2 chapters contains an abstract, introduction, results, discussion etc. Although there are several authors for each paper, I am the first and principal author of both papers.

For the first paper (Chapter 2), I oversaw design and execution of the entire project, under the supervision of my co-supervisors Drs. F. Wang and G. Stern. I led all field studies except the last one in the summer of 2005, which was led by the second author J. Carrie. I was responsible for sample analysis and data interpretation. I wrote the draft of the manuscript that was then polished by my co-supervisors and other co-authors.

For the second paper (Chapter 3), I again oversaw the design and execution of the entire project under the supervision of Drs. F. Wang and G. Stern. I led all field studies with the assistance of Dr. Wayne Pollard’s group at McGill University, and executed all sample-analysis pertinent to this paper with the exception of the radioactive dating. I interpreted the data and drafted the manuscript that has since been edited by both co-supervisors.

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Chapter 1 – Introduction

The objective of the overall study is to probe processes responsible for mercury (Hg) contamination in marine mammals in the Beaufort Sea and their response to climate variation. The objectives of this specific study are to:

- (1) assess current Hg and methylmercury (MeHg) levels and distribution in water throughout the lower Mackenzie Basin,
- (2) estimate the flux of Hg from both the Mackenzie River and permafrost degradation to the Beaufort Sea, working towards calculating a Hg budget for the Beaufort Sea,
- (3) probe conditions that result in higher Hg discharges, and
- (4) commence long-term monitoring of the Mackenzie River and its tributaries.

Hg is a contaminant of concern because it is a toxic metal that has been found at high levels in aquatic and marine animals in the Arctic (AMAP, 2002; Lockhart and Evans, 2000; Wagemann et al., 1995; 1997). As Hg biomagnifies up the food web, it has been shown to have adverse effects on human populations who consume these animals as part of their diet (Grandjean et al., 1998; Stein et al., 2002; Walker et al., 2006), with Inuit people being among the most affected in Canada (Walker et al., 2006).

As with many contaminants, Hg is largely emitted from more southern industrial areas and carried thousands of kilometres to the Arctic via atmospheric transport (Macdonald et al., 2005). Although Minamata disease has never been reported in the western Arctic, Hg in some Arctic marine mammals has been observed at levels high enough to cause concern. Lockhart et al. (2005) found that levels of Hg in beluga liver from the Mackenzie Delta area

increased drastically (approximately 4-fold) in concentration between the early 1980s and the late 1990s, peaking at an average of 29.0 µg/g wet weight in 1996 (age-corrected; Figure 1). Although no guidelines exist for marine mammals, this is almost 60 times higher than the recommended consumption guidelines for fish (0.5 µg/g wet weight, Health Canada). Levels have since decreased to 13.5 µg/g wet weight, which still doubles the Hg levels from the early 1980s and nearly 30 times the recommended fish consumption guideline. Although not as frequently consumed as muktuk (whale blubber and skin), liver is used as an indicator organ. Muktuk, which is more frequently consumed by local populations, had mean levels that were still above recommended consumption guidelines (between 0.57 and 1.15 µg/g wet weight; Lockhart et al., 2005). Consumption of fish and marine mammals is recognized as the primary source of Hg to northern indigenous peoples (Kuhnlein and Chan, 2000), and higher blood Hg levels in Inuit are a function of the frequency of consumption, and the level of Hg in the tissue consumed (Walker et al., 2006).

The origin of this recent mercury increase is unclear. Lu et al. (2001) used deposition rates calculated in the Beaufort Sea area to estimate that 17 tonnes of Hg are atmospherically deposited to the entire High Arctic Ocean annually. This amounts to 1.4 tonnes of Hg/yr atmospherically deposited to the Beaufort Sea. This is likely an over-estimate of net atmospheric Hg flux, as the fraction of atmospherically deposited Hg that enters the marine system is currently being debated. A growing body of evidence suggests that much of this Hg is photoreduced to Hg⁰ and released back to the atmosphere (Ferrari et al., 2004; Lahoutifard et al., 2005; Lalonde et al., 2002; St. Louis et al., 2005; Steffen et al., 2005). Although it is well recognized that anthropogenic Hg is atmospherically deposited to the Arctic via long-

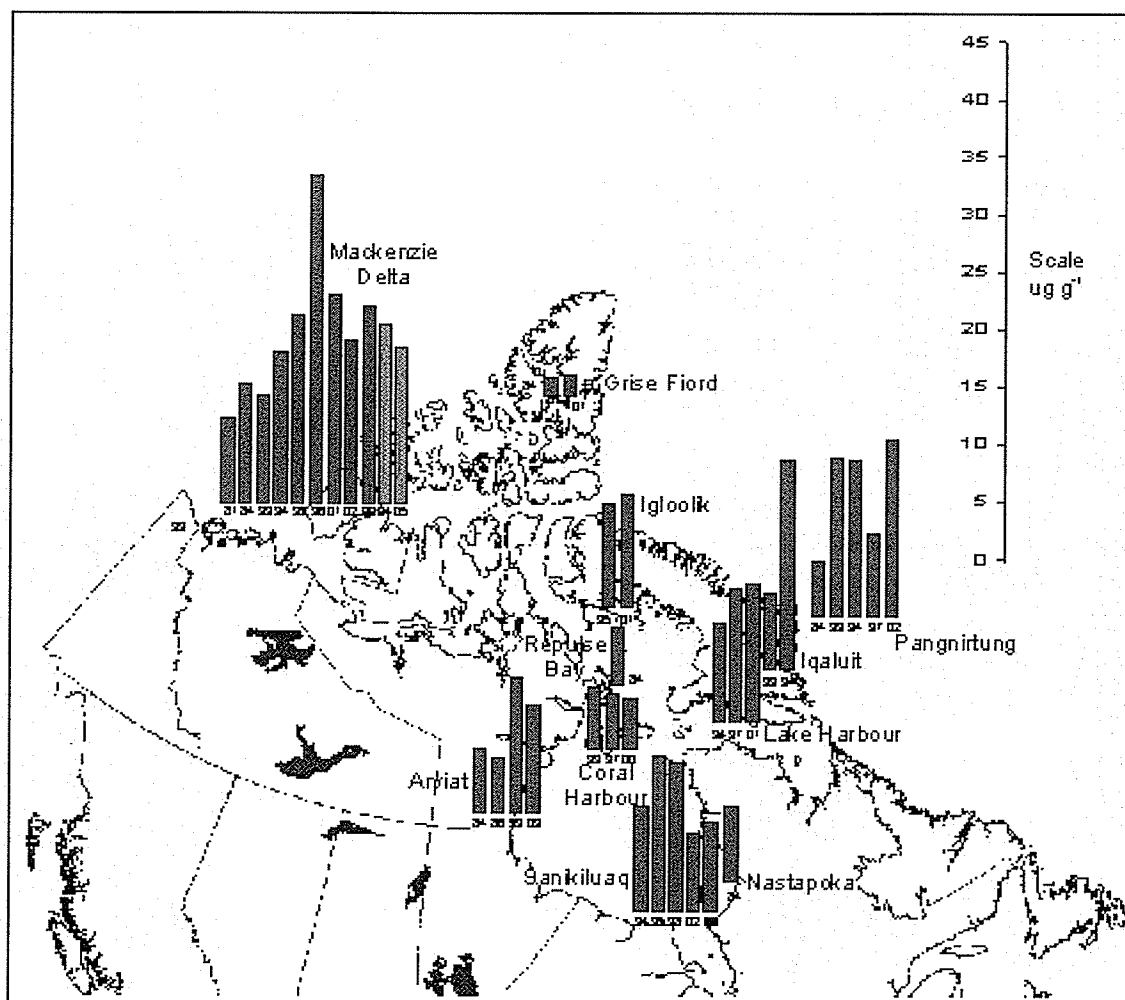


Figure 1. Mercury levels in liver ($\mu\text{g/g}$ wet weight) of beluga whales (age-adjusted to age 13.1 years) (personal communication, G. Stern, DFO).

range transport (Bard, 1999; Macdonald et al., 2000; Pacyna and Keeler, 1995), levels of Hg in the atmosphere have remained relatively constant over the past 2 decades (Slemr et al., 2003; Steffen et al., 2005). It would therefore appear as though atmospheric deposition alone cannot explain the recent increases of Hg in marine mammals in the Mackenzie Delta area. Several other processes could potentially result in higher Hg in the marine mammals of the Beaufort Sea. These processes include: (1) increased Hg transport by the Mackenzie River, (2) permafrost degradation, (3) a change in feeding behavior of beluga, and (4) changes in oceanic currents (see Figure 2).

As part of a broader study including several other students and researchers, this project investigates the Hg contribution to the Beaufort Sea from (1) the Mackenzie River, and (2) permafrost degradation. We believe both of these sources have the potential to discharge a significant amount of Hg to the Beaufort Sea annually. We also believe these processes to be susceptible to climate variation. Climate warming has been shown to be more pronounced at higher latitudes, and the Mackenzie Basin has been identified as an area receiving some of the most dramatic temperature increases in the world (Stewart, 1998). It is predicted that higher temperatures would increase permafrost melt and coastal erosion throughout the Mackenzie Basin and the Beaufort Sea coast (Lantuit and Pollard, 2005). As well, Hg methylation (process by which the more toxic MeHg is produced) may increase with higher temperatures (Chen et al., 2005).

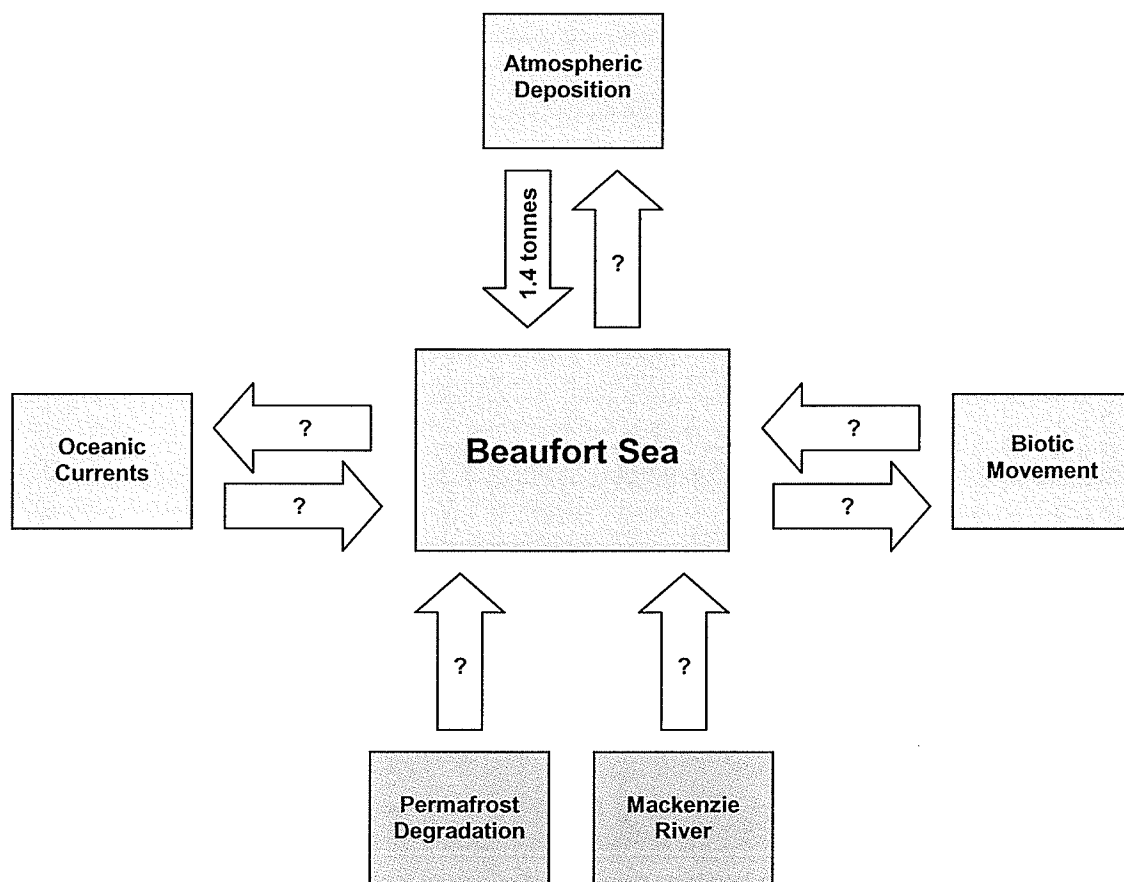


Figure 2. Potential mercury sources to the Beaufort Sea.

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Chapter 2 – The Delivery of Mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River

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Abstract

Very high levels of mercury (Hg) have recently been reported in marine mammals and other lower trophic-level biota in the Mackenzie Delta and Beaufort Sea of the western Arctic Ocean. To quantify the input of Hg (particulate, dissolved and methylated) by the Mackenzie River as a potential source of Hg in the ecosystem, surface water and sediment samples were taken from 79 sites in the lower Mackenzie Basin during three consecutive summers (2003-2005) and analyzed for Hg and methylmercury (MeHg). Intensive studies were also carried out in the Mackenzie Delta during the freshets of 2004 and 2005. Large seasonal and annual variations were found in Hg concentrations in the river, coincident with the variations in water discharge. Increased discharges during spring freshet and during the summers of 2003 and 2005 compared to 2004 were mirrored by higher Hg concentrations. The correlation between Hg concentration and riverflow suggests additional Hg sources during periods of high water, potentially from increased surface inundation and increased bank erosion. The increase in the Hg concentration with increasing water discharge amplifies the annual Hg and MeHg fluxes during high water level years. For the period 2003-2005, the Hg and MeHg fluxes from the Mackenzie River to the Beaufort Sea averaged 2.2 ± 0.9 tonnes/yr and 15 ± 11 kg/yr, respectively, the largest known Hg source to the Beaufort Sea. These results, together with the observation that approximately half of the Hg fluxes occur during the short spring freshet season which coincides with the fast growth season of marine biota, imply that the Mackenzie River input may play a major role in the elevated Hg concentrations in marine mammals in the Beaufort Sea. The Hg and MeHg fluxes from the Mackenzie

River are expected to further increase with projected climate warming in the Mackenzie Basin.

Keywords: Mercury; Arctic Ocean; Climate variation

Introduction

Extensive studies during the past 20 years have demonstrated that the Arctic is not as pristine as traditionally perceived (Macdonald et al., 2000, 2005; Muir et al., 1999). Among all the contaminants found in the Arctic ecosystems, Macdonald and Bowers (1996) flagged mercury (Hg) as perhaps the most troubling because concentrations in certain biota appeared to be increasing rapidly whereas sources and environmental processes of Hg in the Arctic remained very poorly understood. Data collected since that time highlight especially marine mammals from the Mackenzie Delta and Beaufort Sea. A four-fold increase in Hg concentration has been observed in livers of beluga whales from the Beaufort Sea area since 1982, peaking at 29.0 µg/g (wet wt., age corrected; 41.5 µg/g without age correction) in 1996, and remaining as high as 13.5 µg/g in 2002 (wet wt., age corrected) (Lockhart et al., 2005). Hg concentrations as high as 200 µg/g have been found in livers of some ringed seals collected in 2004 from Holman, Sachs Harbour and Tuktoyaktuk (G. Stern, unpublished results). These concentrations are 2-3 orders of magnitude higher than is considered to be the safe limit for subsistence consumption (the Health Canada subsistence consumption guideline for Hg in commercial fish is 0.5 µg/g wet wt; CFIA, 2001) and may pose reproductive, immunosuppressive and neurobehavioural risks to marine mammals (Givelet et al., 2005). Indeed, the Arctic is

probably experiencing one of the most severe, large-scale Hg problems (Hylander and Goodsite, 2006), which raises serious concerns over the health of the fragile Arctic ecosystem and of the local community people who consume marine mammal tissues as part of their traditional diets.

Given both natural and anthropogenic sources of Hg, the cause of such high Hg burdens and large variations remains a mystery. Global anthropogenic emissions have reportedly declined during the past two decades (Pacyna and Pacyna, 2002) and median atmospheric Hg concentrations in the Arctic have remained essentially constant for at least the past 10 years (Berg et al., 2004; Steffen et al., 2005). Nevertheless, atmospheric Hg deposition in the Arctic has received much scientific attention, due mainly to the discovery of atmospheric mercury depletion events (MDEs) in the mid-1990s (Schroeder et al., 1998). After polar sunrise, the concentration of atmospheric elemental mercury (Hg^0) was found to drop significantly with a corresponding increase in Hg concentrations in surface snow, showing a potential mechanism of altering surface flux of Hg in the Arctic. It is now clear that photochemically driven MDEs remove Hg^0 from the lower km of the atmosphere after polar sunrise and deposit it to surfaces in a reactive, biologically available form (Lindberg et al., 2002; Steffen et al., 2005). Lu et al. (2001) estimated that about 17 tonnes of Hg are deposited into snowpack of the High Arctic Ocean annually, 90% of which occurred during MDEs. Further studies suggest that much of the Hg deposited in snow during MDEs is photoreduced to Hg^0 , re-enters the atmosphere, and does not actually impinge on Arctic aquatic systems (Ferrari et al., 2004; Lahoutifard et al., 2005; Lalonde et al., 2002; St. Louis et al., 2005; Steffen et al., 2005). Therefore,

MDEs, global emissions and atmospheric trends appear not to provide an explanation for the recently observed Hg increases and variation in Arctic aquatic ecosystems.

We hypothesize that other processes likely play a more important role in the Hg distribution and trends in western Arctic ecosystems. Examples of such processes include the riverine Hg discharge, direct terrestrial Hg input from melted permafrost and coastal erosion, oceanic Hg transport, sea ice loss, and changes in marine mammal feeding habitats and food web structures, each of which is sensitive to climate variation and none of which has been studied in any detail.

As part of a long-term effort to understand what controls the Hg levels in marine mammals in the western Arctic, we here report the results from a multi-year study on the distribution and speciation of Hg in the Mackenzie River and the relative importance of this river as a Hg and MeHg source to the Beaufort Sea. As the Mackenzie River is the largest river discharging to the Beaufort Sea, it is expected to be the dominant riverine Hg source. Within the Beaufort Sea, zooplankton from the Canada Basin have been shown to have Hg levels approximately 2 times higher than zooplankton collected from the Chukchi Plateau, suggesting inputs from the Mackenzie River may be an important factor in the regional distribution of Hg (Stern and Macdonald, 2005).

Materials and Methods

The Lower Mackenzie Basin

Within the Arctic, the Mackenzie River is the largest riverine source of suspended sediments, the second largest in dissolved matter (after the Yenisei), and the fourth in water discharge (after the Russia's Lena, Yenisei and Ob rivers) (Milot et al., 2003). Originating from the headwaters of the Peace River in the Rocky Mountains, the main channel of the Mackenzie River flows northward, draining an area of 1.78×10^6 km² through British Columbia, Alberta, Saskatchewan, and the Yukon and Northwest Territories before emptying into the Beaufort Sea. At its mouth, the Mackenzie splits into many branched channels forming the largest delta in Canada and the second largest in the Arctic (after the Lena).

The present study covers the lower Mackenzie basin, which comprises the Mackenzie River valley from Great Slave Lake to the Delta (Figure 1). The landscape of the valley is primarily a product of the last continental glaciation about 30 Ka ago (Duk-Rodkin and Lemmen, 2000). The lower Mackenzie basin is dominated by two major structural and geological units: the North American Cordillera to the west, and the Precambrian Canadian Shield to the east (Milot et al., 2003). Most of the basin is underlain with continuous or extensive discontinuous permafrost.

In winter, cold, dry air from the Arctic region dominates the lower Mackenzie basin, whereas low-pressure systems from the Pacific Ocean can access from the west and south

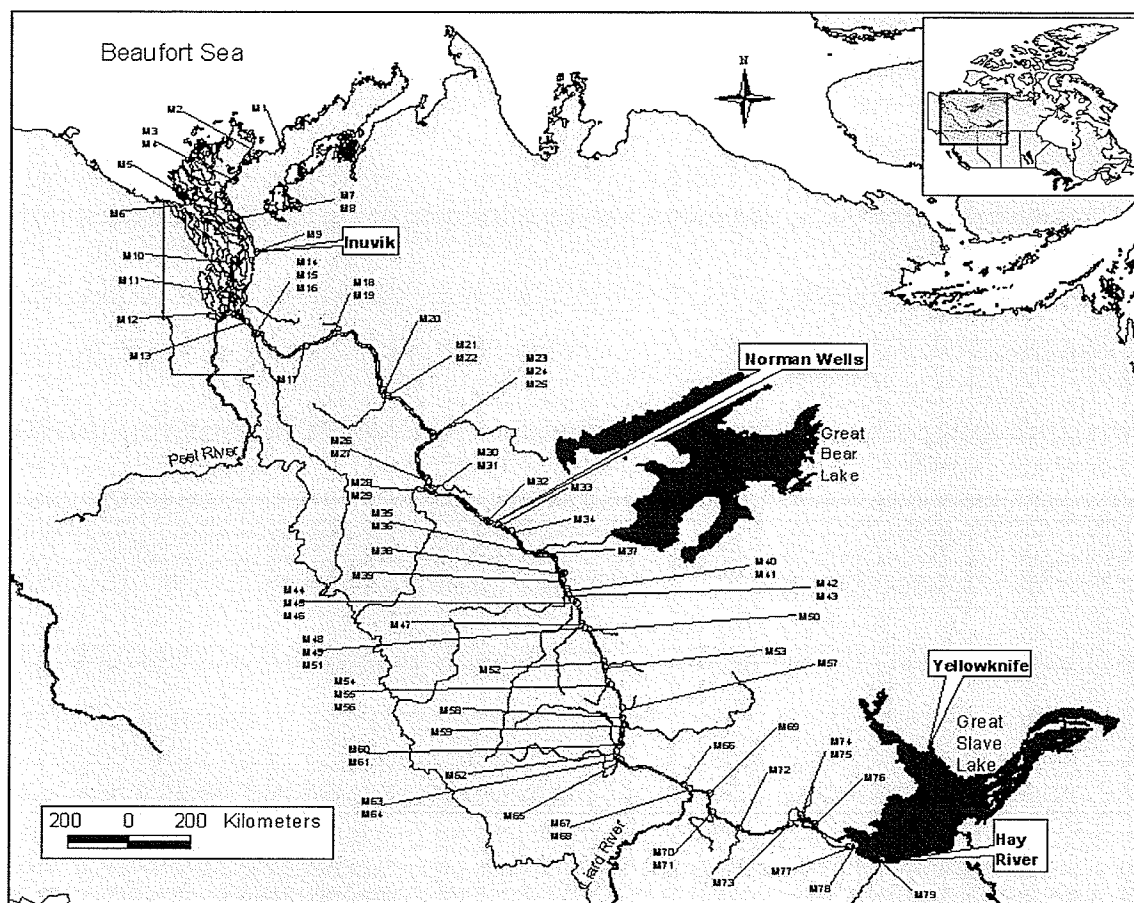


Figure 1. Summer sampling sites (M1 – M79) along the lower Mackenzie basin.

in summer. The mean monthly temperature for the valley ranges from -30 – -20 °C in January to 10 – 15 °C in July. Annual precipitation averages from 300 to 400 mm throughout most of the lower Mackenzie basin, and 125 to 250 mm along the Delta and coastal area (Dyke, 2000), but there is a large seasonal and annual variation. Approximately 50% of the annual precipitation falls in the summer months of July to September (Stewart et al., 1998). Snowfall is the major form of precipitation in the winter months with snowpack reaching its maximum in February and March (Dyke, 2000). Annual evaporation is estimated to be approximately 87 mm (Walsh et al., 1994). Mean annual water discharge of the Mackenzie River at its mouth has been estimated at ~300 – 330 km³ (Macdonald et al., 1998; Millot et al., 2003). The river flow varies seasonally with the maximum occurring between June and September and the minimum between November and April (Millot et al., 2003)

The lower Mackenzie basin is sparsely settled with a human population of less than 50,000 (35 settlements, 83% of which have less than 1,000 people) (Bone et al., 1997). With areas underlain by coal-bearing strata ranging from Mississippian to Oligocene in age (Cameron and Beaton, 2000), the Mackenzie basin is the most important area in Canada for energy production (MRBC, 1981). Major petroleum and gas reserves have been identified and are being developed in the lower Mackenzie basin, particularly around Norman Wells and in the Delta and Beaufort Sea area. Several large hydro-electric dams have also been built in the upper Mackenzie basin (among the largest are the W.A.C. Bennett Dam and the Peace Canyon Dam) creating large reservoirs and

wetlands. Mining industries have been active in certain areas of the basin (e.g., gold and diamond mines near Yellowknife).

Sampling

Five sampling campaigns were carried out during the period of 2003-2005, three of which were in the consecutive summers of 2003-2005, and the other two were during the spring freshets of 2004 and 2005 (a freshet is a sudden rise in water level associated with rainfall or snowmelt).

During the summer sampling, surface water samples were collected along the entire length of the lower Mackenzie River from Hay River ($60^{\circ}51.558'N$, $115^{\circ}43.812'W$) to the Delta ($69^{\circ}27.438'N$, $133^{\circ}02.173'W$), as well as at the lower reaches of the major tributaries. Sampling was conducted onboard the Canadian Coast Guard Ships Dumit and Eckaloo from August 6 to September 8 in 2003, July 24 to September 8 in 2004, and August 4 to 31 in 2005 (Figure 1). Except for the second half of the 2005 Expedition (from Normal Wells downstream to Inuvik), the ships travelled upstream to minimize cross-contamination from ship exhaust and to avoid the possibility of sampling the same water mass.

Where possible, sampling was carried out from the middle of the river. Where the current was too fast to use the anchor, sampling was conducted with the boat pulled up to shore. Surface water samples were collected from approximately 10 cm below the surface using an *in situ* water filtration sampler (Masterflex E/S Portable Sampler, Cole Parmer) with

acid-cleaned all-Teflon sampling lines following ultraclean sampling techniques (St. Louis et al., 1994). The water samples were filtered in situ through 0.45 μm GHP polypropylene membranes (Pall Corporation). The filtrates were directly collected in pre-treated 50-mL Teflon bottles (Savillex) or new sterilized Falcon polypropylene tubes (VWR) for the analyses of dissolved Hg (Hg_D), and in 500mL amber HDPE bottles for dissolved MeHg (MeHg_D). The particulates retained on the filters were collected in Falcon tubes for the analyses of suspended particulate matter (SPM) and particulate Hg (Hg_P). In the summer of 2005, unfiltered raw water samples were also collected for the analysis of total Hg (Hg_T) and MeHg (MeHg_T). Prior to use in the field, the Teflon and amber HDPE bottles were pre-cleaned in a 4-M HCl acid bath, rinsed with ultrapure water (Milli-Q Element), dried, and then spiked with 0.5% Optima grade HCl (Fisher Scientific) in metal-free Class 10 – 1,000 cleanrooms at the Ultra Clean Trace Elements Laboratory (UCTEL) at the University of Manitoba. The Falcon tubes were used as supplied without any further cleaning; extensive testing showed that the sterilized, disposable Falcon tubes have very low Hg background ($<0.1 \text{ ng/L}$). Once filled with samples in the field, the bottles were double bagged in polyethylene Ziploc bags and transported in coolers to the laboratory where they were refrigerated until analysis. Water samples for dissolved organic carbon (DOC), chloride (Cl^-), and sulphate (SO_4^-) were collected in 500 mL HDPE bottles. Sample bottles were rinsed 3 times in the sample water prior to collection. Samples were kept refrigerated until analysis.

During the spring freshet sampling, surface water samples were collected from the Mackenzie Delta area from June 1 to 10 in 2004 and May 26 to June 6 in 2005 (Figure 2).

Water samples were collected near the riverbank due to the presence of moving ice in the open water, following the same protocol as in the summer sampling.

In the summers of 2003 and 2004, surface sediment was also sampled wherever accessible for the analysis of total Hg (Hg_S). The sediment was retrieved using an Ekman or Ponar dredge. The sediment 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.

Sample Analysis

The analysis of Hg_D and Hg_T in the water samples was performed by cold-vapour atomic fluorescence spectroscopy (CVAFS) on a Tekran 2600 Hg analyzer at the UCTEL, following U.S. EPA Method 1631 (U.S. EPA, 2002) with a method detection limit of 0.2 ng/L. Certified reference materials ORMS-2 and ORMS-3 (National Research Council of Canada) were used for quality control, and were within 5% of their certified values. An ongoing precision and recovery (OPR) Hg standard of 5 ng/L was also used, and was always within 10% of its value. Further QA/QC was successfully conducted as part of the inter-laboratory comparison program under the Collaborative Mercury Research Network (COMERN) of Canada. The analysis of $MeHg_D$ in the water samples was conducted at the University of Ottawa laboratories using capillary gas chromatography coupled with atomic fluorescence spectroscopy as described by Cai et al. (1996). The detection limit was 0.02 ng/L.

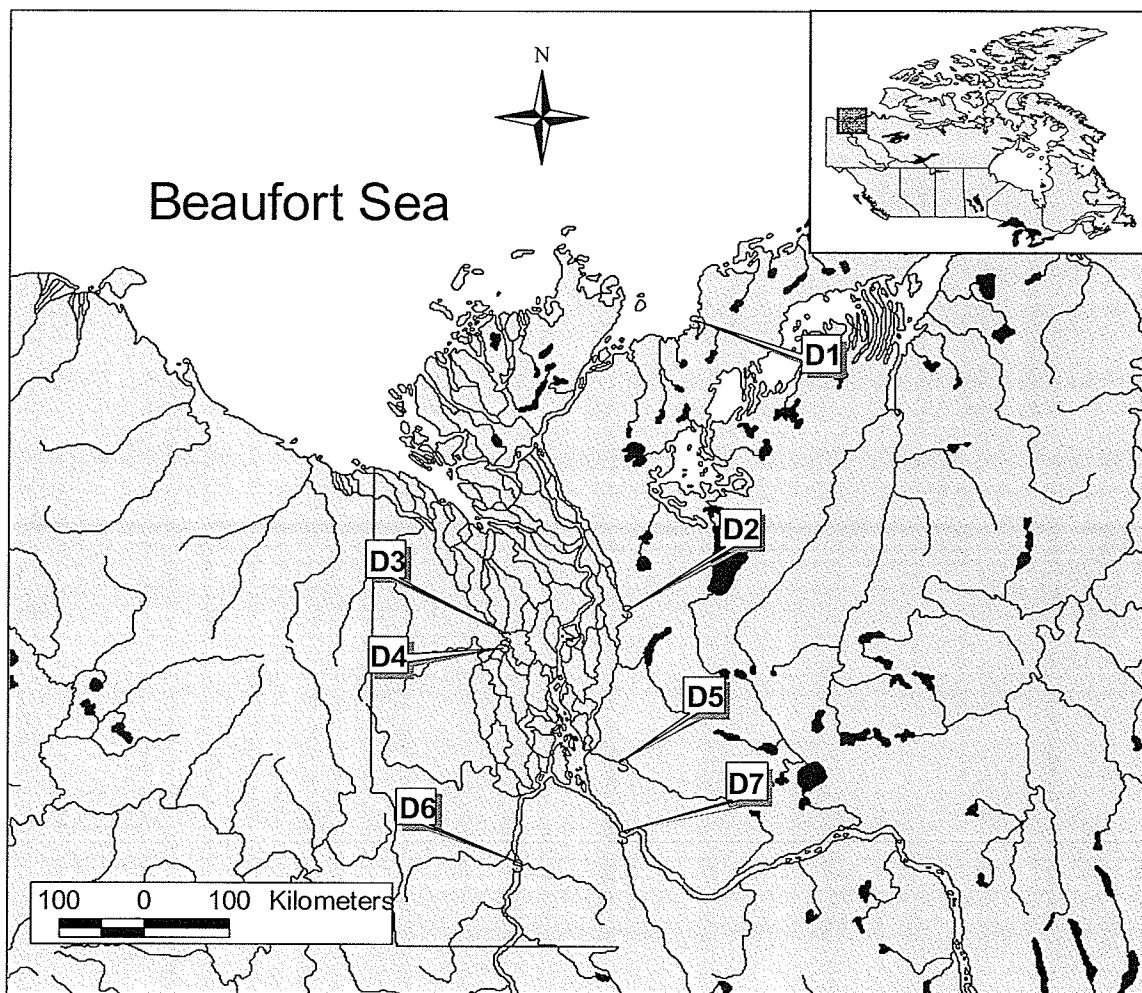


Figure 2. Spring freshet sampling sites (D1-D7) in the Mackenzie Delta.

Hg_P and Hg_S were analyzed at the Freshwater Institute laboratories using a procedure adapted from Method CAS-AM-70.13 by Dow Chemical of Canada Ltd (as described in detail elsewhere, i.e., Lockhart et al., 1998). In brief, SPM samples were dried in an oven and sediment samples were dried in a freeze-dryer. Samples were then boiled in an aqua regia solution at 120°C for 30 min in a digestion block to oxidize organic Hg to inorganic Hg. Sample extracts were then analyzed for Hg by cold vapour atomic absorption spectroscopy (CVAAS) on a 3200 Elemental Mercury Detector (Thermo Separation Products). Certified reference materials MESS-3 and LKSD-1 (National Research Council of Canada) were used and found to be within 15% of their certified values.

Here we define [Hg]_D and [MeHg]_D as Hg and MeHg concentrations present in the water fraction that passes through the 0.45-μm GHP polypropylene membrane during the *in situ* filtration. The proportion of Hg retained on the membrane is referred to as the particulate fraction ([Hg]_P). [Hg]_T refers to the Hg concentration in the unfiltered, raw water samples. In the summers of 2003 and 2004 and the spring of 2004, where no raw water samples were collected for analyses, [Hg]_T was calculated as the sum of [Hg]_D and [Hg]_P. In the summer of 2005, raw water samples were collected, along with dissolved and particulate fractions, which allowed a comparison between calculated [Hg]_{T-calc} and measured [Hg]_{T-meas}. The good correlation ($r^2=0.78$), slope of close to one (1.18) and intercept of close to zero (-1.08) suggest that *in situ* filtration in the field provides a simple, alternative way to separate Hg_D and Hg_P (Figure 3).

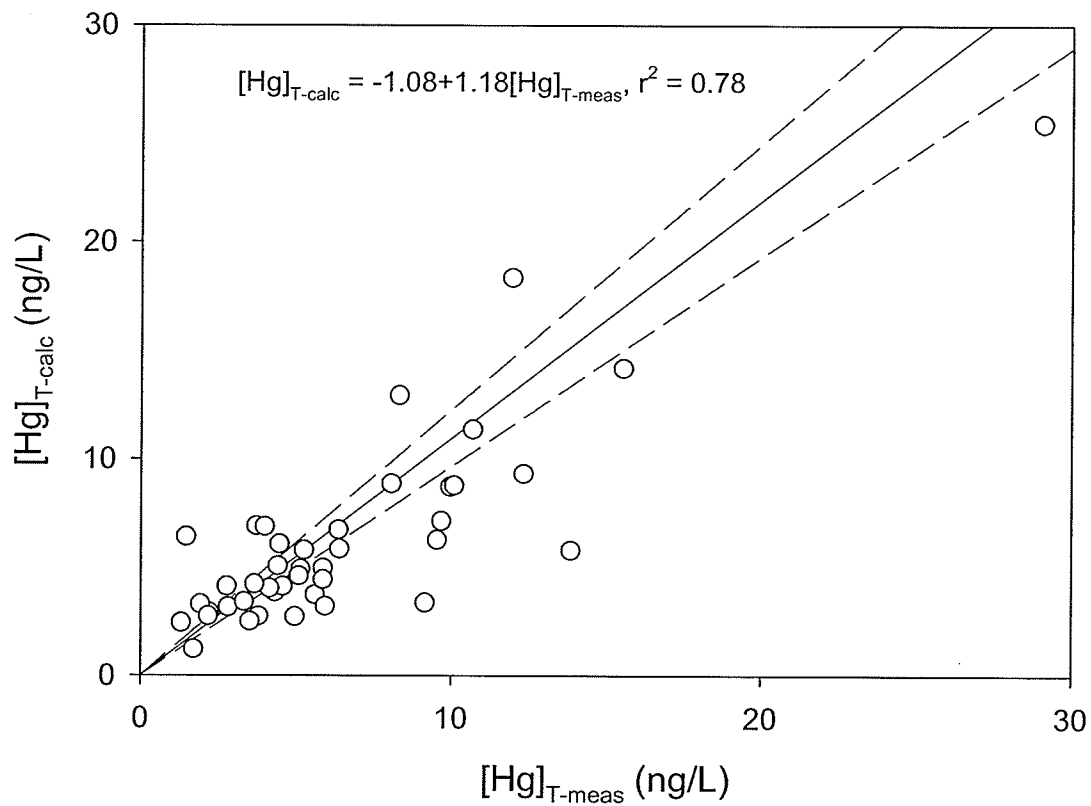


Figure 3. Comparison of total Hg ($[\text{Hg}]_{\text{T}}$) calculated by summation of dissolved and particulate measurements ($[\text{Hg}]_{\text{T-calc}} = [\text{Hg}]_{\text{D}} + [\text{Hg}]_{\text{P}}$) and total Hg directly measured $[\text{Hg}]_{\text{T-meas}}$ in unfiltered samples collected throughout the Mackenzie Basin during summer, 2005. The solid line is the regression line, and the dashed lines show the 95% confidence intervals of the regression line.

DOC was analyzed by infra-red spectroscopy at the Freshwater Institute laboratories (Method No. FWI-DOC-2.0). Cl^- and SO_4^{2-} were analyzed by ion chromatography (Method No. FWI- $\text{Cl}^-/\text{SO}_4^{2-}$). All methods are described in Stainton et al. (1977).

Results

Table 1 summarizes the multi-year average concentrations of dissolved mercury ($[\text{Hg}]_{\text{D}}$), particulate mercury ($[\text{Hg}]_{\text{P}}$), total mercury in surface water ($[\text{Hg}]_{\text{T}}$), dissolved MeHg ($[\text{MeHg}]_{\text{D}}$), and total mercury in surface sediment ($[\text{Hg}]_{\text{S}}$) in the Mackenzie River and its major tributaries in the summers of 2003-2005. Only those sites that have been monitored for more than one summer are included in the table. Table 2 shows the Hg and MeHg concentrations in the Mackenzie Delta during spring freshet of 2004 and 2005. The complete dataset can be found elsewhere (Appendices 1 & 2).

Annual Variation of Hg in the Mackenzie River

During the summers of 2003-2005, the median concentrations of $[\text{Hg}]_{\text{D}}$, $[\text{Hg}]_{\text{P}}$, $[\text{Hg}]_{\text{T}}$, and $[\text{MeHg}]_{\text{D}}$ throughout the lower Mackenzie Basin were 2.02, 2.71, 6.22, 0.065 ng/L, respectively (Table 1), similar to the Hg concentrations in other large rivers (e.g., Cossa et al., 1996; Quémérais et al., 1999). However, great variation was found in $[\text{Hg}]_{\text{D}}$, $[\text{Hg}]_{\text{P}}$ and $[\text{Hg}]_{\text{T}}$ among the 3 consecutive summers (Figure 4). $[\text{Hg}]_{\text{T}}$ in water ranged from 1.69 - 29.66 ng/L (median 7.57 ng/L) in the summer 2003, but was considerably lower during the summer of 2004, ranging from 0.36 - 8.76 ng/L (median: 1.76 ng/L). In the summer of 2005 $[\text{Hg}]_{\text{T}}$ was comparable to levels observed in 2003, ranging from 1.20 - 31.48

Table 1. Average mercury (Hg) and methylmercury (MeHg) concentrations at selected stations in the lower Mackenzie basin in the summers of 2003-2005.

River	Station ID	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _T (ng/L)	[MeHg] _D (ng/L)	[Hg] _S (µg/g)
<i>Mainstream of the Mackenzie</i>						
East Channel	M9	1.53	4.13	5.61	0.060	0.025
Horseshoe bend	M10	1.39	4.03	6.01	0.059	0.017
Point Separation	M13	1.53	6.64	8.79	0.128	-
Benoit Creek	M17	1.67	2.48	4.29	0.062	0.007
Downstream Travaillant R.	M19	1.18	2.38	3.56	0.145	0.016
Downstream Ontaritue R.	M20	7.49	2.94	11.01	0.099	0.009
Upstream Ontaritue R.	M22	6.31	2.46	8.77	0.020	0.008
Upstream Hare R.	M25	2.16	3.40	6.44	0.071	0.017
Downstream Mountain R.	M26	9.47	5.73	19.81	0.020	0.044
Upstream Mountain R.	M29	5.51	8.15	16.26	0.048	0.012
Downstream Norman Wells	M32	4.89	6.10	10.86	0.060	0.011
Upstream Norman Wells	M33	3.01	3.22	6.08	0.039	0.007
Upstream Great Bear R.	M36	4.16	5.47	9.63	0.041	0.012
Upstream Keele R.	M43	5.67	5.02	10.68	0.115	0.023
Downstream Redstone R.	M44	1.50	4.86	6.35	0.049	0.031
Upstream Redstone R.	M46	3.80	3.60	7.39	0.097	0.018
Downstream Dahadini R.	M47	1.43	4.26	5.69	0.086	0.026
Between Dahadini and Blackwater R.	M49	2.54	8.18	11.78	0.155	0.029
Upstream Blackwater R.	M51	1.03	2.24	3.27	0.076	0.012
Upstream Wrigley	M56	1.65	14.20	15.85	0.187	0.010
Between Two Mountains	M57	1.45	0.99	3.34	0.042	-
Downstream Willowlake R.	M58	1.15	1.94	3.32	0.035	0.009
Camsell Bend	M63	1.91	2.44	5.15	0.055	-
Upstream N. Nahanni R.	M65	0.93	1.20	8.90	0.081	-
Downstream Liard R.	M66	2.55	4.47	7.02	0.053	0.009
Upstream Liard R.	M68	2.98	1.43	4.25	0.020	-
Upstream Jean Marie R.	M71	1.01	0.86	2.24	0.057	-
Downstream Mills Lake	M73	1.38	1.38	3.31	0.100	-
Upstream Mills Lake	M74	1.07	0.78	2.64	0.133	-
Fort Providence	M76	2.66	0.87	4.21	0.079	-
South Channel	M77	1.48	0.68	2.65	0.069	0.015
Great Slave Lake (West corner)	M78	2.23	1.31	4.52	0.107	-
<i>Tributaries</i>						
Peel R.	M12	1.71	3.58	6.72	0.042	0.053
Arctic Red R.	M15	1.96	5.06	7.02	0.098	0.084
Ontaritue R.	M21	5.29	1.89	7.17	0.138	0.057

River	Station ID	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _T (ng/L)	[MeHg] _D (ng/L)	[Hg] _S (µg/g)
Hare Indian R.	M24	6.11	0.09	9.07	0.094	0.020
Mountain R.	M28	2.07	6.46	9.44	0.041	0.036
Great Bear R.	M35	2.16	0.61	3.71	0.032	0.029
Big Smith Creek	M39	0.98	0.11	1.46	0.020	0.035
Keele R.	M42	1.41	2.42	3.83	0.045	0.028
Redstone R.	M45	1.88	5.09	6.97	0.049	0.035
Dahadini R.	M48	2.51	6.26	7.25	0.025	0.055
Blackwater R.	M50	1.35	0.17	1.98	0.089	0.015
Ochre R.	M53	8.62	1.00	13.67	0.054	0.024
Wrigley R.	M55	0.95	8.27	8.10	0.084	0.025
Willowlake R.	M59	2.73	1.14	4.95	0.103	0.036
Root R.	M61	0.99	3.86	5.50	0.075	0.023
North Nahanni R.	M64	2.44	4.42	7.94	0.028	0.011
Liard R.	M67	3.13	4.87	8.00	0.081	0.011
Jean Marie R.	M70	2.85	1.68	4.59	0.133	0.015
Trout R.	M72	2.59	0.80	4.51	0.175	0.019
Horn R.	M75	1.05	1.46	3.21	0.020	0.025
<i>Statistics of the Mainstream</i>						
Average		2.77	3.68	7.18	0.076	0.017
Standard deviation		2.11	2.85	4.31	0.041	0.009
Median		1.79	3.08	6.05	0.065	0.014
10% percentile		1.07	0.88	3.27	0.035	0.008
90% percentile		5.65	6.59	11.70	0.133	0.029
<i>Statistics of the Basin</i>						
Average		2.72	3.40	6.82	0.074	0.024
Standard deviation		2.03	2.70	3.82	0.042	0.016
Median		2.02	2.71	6.22	0.065	0.020
10% percentile		1.03	0.78	3.22	0.025	0.009
90% percentile		5.65	6.44	11.00	0.133	0.043

Table 2. Mercury (Hg) and methylmercury (MeHg) concentrations in surface waters in the Mackenzie Delta during the spring freshet 2004-2005.

ID	Freshet 2004				Freshet 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _T (ng/L)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _T (ng/L)	[MeHg] _D (ng/L)
D1	1.34 ± 0.22	3.79	5.13	0.070 ± 0.021	1.57 ± 1.01	3.10	4.67 ± 1.01	0.359
D2	2.93 ± 0.55	16.39	19.32	<0.020	2.81 ± 0.93	6.12	8.93 ± 1.16	0.322 ± 0.368
D3	1.62 ± 0.24	20.89	22.51	<0.020	2.00 ± 0.37	20.02	22.02 ± 1.97	0.244
D4	1.88 ± 0.25	8.30	10.18	0.033 ± 0.018	2.82 ± 2.72	19.05	21.87 ± 4.79	0.449
D5	4.16 ± 0.32	6.68	11.84	0.311	4.76 ± 0.46	0.92	5.68 ± 0.84	<0.020
D6	1.98 ± 0.19	12.48	14.46	0.031	2.14 ± 0.96	10.94	13.08 ± 4.59	0.335
D7	1.31 ± 0.15	14.89	16.20	<0.020				

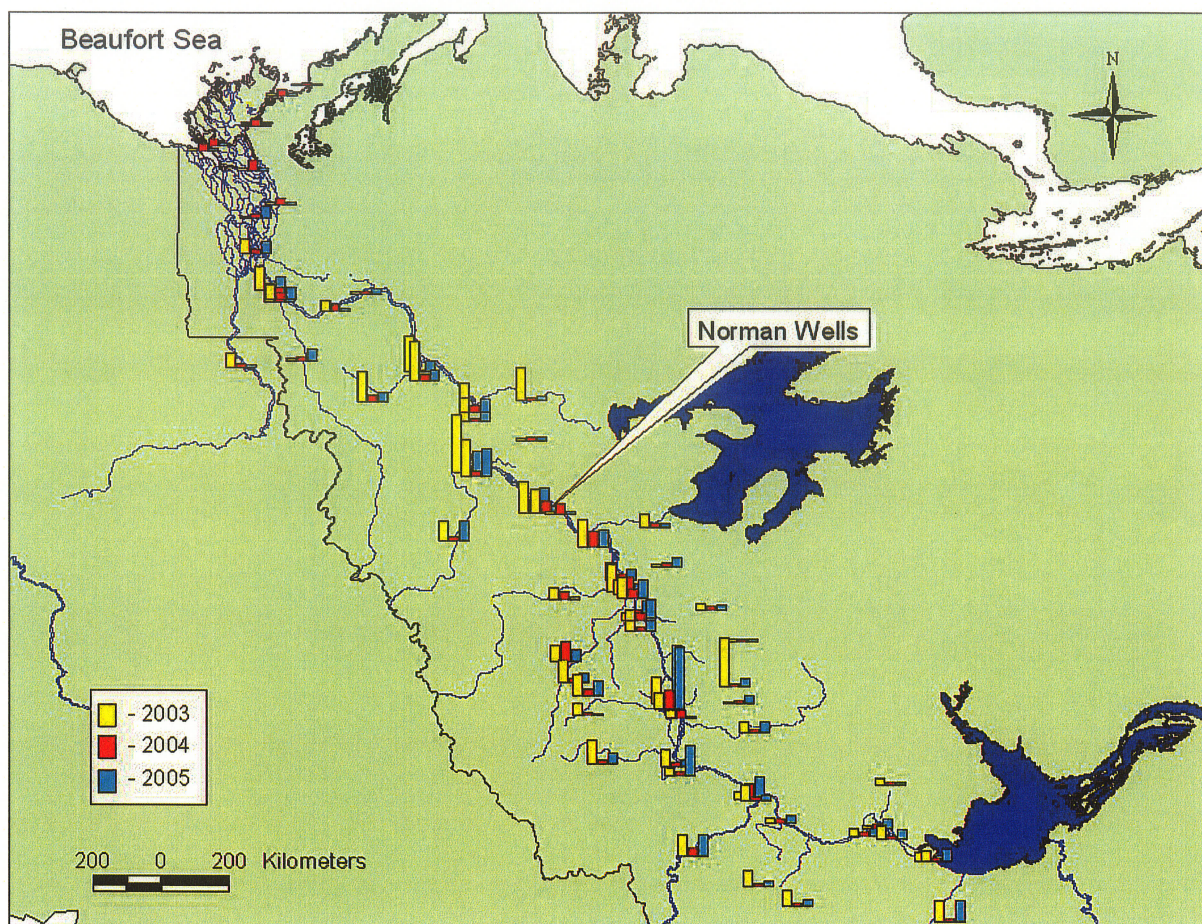


Figure 4. Spatial and temporal variation of total mercury ($[Hg]_T$) in the lower Mackenzie Basin (bars have been repositioned to more easily show tributaries).

ng/L (median 4.58 ng/L). Similarly, $[\text{Hg}]_P$ in the Mackenzie was higher in the summers of 2003 (median of 2.90 ng/L) and 2005 (median of 3.08 ng/L), but lower in the summer of 2004 (median of 1.76 ng/L). The most dramatic change was found in $[\text{Hg}]_D$, which was very low in the summer of 2004 compared with the summers of 2003 and 2005. $[\text{MeHg}]_D$ showed less variation, ranging from 0.02 - 0.266 ng/L (median: 0.085 ng/L) in 2003 and 0.02 - 0.140 ng/L (median: 0.026 ng/L) in 2004. In contrast, no significant change was evident in $[\text{Hg}]_S$ between 2003 and 2004, ranging from 0.006 - 0.089 $\mu\text{g/g}$ (dry weight) in 2003 and 0.004 - 0.079 $\mu\text{g/g}$ in 2004.

Similarly, Hg and MeHg concentrations also varied during the spring freshet seasons of 2004 and 2005 (Table 2). $[\text{Hg}]_D$ in the Mackenzie Delta had median values of 1.88 and 2.48 ng/L in spring 2004 and 2005, respectively. $[\text{Hg}]_P$ was much higher with median values of 12.48 and 15.00 ($[\text{Hg}]_{P\text{-calc}}$) ng/L in 2004 and 2005, respectively. The median $[\text{MeHg}]_D$ in the spring of 2004 was 0.031 ng/L, but reached as high as 0.335 ng/L in the spring of 2005.

Seasonal Variation of Hg in the Mackenzie River

In addition to the annual variations, much higher $[\text{Hg}]_D$ and $[\text{Hg}]_P$ concentrations were generally observed during the spring freshet season than later in the summer. Among the sites in the Delta that were visited both in the spring and summer, levels of $[\text{Hg}]_D$ and $[\text{Hg}]_P$ were both ~7-fold higher during the freshet than in the summer. In contrast to inorganic Hg, $[\text{MeHg}]_D$ remained relatively constant throughout freshet and into summer.

Spatial Variation of Hg and MeHg in the Mackenzie River

Hg varied significantly across the lower Mackenzie Basin (Table 1, Figure 4). Most obvious geographical variations in $[\text{Hg}]_D$ were recorded in the summer of 2003. $[\text{Hg}]_D$ at most sampling sites was <5 ng/L, but exceeded 10 ng/L at locations which tended to be located in the middle reaches of the river centred around Norman Wells, roughly between sample sites M20 and M36, and at a few sites farther upstream. Concentrations in the Delta were consistently around 2-3 ng/L. In 2005, the highest $[\text{Hg}]_D$ values, 5.59 and 4.40 ng/L, were found at M66 (the Mackenzie R. below the Liard R.) and M59 (the Willowlake R.) respectively. No trends were evident in the summer of 2004 due to much lower $[\text{Hg}]_D$ observed for that year (see discussion below). There are no regional hotspots for $[\text{MeHg}]_D$.

$[\text{Hg}]_P$ was consistently lower on the Mackenzie main-channel upstream from the Liard River (Figure 4) and was much lower in tributaries draining the east side of the river (median for all three years: 0.17 ng/L), compared to tributaries draining the west side (2.46 ng/L) or the main-channel Mackenzie River (2.18 ng/L).

River-bottom sediments ($[\text{Hg}]_S$) in the Mackenzie River averaged 0.016 ± 0.011 $\mu\text{g/g}$ in 2003 and 0.026 ± 0.017 $\mu\text{g/g}$ in 2004. This falls within ranges reported for Mackenzie Shelf sediments ($<0.01 - 0.1$ $\mu\text{g/g}$) (Macdonald and Thomas, 1991) and sediments from the Beaufort Shelf north of Alaska (0.041 ± 0.029 $\mu\text{g/L}$) (Trefry et al., 2003). Higher $[\text{Hg}]_S$ values were found in rivers that drained into the Mackenzie on the west side, such

as the Peel (0.030 - 0.076 $\mu\text{g/g}$), Arctic Red (0.089 - 0.079 $\mu\text{g/g}$), Ontaritue (0.059 - 0.070 $\mu\text{g/g}$), and the Hay (0.089 $\mu\text{g/g}$) rivers.

Discussion

Processes Controlling Mercury Concentrations in the Mackenzie River

Water Discharge

It has long been known that the water composition of a river depends on the hydrological regime, and that the relationship between changes in water discharge and concentrations of various substances often indicate the major sources of substances (Chapman, 1992).

For the Mackenzie River, much higher Hg concentrations are generally observed during the spring freshet than later in summer. The increase in Hg concentration with water flow runs counter to the behaviour of most solutes, which tend to decrease with flow, exhibiting a dilution effect (e.g., see Bishop et al., 1995), and suggests that Hg release from drainage-basin soils must increase with moisture. Among sites that were visited both in the spring and summer, concentrations of $[\text{Hg}]_{\text{D}}$ and $[\text{Hg}]_{\text{P}}$ were ~ 7 -fold higher during the freshet than in the summer. This trend of higher $[\text{Hg}]_{\text{D}}$ during high water has also been observed on the St. Lawrence River (Qu  marais et al., 1999), the Wisconsin River (Hurley et al., 1995), the Sacramento River (Domagalski, 2001) and the Sleepers River (Stanley et al., 2002). Correlation with riverflow implies that Hg transport is biased toward high flow periods which is very significant for the Mackenzie because $\sim 80\%$ of the annual discharge occurs during the four summer months, when high-flow events of

short duration frequently occur (Figure 5). In contrast to inorganic Hg, [MeHg]_D remains relatively constant with flow suggesting that hydrological control differs for this form of Hg.

The large seasonal and annual differences in the Hg concentrations in the Mackenzie River warrant further attention. A comparison with the hydrograph of the Mackenzie River during the period of sample collection (Figure 5) reveals a strong co-variation between the water discharge and the Hg concentrations in the water both at seasonal and annual scales. Much higher [Hg]_T was found during the high-water flow, spring freshet season than in the summer when the water discharge was lower. On an annual scale, Figure 4 reveals that the water discharge in the Mackenzie River was much lower in the summer of 2004 compared to that in the summers of 2003 and 2005. Coincidentally, a much lower [Hg] was also found in the river in the summer of 2004 (Figure 4). Similar co-variations have also been observed in the Carson River, Nevada, where high water levels were highly correlated with higher levels of Hg in water (Carroll et al., 2004), in the Vistula River, Poland, where fish exhibited a 2.5-fold increase in Hg levels after a flood period (Zarski et al., 2002), and in northeastern Minnesota lakes where Hg levels in the young-of-the-year yellow perch varied with annual water-levels in these lakes (higher water levels resulting in higher Hg concentrations) (Sorensen et al., 2005).

The relationship between [Hg]_P and water discharge is robust ($r^2 = 0.73$), being maintained at the Mackenzie River at the Arctic Red River sampling station throughout

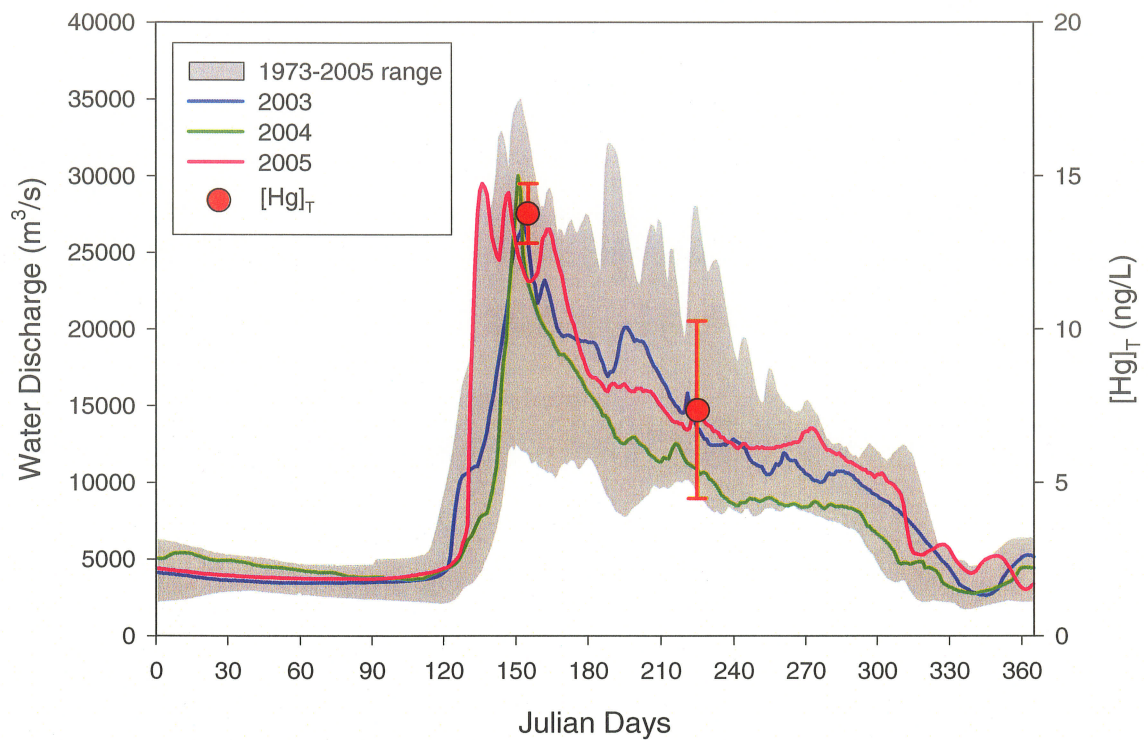


Figure 5. Water discharge of the Mackenzie River at the Arctic Red River in 2003-2005 relative to the range between 1972 and 2005 (the grey area). Data were compiled from HYDAT, Environment Canada. The red circles and error bars show the total Hg concentration during the spring freshet and later in summer in 2003.

several sampling campaigns in 2003-2005 (Figure 6a). During peak flow, $[\text{Hg}]_P$ was as much as 5-fold higher than during the spring freshet season. Intensive sampling conducted in the Mackenzie Delta (East Channel) near Inuvik over the span of 9 days in June 2004 during the spring freshet season (Figure 6b) showed that $[\text{Hg}]_P$ was as high as 35 ng/L (June 1) just before the peak flow (June 3), and then dropped sharply to <10 ng/L within a few days after the peak flow. The limited data suggest that the $[\text{Hg}]_P$ peak precedes the water discharge peak. A similar time trend was also found, but with a delay, at a downstream site near Tuktoyaktuk (Appendix 3). The water discharge effect on $[\text{Hg}]_D$ at the downstream sites was, however, not significant. The Mackenzie River at the Arctic Red River (upstream from the Delta) was also sampled during the spring with a decrease in $[\text{Hg}]_P$ observed after peak flow and no change in $[\text{Hg}]_D$ (Appendix 4).

The correlation between $[\text{Hg}]$ and flow suggests that increasing surface run-off from the basin mobilizes Hg. Hg is known to bind strongly with soil organic matter which is susceptible to erosion with high water flows. Unfortunately, particulate organic carbon (POC) was not measured in this study. However, DOC measured during this study confirmed that concentrations in the spring freshet season (10.90 ± 3.07 mg C/L) were much higher than in the summer (3.71 ± 0.22 mg C/L) in the Mackenzie Delta region and higher during a high flow year (2005: 11.04 ± 6.79 mg C/L) compared to a low flow year (2004: 4.75 ± 3.43 mg/L). A similar relationship between DOC and flow has been observed in other rivers (Boyer et al., 1997; Cauwet and Sidorov, 1996; Guo and Macdonald, 2006; Hornberger et al., 1994). In this latter study of the Yukon River, ^{14}C measurements showed that DOC and colloidal organic carbon (COC) were relatively

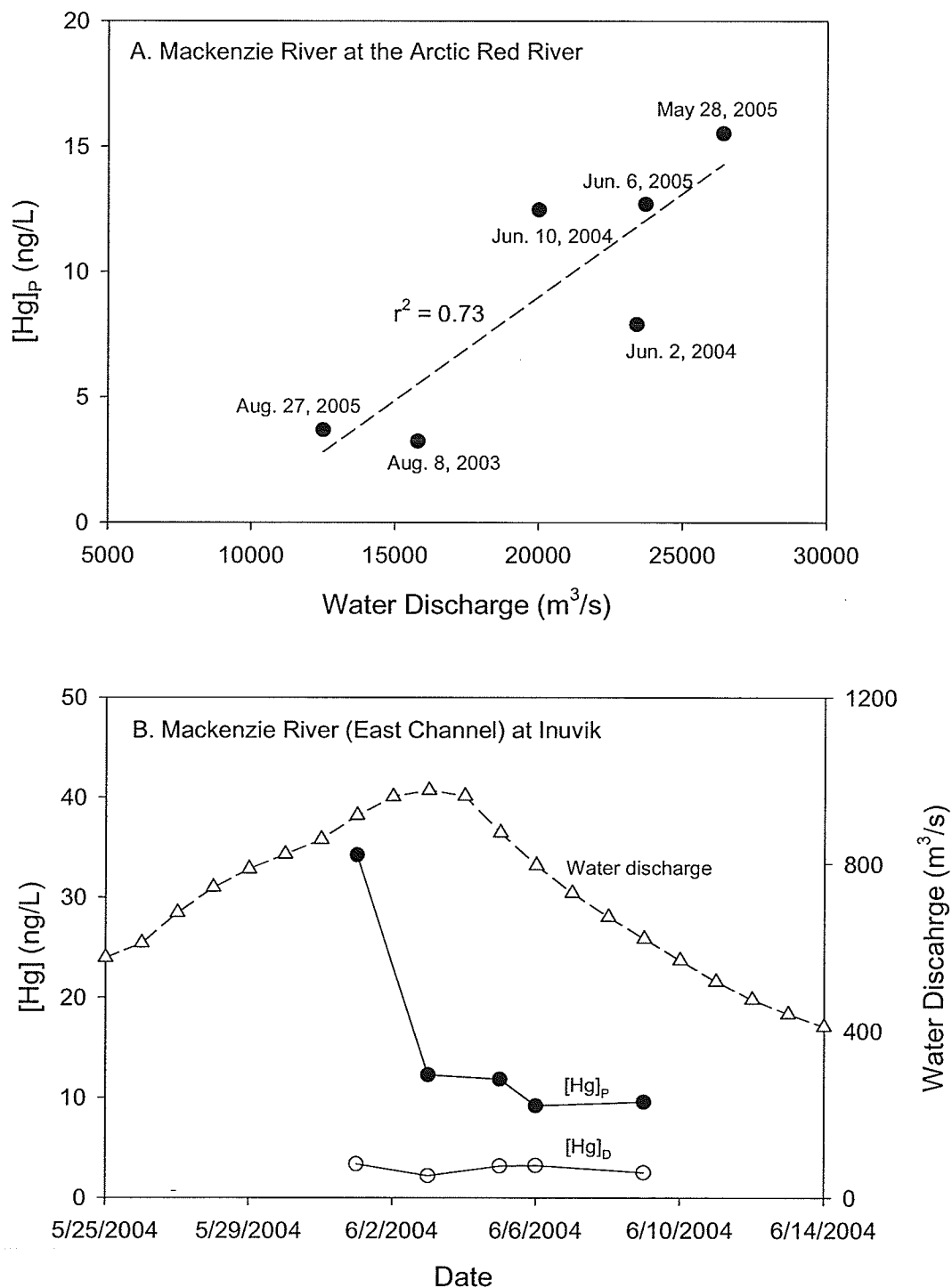


Figure 6. Relationship between a) particulate mercury and water discharge in the Mackenzie River at Arctic Red River between 2003 and 2005, and b) particulate mercury and water discharge measured between June 1 and June 9, 2004 at the East Channel near Inuvik.

young (hundreds of years old) compared to POC (2,300 – 5,000 yBP). Accordingly, higher DOC in the Mackenzie River at high water levels likely results from increased water percolating through relatively young litterfall, followed by the release of DOC-rich interstitial water in the upper soil horizons into surface water run-off (Cauwet and Sidorov, 1996; Guo and Macdonald, 2006; Rember and Trefry, 2004).

Geomorphology

The observation that tributaries draining mountainous terrain to the west of the Mackenzie (e.g., the Peel, Arctic Red, Ontonagon, and Liard) have higher [Hg]_p and [Hg]_s than those on the flatter east side suggests that geomorphology also plays a role in controlling Hg concentrations in the river. This could be due to the rapid response of mountainous, less treed catchments to rainstorms and snowmelt compared to those of lowlands and plains that are less responsive (Brooks, 2000). Sorensen et al. (1990) found significant correlations between [Hg] in lakes and the percentage forest cover of the catchment. There are also more lakes and wetlands to trap sediment on the east side of the Mackenzie River. In particular, approximately 50% of the sediment discharged by the Mackenzie River at its mouth is derived from the Liard River which has very high levels of particulate matter due to the mountainous terrain and the absence of large lakes within its basin (Hirst et al., 1987).

Geology

The Hg hot spots near the Norman Wells area are potentially related to regional geology

(Figure 4). Norman Wells is one of the major petroleum and gas reserves in the Mackenzie basin. Although we do not yet have Hg concentration data for geological materials in this area, the coal and organic carbon-bearing materials are expected to be relatively enriched in Hg due to the strong affinity of Hg to sulphur (Wolfenden et al., 2005). It remains, however, unclear whether the hot spots are caused by natural weathering of Hg-enriched geological materials or by anthropogenic petroleum and gas production.

Forest fire

Another possible contributor to annual variation in Hg concentration is the frequency and extent of forest fire. A wide range of substances including Hg have been found to be associated with runoff from forest fires (especially with particulate matter) (Westerhoff et al., 2004). Most of the Hg from atmospheric deposition accumulates in the organic matter in the upper layer of soil (Meili, 1991) and this layer becomes exposed to erosion following fire. The transfer of POC, DOC (Hobbie and Likens, 1973), and associated Hg to the aquatic system hence increases after forest fires (Garcia and Carignan, 1999). Caldwell et al. (2000) reported a two-fold increase in [Hg] in water in a reservoir after a forest fire followed by a storm. In 2003, there were several fires in the Norman Wells area, where we observed the highest concentrations of Hg, about 1 week before our sampling campaign.

Hg Speciation in the Mackenzie River

On average, $[\text{Hg}]_{\text{D}}$ accounted for $62 \pm 21\%$, $11 \pm 5\%$, and $37 \pm 26\%$ of $[\text{Hg}]_{\text{T}}$ in the lower Mackenzie basin in the summer of 2003, 2004, and 2005, respectively (Appendix 2). No significant relationship was found between $[\text{Hg}]_{\text{D}}$ ($\mu\text{g/L}$) and $[\text{Hg}]_{\text{P}}$ ($\mu\text{g/g}$) in the surface water or $[\text{Hg}]_{\text{S}}$, suggesting that thermodynamic equilibrium has either not yet been reached between dissolved and particulate Hg, or that Hg complexing ligands are present throughout the river at very different concentrations, or that variation in matrix $[\text{Hg}]$ in suspended solids confounds any evidence of equilibrium between particulate surfaces and the water, or due to the loss of $[\text{Hg}]_{\text{D}}$ to the atmosphere. A simple distribution coefficient (i.e., $K_{\text{D}} = [\text{Hg}]_{\text{P}}/[\text{Hg}]_{\text{D}}$) is thus not applicable to this system.

No significant relationship was found between $[\text{Hg}]_{\text{D}}$ and $[\text{DOC}]$ or $[\text{Cl}^-]$ throughout the basin (Appendix 1). However, as mentioned earlier, when examining the water chemistry data at a specific site in the summers of 2004 and 2005, $[\text{Hg}]_{\text{D}}$ was consistently higher in the summer of 2005 when $[\text{DOC}]$ was higher in the river.

On average, $[\text{MeHg}]_{\text{D}}$ accounted for $4 \pm 3\%$, $18 \pm 14\%$, and $32 \pm 30\%$ of $[\text{Hg}]_{\text{D}}$ in the lower Mackenzie basin in the summers of 2003, 2004, and 2005 respectively. MeHg in particulate matter was not determined in this study; it has been reported that MeHg is primarily associated with the dissolved phase in natural waters (Shiels et al., 2001).

As $[\text{MeHg}]$ did not change significantly between seasons and $[\text{Hg}]_{\text{T}}$ was much higher in spring, MeHg contributed a lower percentage of Hg_{T} during spring than summer. This

could be explained by higher levels of inorganic Hg being eroded as old weathered soil particulates in the spring relative to MeHg which may be more associated with the young organic carbon in surface soils. If inorganic Hg and MeHg are equally affected by the higher water levels in spring, the higher percentage of MeHg in summer could be due to a higher methylation rate in response to the higher temperatures (Chen et al., 2005).

Riverine Hg and MeHg Fluxes to the Beaufort Sea

Because the Mackenzie River exhibits a nival flow regime whereby spring flow is very high due to snowmelt accompanied by ice breakup (Figure 5), we divided the annual flow regime into two periods for the purpose of flux calculations: i) the freshet, which is defined here as the period when the flow attains 1.5x the average flow of the preceding 30 days, to the peak flow, and then 10 days after; and ii) the remainder of the year. During the freshet, the river experiences very high water levels and increased shoreline erosion, and hence high amounts of suspended sediment. During the rest of the year, the water levels are much lower, more consistent, and there is much less suspended sediment.

The annual flux (J) of Hg or MeHg is then calculated as:

$$J = C_f Q_f + C_r Q_r$$

where C_f and C_r are the median concentrations of Hg ($[Hg]_D$, $[Hg]_P$, or $[MeHg]_D$) in the Delta region during the freshet (as measured in the spring; Table 2) and the rest of the

year (as measured in the summer; Table 1, respectively. Q_f and Q_r are the total water discharge during the freshet and the rest of the year, respectively.

Since the gauging station on the Mackenzie River at the Arctic Red River is the most downstream station before it splits into many channels in the Delta, we used the daily water discharge data at this station (HYDAT, Environment Canada; <http://www.wsc.ec.gc.ca/hydat/H2O>) (Figure 5) to calculate Q_f and Q_r . The drainage area at this station is $1.68 \times 10^6 \text{ km}^2$ or 94% of the total Mackenzie catchment, missing only the Peel River and several small rivers such as the Rengleng River that drain into the Delta.

As shown in Table 3, our calculations suggest that the Mackenzie River delivered an annual total Hg flux of 2.4, 1.2 and 2.9 tonnes to the Beaufort Sea in 2003, 2004, and 2005, respectively. The majority of the total Hg flux is carried in the form of particulate Hg, which accounts for 73-87% of the annual Hg flux in the past 3 years. The annual dissolved MeHg flux from the Mackenzie River to the Beaufort Sea was 22 and 7 kg in 2003 and 2004, respectively. Since MeHg is mostly associated with the dissolved phase in natural waters (Shiels et al., 2001), the dissolved MeHg flux is likely a good estimate of the total MeHg flux from the river. This amount of MeHg is sufficient to directly contaminate 7,000-30,000 tonnes of beluga muscle (or 6,400 to 27,000 adult beluga whales; assuming an average body weight of 1500 kg, 30% of which is blubber which contains negligible MeHg; pers. comm., L. Loseto, University of Manitoba) to a MeHg level of $1 \mu\text{g/g}$. A fraction of the inorganic Hg transported by the Mackenzie River will eventually be methylated and further contribute to the MeHg pool in the Beaufort Sea.

Table 3. Mercury (Hg) and methylmercury (MeHg) fluxes from the Mackenzie River to the Beaufort Sea.

Year	Season	Water discharge (km ³)	Flux of Hg species (kg)			Total Annual Flux (kg/yr)	
			Hg _D	Hg _P	MeHg _D	Hg _T	MeHg _D
2003 ^a	Freshet	61	134	844	2	2900	22
	Rest of the Year	236	657	1286	20		
2004	Freshet	46	86	680	1	1200	7
	Rest of the Year	206	60	350	6		
2005	Freshet	61	150	920	<1	2400	-
	Rest of the Year	260	510	830	-		

^a river was only sampled in the summer time; see the text for detail.

The high inter-annual variation in the Hg and MeHg flux results from the inter-annual variation in river discharge and the variation of [Hg] with water discharge. It should be noted that in 2003 the river was only sampled once in the summer. In order to get as accurate an estimate as possible, [Hg] from the freshet of 2004 and 2005 were averaged and used to represent the freshet time of year for the loading estimate.

The dissolved and particulate Hg fluxes of several major tributaries in the lower Mackenzie basin were also estimated (Table 4, Figures 7 and 8). Since these rivers were sampled only during summer, the dissolved Hg flux was calculated from the summertime $[Hg]_D$ and the annual water discharge, which likely underestimates the flux. Since the SPM fluxes are available for several of the rivers (Carson et al., 1998), the particulate Hg flux was calculated from the $[Hg]_P$ (expressed in $\mu\text{g/g}$ – which is less sensitive to water discharge) and the SPM flux.

The main-channel of the Mackenzie River upstream of the Liard River confluence delivers approximately 380 kg/yr of dissolved Hg. From there downstream, the Liard River is the largest contributor of Hg_D with a flux of 240 kg/yr. Much smaller Hg_D fluxes are brought into the river by all other tributaries (Figure 7). The Liard River also dominates the particulate Hg flux; it delivers about 3.5 tonnes of Hg_P annually to the Mackenzie River. The Peel River delivers another 1.3 tonnes/yr of Hg_P . It is clear that Hg_P originates almost entirely from the west side of the Mackenzie River from more mountainous terrain with less than 0.2 tonnes originating from all the rivers on the east side combined (Figure 8). This could be partially attributed, at least in the case of the

Table 4. Dissolved and particulate Hg (Hg_D, Hg_P) fluxes of major tributaries of the Mackenzie River.

River	Water Discharge ^a (km ³ /year)	Flux of Suspended Particulate Matter (SPM) ^b (10 ⁶ tonnes/yr)	Average [Hg] _P (ng/g dry wt.)	Average Hg Flux (kg/yr)	
				Hg _D	Hg _P
<i>Draining from the west:</i>					
Peel R.	22	15-25	0.064	37	1280
Arctic Red R.	5.1			10	
Mountain R.	3.9	<5	0.065	8	<330
Keele R.	4.5	5-15	0.083	6	825
Redstone R.	4.6	5-15	0.053	9	540
Root R.	3.1	<5	0.034	3	<170
N. Nahanni River		<5	0.061		<300
Liard R.	78	35-45	0.088	244	3500
Upper Mackenzie (above the Liard)	144 ^c	<5	0.044	379	<220
<i>Draining from the east:</i>					
Willowlake R.	2			14	
Blackwater R.	1.6			7	
Trout R.	1.1			13	
Jean Marie R.	0.14			15	
Wrigley R.	0.22			5	
Big Smith R.	0.18			5	
Great Bear R.	16.7			11	
Hay R.	3.55			23	
All eastern tributaries		<5	0.035		<180

^a HYDAT Data

^b from Carson et al. (1998)

^c At Strong Point

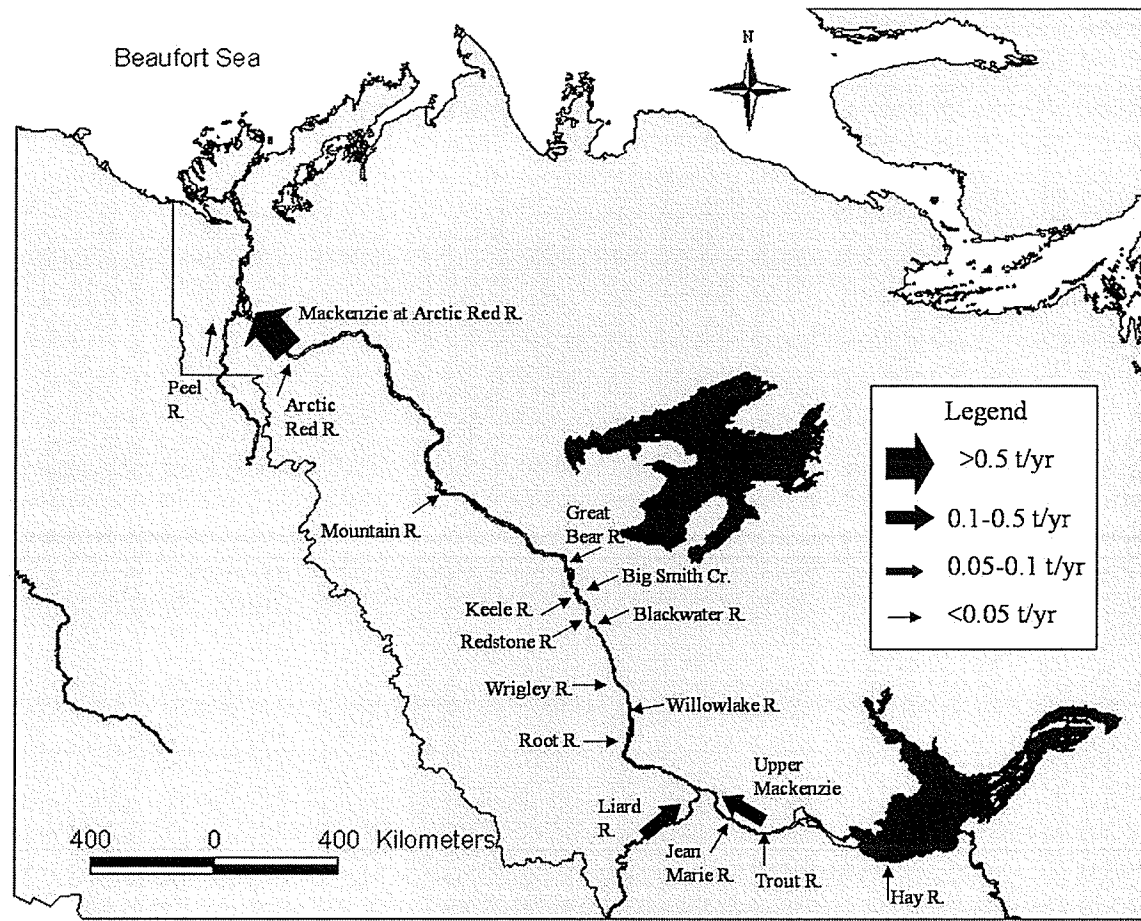


Figure 7. Dissolved Hg fluxes in the lower Mackenzie Basin estimated from water flow data (Environment Canada) and dissolved Hg measurements (this study).

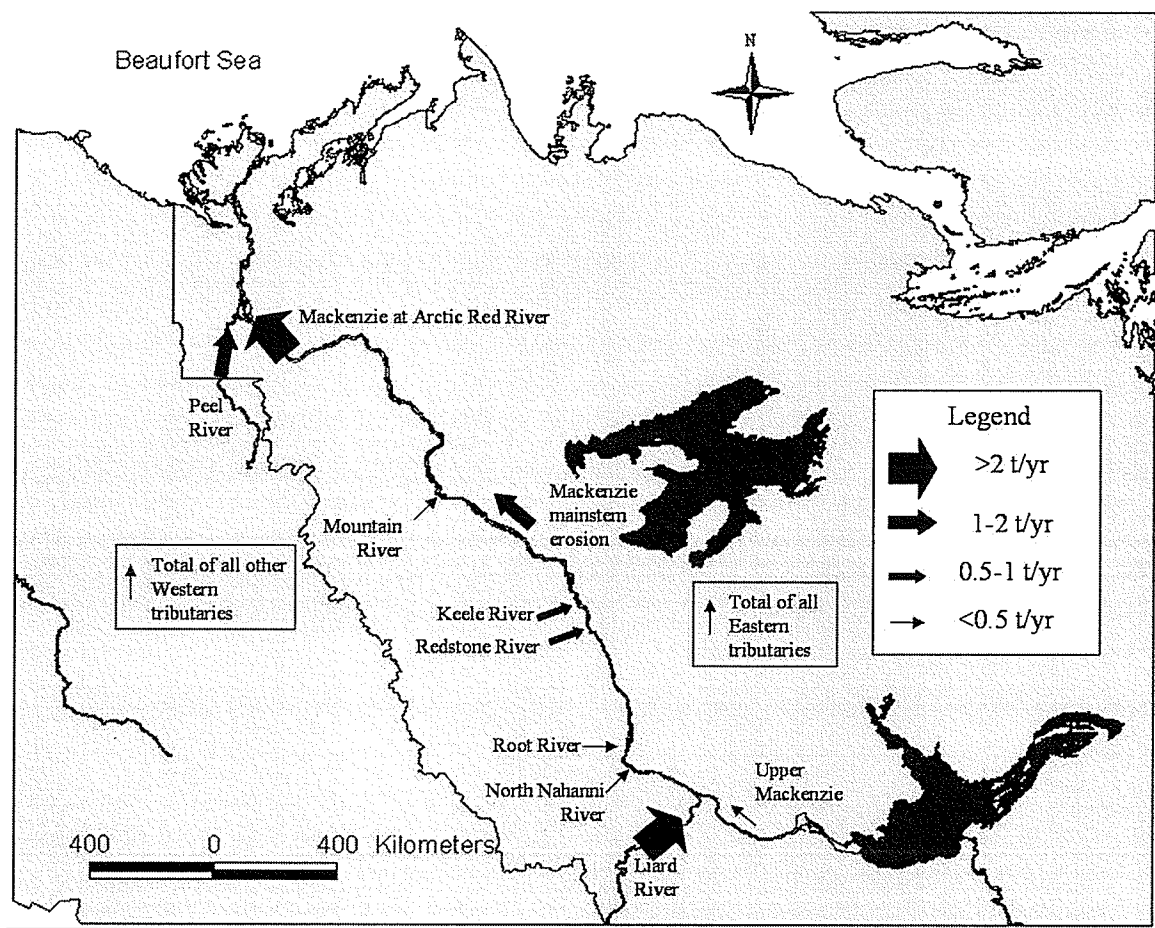


Figure 8. Particulate Hg fluxes in the lower Mackenzie Basin calculated from sediment Hg concentrations and sediment fluxes estimated by Carson et al. (1998).

Mackenzie River and the Great Bear River, to the rivers having large headwater lakes and wetlands, which act as sediment traps. Since the Hg_P flux in the Mackenzie at the Liard River is much higher than that at the downstream site at the Arctic Red River, a significant fraction of Hg_P must have been trapped in the sediment of the Mackenzie River or volatilized between these two sites.

Total Hg Budgets to the Beaufort Sea

Our estimate of the Hg flux from the Mackenzie River compares well with those estimated by Coquery et al. (1995) for the three major Russian Arctic Rivers, the Lena, the Ob and the Yenisei (Table 5). It should be noted, however, that the Russian rivers were sampled only once in late summer which would lead to an underestimate of flux due to the higher concentrations generally found during the freshet.

No reliable estimate has been made for net atmospheric deposition of Hg to the Beaufort Sea or the Arctic Ocean. Assuming that mercury depletion events (MDE) led to the enhanced snowpack $Hg(II)$ concentrations observed in the spring of 1998 at SHEBA in the Canada Basin and prorating this deposition to the entire High Arctic ($7 \times 10^6 \text{ km}^2$), Lu et al. (2001) estimate that MDEs deposit ~ 17 tonnes of Hg to the surface of the Arctic Ocean. For the area of the Beaufort Shelf adjacent to the Mackenzie River ($60,000 \text{ km}^2$), a similar estimate suggests a deposition of 0.15 tonnes/yr or, for the entire Beaufort Sea ($590,000 \text{ km}^2$), 1.4 tonnes/yr. Given recent findings that much of the $Hg(II)$ deposited in the snowpack during MDEs is photoreduced and released back to the atmosphere (e.g.,

Table 5. Hg flux estimates to the Arctic Ocean.

Source	Total Hg Flux (tonnes/yr)		Reference
	Beaufort Sea	Entire High Arctic Ocean	
Mackenzie R.	2.2± 0.9	2.2 ± 0.9	This study
Lena R.		4.0 ^a	Coquery et al., 1995
Ob R.		1.3 ^a	Coquery et al., 1995
Yenisei R.		0.7 ^a	Coquery et al., 1995
Atmosphere	<<1.4 ^b	<<17 ^b	Lu et al., 2002
Coastal erosion	0.6	?	Leitch, 2006

^a Calculated based on one sampling event only in late summer

^b Assuming all the Hg(II) from MDEs ends up in the ocean

Poulain et al., 2004), the actual atmospheric contribution to Hg in the Arctic by this process is likely much smaller.

Given that coastal erosion in the Beaufort Sea contributes much smaller loadings of sediments and water than the Mackenzie River (Macdonald et al., 1998), and that this material does not contain anomalously high mercury concentrations (Leitch, 2006) this source appears unlikely to support Hg fluxes greater than ~ 0.6 tonnes/yr.

Based on the above estimates and the Table 5 compilation, we conclude that riverine input is likely to be the largest source for Hg to the Arctic Ocean and that the Mackenzie River is the largest Hg source to the Beaufort Sea. This finding is very different from the general conclusion that, globally, rivers account for only about 10% of total inputs to oceans. This may not be surprising, as the Arctic Ocean is an exception in the world's oceans in its domination by river inputs of runoff, sediments and organic carbon (Shiklomanov, 2000; Stein and Macdonald, 2004). Indeed, the Arctic Ocean is the only ocean where the drainage area is considerably larger than the ocean surface area itself (1.5x more land area than ocean area) (Peterson, 2002; Shiklomanov and Shiklomanov, 2003).

As shown in Table 3, ~50% of the annual total Hg flux by the Mackenzie occurs during the spring freshet. Semkin et al (2005) also found that the spring freshet was the major source of Hg_T to a High Arctic Canadian lake. The significance of these springtime loadings is that they occur at, or just before primary production commences in the estuary and when many Arctic animals (including marine mammals) are most sensitive to

bioaccumulative contaminants such as Hg due to active foraging and rapid growth rates after the long winter (Lindberg et al., 2002; Lu et al., 2001).

Implications of Climate Variation in the Mackenzie Basin

As a dominant component of the cryosphere, the Arctic is especially vulnerable to climate change (ACIA, 2004). Estimates of the temperature increase in the Mackenzie basin vary between an average increase of air temperature of 1.5°C over the last 50 years (Zhang et al., 2000) to 2°C/decade (Stewart et al., 1998). Climate stations have also shown varying degrees of temperature increase with more northerly stations showing more drastic increases: Inuvik: +0.9°C/decade, Yellowknife: +0.7°C/decade, Fort McMurray: +0.5°C/decade (Woo and Thorne, 2003). The warming of the Mackenzie Basin is expected to significantly change the Hg cycle in the Mackenzie Basin and its downstream coupling with the Beaufort Sea in several ways.

i) Water discharge: Regression analysis shows that the water discharge of the Mackenzie River has been increasing at a rate of 0.6 km³/year over the past 35 years (Peterson, 2002). This will produce a very modest increase in Hg flux to the Beaufort Sea by means of a simple increase water volume discharged, as well as due to the increased Hg concentration because of surface runoff and bank erosion caused by higher water levels, as demonstrated in 2003-2005.

ii) Freshet and flooding events: The warming of the Mackenzie Basin has been shown to be especially significant in April (Woo and Thorne, 2003), which could further advance

the dates of snowmelt and spring break-up. Spring breakup on the Mackenzie has already advanced by an average of 3 days per decade since 1973 (Woo and Thorne, 2003). As the freshet season discharges approximately 50% of the total Hg flux, an advance in the freshet season would further align the peak Hg input time with the rapid growth season of marine biota. One of the manifestations of climate change is likely to be storm events which then lead to flushing of sediments and inundation of low-lying flood plains (cf. ACIA, 2005). In particular, the interaction between deltaic lakes and the river during freshet seems likely to impact the Hg cycle. This interaction depends strongly on water level which itself depends on flow and, during spring, ice jamming, both of which are subject to climate change. Flushing of shallow deltaic lakes leads to trapping of sediments and organic carbon (see, for example, Burn, 1995; Rouse et al., 1997) and, potentially, the entry of MeHg from wetlands and lakes, which are likely to be sites of enhanced Hg methylation.

iii) Forest fires: The warming of the Mackenzie Basin is predicted to increase the occurrence of forest fires in the basin (Flannigan et al., 2005; Kadonaga, 1997; Kochtubajda et al., 2006). The area burned within the Mackenzie Basin is predicted to increase by 39% to 57% above current levels with a tripling of CO₂ by 2100 (Flannigan et al., 2005). As the population of the Mackenzie basin is increasing (Bone et al., 1997), human-caused forest fires are also likely to increase. An increase in forest fire occurrence and extent will likely result in increased Hg runoff to the Mackenzie River during high water flow events (e.g., freshet, storms).

iv) Temperature rise: Increase in temperature may have several effects, one of which will be the release – or partial release – of contaminant Hg stored in snow and soils during the past two centuries. A second effect will be the likely increase in Hg methylation due either to the kinetic increase of methylation itself or the increase in organic loading (terrestrial and aquatic), brought about by change, which then produces more widespread methylating environments. Hg methylation is thought to be mainly mediated by sulphate-reducing bacteria in wet locations, the activity of which is promoted at higher temperature. Since MeHg is the most toxic Hg form that bioaccumulates and biomagnifies, any increase in the MeHg flux to the Beaufort Sea will exacerbate the Hg problem in marine mammals.

Concluding Remarks

The Mackenzie River is the largest river flowing to the Beaufort Sea, and one of the largest rivers emptying into the Arctic Ocean. Flowing through a vast terrain in Northern Canada, which has been experiencing one of the most noticeable climate warming trends in North America, this river plays a major role in the biogeochemical cycles of major and trace elements in the continental-ocean-atmosphere system of the western Arctic. Several locations in the lower Mackenzie basin seem to have elevated Hg concentrations, including the Liard River and the Norman Wells area. It remains unknown at this time whether this is due to geological enrichment, forest fire, or other processes. Based on an intensive study along the lower Mackenzie Basin and the Delta region during 2003-2005, we estimate that the Mackenzie River discharges 2.2 ± 0.9 tonnes/yr of total Hg into the Beaufort Sea, a portion of which (7-22 kg) is in the form of MeHg. When compared with

limited literature on other potential Hg sources, the Mackenzie River seems to be overwhelmingly the largest source of Hg to the Beaufort Shelf and, potentially, the largest source of Hg to the upper ocean of the Beaufort Sea.

Because the annual Hg flux of the Mackenzie River co-varies strongly with the water discharge, the average annual Hg flux value (i.e., 2.2 tonnes/yr for 2003-2005) needs to be viewed with caution. In a high water-level year, not only will seaward water discharge increase, but also the Hg concentration carried in the water will increase resulting in magnification of the Hg flux. For example, the annual water discharge in 2003 (298 km³) and 2005 (321 km³) was about 1.2 times that of 2004 (253 km³/yr), but the Hg flux in 2003 and 2005 (2.9 and 2.4 tonnes) was more than double that of 2004 (1.2 tonnes). Accordingly, future change manifest in more frequent flood events will likely be a sensitive mechanism to enhance Hg loading to the Mackenzie's estuary.

The finding that ~50% of the annual seaward Hg flux is delivered in a rather short freshet period (45 days as defined in this study) warrants particular attention, as this is close to the fast growth season of many animals including marine mammals. It is of critical importance to probe whether this has played a major role in the extremely high Hg concentration in beluga in the Beaufort Sea area, and how this will change with climate variations in the Mackenzie Basin.

Furthermore, the problem of elevated Hg concentrations in marine mammals in the Beaufort Sea cannot be viewed appropriately without a better understanding of the

continent-ocean-atmosphere interactions in the entire Arctic Ocean. Although progress has been made on constraining the riverine Hg input (e.g., Coquery et al., 1995 and this study), further work is needed to quantify the relative importance of other fluxes (e.g., atmospheric deposition, coastal erosion, oceanic circulation, biotic transport), as well as the uptake and transport of Hg and MeHg in the Arctic food webs.

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Chapter 3 – Permafrost melt and coastal erosion as a source of mercury to the Beaufort Sea

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Abstract

Levels of Hg in marine mammals in the Beaufort Sea have been recently reported to be extremely high. To investigate the role of permafrost melt and coastal erosion as a potential contributor of Hg to the marine environment, permafrost cores were taken from 5 sites along the Canadian portion of the southern Beaufort Sea coastline. Samples showed two distinct profiles; one with a Hg peak near the surface, and another with no peak. This is possibly due to a loss of the upper layer by erosional processes. Two cores were also dated to investigate the possibility of using permafrost to re-construct historic atmospheric Hg deposition rates. Using existing permafrost degradation rates, we calculate that approximately 610 kg of Hg is deposited into the Beaufort Sea marine environment via permafrost degradation annually. As increases in temperature, storms, waves, open water, and sea level are currently being observed and predicted to further increase in the future, it is anticipated that permafrost melt and coastal erosion will also increase. This would subsequently increase Hg flux to the Beaufort Sea.

Introduction

Recently it has been reported that mercury (Hg) levels in beluga livers in the Beaufort Sea area have increased significantly over the past 20 years (Lockhart et al., 2005). Although no guidelines exist for marine mammals in Canada, the levels are 27-58 times higher than Canadian guidelines for consumption of commercial fish tissue (0.5 µg/g wet weight, CFIA). This raises concerns over the health of marine mammals and the indigenous peoples who consume marine mammal tissues as part of their traditional diet.

The source of elevated Hg levels in the western Arctic is not yet known. Although long-range atmospheric transport of anthropogenic Hg is thought to be an important source of Hg to the Arctic (Macdonald et al., 2000), atmospheric levels have remained relatively stable over at least the past 10 years (Steffen et al., 2005). Recently, mercury depletion events (MDEs) were thought to be responsible for depositing massive quantities of Hg to the Arctic (Lu et al., 2001; Schroeder et al., 1998), but it has been shown that much of the deposited Hg is quickly photoreduced to Hg⁰ and released back to the atmosphere (Lalonde et al., 2002; Poulain et al., 2004; St. Louis et al., 2005; Steffen et al., 2005). We thus believe processes other than atmospheric transport are responsible for the increasing Hg levels in the western Arctic. Among potentially important processes are fluvial Hg transports from rivers emptying into the western Canadian Arctic (e.g., the Mackenzie River; Leitch et al., under review – Chapter 2), direct terrestrial Hg transport via permafrost degradation (melted permafrost and coastal erosion), oceanic Hg transport from other more contaminated marine sites, and changes in beluga feeding habits and food web structures.

As part of a broader study, here we assess the potential influence of permafrost thaw and coastal erosion as a source of Hg to the Beaufort Sea. Permafrost is defined as soil that remains below 0°C for at least two consecutive years (IPA, 1998). Because the western Arctic has been identified as an area of potentially significant climate change (Mitchell et al., 1995; Zwiers, 2002), already high rates of coastal erosion and permafrost melt are expected to accelerate (Lantuit and Pollard, 2005). A reduction in sea ice extent and duration (Cavalieri, 1997; Chapman and Walsh, 1993), sea level rise, increased wave activity, and thawing permafrost (Nelson et al. 2002; Pavlov, 1994) have already been observed in the western Arctic. The southern Beaufort Sea coast is also one of the most ice-rich areas in the entire Canadian Arctic (Lantuit and Pollard, 2006) making it especially vulnerable to an increase in air temperature (Aylsworth et al., 2000). Predictions anticipate a further increase in open water and occurrence of large waves (McGillivray et al., 1993). As a result, permafrost is recognized as a large potential source of greenhouse gases, organic carbon (Bockheim et al., 1999; Heginbottom, 2000; Jorgenson and Brown, 2005; Oechel et al., 1995), and organically bound trace metals including mercury to the Arctic Ocean (Macdonald et al., 2005). No quantitative studies have been reported on the contribution of Hg from permafrost degradation. Givelet et al. (2004) were the first to report Hg profiles in dated peat cores (including both the active layer and permafrost) in the Canadian High Arctic. The record obtained from two sites on Bathurst Island was used to reconstruct historical atmospheric Hg deposition rates in the High Arctic, the validity of which has been complicated by the vertical mixing due to processes such as desiccation cracks (Bindler et al., 2005; Givelet et al., 2004; Shotyk et al., 2005).

Here we report the first attempt to quantify the potential importance of permafrost melt and erosion as a source of Hg to the Arctic Ocean. Mercury profiles in 6 permafrost cores across the southern coastline of the Beaufort Sea were obtained. The surface active layer of two of the cores was further dated using the ^{210}Pb and ^{137}Cs methods to evaluate the possibility of reconstructing Hg depositional chronology in the past 200 years. Our focus, however, was on the potential quantity of Hg released via permafrost degradation, and its response to ongoing climate change.

Materials and Methods

Study Area

The southern coastline of the Beaufort Sea is within the Arctic Coastal Plain (Bostock 1967). The Canadian portion is more than 2000 km long reaching from the Yukon-Alaska border to Tuktoyaktuk peninsula (Figure 1). With the exception of deep lakes and river channels, the entire area is underlain by continuous permafrost. The presence of ice in the surficial sediments strongly affects coastal morphology and stability (Harper, 1990). Approximately 80% of the Canadian Beaufort Sea coast is considered to be erosional (Harper, 1990). The coastline is comprised mainly of unconsolidated Quaternary sediments including fluvial, glacial and marine deposits, which are locally capped by organic deposits (Harper and Penland, 1982; Wolfe et al., 2000).

Harper and Penland (1982) divide the area into 3 geographic regions: (1) Tuktoyaktuk peninsula, which generally has low (<5 m) variable-ice bluffs with many thermokarst

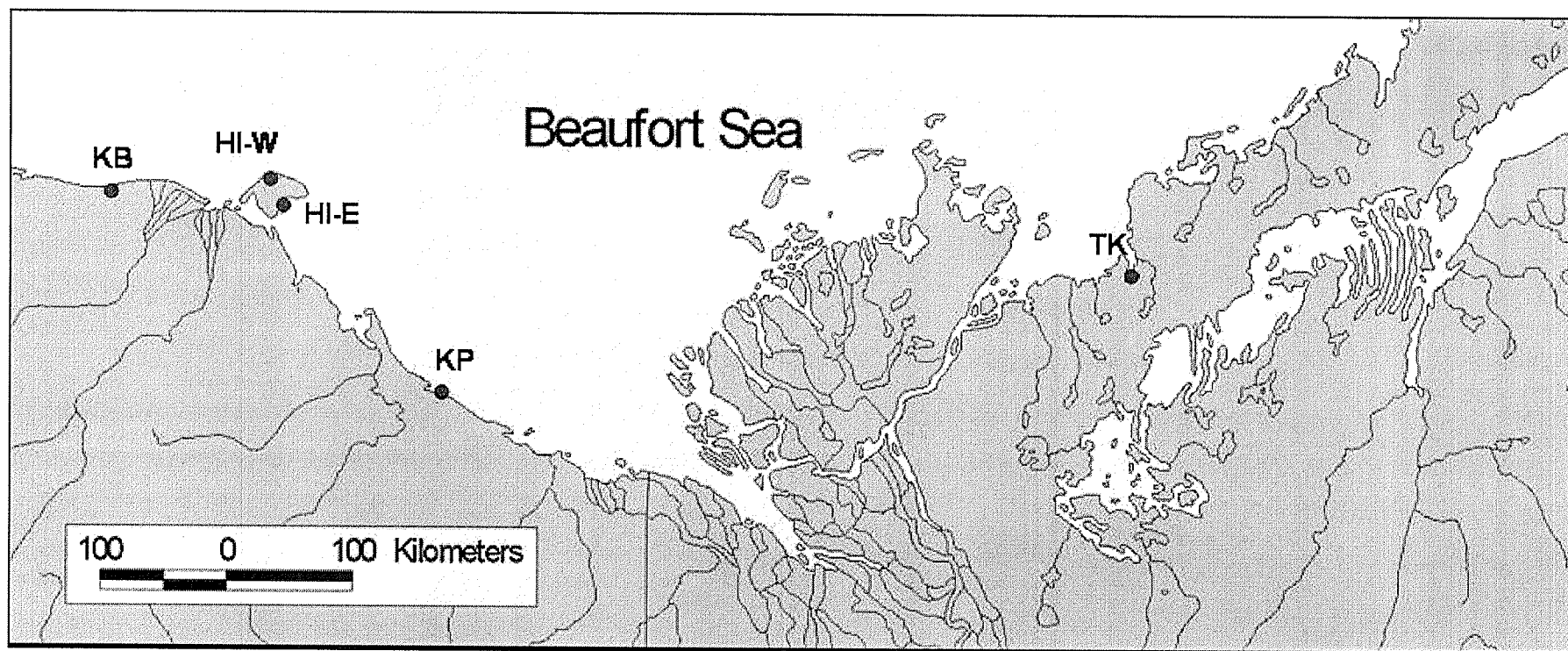


Figure 1. Permafrost sampling sites along southern Beaufort Sea coast (KB – Komakuk Beach, HI-W – Herschel Island West, HI-E – Herschel Island East, KP – King Point, TK – Tuktoyaktuk).

lakes and pingos off shore (Harper, 1990; Rachold et al., 2000). This area is dominated by fine ice-rich organic deposits (Rampton and Mackay, 1971). (2) The Mackenzie River Delta and outer islands, which have low (<1.5 m) bluffs composed of fine deltaic organic-rich sediments and glacial-marine sediments (Mackay, 1963; Rachold et al., 2000), and (3) The Yukon Coastal plain, which is composed of variable-sized bluffs (up to 30 m) with variable ice content (Rachold et al., 2000). Sediments here are mainly of glacial and glacial-marine deposits (Rampton, 1982). Just off shore from the Yukon Coastal plain, Herschel Island is a remnant of a glacial ice-thrust formed during the Wisconsin glaciation and is characterized by fine-grained marine sediments and coarser grained coastal deposits (Lantuit and Pollard, 2006) and a rolling topography rising to a maximum elevation of 183 m (de Krom, 1990 *in* Kokelj et al., 2002; Mackay, 1959; Lantuit and Pollard, 2006).

The climate in this area has been described as polar continental (Turner, 2004). Surface air temperatures vary between monthly averages of -25°C and -26°C in February and +8°C and +11°C in July for Komakuk Beach and Tuktoyaktuk respectively, but can drop to as low as -50°C in winter, and as high as +30°C in summer. The region is arid, receiving only ~150 mm total precipitation annually, of which approximately ½ is in the form of snow. The ground is generally snow-free for approximately 4-5 months a year (June-Sept./Oct.) (Environment Canada). The Beaufort Sea is ice-free for 3-4 months each year and is completely covered by sea-ice from mid-October to the end of June (Solomon, 2005). Dominant winds on the eastern Beaufort Sea tend to be from the northwest and southeast, while further west near Komakuk beach, dominant winds are

from the east and west (Harper and Penland, 1982). Storm winds prominently come from the north-west (Harper and Penland, 1982). Waves are predominantly from the northwest, especially larger waves (>2 m) (Baird and Hall, 1980 *in* Hill et al., 1991).

Sample Location and Collections

Six permafrost cores were collected from 5 sites along the coast of the Canadian Beaufort Sea, stretching from Tuktoyaktuk to Komakuk Beach (Table 1). Sampling sites were chosen in areas of high permafrost degradation activity.

Tuktoyaktuk ($69^{\circ}24.111\text{N}$, $133^{\circ}01.677\text{W}$) is located east of the Mackenzie Delta approximately 120 km north of Inuvik. The sample site was situated approximately 100 m from a bay connected to the Beaufort Sea. The vegetation was very short with some knee-high willow-like vegetation. Two replicate cores were taken from the same site.

King Point ($69^{\circ}05.512\text{N}$, $137^{\circ}56.741\text{W}$) is located 190 km northwest of Inuvik and 70 km southeast of Herschel Island. The core was taken 5-10 m from the top edge of a high coastal bluff (5-10 m elevation) undergoing active coastal erosion.

Herschel Island is approximately 60 km east of the Yukon/Alaska border and 3 km north of mainland Yukon. Two sites were sampled on the island. The sample site on the west shore ($69^{\circ}38.006\text{N}$, $139^{\circ}04.134\text{W}$) was situated atop a high cliff (~ 50 m elevation) above an area of active coastal erosion. The site on the east coast of Herschel Island (69°

Table 1. Description of permafrost sampling sites.

Sample ID	Sample Site	Latitude	Longitude	Date of Sampling	Active layer depth (cm)	% Moisture
TK-1	Tuktoyaktuk	69°24.111 N	133°01.677 W	Sept. 10, 2003	37	-
TK-2	Tuktoyaktuk	69°24.111 N	133°01.677 W	Sept. 10, 2003	49	-
HI-W	Herschel Island – West	69°38.006 N	139°04.134 W	Aug. 11, 2004	52	22±4
HI-E	Herschel Island - East	69°32.736 N	139°03.440 W	Aug. 16, 2004	88	20±5
KP	King Point	69°05.512 N	137°56.741 W	Aug. 13, 2004	32	53±16
KB	Komakuk Beach	69°35.575 N	140°13.643 W	Aug. 17, 2004	43	82±7

32.736N, 139° 03.440W) was situated approximately 5 m back from the headwall of a large retrogressive thaw slump at an elevation of ~20 m. Retrogressive thaw slumps are a backwasting type of thermokarst (irregular, hummocky terrain formed by the melting of permafrost), generally initiated by coastal erosion, where large volumes of sediment are eroded in an inland direction (French, 1996). Slumping had previously occurred at the sample site, but has been re-vegetated.

Komakuk Beach (69°35.575N, 140°13.643W) is situated within Ivvavik National Park. We sampled several kilometers to the west of a Distant Early Warning (DEW) military site. This area was covered with polygons formed by ice wedges (referred to as ice wedge polygons). The permafrost core was taken from the middle of a polygon, ~5 m from the edge of a low (5 m) cliff overlooking the Beaufort Sea in an area of abundant active coastal erosion.

Samples from Tuktoyaktuk were collected in early September of 2003, while samples from west of the Delta were collected in mid-August of 2004.

Active layer (defined as the portion of the ground that thaws in summer) samples were collected at intervals of 1 cm for the upper 20 cm generally, and then 2 cm thereafter, using a stainless steel saw and stainless steel knife. Permafrost samples were collected with a modified CRREL coring auger with a Stihl 4308 model powerhead (with gear reduction to 150:1) and a 3" (7.6 cm) diameter stainless steel core barrel (supplied by the Geological Survey of Canada). Cores were kept frozen and intact and brought back to the

laboratory where they were sliced (while frozen) using a stainless steel hacksaw blade. 1- or 2-cm slices were sub-sectioned every 3 to 5 centimetres. All samples were stored in Ziploc bags and kept frozen until analysis.

Analytical Methods

Samples were freeze-dried in the laboratory at the Freshwater Institute in Winnipeg. Sample weights were recorded before and after freeze-drying to obtain the percent moisture. Samples were mixed within the Ziploc bag, and when necessary (hard chunks present), ground into a homogenous mix using a clean mortar and pestle.

For Hg analysis, ~0.3 g of dry sediment from each slice was weighed out into clean test tubes. Samples were then boiled in an aqua regia (3:1 hydrochloric and nitric acid) solution at 120°C for 30 min in a digestion block to oxidize organic Hg into inorganic Hg (using a procedure adapted from Method CAS-AM-70.13 by Dow Chemical of Canada Ltd., described in detail elsewhere, i.e Lockhart et al., 1998). Sample extracts were then analyzed for total Hg by Cold Vapour Atomic Absorption Spectrophotometry on a Mercury Monitor 3200 Elemental Mercury Detector (Thermo Separation Products) where a SnCl_2 reductant was added to reduce Hg to the elemental state. Certified reference materials MESS-3 and LKSD-1 (the National Research Council of Canada) were used and found to be within 15% of their certified values of 0.091 and 0.110 $\mu\text{g/g}$ respectively.

Permafrost Core Dating

From the homogenized slices, sub-samples were taken for radioisotope dating. Two cores were dated by measuring the ^{210}Pb and ^{137}Cs activity, as described elsewhere (Lockhart et al., 2000). Both linear and constant rate of supply (CRS) models (Robbins, 1978) were used to estimate sedimentation rates.

Results and Discussion

Vertical distribution of Hg

Hg concentrations in the permafrost cores ranged between 26 and 303 ng/g (dry weight) along the Beaufort coastline (Figure 2). In general, two different types of Hg profiles were observed.

The first type of profile shows a near-surface peak in the Hg concentration followed by a much lower, relatively constant “background” Hg concentration in the deeper layer of the core, similar to what was reported by Givelet et al. (2004). This includes the two replicate cores from Tuktoyaktuk (TK-1, TK-2) and the cores from King Point (KP) and Komakuk Beach (KB), but the background level and the location and magnitude of the peak Hg concentration differed from site to site. The background Hg levels at Tuktoyaktuk and King Point were approximately 100 ng/g (dry weight). The Hg concentration peaked at levels near 300 ng/g (dry weight) in each of these cores, approximately 3x higher than background levels. In the uppermost 2 or 3 cm, Hg levels decreased. The core from Komakuk Beach was similar to these cores, but with lower levels of Hg. The background

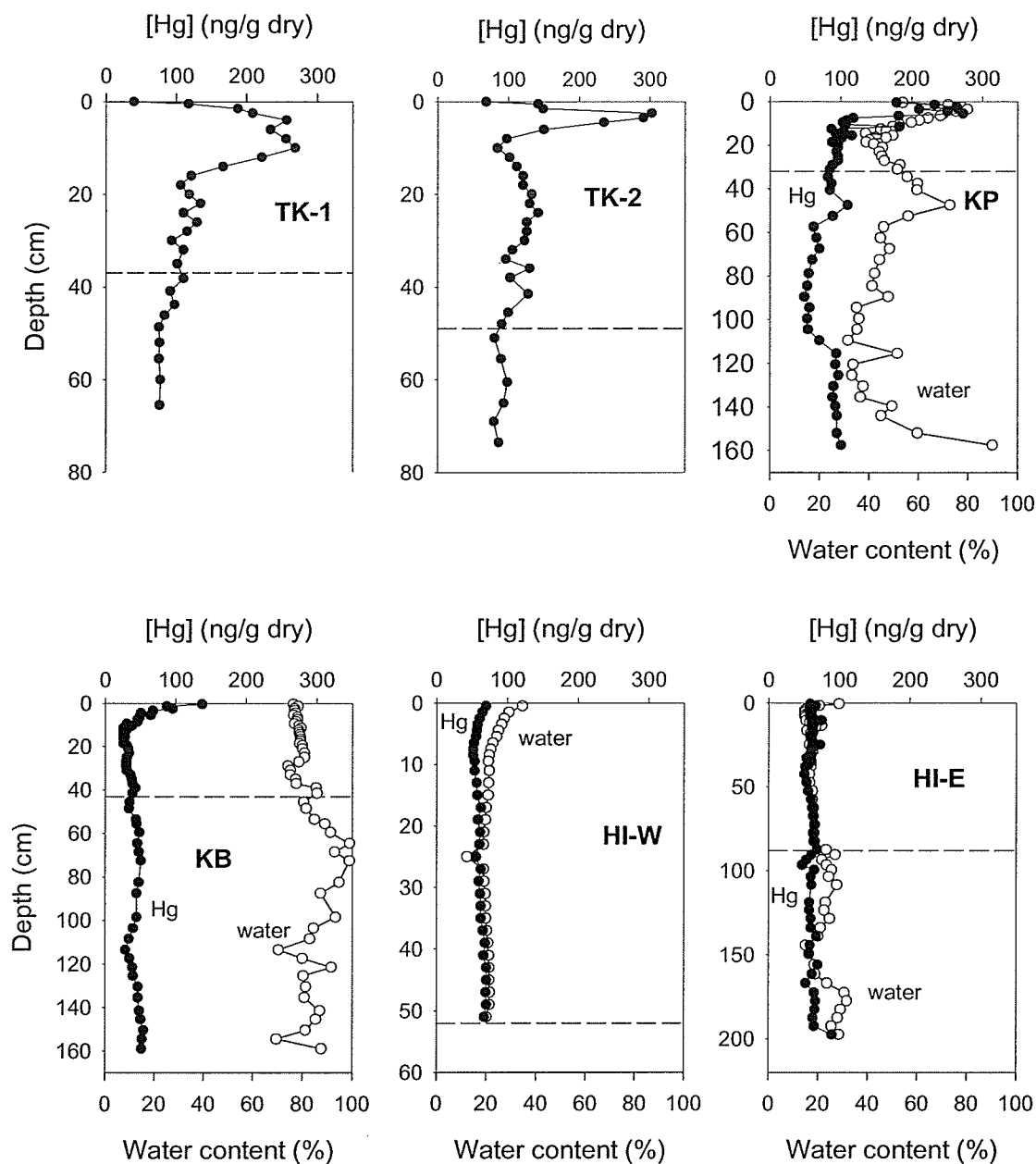


Figure 2. Profiles of the Hg concentration and water content in the permafrost cores. The dashed line represents the boundary between the surface active layer and bottom permafrost.

was approximately 40 ng/g (dry weight), the peak increased to only about 150 ng/g, and there was no decrease right at the surface as there was with the other 3 cores.

In contrast, the two cores from Herschel Island showed no peak in Hg. Although taken from opposite ends of the island, both cores showed a straight line of steady Hg levels of about 60 ng/g (dry weight). No cores showed any change before or after the permafrost-active layer interface. While we do not have conclusive evidence, we suspect that the straight Hg profile obtained in Herschel Island might be a “pseudo” profile, due to the recent loss of the Hg-enriched surface layer (e.g., slumping) or, less likely, vertical transport and mixing of the Hg, as supported by the ^{137}Cs profile discussed below.

^{210}Pb and ^{137}Cs dating

Figure 3 shows the ^{210}Pb and ^{137}Cs dating results for the surface section of the cores from King Point (KP) and Hershel Island (HI-W). These cores were selected because they represent the two types of profiles observed. Neither sites were peat bogs, but a layer of peat did exist (especially at KP). In the future, we intend to analyse ash content of the cores to ascertain the ombrotrophic (receiving moisture solely from the atmosphere) or minerotrophic (receiving moisture from both atmosphere *and* groundwater) status of the peat. Ombrotrophic peat bogs are recognized as the best stores of historical Hg. The KP core showed reasonable chronological results with a well preserved ^{137}Cs activity peak (Figure 3, Appendix 5). Although the ^{137}Cs activity apparently peaked later than expected (1977 vs. expected 1964), this is likely due to the low temporal resolution of the core sectioning. This could also be the result of the ^{137}Cs mobility in sediments with minimal

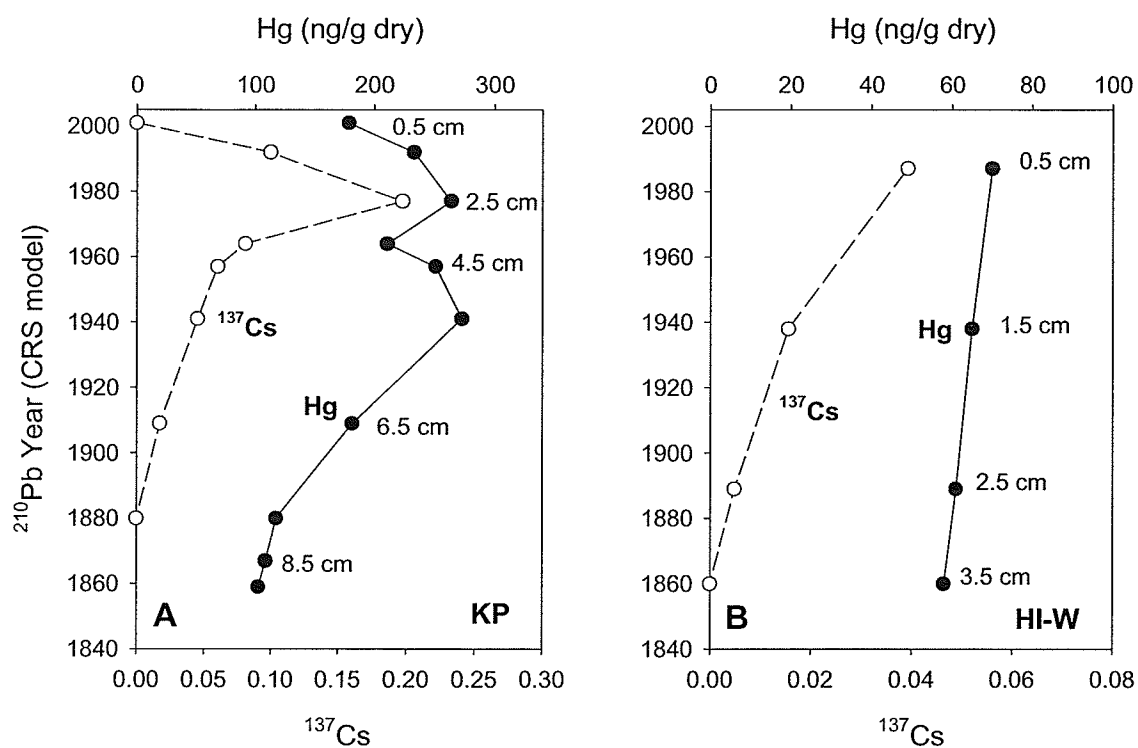


Figure 3. ^{210}Pb dated vertical distribution of Hg at a) King Point and b) Herschel Island – West.

clay (Davis et al., 1984). The calculated peat accumulation rate was approximately 0.05 cm/year for the past 140 years. Since the cores were cut into 1 cm section, each section thus represents the accumulation in approximately 20 years. Much thinner sections would be required to confirm the exact location of the ^{137}Cs peak.

In contrast, the ^{137}Cs peak was absent in the HI-W core. ^{210}Pb years for this core were also more compressed (i.e. more years were represented within a smaller vertical distance) than the KP core (Figure 3, Appendix 6). Although the HI-W site showed no obvious sign of previous erosion (as HI-E did), together with the lack of a subsurface Hg peak, we suspect that the top layer of the recently accumulated material at this site has been disturbed (either eroded away or, less likely, vertically mixed). It could also be a result of the “coarse” sampling resolution with such slow peat accumulation, where 1 cm slices represent approximately 36 years. This would make it difficult to distinguish both the ^{137}Cs and the Hg peaks. Another possible reason for the very different profiles could be the different origin of sediment as compared to other areas along the Beaufort Sea coast. As previously discussed, Herschel Island was formed from a glacial ice-thrust and is composed of fine-grained marine sediments. Perhaps this substrate is more subject to the vertical movement of contaminants.

Assuming that the Hg within the cores originated solely from atmospheric deposition (Givelet et al., 2004; Shotyk et al., 2003), the King Point core shows that Hg deposition began increasing in the early 1900s. Levels peaked between 1940 and 1980, and have been declining since. At its peak, levels were ~2.5x ‘background’ baseline values, which

is comparable to inferred atmospheric deposition increases found elsewhere in the Arctic (Asmund and Nelson, 2000; Coggins et al., 2006; Jensen and Jensen, 1991; Lockhart et al., 1996), although it has been suggested that many similar studies did not show true background levels because of either other Hg sources, or from overly short cores that did not look far enough back in time (Bindler, 2003). The peak coincides temporally with atmospheric emissions and Hg peaks found elsewhere as well (Bindler, 2003; Givelet et al., 2003; Hylander and Meili, 2003; Norton et al., 1997). The decline after 1980 coincides with a decrease in anthropogenic Hg emissions circa 1970 (Hylander and Meili, 2003). We will analyze for Br and Se in the future to help tell us the anthropogenic versus natural Hg contributions.

Hg Flux from coastal erosion

Coastal retreat has been widely documented at different areas along the southern Beaufort Sea coast (for example: Harper and Penland, 1982; Hill et al., 1991; Jorgenson and Brown, 2005; Lantuit and Pollard, 2006; Solomon, 2005). More recent estimates have placed coastal retreat in the order of 0.45 m/yr (Herschel Island) to 0.6 m/yr (Mackenzie Delta region) (Lantuit and Pollard, 2006; Solomon, 2005). Locally, retreat varies significantly with variations in coastal bluff height, coastal geology, ice content, and exposure, with some areas eroding at rates in excess of 20 m/yr (Harper, 1990; Hequette and Barnes, 1990; Macdonald et al., 1998; Solomon, 2005). The highest rates tend to be in areas most exposed to north-west winds (Solomon, 2005). Silty sediments tend to erode at a greater rate than sandy soils (Jorgenson and Brown, 2005). Year to year variability is also quite high (Solomon, 2005).

The first comprehensive volumetric estimate of the coastal erosion rate along the southern Beaufort Sea coast came from Harper and Penland (1982), and was estimated to be $2.9 \times 10^6 \text{ m}^3/\text{yr}$. This value was updated by Hill et al. (1991) to $3.51 \times 10^6 \text{ m}^3/\text{yr}$ or $5.62 \times 10^6 \text{ tonnes/yr}$ (assuming a density of 1.6 kg/L). Hill et al. (1991) further divided the southern coastline of Beaufort Sea to the following 4 regions and provided an estimated erosion rate for each region: Yukon Coastal Plain, Mackenzie Delta, Outer Delta Islands, and Tuktoyaktuk peninsula.

Since no recent estimates on the erosion rate are available in the literature, we based our Hg flux calculations on the erosion rates estimated by Hill et al. (1991) (Table 2). Volumetric erosion rates were converted to weight values by using the same assumed density. Because we do not have samples from the Mackenzie Delta region (composed of Mackenzie Delta and Outer Islands), values from the Tuktoyaktuk peninsula were used to represent this region due to their relative proximity, and the fact that both regions are composed of fine organic-rich sediments due to the influence of the Mackenzie River (Pelletier, 1975; Rachold et al., 2000; Rampton and Mackay, 1971). Herschel Island, which was not included in Hill's (1991) estimate, has been estimated to discharge an additional 1.38 Mt of sediment to the Beaufort Sea annually (N. Couture, McGill University, unpublished data).

Using median [Hg]s from cores found within each region, and based on the erosion rates above, we estimate that approximately 610 kg of Hg are released via eroded and melted

Table 2. Estimates of Hg inputs to the Beaufort Sea via erosion.

Region	Volume of sediment eroded (m ³ /a)*	Converted to weight (Mt/a)**	Median [Hg] (µg/g)	Kg of Hg/yr
Tuktoyaktuk Peninsula	4.70×10 ⁵	0.75	0.1138	86 (14%)
Mackenzie River Delta & Outer Islands	1.50×10 ⁶	2.40	0.1138***	273 (45%)
Herschel Island	-	1.38 [†]	0.0613	85 (14%)
Yukon Coast	1.54×10 ⁶	2.47	0.0668	165 (27%)
TOTAL	3.51×10⁶	5.62		609

* As estimated by Hill et al., 1991 (except Herschel Island)

** Using the conversion factor from Hill et al., 1991

*** Represented by Tuktoyaktuk values

[†] As estimated by N. Couture, 2006

permafrost along the southern Beaufort Sea annually (Table 2). This is however a maximum value, as a relatively high proportion of this sediment is likely to be sand and gravel (Hill et al., 1991), which will have lower levels of Hg due to lower surface area and different surface properties (Boszke et al., 2004; Moore et al., 1989), and is less likely to be transported away from the coast. Of the 610 kg of Hg, 45% is from the Mackenzie Delta and Outer Islands, 27% is from the Yukon Coastal Plain, 14% is from Tuktoyaktuk peninsula, and 14% is from Herschel Island. Relative to other estimated inputs to Beaufort Sea, this is a significant amount of Hg (Table 3).

Although the amount of sediment discharged annually from coastal erosion (5.6 ± 2.5 Mt) is only 4% of the average annual sediment discharge of the Mackenzie River (127 ± 6 Mt), the relative Hg discharge is much higher. With estimates of annual Hg flux from the Mackenzie at 2.2 ± 0.9 tonnes (Leitch et al., under review – Chapter 2), coastal erosion and permafrost melt discharges a sea-ward Hg flux as much as 28% of that directly carried by the Mackenzie River. Permafrost degradation inputs a significant amount of Hg relative to the estimates of atmospheric Hg deposition as well. With Lu et al. (2001) estimating 1400 kg of Hg atmospherically deposited to the Beaufort Sea annually, permafrost degradation amounts to 44% of this. As it is recognized that much of the atmospherically deposited Hg is photoreduced to Hg^0 and re-emitted to the atmosphere (Lalonde et al., 2002; Poulain et al., 2004; St. Louis et al., 2005; Steffen et al., 2005), the contribution of Hg from permafrost degradation may exceed that of atmospheric deposition (Table 3).

Table 3. Comparison of Hg fluxes to the Beaufort Sea

Source	Hg flux (kg)	Source
Permafrost Degradation	609	This study
Mackenzie River	2200 ± 900	Leitch et al., in review – Chapter 2
Atmospheric Deposition	1400*	Lu et al., 2001

*obtained by dividing an estimate of 17 tonnes to entire high Arctic Ocean by relative surface area of the Beaufort Sea (Lu et al., 2001).

*also note that most (if not all) of atmospheric flux is re-reduced and evades to the atmosphere

Additionally, Jorgenson and Brown (2005) have estimated that 3.3 Mt of sediment are eroded annually from the Alaskan portion of the southern Beaufort Sea coast (~2000 km of coast). Although the Canadian and American Beaufort Sea coasts differ in aspects of coastal processes, if we assume a comparable [Hg] to those found in the western Yukon, this results in an additional ~220 kg of Hg discharged into Alaskan portion of the southern Beaufort Sea annually. Contributions from the Russian coast are also likely quite significant, with estimates of 58.4 Mt of sediment eroding annually from the Laptev Sea coast (2400 km long) (Grigoriev and Rachold, 2003). Using median Hg values obtained from the Canadian Beaufort Sea coast, this would result in ~4 tonnes of Hg/yr to the Arctic Ocean.

Moreover, contributions from permafrost degradation from within the Mackenzie Basin should not be overlooked. As temperatures increase, increasing permafrost melt and active layer detachments (some of which form retrogressive thaw slumps) have been observed (Heginbottom, 2000; Pollard, 1990). An increase in slope failure is also predicted. As a large part of the Mackenzie Basin is within the discontinuous permafrost region, which is predicted to be adversely affected by temperature increases, it is likely there will be a significant increase in future permafrost degradation in the upper reaches of the Mackenzie Basin (Burgess et al., 2000). This sediment will enter the Mackenzie River and subsequently the Delta.

What happens with the Hg from degraded permafrost once it is discharged into the Beaufort Sea is not known. If a high portion of the Hg is organically-bound, one would

expect a larger portion assimilates into the bottom of the food web. Less effect would be expected if the Hg was largely inorganic.

Response to Climate Change

Although some studies show an increase in coastal erosion over the 20th century (Lantuit and Pollard, 2003), the most recent studies have shown a decrease in coastal retreat rates. Lantuit and Pollard (2006) found that average retreat rates decreased from 0.61 m/yr for the period of 1952-1970, to 0.45 m/yr for the period of 1970-2000 on Herschel Island. Solomon (2005) found that retreat rates in the Mackenzie Delta and Tuktoyaktuk peninsula region decreased by 15% in the period of 1985-2000 as compared to 1972-1985. It is unlikely however that there will be a long-term decrease in coastal erosion rates. The decreasing erosion rates in recent years are likely attributable to the decrease in number of storm events since 1980 (Solomon, 2005), as well as the increasing variability in the direction of origin of storms (Lantuit and Pollard, 2006). There is a strong correlation between storms and coastal erosion rates (Solomon et al., 1994). Solomon (2005) also observed that the areas of decreasing coastal retreat are in areas of lower average retreat rates, but that trend was not reflected in zones with higher retreat rates. Lantuit and Pollard (2006) also noted that retrogressive thaw slumps increased dramatically in both number and area.

As the amount of annual coastal retreat in the area is controlled by the combined effects of wave action, the extent of the open-water season, storm surges and thaw controls, any changes in these variables will result in a corresponding change in coastal retreat rates

(Turner, 2004). Climate models unanimously forecast an increase in global temperature (Anisimov and Nelson, 1996; Cohen, 1997; IPCC, 2001; Woo and Thorne, 2003), with areas such as the western Arctic expected to exhibit the most dramatic climate change (Chapman and Walsh, 1993; Serreze et al., 2000). Warmer temperatures are linked to increasing amounts of open water, both in extent and duration, rising sea levels, and the thawing of permafrost (Lynch et al., 2004; Proshutinsky et al., 2001). Storms only adversely affect coastal erosion during the open-water season, therefore if the open-water season increases from 4 to 5 months (i.e. 25% increase), there will be a corresponding 25% increase in open-water season storms, as storms tend to be relatively evenly distributed throughout the open-water season (Solomon et al., 1994). Furthermore, storms at the end of the summer/fall have more dramatic effects than summer storms because the active layer is at its deepest and thermokarst process are at their maximum (Turner, 2004).

Further warming is predicted to more than double the open water season, further decrease the extent of ice by hundreds of kilometres (hence increasing fetch), decrease the thickness of first-year ice by 50-75%, and increase the occurrence of large waves (McGillivray et al., 1993). Additionally, the rate of global sea level rise is predicted to as much as double the current rate of 3 mm/yr (Solomon et al.1994) (and up to 0.5-0.7 m over the next 100 years (IPCC, 2001)). As the Beaufort Sea is among 3% of Canada's coast that has been classified as "highly sensitive to sea-level rise" (Shaw et al., 1998), the projected increases in sea level, warmer temperatures, open water, wave energy and number of storms are very likely to increase coastal erosion and permafrost melt rates

along the southern Beaufort Sea coast. Turner (2004) has applied a model created by Kobayashi et al. (1999) to predict an increase in erosional rate of 56% on the southern Beaufort Sea coast over the next 30 years. If sediment discharge increases by 56%, Hg discharge will also increase by 56% up to 950 kg/yr. Additionally, permafrost degradation leads to altered hydrology, which could potentially lead to an increase in wetlands and fluxes of organic carbon to the aquatic environment (Macdonald et al., 2005). Elevated levels of methylmercury (the bio-accumulative form of Hg) have been observed in small ponds in the Canadian high Arctic (Loseto et al., 2004; St. Louis et al., 2005) and Arctic wetlands have been shown to produce MeHg (Loseto et al., 2004).

Conclusion

In this study we have provided the first estimate of Hg flux to the Arctic Ocean by means of permafrost degradation. Based on the Hg distribution profiles from 5 sites across the southern coastline of Beaufort Sea and with the scarcely available erosion rate data, we estimate that approximately 610 kg of Hg are currently discharged into the Beaufort Sea on an annual basis. As permafrost degradation is occurring at rapid rates in the circumpolar Arctic, and is likely to increase dramatically in concert with higher temperatures, increased open water, more large waves, more storms, and an increase in sea level, it is likely that this flux will increase to over 950 kg in the next 30 years. This is a significant increase in Hg flux to the Beaufort Sea relative to other sources. In the future, the fate of the Hg once it enters the marine environment should be further examined to understand the relative contribution of Hg from permafrost degradation has

to the biological food web. To investigate this, speciation of Hg from degraded permafrost should be assessed.

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Chapter 4 – Conclusion

The aims of the study were to (1) assess Hg and MeHg levels and distribution in water within the lower Mackenzie Basin, (2) estimate the flux of Hg from the Mackenzie River and permafrost degradation on an annual basis, (3) probe conditions which result in higher Hg discharges, and (4) commence long-term monitoring of Hg in the Mackenzie River and its tributaries.

In conclusion, levels of Hg in the water throughout the lower Mackenzie Basin vary dramatically both inter- and intra-annually. Higher Hg levels are present with higher water levels. This applies within the same year, (with Hg levels in the spring freshet being approximately 7x higher than later in the summer), as well as between years (with higher Hg levels being present in summers with high flow versus summers with low flow). Particulate Hg is especially susceptible to changes in water levels, accounting for ~75% of total Hg inputs to the Beaufort Sea.

Both the Mackenzie River and permafrost degradation supply significant quantities of Hg to the Beaufort Sea. We conclude that the Mackenzie River is in fact the most important source of Hg to the Beaufort Sea discharging 2.2 ± 0.9 tonnes of Hg annually, surpassing estimates of atmospheric deposition to the Beaufort (see Figure 1). Permafrost degradation is also inputting approximately 0.6 tonnes into the Beaufort annually. Of the other potential sources of Hg to the Beaufort Sea, oceanic currents merit some attention, as massive volumes of water likely flow in and out of the Beaufort Sea.

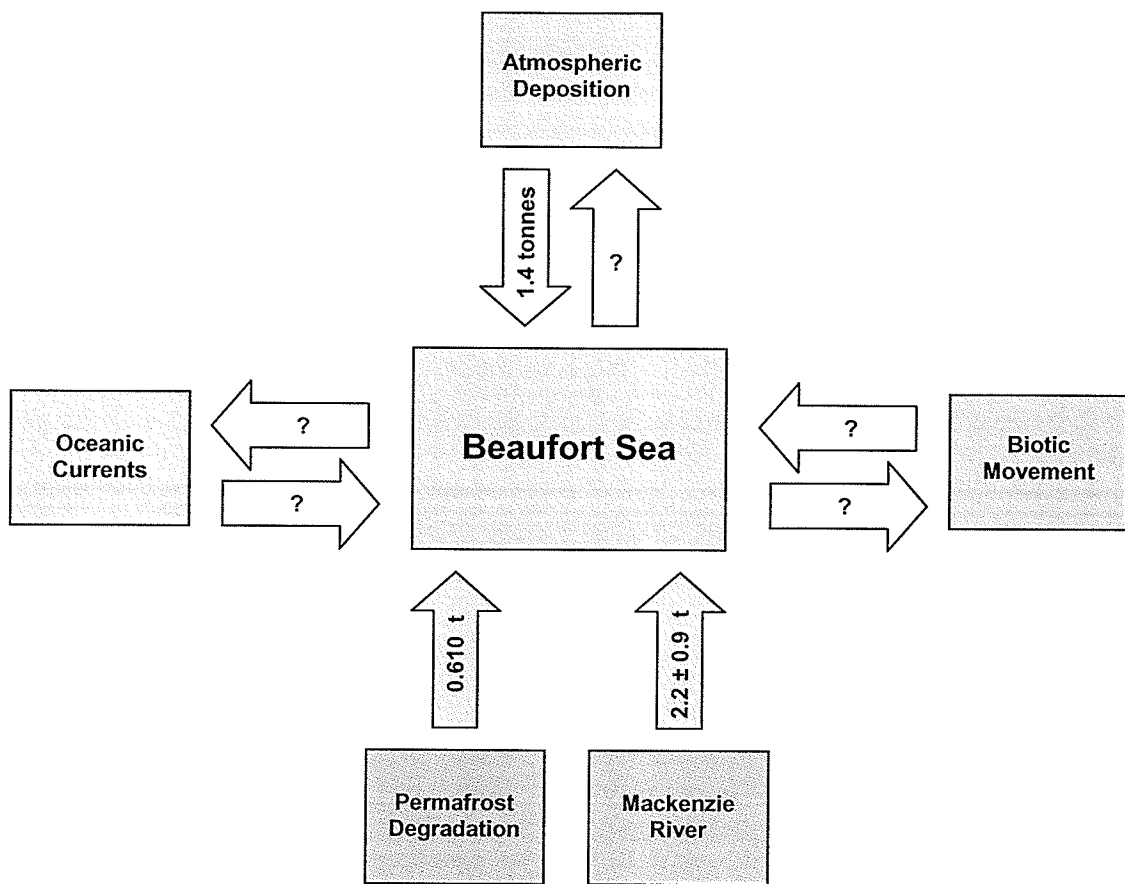


Figure 1. Mercury sources to the Beaufort Sea.

In the future, it is important that long-term monitoring of the Mackenzie River be continued. Due to the high variability in the water discharge of the Mackenzie River, a longer-term database will be much more valuable when it comes to observing trends and anticipating future change. It would also be desirable to increase the number of sampling events throughout the year. As the costs of travel to the north can be prohibitive, perhaps this can be achieved with a community-based monitoring program. Perhaps one or two years could confirm (or refute) our assumptions that summer concentrations are representative of fall and winter. Further investigation into the occurrence and impact of forest fires within the basin should also be examined.

For permafrost, better spatial resolution would be desirable. This is currently being addressed. A more recent estimate of permafrost erosion and melt rates would also lead to more accurate estimates of the actual Hg flux from permafrost. To assess relative importance of Hg sources to the Arctic, further research is required to assess the *net* atmospheric flux. It would also be beneficial if ash content could be analyzed in the permafrost cores to help us ascertain whether the site is more ombrotrophic or minerotrophic. Ombrotrophic sites (atmospherically fed) are more reliable for estimating past Hg deposition, while minerotrophic sites (atmospherically *and* ground fed) are subject to higher background Hg levels).

As the Beaufort Sea is not a static system, it is important to extend the scope of this research to the entire circumpolar region. The Arctic is a dynamic system related by variables such as currents, winds and biota. There are still many gaps in Arctic Hg

research that need to be filled to fully understand the contamination problems. This is important for the marine mammals that have been found with extremely high levels of Hg, as well as the indigenous people who consume marine mammals as part of their traditional diet.

Appendices

Appendix 1. Coordinates and chloride, sulphate, and dissolved organic carbon data for all sampling sites in the lower Mackenzie Basin.

ID ^a	Latitude	Longitude	Cl ^{-b} (mg/L)	SO ₄ ^{2-b} (mg/L)	DOC ^b (mg/L)	Site Description
M1	69°27.438'	133°02.173'	1390	10370	1.27	Tuktoyaktuk
D1	69°27.390'	133°02.242'	80	32.5	7.50	Tuktoyaktuk
M2	69°22.503'	133°42.097'	118	55.1	3.80	Kittigazuit Bay
M3	69°06.763'	134°21.136'	8.36	32.4	4.97	Holmes Creek
M4	69°05.586'	134°22.965'	8.65	37.7	3.84	Mackenzie R. at Swimming Point (in Delta)
M5	68°54.813'	135°30.656'	14.4	36.5	3.53	Reindeer Channel (in Delta)
M6	68°51.828'	135°45.695'	9.50	38.2	3.70	Shallow Bay (in Delta)
M7	68°41.848'	134°28.036'	9.03	39.4	3.70	Mackenzie R. at Axel Creek (in Delta)
M8	68°41.487'	134°29.773'	9.34	40	4.06	Axel Creek (in Delta)
D2	68°21.148'	133°43.589'	9.40	29.50	12.50	Mackenzie R., East Channel
M9	68°21.101'	133°43.701'	9.6	39.4	3.96	Mackenzie R., East Channel (in Delta)
D3	68°14.886'	135°00.992'	<9	36	10	Mackenzie R., Aklavik Channel
M10	68°14.734'	134°24.174'	11.6	43.1	3.48	Mackenzie R. at Horseshoe Bend (in Delta)
D4	68°13.095'	135°01.312'	<9	43	7	Mackenzie R., Peel Channel
M11	67°54.612'	134°23.118'				Mackenzie R. below Peel R. (in Delta)
D5	67°45.027'	133°45.381'	<9	10.50	21.00	Rengleng R.
M12	67°41.616'	134°31.415'	2.75	80.6	0.78	Peel R.
M13	67°35.366'	134°01.714'	9.87	40.2	3.44	Mackenzie R. at Point Separation
M16	67°27.393'	133°44.282'	11.6	43.7	3.54	Mackenzie R. above Arctic Red R.
D6	67°27.387'	133°45.928'	9	29.50	8.50	Mackenzie R. below Arctic Red
M14	67°27.018'	133°46.650'				Mackenzie R. below Arctic Red R.
M15	67°26.399'	133°45.116'	0.83	128	1.31	Arctic Red R.
D7	67°20.291'	134°52.375'	<9	43	7	Peel River (at Dempster)
M17	67°19.129'	132°18.411'	9.86	38.2	3.59	Mackenzie R. at Benoit Creek
M18	67°27.903'	131°29.408'				Travaillant R.
M19	67°27.604'	131°29.727'	10.6	41.8	3.00	Mackenzie R. at Travaillant R.

ID ^a	Latitude	Longitude	Cl ^{-b} (mg/L)	SO ₄ ^{2-b} (mg/L)	DOC ^b (mg/L)	Site Description
M21	66°45.592'	130°02.408'	11.8	43.5	3.53	Ontaritue R.
M22	66°45.299'	129°57.811'	9.73	37.5	3.79	Mackenzie R. above Ontaritue R.
M23	66°19.254'	128°38.484'				Mackenzie R. below Hare Indian R.
M24	66°17.608'	128°37.624'	4.49	408	4.82	Hare Indian R.
M25	66°17.420'	128°38.593'	10.4	38.3	3.41	Mackenzie R. above Hare Indian R.
M26	65°47.874'	128°50.381'	4.52	113	1.38	Mackenzie R. below Mountain R. and Stinky Creek
M27	65°46.167'	128°46.126'	46.9	147	16.15	Stinky Creek
M28	65°41.247'	128°49.474'	2.58	113	1.38	Mountain R.
M29	65°40.816'	128°49.143'	20.6	45.1	4.21	Mackenzie R. above Mountain R.
M30	65°39.499'	128°44.474'				Mackenzie R. below Carcajou R.
M31	65°38.629'	128°42.034'				Mackenzie R. above Carcajou R.
M32	65°17.897'	127°05.297'	7.98	37.1	3.26	Mackenzie R. below Norman Wells
M33	65°14.908'	126°45.882'	7.25	30.4	3.71	Mackenzie R. above Norman Wells
M34	65°09.822'	126°24.404'	8.34	25.7	3.61	Above Norman Wells at S. tip of 10-mile Island
M35	64°54.647'	125°35.638'	5.03	11.3	1.94	Great Bear R.
M36	64°53.405'	125°32.480'	6.63	34.9	3.78	Mackenzie R. above Great Bear R.
M37	64°53.501'	125°24.519'				Mackenzie R. further above Great Bear R.
M38	64°39.644'	124°54.016'				Mackenzie R. below Big Smith Creek
M39	64°34.447'	124°54.236'	226	461	5.46	Big Smith Creek
M40	64°27.924'	124°47.916'				Mackenzie R. below Keele R.
M41	64°25.247'	124°47.245'				Mackenzie R. near Keele R.
M42	64°24.751'	124°47.858'	7.95	113	1.61	Keele R.
M43	64°23.570'	124°45.536'	7.3	43.4	3.31	Mackenzie R. above Keele R.
M44	64°18.326'	124°36.758'	8.26	77.8	2.30	Mackenzie R. below Redstone R.
M45	64°17.402'	124°32.719'	8.09	92.9	1.69	Redstone R.
M46	64°16.966'	124°30.630'	10	30.2	4.30	Mackenzie R. above Redstone R.
M47	64°00.728'	124°23.283'				Mackenzie R. below Dahadini R.
M48	63°59.122'	124°22.171'	1.76	191.2	6.06	Dahadini R.
M50	63°56.527'	124°10.500'	48.8	65.6	10.20	Blackwater R.
M51	63°58.095'	124°18.119'	13.8	31.1	4.51	Mackenzie R. above Blackwater R.
M52	63°31.986'	123°44.387'	6.53	34.4	3.90	White Sands Creek

ID ^a	Latitude	Longitude	Cl ^{-b} (mg/L)	SO ₄ ^{2-b} (mg/L)	DOC ^b (mg/L)	Site Description
M53	63°27.989'	123°42.226'	96.1	99	4.51	Ochre R.
M54	63°16.398'	123°36.690'				Mackenzie R. below Wrigley R.
M55	63°14.514'	123°34.150'	95.9	69	5.29	Wrigley R.
M56	63°14.129'	123°32.851'	3.71	36.8	4.28	Mackenzie R. above Wrigley R.
M57	62°56.156'	123°12.982'	6.61	18.6	9.79	R. Between Two Mountains
M58	62°48.538'	123°12.666'	8.29	26.1	4.38	Mackenzie R. below Willowlake R.
M59	62°41.919'	123°07.056'	100	33.6	11.63	Willowlake R.
M60	62°26.659'	123°13.783'				Mackenzie R. below Root R.
M61	62°26.180'	123°17.745'	6.64	85.4	1.75	Root R.
M62	62°20.974'	123°22.977'				Mackenzie R. below Camsell Bend
M63	62°16.698'	123°21.803'	9.16	2.06	4.87	Mackenzie R. at Camsell Bend
M64	62°15.059'	123°19.673'	15.4	79.4	2.09	North Nahanni R.
M65	62°14.594'	123°15.263'	9.62	21.6	4.32	Mackenzie R. above North Nahanni R.
M66	61°54.095'	121°26.910'	1.47	36.2	5.08	Mackenzie R. below Liard R.
M67	61°50.189'	121°17.225'	0.85	38.8	4.63	Liard R.
M68	61°51.132'	121°15.875'	8.09	2.02	4.38	Mackenzie R. above Liard R.
M69	61°46.925'	120°41.586'				Rabbitskin R.
M70	61°31.619'	120°37.993'	2.83	12.1	12.53	Jean Marie R.
M71	61°31.416'	120°36.590'	7.82	20.5	4.81	Mackenzie R. above Jean Marie R.
M72	61°18.769'	119°51.294'	1.06	8.02	11.50	Trout R.
M73	61°22.129'	118°23.695'	8.52	21.6	4.44	Mackenzie R. below Mills Lake
M74	61°27.941'	118°03.368'	8.32	21.7	4.26	Mackenzie R. above Mills Lake
M75	61°29.511'	118°04.834'	59.4	257.5	19.91	Horn R.
M76	61°21.381'	117°40.974'	6.46	21.1	4.42	Mackenzie R. at Fort Providence
M77	61°03.164'	116°40.967'	9.39	24.8	4.28	Mackenzie R. at South Channel
M78	61°04.197'	116°30.050'	8.04	21.3	4.45	Great Slave Lake (West corner)
M79	60°51.558'	115°43.812'				Hay River

a. M denotes the summer sampling stations and D denotes the freshet sampling stations.

b. measured in the summer 2004.

Appendix 2. Mercury (Hg) and methylmercury (MeHg) concentrations in the lower Mackenzie basin in the summers of 2003-2005.

ID	Summer 2003					Summer 2004					Summer 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[MeHg] _D (ng/L)
M1						0.27 ± 0.01	<1.67 ^A	<1.94		<0.020				
M2						0.31 ± 0.05	1.77	2.08		0.025				
M3						0.49 ± 0.13	<1.82 ^A	<2.31	0.058	0.051				
M4						0.31 ± 0.07	1.96	2.27	0.023	0.051				
M5						0.30 ± 0.09	1.89	2.19	0.045	0.044				
M6						0.27 ± 0.05	<1.67 ^A	<1.94	0.054	<0.020				
M7						0.29 ± 0.02	3.74	4.03	0.040	0.027				
M8						0.38 ± 0.03	2.10	2.48	0.067	<0.020				
M9		5.43		0.029	0.091	0.28 ± 0.05	<0.87 ^A	<1.15	0.021 ± 0.0021	0.029 ± 0.012	2.78	2.83	5.61 ± 0.47	
M10	2.00	4.87	6.87	0.006	0.034	0.22 ± 0.04	<1.67 ^A	<1.89	0.027	0.084	1.96 ± 0.91	3.19	5.15 ± 0.71	
M11	3.59	5.44	9.03	0.009	0.104									
M12	3.14	3.58	6.72	0.030	0.063									
M13	2.78	8.85	11.63		0.128	0.28 ± 0.05	<2.11 ^A	<2.39	0.076	<0.020				
M14	6.16	3.24	9.40	0.040	0.035						1.51 ± 0.80	4.43	5.94 ± 0.18	
M15	3.17	5.46	8.63	0.089	0.055	0.21	6.35	6.56	0.079	0.140	1.64 ± 0.29	3.69	5.33 ± 0.18	
M16						0.23 ± 0.00	<10.00 ^B				2.50 ± 0.19	3.38	5.87 ± 0.64	
M17	3.01 ± 1.04	3.21 ± 0.54	6.22	0.007 ± 0.0014	0.082 ± 0.014	0.32 ± 0.02	1.74	2.06	0.006	0.041 ± 0.029	1.24 ± 0.73	3.74	4.97 ± 0.76	
M18											-	-	4.58 ± 0.98	
M19	2.02	2.57	4.59	0.022	0.200	0.34 ± 0.18	2.18	2.52	0.009	0.089	0.82 ± 0.20	0.90	1.72 ± 0.04	

ID	Summer 2003					Summer 2004					Summer 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[MeHg] _D (ng/L)
M20	13.13	4.56	17.69	0.009	0.099	-	1.78				1.84 ± 1.61	2.49	4.33 ± 1.00	
M21	13.40	1.73	15.13	0.059	0.205	0.25	2.34	2.59	0.055	0.070	2.21 ± 0.23	1.59	3.80 ± 0.91	
M22	16.11	3.67	19.78	0.009	-	0.37 ± 0.10	1.73	2.10	0.007	<0.020	2.44 ± 1.41	1.98	4.42 ± 1.11	
M23	14.77	4.55	19.32	0.011	0.029						1.89 ± 0.35	3.38	5.26 ± 0.48	
M24	16.63	0.13	16.76	0.012	0.079	0.36 ± 0.07	<1.67 ^A	<2.03	0.028 ± 0.0089	0.109	1.35 ± 0.33	0.04	1.38 ± 0.44	
M25	3.25	3.75	7.00	0.017	0.071	0.40 ± 0.10	<3.33 ^A	<3.73			2.84 ± 0.77	3.04	5.87 ± 0.64	
M26	26.67	2.99	29.66	0.043	-	0.25 ± 0.08	<1.67 ^A	<1.92	0.045	<0.020	1.50 ± 0.54	8.46	9.96 ± 1.79	
M27						0.66 ± 0.20	<1.67 ^A	<2.33	0.024	0.139	1.12 ± 0.38	0.08	1.20 ± 0.41	
M28	5.59	3.74	9.33	0.027	0.061	0.24 ± 0.02	<1.67 ^A	<1.91	0.044	<0.020	0.38 ± 0.05	9.17	9.54 ± 2.25	
M29	14.52 ± 2.47	4.12 ± 0.35	18.64	0.012 ± 0.0021	0.076 ± 0.021	0.32 ± 0.00	<1.67 ^A	<1.99	-	<0.020	1.70	12.17	13.87 ± 1.29	
M30											2.54 ± 1.36	5.30	7.84 ± 0.79	
M31											2.36 ± 0.45	4.04	6.39 ± 1.13	
M32	12.41	2.98	15.39	0.007	0.099	0.40 ± 0.02	5.23	5.23	0.015 ± 0.0059	<0.020	1.86 ± 0.65	10.10	11.96 ± 0.31	
M33	7.06	4.41	11.47	0.007	0.058	0.44 ± 0.06	4.56	4.56	-	<0.020	1.52 ± 0.00	0.70	2.22 ± 0.33	
M34						0.35 ± 0.01	3.93	4.28	-	<0.020				
M35	5.31	0.80	6.11	0.025	0.043	0.26 ± 0.02	<1.54 ^A	<1.80	0.032	<0.020	0.90 ± 0.14	0.41	1.31 ± 0.37	
M36	10.20 ± 4.60	3.31 ± 0.25	13.51	0.011 ± 0.0017	0.057 ± 0.008	0.44 ± 0.01	6.87	7.31	0.012	0.024	1.84 ± 0.30	6.23	8.06 ± 0.13	
M37						0.35 ± 0.01	7.45	7.80	0.013	<0.020				
M38								0.00			1.46 ± 0.03	2.27	3.73 ± 0.34	

ID	Summer 2003					Summer 2004					Summer 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (μg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (μg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[MeHg] _D (ng/L)
M39						0.60 ± 0.02	<1.67 ^A	<2.27	0.035 ± 0.0145	<0.020	1.35 ± 0.24	0.11	1.46 ± 0.27	
M40	5.68	1.84	7.52	-	0.132						0.92 ± 0.06	3.08	4.00 ± 0.19	
M41											0.61 ± 0.04	1.11	1.71 ± 0.25	
M42	2.51 ± 2.48	2.31	4.82	0.019	0.069	0.31 ± 0.03	2.52	2.83	0.036 ± 0.0215	<0.020				
M43	10.91	2.50	13.41	0.029	0.209	0.42 ± 0.02	7.53	7.95	0.016 ± 0.0051	<0.020				
M44	3.12 ± 2.26	3.45 ± 0.60	6.57	0.022 ± 0.0102	0.077 ± 0.026	0.43 ± 0.03	7.59	8.02	0.040	<0.020	0.94 ± 0.12	3.54	4.47 ± 0.34	
M45	4.34	2.81	7.15	0.034	0.077	0.43 ± 0.02	8.76	9.19	0.035	<0.020	0.87 ± 0.03	3.71	4.58 ± 0.41	
M46	9.00	1.13	10.13	0.023	0.173	0.45 ± 0.01	3.29	3.74	0.013	<0.020	1.94 ± 0.13	6.37	8.31 ± 0.75	
M47	1.65	1.69	3.34	0.016	0.152	0.45 ± 0.01	4.12	4.57	0.035	<0.020	2.20 ± 0.01	6.96	9.16 ± 0.20	
M48	4.24	6.26 ± 0.51	10.50	0.055	<0.020	0.78 ± 0.02	<1.67 ^A	<2.45	-	0.029	-	-	4.00 ± 0.16	
M49	5.35	2.64	7.99	0.032 ± 0.0085	0.155	0.43 ± 0.03	<1.67 ^A	<2.10	0.026	-	1.85 ± 0.46	13.72	15.56 ± 2.11	
M50	1.93	0.17	2.10	0.025	0.112	0.76 ± 0.00	<1.67 ^A	<2.43	0.004	0.066	-	-	1.86	
M51	1.68	2.29	3.97	0.006	0.077	0.37 ± 0.04	2.19	2.56	0.017	0.075 ± 0.014				
M52	10.14	<DL		0.009	0.044	0.44 ± 0.02	<1.54 ^A	<1.98	0.012	0.059				
M53	24.22	0.29	24.51	0.037	0.088	0.51 ± 0.10	<1.54 ^A	<2.05	0.011	<0.020	1.13 ± 0.01	1.70	2.82 ± 0.48	
M54	7.72	4.71	12.43	0.010	0.085						2.59	26.48	29.07 ± 2.67	
M55	1.31	8.27	9.58	0.033	0.113	0.58 ± 0.01	<1.67 ^A	<2.25	0.017	0.055	-	-	6.62 ± 3.96	
M56	1.48	6.13	7.61	0.010	0.266	0.63 ± 0.07	7.82	8.45	-	0.108	2.84 ± 0.00	28.64	31.48 ± 12.76	
M57						0.55 ± 0.04	<1.67 ^A	<2.22	-	0.042	2.35 ± 0.19	0.99	3.34 ± 0.47	

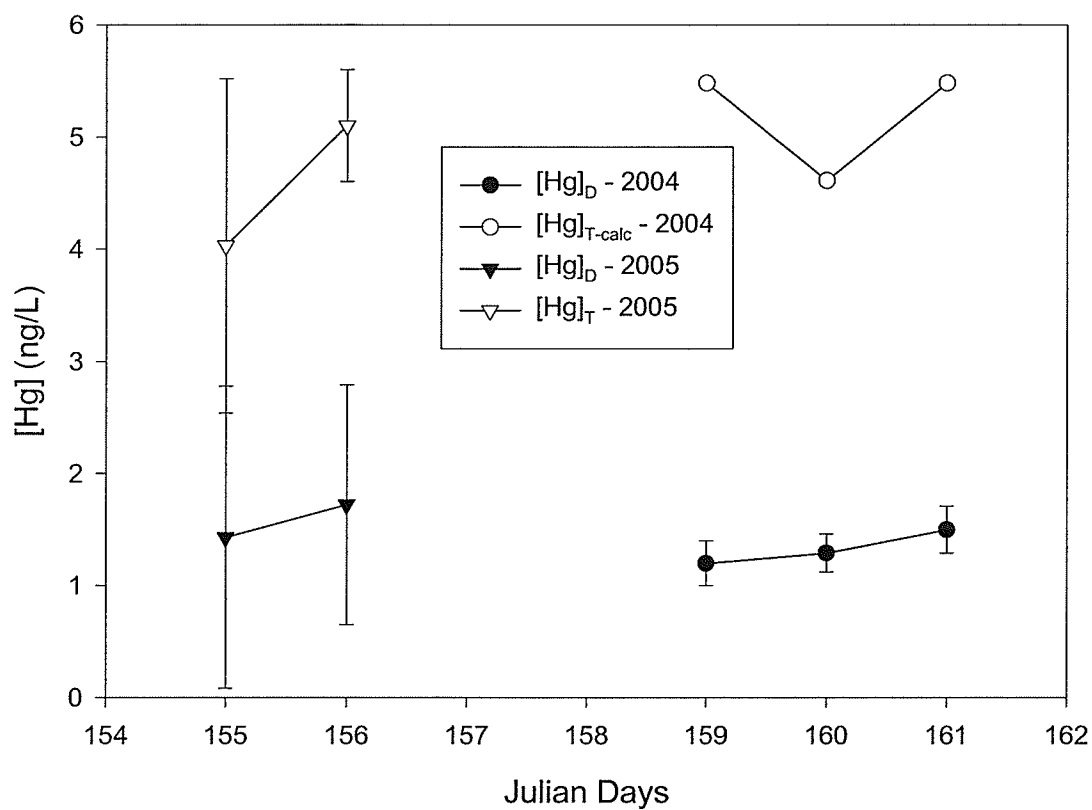
ID	Summer 2003					Summer 2004					Summer 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (μg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (μg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[MeHg] _D (ng/L)
M58	2.36	0.88	3.24	0.009	0.050	0.41 ± 0.01	2.99	3.40	-	<0.020	0.69 ± 0.58	-	-	
M59	3.22	1.63	4.85	0.042	0.148 ± 0.006	0.58 ± 0.01	<1.67 ^A	<2.25	0.030	0.057	4.40 ± 0.30	0.64	5.04 ± 1.09	
M60											1.39 ± 0.21	4.99	6.37 ± 0.30	
M61	1.64	3.86	5.50	0.038	0.079	0.33 ± 0.00	<1.67 ^A	<2.00	0.007	0.071				
M62											2.47 ± 0.16	9.86	12.33 ± 0.91	
M63	4.57	3.24 ± 0.50	7.81	-	<0.020	0.31 ± 0.03	<1.90 ^A	<2.21	-	0.090	0.85 ± 0.21	1.63	2.48 ± 0.43	
M64	4.94	6.78	11.72	0.011	-	0.28 ± 0.06	<1.67 ^A	<1.95	0.011	0.028	2.10 ± 0.10	2.05	4.15 ± 0.43	
M65	1.63	1.20	2.83	-	0.128	0.23 ± 0.02	<1.67 ^A	<1.90	-	0.034	-	-	14.97 ± 2.78	
M66	1.23	1.83	3.06	0.009	0.049	0.84 ± 0.00	6.47	7.31	-	0.057 ± 0.052*	5.59 ± 3.19	5.10	10.69 ± 1.36	
M67	6.14 ± 2.60	4.31 ± 0.63	10.45	0.011 ± 0.0040	0.102 ± 0.037	0.83 ± 0.03	2.63	3.46	-	0.059 ± 0.006	2.43 ± 0.97	7.67	10.09 ± 2.31	
M68	5.66	1.43	7.09	-	<0.020	0.30 ± 0.04	<1.67 ^A	<1.97	-	<0.020	-	-	1.40 ± 0.26	
M69											2.97	0.70	3.67 ± 0.69	
M70	5.57	1.68	7.25	-	-	0.55 ± 0.03	<1.67 ^A	<2.22	0.015	0.133	2.42 ± 0.98	<DL	1.93 ± 0.33	
M71	0.82	0.87	1.69	-	0.094	0.28 ± 0.00	<1.67 ^A	<1.95	-	<0.020	1.93 ± 0.06	0.85	2.78 ± 0.24	
M72	5.87	0.96	6.83	0.019	0.238	0.34 ± 0.00	<1.67 ^A	<2.01	-	0.112	1.55 ± 0.14	0.63	2.18 ± 0.80	
M73	2.02 ± 1.34	1.07 ± 0.07	3.09	-	0.068 ± 0.006	0.26 ± 0.01	<1.67 ^A	<1.93	-	0.131	1.85 ± 1.14	1.68	3.52 ± 1.68	
M74	1.86	0.78	2.64	-	0.133	0.27 ± 0.00	<1.67 ^A	<1.94	-					
M75	-	1.38		0.025	<0.020	0.42 ± 0.01	<1.67 ^A	<2.09	-	<0.020	1.68 ± 0.16	1.53	3.21 ± 1.48	
M76	4.40	0.87 ± 0.07	5.27	-	0.137 ± 0.081	0.26 ± 0.04	<1.67 ^A	<1.93	-	<0.020	3.33 ± 1.52	<DL	3.15 ± 0.85	

ID	Summer 2003					Summer 2004					Summer 2005			
	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[Hg] _S (µg/g)	[MeHg] _D (ng/L)	[Hg] _D (ng/L)	[Hg] _P (ng/L)	[Hg] _{T-calc} (ng/L)	[MeHg] _D (ng/L)
M77	2.75	0.87	3.62	0.016	0.117	0.26 ± 0.03	<1.67 ^A	<1.93	0.014	<0.020	1.42 ± 0.09	0.48	1.68 ± 0.47	
M78	3.08	0.87	3.95	-	0.107	0.25 ± 0.06	<6.67 ^B		-	-	3.35 ± 0.48	1.74	5.09 ± 0.73	
M79	5.42	4.69 ± 0.01	10.11	0.089	0.222						3.63 ± 0.45	6.05	9.68 ± 0.15	
Min.	0.82	0.13	1.69	0.006	0.020	0.21	0.10	0.36	0.004	0.02	0.38	0.04	1.2	
Max	26.67	8.85	29.66	0.089	0.266	0.84	8.76	9.19	0.079	0.14	5.59	28.64	31.48	
Median	4.40	2.90	7.57	0.019	0.085	0.35	1.76	2.08	0.025	0.026	1.85	3.08	4.58	
Average	6.24	3.02	9.18	0.024	0.099	0.39	2.50	2.89	0.029	0.046	1.96	4.66	6.36	

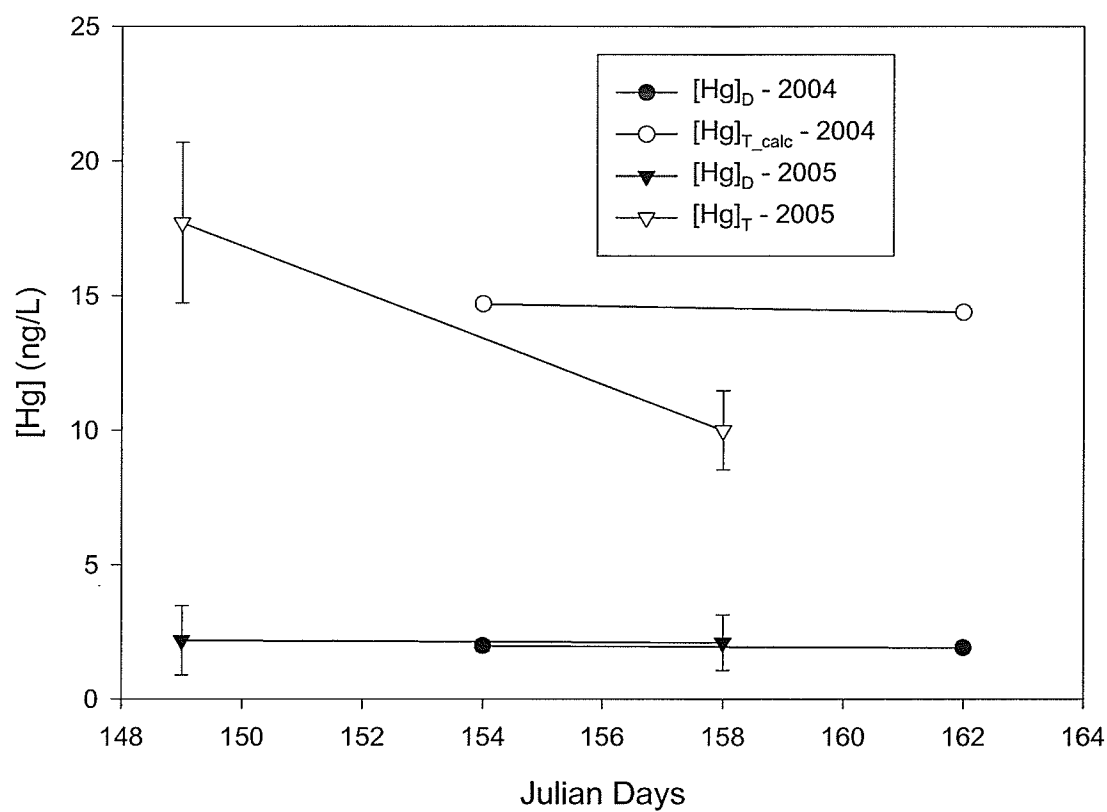
^A [Hg]_P was below the detection limit (DL), which is dependent on the volume of the water sample filtered.

^B A low water sample volume was filtered which resulted in a very high DL of [Hg]_P.

Appendix 3. Spring $[\text{Hg}]_{\text{D}}$ and $[\text{Hg}]_{\text{T}}$ at Tuktoyaktuk.



Appendix 4. Spring $[\text{Hg}]_{\text{D}}$ and $[\text{Hg}]_{\text{T}}$ at the Mackenzie River at the Arctic Red River.



Appendix 5. ^{210}Pb and ^{137}Cs dating of King Point permafrost core.

Average Depth (cm)	Excess Pb-210	Pb-210 Activity (Bq/g +/- 2SD)	Cs-137 Activity (Bq/g +/- 2SD)	Linear Model		CRS Model		Sedimentation Rate (g/m ² /yr)
				# years/slice	Median year of deposition	# years/slice	Median year of deposition	
0.5	2.20×10^1	$2.32 \times 10^1 \pm 5.23 \times 10^3$	0	9.2	2000	7.4	2001	257
1.5	1.75×10^1	$1.87 \times 10^1 \pm 5.19 \times 10^3$	$9.96 \times 10^2 \pm 4.81 \times 10^3$	13.2	1989	11.2	1992	242
2.5	1.45×10^1	$1.57 \times 10^1 \pm 4.25 \times 10^3$	$1.97 \times 10^1 \pm 9.16 \times 10^3$	17.1	1974	18.9	1977	185
3.5	7.61×10^2	$8.81 \times 10^2 \pm 3.41 \times 10^3$	$8.10 \times 10^2 \pm 1.00 \times 10^2$	7.3	1962	6.4	1964	234
4.5	5.98×10^2	$7.18 \times 10^2 \pm 2.47 \times 10^3$	$6.02 \times 10^2 \pm 6.86 \times 10^3$	9.5	1953	8.2	1957	238
5.5	4.94×10^2	$6.14 \times 10^2 \pm 2.26 \times 10^3$	$4.53 \times 10^2 \pm 6.17 \times 10^3$	20.9	1938	24.0	1941	178
6.5	1.71×10^2	$2.91 \times 10^2 \pm 1.67 \times 10^3$	$1.75 \times 10^2 \pm 2.76 \times 10^3$	38.1	1908	39.3	1909	199
7.5	5.04×10^3	$1.70 \times 10^2 \pm 1.09 \times 10^3$	0	23.5	1878	18.3	1880	263
8.5	1.17×10^3	$1.32 \times 10^2 \pm 8.56 \times 10^4$		32.1	1850	9.0	1867	733
9.5	4.83×10^4	$1.25 \times 10^2 \pm 8.32 \times 10^4$		41.3	1813	6.0	1859	1405
10.5		$1.25 \times 10^2 \pm 8.32 \times 10^4$						
		$1.19 \times 10^2 \pm 7.77 \times 10^4$						
		$1.33 \times 10^2 \pm 8.11 \times 10^4$						
		$1.40 \times 10^2 \pm 7.55 \times 10^4$						
		$1.26 \times 10^2 \pm 6.63 \times 10^4$						
		$1.43 \times 10^2 \pm 7.42 \times 10^4$						

Appendix 6. ^{210}Pb and ^{137}Cs dating of Herschel Island - W permafrost core.

Average Depth (cm)	Excess Pb-210	Pb-210 Activity (Bq/g +/- 2SD)	Cs-137 Activity (Bq/g +/- 2SD)	Linear Model		CRS Model		Sedimentation Rate (g/m ² /yr)
				# years/slice	Median year of deposition	# years/slice	Median year of deposition	
0.5	8.68×10^2	$1.01 \times 10^1 \pm 2.42 \times 10^3$	$3.92 \times 10^2 \pm 2.15 \times 10^3$	34.2	1988	34.8	1987	500
1.5	1.83×10^2	$3.23 \times 10^2 \pm 1.18 \times 10^3$	$1.56 \times 10^2 \pm 6.48 \times 10^4$	72.0	1934	64.5	1938	566
2.5	4.52×10^3	$1.85 \times 10^2 \pm 8.62 \times 10^4$	$4.87 \times 10^3 \pm 1.29 \times 10^3$	29.1	1884	33.2	1889	445
3.5	8.90×10^4	$1.49 \times 10^2 \pm 8.25 \times 10^4$	0	44.5	1847	25.3	1860	891
4.5		$1.41 \times 10^2 \pm 6.08 \times 10^4$	0					
5.5		$1.39 \times 10^2 \pm 6.78 \times 10^4$						
6.5		$1.44 \times 10^2 \pm 7.10 \times 10^4$						
7.5		$1.40 \times 10^2 \pm 6.47 \times 10^4$						
8.5		$1.35 \times 10^2 \pm 9.40 \times 10^4$						
9.5		$1.43 \times 10^2 \pm 9.42 \times 10^4$						
11		$1.60 \times 10^2 \pm 1.12 \times 10^3$						
13		$1.53 \times 10^2 \pm 9.43 \times 10^4$						