UVicSPACE: Research & Learning Repository

University of Victoria

Faculty of Social Science

Faculty Publications

Mercury in freshwater ecosystems of the Canadian Arctic: Recent advances on its cycling and fate

John Chételat, Marc Amyot, Paul Arp, Jules M. Blais, David Depew, Craig A. Emmerton, Marlene Evans, Mary Gamberg, Nikolaus Gantner, Catherine Girard, Jennifer Graydon, Jane Kirk, David Lean, Igor Lehnherr, Derek Muir, Mina Nasr, Alexandre J. Poulain, Michael Power, Pat Roach, Gary Stern, Heidi Swanson, Shannon van der Velden

2015

Crown Copyright © 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

This article was originally published at:
http://dx.doi.org/10.1016/j.scitotenv.2014.05.151

Citation for this paper:

Chételat, J.,Amyot, M., Arp, P., Blais, J.M., Depew, D., Emmerton, C.A. & van der Velden, S. (2015). Mercury in freshwater ecosystems of the Canadian Arctic: Recent advances on its cycling and fate. *Science of the Total Environment,* 509-510, 41-66. http://dx.doi.org/10.1016/j.scitotenv.2014.05.151

Science of the Total Environment 509–510 (2015) 41–66

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Mercury in freshwater ecosystems of the Canadian Arctic: Recent advances on its cycling and fate

John Chételat [a,*], Marc Amyot [b], Paul Arp [c], Jules M. Blais [d], David Depew [e], Craig A. Emmerton [f], Marlene Evans [g], Mary Gamberg [h], Nikolaus Gantner [i,1], Catherine Girard [b], Jennifer Graydon [f], Jane Kirk [e], David Lean [j], Igor Lehnherr [k], Derek Muir [e], Mina Nasr [c], Alexandre J. Poulain [d], Michael Power [l], Pat Roach [m], Gary Stern [n], Heidi Swanson [l], Shannon van der Velden [l]

[a] Environment Canada, National Wildlife Research Centre, Ottawa, Ontario K1A 0H3, Canada
[b] Centre d'études nordiques, Département de sciences biologiques, Université de Montréal, Montreal, Quebec H3C 3J7, Canada
[c] Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada
[d] Department of Biology, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada
[e] Environment Canada, Canada Centre for Inland Waters, Burlington, Ontario L7R 4A6, Canada
[f] Department of Biological Sciences, University of Alberta, Edmonton, Alberta T6G 2E9, Canada
[g] Environment Canada, Aquatic Contaminants Research Division, Saskatoon, Saskatchewan S7N 3H5, Canada
[h] Gamberg Consulting, Whitehorse, Yukon Y1A 5M2, Canada
[i] Department of Geography, University of Victoria, Victoria, BC V8W 3R4, Canada
[j] Lean Environmental, Apsley, Ontario K0L 1A0, Canada
[k] Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
[l] Department of Biology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
[m] Aboriginal Affairs and Northern Development Canada, Whitehorse, Yukon Y1A 2B5, Canada
[n] Centre for Earth Observation Science, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

HIGHLIGHTS

- New data are available on mercury concentrations and fluxes in Arctic fresh waters.
- Mercury fluxes to Arctic lake sediments have increased during the Industrial Era.
- No geographic patterns are evident for mercury levels in freshwater fish species.
- Mercury has increased in some freshwater fish populations in recent decades.
- Climate change may be impacting mercury cycling and fate in the Canadian Arctic.

ARTICLE INFO

Article history:
Received 16 December 2013
Received in revised form 1 May 2014
Accepted 27 May 2014
Available online 30 June 2014

Editor: Jason Stow

Keywords:
Arctic
Mercury
Fresh water
Bioaccumulation
Biogeochemistry
Temporal trends

ABSTRACT

The Canadian Arctic has vast freshwater resources, and fish are important in the diet of many Northerners. Mercury is a contaminant of concern because of its potential toxicity and elevated bioaccumulation in some fish populations. Over the last decade, significant advances have been made in characterizing the cycling and fate of mercury in these freshwater environments. Large amounts of new data on concentrations, speciation and fluxes of Hg are provided and summarized for water and sediment, which were virtually absent for the Canadian Arctic a decade ago. The biogeochemical processes that control the speciation of mercury remain poorly resolved, including the sites and controls of methylmercury production. Food web studies have examined the roles of Hg uptake, trophic transfer, and diet for Hg bioaccumulation in fish, and, in particular, advances have been made in identifying determinants of mercury levels in lake-dwelling and sea-run forms of Arctic char. In a comparison of common freshwater fish species that were sampled across the Canadian Arctic between 2002 and 2009, no geographic patterns or regional hotspots were evident. Over the last two to four decades, Hg concentrations have increased in some monitored populations of fish in the Mackenzie River Basin while other populations from the Yukon and Nunavut showed no change or a slight decline. The different Hg trends indicate that the drivers of temporal change may be regional or habitat-specific. The Canadian Arctic is undergoing profound environmental change, and preliminary evidence suggests that it may be impacting the cycling and bioaccumulation of mercury. Further research is needed to investigate climate

* Corresponding author. Tel.: +1 613 991 9835; fax: +1 613 998 0458.
E-mail address: John.Chetelat@ec.gc.ca (J. Chételat).
[1] Current address: Department of Chemistry, Trent University, Peterborough, Ontario K9J 7B8, Canada.

http://dx.doi.org/10.1016/j.scitotenv.2014.05.151
0048-9697/Crown Copyright © 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

change impacts on the Hg cycle as well as biogeochemical controls of methylmercury production and the processes leading to increasing Hg levels in some fish populations in the Canadian Arctic.

Crown Copyright © 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Contents

1. Introduction . . . 42
2. Water . . . 43
2.1. Ecosystem and geographic variation in water Hg concentrations . . . 43
2.2. Mackenzie River mercury concentrations and export to the Arctic Ocean . . . 44
2.3. Speciation of Hg in the upper Yukon River Basin . . . 45
2.4. Exports of Hg from the sub-Arctic Nelson and Churchill rivers . . . 45
2.5. Snowmelt delivery of Hg to High Arctic lakes . . . 45
3. Sediment . . . 46
3.1. Spatial analysis of Hg levels in bulk sediment from Arctic streams and lakes . . . 46
3.2. Mercury fluxes to Arctic lake sediments . . . 48
3.2.1. Spatial and temporal trends of Hg fluxes inferred from lake sediments . . . 48
3.2.2. Agreement of Hg fluxes inferred from lake sediment with modeled deposition . . . 49
3.2.3. Interpretation of Hg fluxes to lake sediments . . . 49
3.3. Impact of permafrost thawing on Hg transport to Arctic lakes . . . 51
4. Biogeochemical transformations of Hg . . . 51
4.1. Microbial transformations of Hg . . . 51
4.2. Photochemical transformations of Hg . . . 52
4.2.1. Photoreduction and photooxidation . . . 52
4.2.2. Photodemethylation . . . 52
4.3. Mass balance of MeHg in High Arctic ponds . . . 53
5. Trophic transfer in food webs . . . 53
5.1. Trophic transfer of Hg in coastal Arctic lakes with and without anadromous Arctic char . . . 53
5.2. Trophic transfer of Hg in lakes with landlocked Arctic char . . . 54
5.3. Factors affecting Hg bioaccumulation in Arctic invertebrates . . . 55
5.4. Tracing the source(s) of Hg in lake food webs using Hg stable isotopes . . . 55
6. Fish . . . 56
6.1. Geographic and species variation in fish Hg concentrations . . . 56
6.2. Arctic char . . . 57
6.2.1. Comparison of Hg bioaccumulation in sea-run and lake-dwelling Arctic char . . . 57
6.3. Lake trout . . . 59
6.3.1. Anadromous lake trout in the West Kitikmeot . . . 59
6.3.2. Lake trout in the Mackenzie River Basin . . . 59
6.4. Temporal trends of Hg in Arctic fish populations . . . 59
6.4.1. Temporal trends of Hg in Mackenzie River burbot . . . 60
6.4.2. A multi-species assessment of temporal Hg trends in Great Slave Lake . . . 61
7. Wildlife in freshwater ecosystems . . . 61
7.1. Waterfowl . . . 61
7.2. Small mammals . . . 61
8. Summary . . . 61
Acknowledgments . . . 63
References . . . 63

1. Introduction

The Canadian Arctic contains vast fresh waters that cover about 140,000 km^2 of land north of 60° latitude (Prowse et al., 2009). Freshwater fish are important in the diet of many Northerners, particularly in central and sub-Arctic regions of the Northwest Territories, Yukon, Nunavut and northern Quebec. The Canadian Government's Northern Contaminants Program (NCP) has collected extensive information on mercury (Hg) in Arctic fresh waters since the early 1990s. During the first two phases of the program (Phase I: 1991 to 1997; Phase II: 1998 to 2003), investigations focused primarily on fish surveys involving measurements of Hg (and other metals) in a variety of fish species, particularly Arctic char (*Salvelinus alpinus*), lake trout (*Salvelinus namaycush*), northern pike (*Esox lucius*) and burbot (*Lota lota*) (NCP, 1997, 2003). Monitoring programs were also established to detect temporal trends of Hg for a few fish populations in different regions of the Canadian Arctic including Yukon, Mackenzie River Basin in the Northwest Territories, and High Arctic islands in Nunavut (NCP, 2003). These investigations identified some lakes where concentrations of Hg in top predator species exceeded Health Canada's consumption guideline for commercial sale of fish. While trophic position, age, and size of fish were identified as important factors, no geographic trends were discernible for the elevated Hg levels (Evans et al., 2005a).

Since 2002, activities under the NCP were expanded to include more focused research of transport, biogeochemical and food web processes that control the fate of Hg in northern aquatic ecosystems and to better understand the high lake-to-lake variability of Hg in freshwater fish. The discovery in the 1990s of enhanced Hg deposition from atmospheric mercury depletion events (AMDEs) (Schroeder et al., 1998) stimulated extensive research on potential impacts to aquatic ecosystems in the Canadian Arctic. Climate change was also highlighted as a potentially important driver of Hg cycling that required further research (NCP, 2003).

Over the last decade, important advances have been made in our understanding of the Hg cycle in Arctic freshwater ecosystems. Water concentrations and speciation of Hg are now available for lakes, ponds, and several large rivers in the Canadian Arctic. Mercury profiles in lake sediments provide new estimates of deposition rates. Production and loss of MeHg in ponds as well as snowmelt fluxes of MeHg to lakes were

investigated. To determine factors influencing lake-to-lake variability in Hg bioaccumulation, food webs were studied in Arctic lakes where landlocked char or lake trout are the top predator fish. A novel approach to trace Hg sources using Hg stable isotopes was also applied to some of these Arctic lake food webs. Recent studies examined potential influences of climate change on Hg bioaccumulation in fish and on Hg sequestration in lake sediments. Impacts of thawing permafrost on Hg transport to lakes were investigated in the Mackenzie River Basin. More frequent monitoring under the NCP of key fish species has further strengthened the temporal trend datasets for the freshwater environment.

This review summarizes our current state of knowledge on mercury in freshwater ecosystems of the Canadian Arctic. An emphasis is placed on geographically-linked information specific to Canada, which complements a recent more generalized review for the circumpolar Arctic (Douglas et al., 2012). Much of the information describe herein was collected under NCP-funded research and monitoring, although every effort was made to include other sources including the published literature and studies funded under the International Polar Year and ArcticNet programs. The main objective of this review is to highlight recent scientific advances since 2002—an update of Evans et al. (2005b)—and to identify knowledge gaps and important directions for future research.

2. Water

2.1. Ecosystem and geographic variation in water Hg concentrations

Over the last decade, much new information has been collected on water concentrations of total Hg (THg) and MeHg in fresh waters of the Canadian Arctic (Table 1; Fig. 1). Most available data are for lakes and large rivers although some ponds, streams, and wetlands have also been sampled in recent years. The most extensively sampled areas are two High Arctic islands in Nunavut (Cornwallis, Ellesmere) and the Mackenzie River Basin in the Northwest Territories.

Water concentrations of unfiltered THg ranged widely from 0.1 to 19.8 ng L^{-1} in different water bodies of the Canadian Arctic (Fig. 1; Table 1). Lakes, ponds, and wetlands from several Arctic regions had relatively low concentrations—generally less than 3 ng L^{-1}—whereas rivers often had considerably higher levels. Elevated concentrations were mostly measured in the Mackenzie River or its tributaries and were largely associated with particulate matter. The Mackenzie had more particulate Hg during periods of high flow due to increased erosion in the basin (Leitch et al., 2007). Concentrations of THg were generally lower in other rivers and streams including sites on Cornwallis Island and the Nelson and Churchill rivers (Table 1). Geographic variation in hydrology and drainage basin characteristics may influence concentrations of THg in flowing waters.

Water concentrations of unfiltered MeHg in Arctic water bodies ranged two orders of magnitude from <0.02 ng L^{-1} (below analytical detection) to 3.0 ng L^{-1} (Fig. 1; Table 1). The majority of lakes, rivers, streams, and wetlands (for which data are available) had low MeHg concentrations (≤0.1 ng L^{-1}). At sites on Ellesmere Island where high concentrations were observed, ponds showed great potential for MeHg production. These shallow water bodies had characteristics known to enhance microbial Hg methylation, namely warm water temperatures and high concentrations of labile organic matter (Lehnherr et al., 2012b; St. Louis et al., 2005). Elevated MeHg concentrations were also observed in Mackenzie Delta lakes (Graydon et al., 2009)

Table 1
Water concentrations of Hg in rivers, streams, lakes, wetlands, and ponds in the Canadian Arctic. Ancillary measurements of water pH and DOC concentrations were included if available.

Location	Date	*n*	pH	DOC (mg L^{-1})	MeHg (ng L^{-1})		THg (ng L^{-1})		Source
					Unfiltered	Filtered	Unfiltered	Filtered	
Rivers and streams									
Yukon River, YT	2004	3	7.9 ± 0.1	2.8 ± 1.8		<0.04		2.2 ± 2.4	1
Yukon River tributaries, YT	2004	14	7.8 ± 0.2	5.1 ± 5.1		<0.04–0.11		1.5 ± 1.2	1
Mackenzie River, NT	2003–2005	37			0.09 ± 0.03	0.08 ± 0.04	7.0 ± 4.3	2.8 ± 2.1	2, 3
Mackenzie River, NT	2007–2010	6			0.08 ± 0.05	0.03 ± 0.01	13.7 ± 8.0	1.4 ± 0.7	4
Mackenzie River tributaries, NT	2003–2005	20				0.07 ± 0.04	6.3 ± 2.9	2.6 ± 1.9	2
Peel River, NT	2007–2010	1			0.10 ± 0.08	0.02 ± 0.02	18.8 ± 12.2	1.6 ± 0.9	4
Cornwallis Island streams, NU	1994–2006	7	8.2 ± 0.1	1.5 ± 1.1	0.07 ± 0.06		1.2 ± 1.1		5, 6, 7
Ellesmere Island streams, NU	2005	4			0.04 ± 0.03		1.1 ± 0.7		8
Devon Island river, NU	2006	1	8.0	0.9	0.05		0.2		5
Churchill River, MB	2003–2007	1		20.5	0.18 ± 0.09	0.14 ± 0.07	2.0 ± 0.8	1.7 ± 0.7	9
Nelson River, MB	2003–2007	1		15.1	0.05 ± 0.03	0.04 ± 0.02	0.9 ± 0.3	0.5 ± 0.2	9
Large rivers in Nunavik, QC	2005–2007	3					1.1 ± 0.1	1.4 ± 0.2	10
Baker Lake outflow, NU	2005–2007	1					0.72		10
Lakes									
Cornwallis Island, NU	2002–2007	18	8.1 ± 0.1	1.1 ± 0.6	0.04 ± 0.01		0.6 ± 0.3		6, 7, 11, 12
Devon Island, NU	2006	6	8.3 ± 0.3	2.0 ± 1.6	0.04 ± 0.02		0.5 ± 0.2		11
Somerset Island, NU	2005–2007	1	7.8	0.5	0.02		0.7		11, 12
Ellesmere Island, NU	2003, 2005–2007	25	8.2 ± 0.4	2.8 ± 2.7	0.05 ± 0.03		0.9 ± 0.5		13, 8, 12
Mackenzie River Basin, NT	1998–2002	18	8.1 ± 0.4	11.5 ± 5.4	0.07 ± 0.04		1.8 ± 0.7		14
Mackenzie Delta, NT	2004, 2010	6			0.10 ± 0.05		2.3 ± 0.6	0.7 ± 0.2	3, 4
Kent Peninsula, NU	2005–2007	3		4.6 ± 2.1			0.5 ± 0.1		12
Victoria Island, NU	2005–2007	1		5.6			0.6		12
Nunavik, QC	2005–2007	2		1.2 ± 0.7			3.2 ± 0.03		12
Wetlands									
Ellesmere Island, NU	2002	2	7.2–7.5	2.2 ± 2.4	<0.02–0.08		0.7 ± 0.1		6
Cornwallis Island, NU	2002	4		1–4.5	0.06 ± 0.03		1.0 ± 0.2		6
Devon Island, NU	2006	4	7.0 ± 0.2	22.4 ± 8.2				4.4 ± 1.3	15
Ponds									
Cornwallis Island, NU	2006	1	8.5	0.9	<0.02		0.4		11
Devon Island, NU	2006	4	8.3 ± 0.2	4.6 ± 2.0	0.08 ± 0.05		1.0 ± 0.4		11
Ellesmere Island, NU	2003, 2005	21	8.4 ± 0.4	18.7 ± 12.1	0.53 ± 0.68		2.2 ± 2.0		8, 13

Notes: mean concentrations are presented (±1 standard deviation), *n* = number of sites sampled, DOC = dissolved organic carbon.
Sources: 1 = Halm and Dornblaser (2007), 2 = Leitch et al. (2007), 3 = Graydon et al. (2009), 4 = Emmerton et al. (2013), 5 = J. Chételat (Environment Canada, unpublished data), 6 = Loseto et al. (2004a), 7 = Semkin et al. (2005), 8 = Lehnherr et al. (2012b), 9 = Kirk and St. Louis (2009), 10 = Hare et al. (2008); 11 = Chételat et al. (2008), 12 = Gantner et al. (2010a,b); 13 = St. Louis et al. (2005), 14 = Evans et al. (2005a), and 15 = Oiffer and Siciliano (2009).

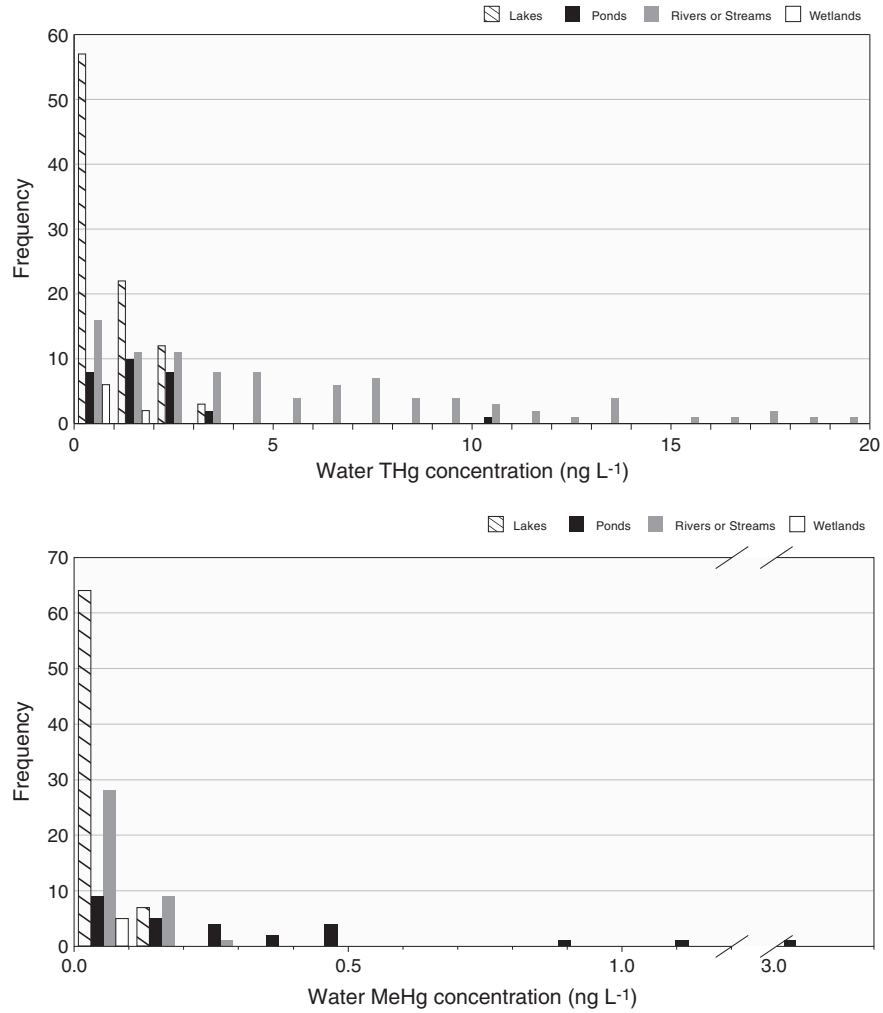

Fig. 1. Frequency distributions of unfiltered THg and MeHg concentrations in water from different freshwater ecosystems in the Canadian Arctic (data sources in Table 1).

and near the outflow of the Churchill River where vast wetlands are the suspected source (Kirk and St. Louis, 2009). In lakes along the Mackenzie River, water concentrations of THg and MeHg, as well as the proportion of THg as MeHg, were higher in smaller lakes where dissolved organic carbon (DOC) concentrations were also higher (Evans et al., 2005a). Wetlands on Cornwallis and Ellesmere Islands were typically water-logged soils overlaid with grass, sedge, or moss and had low aqueous MeHg concentrations (Loseto et al., 2004a).

2.2. Mackenzie River mercury concentrations and export to the Arctic Ocean

The Mackenzie River is the second largest river in Canada, with an immense water discharge (mean > 10,000 $m^3 s^{-1}$) and a heavy sediment load. The hydrology of this river is highly seasonal with low flow during freezing conditions (November to May), snowmelt-induced high flow and flooding of its delta during the snowmelt period (May to June), and decreasing flow during open-water conditions, except during storm events (July to October). This striking flow pattern, its large and diverse watershed (1.8×10^6 km^2), and the effects of ice and its large delta combine to determine Mackenzie Hg concentrations and export to the Arctic Ocean.

Mercury is effectively immobilized in the Mackenzie River Basin during freezing conditions because watershed soils are frozen and the river is ice-covered. Most of the Mackenzie's water at this time originates from Hg-poor sources such as cold oligotrophic lakes. During under-ice, low flow conditions in early May, mean concentrations ($\pm$1 standard deviation) of both THg (unfiltered: 1.05 $\pm$ 0.79 ng L^{-1}, filtered: 0.31 $\pm$ 0.05 ng L^{-1}) and MeHg (unfiltered: 0.025 $\pm$ 0.007 ng L^{-1}, filtered: 0.022 $\pm$ 0.004 ng L^{-1}) were low in the river (Emmerton et al., 2013). As its basin thaws, runoff increases and river ice breaks up. During this time, unfiltered THg (16.92 $\pm$ 5.02 ng L^{-1}) and MeHg (0.085 $\pm$ 0.044 ng L^{-1}) concentrations in the Mackenzie increased substantially. Mercury is predominantly particle-bound during this time (87.7 $\pm$ 5.9%; Emmerton et al., 2013) and originates mostly from mountain-fed rivers in the western portion of the basin (Carrie et al., 2012). Rivers draining mountain areas erode catchment and bank material and mobilize elements that associate closely with particles, including Hg (Benoit et al., 1998). Increases in dissolved concentrations of THg (1.54 $\pm$ 0.41 ng L^{-1}) and MeHg (0.032 $\pm$ 0.015 ng L^{-1}) were also observed in the river during the thaw period suggesting that fine particles (small enough to pass through 0.45 μm filters) were important components of Hg transport in the Mackenzie (Fig. 2; Emmerton et al., 2013). After the ice clears and river discharge peaks, runoff within the Mackenzie River Basin originates from lower in the soil profile, and erosion decreases as river velocities and water levels decline. These factors combine to deliver less organic matter and sediment to the river water, and concentrations of THg and MeHg also decline (Graydon et al., 2009; Leitch et al., 2007). Summer precipitation events and coastal storm surges can mobilize organic matter and sediment through surface runoff and local flooding and may increase Hg concentrations in the Mackenzie River for short periods of time.

The geography, climate and hydrology of the Mackenzie River create an extremely challenging environment within which to measure mass

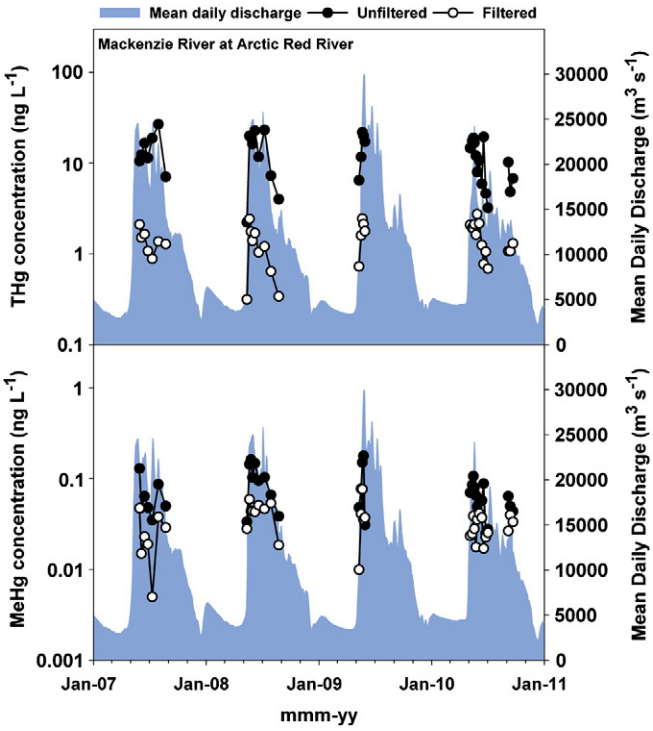

Fig. 2. Filtered and unfiltered concentrations of THg and MeHg in relation to water discharge in the lower Mackenzie River at Arctic Red River between 2007 and 2010. Reprinted with permission from Emmerton et al. (2013). © American Chemical Society.

fluxes of Hg to the Arctic Ocean because: 1) discharge measurements during ice breakup on the river are affected by backwater conditions, 2) annual breakup of river ice is a dangerous environment for collecting water samples; and 3) the Mackenzie River delta may influence Hg concentrations in river water before export to the ocean. Although discharge measurement during ice breakup is currently an ongoing issue in this system, Emmerton et al. (2013) collected samples during the ice-breakup period and Graydon et al. (2009) and Emmerton et al. (2013) investigated the influence of delta processes on river Hg concentrations delivered to the Arctic Ocean. These studies estimated that Hg concentrations in river water exiting the delta were 16 to 19% (unfiltered THg) and up to 10% (unfiltered MeHg) lower than those entering the delta. These differences suggest that northern deltas may be important sinks of river mercury through floodplain processes such as sedimentation, photodemethylation and flooding of soils (Emmerton et al., 2013).

At present, there are few estimates of THg and MeHg export from the Mackenzie River. Emmerton et al. (2013) calculated annual Hg mass fluxes exiting the delta of 1850–3400 kg y^{-1} (unfiltered THg) and 13–20 kg y^{-1} (unfiltered MeHg) to the Arctic Ocean between 2007 and 2010. Approximately 11–13% of unfiltered THg and 39–51% of unfiltered MeHg were in dissolved form. Graydon et al. (2009) calculated export upstream of the delta for 2.5 months (summer 2004) that totalled 1200 kg of unfiltered THg and 8 kg of unfiltered MeHg. Leitch et al. (2007) calculated annual export upstream of the delta of 1200–2900 kg y^{-1} for unfiltered THg and 7–22 kg y^{-1} for filtered MeHg between 2003 and 2005.

2.3. Speciation of Hg in the upper Yukon River Basin

Flowing from its upper reaches in British Columbia and Yukon into Alaska (USA), the Yukon River drains the fourth largest watershed in North America (8.6×10^5 km^2) and discharges into the Bering Sea. The United States Geological Survey measured concentrations of THg and MeHg in waters of the upper Yukon River Basin in Canada, at three stations on the Yukon River and in 14 of its tributaries (Halm and Dornblaser, 2007) as part of a larger, comprehensive study of the entire Yukon River Basin (Schuster et al., 2011). In the summer of 2004, filtered and particulate fractions of Hg were determined on two occasions at each station in Canadian waters.

On average, THg concentrations were equally partitioned between the dissolved and particulate fractions (49 ± 28%, $n = 32$). However, the observed range in particulate THg (<0.06–26.3 ng L^{-1}) was much higher than for the dissolved fraction (0.3–6.4 ng L^{-1}), and elevated THg levels in river water were primarily associated with particulates. Dissolved and particulate MeHg concentrations were below analytical detection at many of the stations, and the maximum observed concentrations were 0.11 ng L^{-1} and 0.07 ng L^{-1}, respectively. In the Yukon River, DOC is primarily terrestrial in origin and a substantial portion is leachate from recent plant production (Guo and Macdonald, 2006; Spencer et al., 2008). A detailed analysis for the outlet of the Yukon River Basin in Alaska showed that water concentrations of dissolved and particulate Hg were strongly related to organic carbon (Schuster et al., 2011). Large reservoirs of organic matter in wetlands and permafrost of northern rivers will likely be impacted by climate change, and transport processes of organic carbon may be important in future watershed delivery of Hg (Schuster et al., 2011).

2.4. Exports of Hg from the sub-Arctic Nelson and Churchill rivers

Annual exports of Hg were determined for two Canadian sub-Arctic rivers that flow into Hudson Bay—the Nelson and the Churchill (Kirk and St. Louis, 2009). In the 1970s, roughly 75% of flow from the Churchill River was diverted into the Nelson River for hydroelectric power development. In recent years, discharge from the Nelson River (3550 m^3 s^{-1}) has been seven times more than that from the Churchill River (550 m^3 s^{-1}) (Kirk and St. Louis, 2009). Based on frequent measurements from 2003 to 2007, unfiltered THg and MeHg concentrations were low in the Nelson River (mean ± standard deviation: 0.88 ± 0.33 and 0.05 ± 0.03 ng L^{-1}, respectively) but higher in the Churchill River, particularly for MeHg (1.96 ± 0.8 and 0.18 ± 0.09 ng L^{-1}, respectively). Hence, the Churchill River may be an important source of MeHg to organisms feeding in its estuary. Despite higher Hg concentrations in the Churchill River, average THg and MeHg exports to Hudson Bay from the Churchill River (37 ± 28 and 4 ± 4 kg y^{-1}, respectively) were less than half of exports from the Nelson River (113 ± 52 and 9 ± 4 kg y^{-1}) because of differences in flow. Interestingly, combined Hg exports to Hudson Bay from the Nelson and Churchill rivers are comparable to estimated THg inputs from spring snowmelt on Hudson Bay ice (177 ± 140 kg y^{-1}) but are about 13 times greater than MeHg inputs from snowmelt (1 ± 1 kg y^{-1}) (Kirk and St. Louis, 2009). Together, Hg inputs from the rivers and snowmelt were estimated to contribute approximately 16% to the THg pool in Hudson Bay waters but account for a lesser portion (6%) of the MeHg pool.

2.5. Snowmelt delivery of Hg to High Arctic lakes

Snow is a large reservoir that accumulates inorganic Hg and MeHg over the long Arctic winter. As spring temperatures warm the snowpack above freezing, Hg is rapidly leached and transported in runoff to fresh waters downstream (Dommergue et al., 2003; Lahoutifard et al., 2005; Lindberg et al., 2002). Intensive sampling of inflow streams to Amituk Lake (Cornwallis Island) showed that stream water concentrations of THg were highest at the onset of spring melt (1.4–4.4 ng L^{-1}) and decreased through spring to a summer low of 0.3–0.4 ng L^{-1} (Loseto et al., 2004a; Semkin et al., 2005). Water concentrations of MeHg in those streams also followed the same decline during the spring melt (Loseto et al., 2004a). The higher Hg concentrations in stream water coupled with high discharge resulted in important amounts of THg and MeHg being delivered during spring (Loseto et al., 2004a; Semkin et al., 2005).

In the Arctic Archipelago, snowmelt is an important source of Hg to lakes. Semkin et al. (2005) calculated that surface runoff was responsible for almost all the THg input to Amituk Lake, about 80% of which

occurred during spring freshet in June and early July. Spring freshet is the critical period of discharge from High Arctic watersheds because most total annual precipitation is deposited in the form of snow during the long polar winter (Woo, 1983). Loseto et al. (2004a) observed that water concentrations of THg and MeHg in lakes on Cornwallis Island were highest in spring due to snowmelt inputs. In two northern Quebec lakes, the top water layer under the ice had higher THg concentrations than deeper waters in May prior to ice thaw (Gantner et al., 2012). Vertical profiles in the water column of Barren Lake on Cornwallis Island indicated that the surface layer, measured initially in the moat between the snow and the floating ice, had the highest THg and MeHg concentrations during the spring melt period (Fig. 3; D. Lean, Lean Environmental, unpublished data). Reflecting the input of snowmelt, the surface water of Barren Lake also had lower conductivities and colder temperatures than deeper layers. Surface water concentrations of THg in Barren Lake were much lower than those associated with snow during AMDEs—but similar to values in local snow just prior to spring melt—whereas MeHg concentrations were similar to those measured in local snow (Lahoutifard et al., 2005). Less information is available on snowmelt delivery of Hg in other regions of the Canadian Arctic, although this spring-time source may be less important in the overall Hg budget of lower latitude Arctic lakes, such as in Alaska, because of differences in watershed characteristics and hydrology (Fitzgerald et al., 2005; Hammerschmidt et al., 2006).

3. Sediment

3.1. Spatial analysis of Hg levels in bulk sediment from Arctic streams and lakes

Watershed-scale processes of Hg accumulation in the active layer of lake and stream sediments were investigated in the Canadian Arctic to identify how THg concentrations relate to sediment attributes as well as the topography, climate, vegetation, and geology of water bodies and their upslope catchments (Nasr et al., 2011). A total of 36,310 sampling locations for THg measurements of bulk sediments (0–30 cm depth) in streams and lakes were examined using the National Geochemical Reconnaissance database (NGR) of the Geological Survey of Canada (GSC, 2008) (Fig. 4). Additional information was obtained for the analysis on geological and lithological specifications (NRCan, 2007), land cover type (GeoBase), stream and lake morphometry (NGR), digital elevation models to evaluate the topographic flow-accumulation and delineate upland or lowland sites (Murphy et al., 2009), and GRAHM (Global/Regional Atmospheric Heavy Metals Model) estimates of atmospheric Hg deposition for 2005 at sampling locations.

Sediment THg concentrations in streams and lakes ranged from 5 to 5950 ng g^{-1} with overall mean and median concentrations of 65 and 40 ng g^{-1} (Fig. 5). The vast majority of sediment samples (99.6%) had values between 5 and 600 ng g^{-1}, with 112 values over 600 ng g^{-1}. There were 20 THg values >1500 ng g^{-1} in Yukon streams, presumably due to upland geogenic or industrial sources. In most cases, there were no industrial upstream disturbances such as surface mining. Notable were the generally higher values (mean: 110 ng g^{-1}) within the Selwyn Basin (Yukon, zone 3), and the generally lower values (mean: 25 ng g^{-1}) on Bathurst Island (Nunavut, zone 4) (Fig. 4).

Within each survey zone with both stream and lake data (Yukon, Labrador), mean THg was lower in streams than in lake sediments (Nasr et al., 2011). On average, this may be related to an increase in Hg concentrations from the more mineral environment in stream beds (mean LOI = 8%, SD = 17%) to the more organically enriched sediments on lake bottoms (mean LOI = 28%, SD = 9%), with LOI referring to loss on ignition at 450 °C, mostly due to organic matter. However, mean stream sediment THg could easily exceed mean lake sediment and vice versa in areas where there would be high upstream THg sources.

Differentiating upland from lowland THg sediment sampling sites by way of digital elevation modeling (uplands were defined by areas 40 m above rivers using methods of Murphy et al., 2009) revealed that sediment THg was significantly higher in upland locations (mean: 49 ng g^{-1} for lakes, 78 ng g^{-1} for streams) than in lowland locations (mean: 39 ng g^{-1} for lakes, 65 ng g^{-1} for streams) (see Table 2 in Nasr et al., 2011). These upland versus lowland trends were also found for lakes within specific survey zones, namely Great Bear Lake (zone 5: 60 vs. 50 ng g^{-1}), Baker Lake (zone 8: 33 vs. 26 ng g^{-1}), the Northwest Territories (zone 7: 52 vs. 42 ng g^{-1}) and southern Nunavut

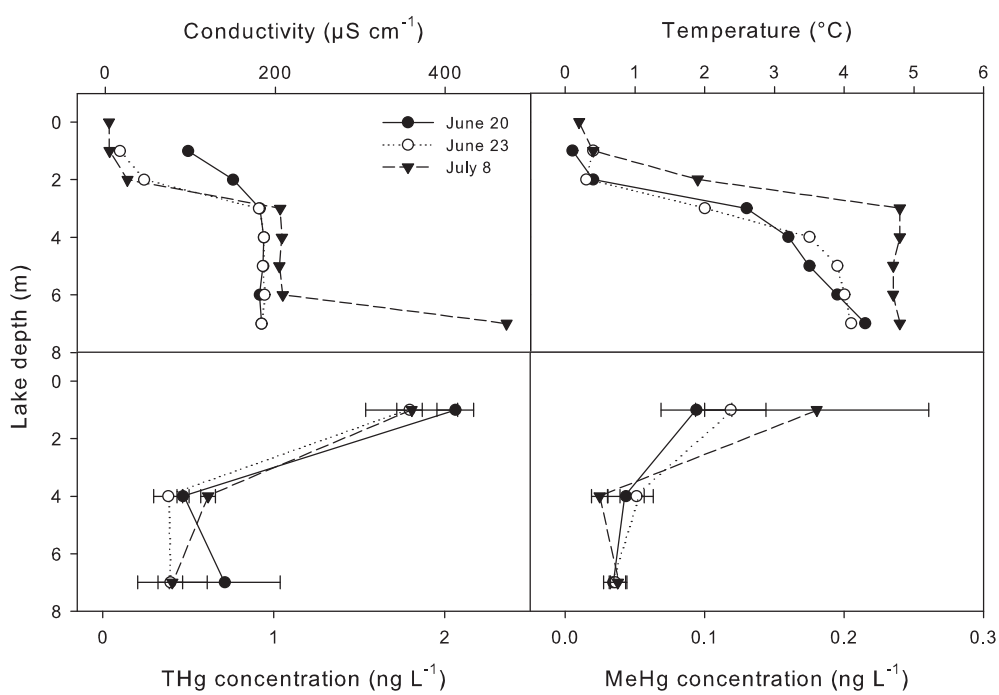

Fig. 3. Vertical profiles of water temperature (°C), specific conductivity (µS cm^{-1}), and concentrations of THg and MeHg (ng L^{-1}; mean ± 1 standard deviation) in the water column of Barren Lake, Cornwallis Island, during spring melt (D. Lean, Lean Environmental, unpublished data).

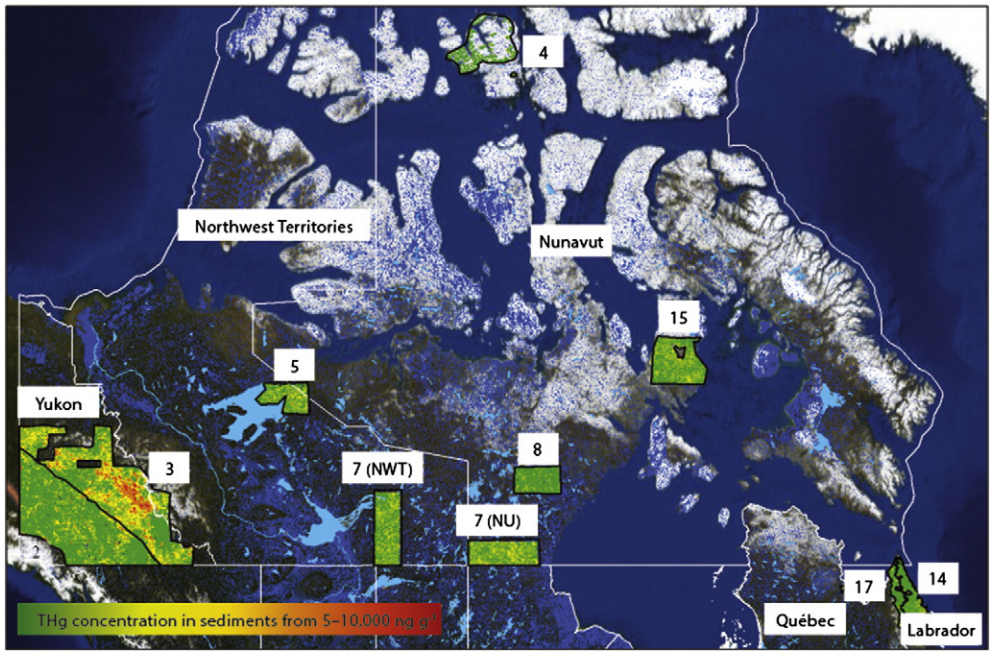

Fig. 4. Map of numbered survey zones examined for THg concentrations in bulk sediment from the National Geochemical Reconnaissance (NGR) database (GSC, 2008). Concentrations inside these zones are categorized by color, from low (green) to high (red). Lowlands (in dark blue) were identified using a national digital elevation model (300 m resolution). Modified from Nasr et al. (2011).

(zone 7: 62 vs. 51 ng g^{-1}). Upland stream sites had significantly higher THg compared to lowland sites in the east Yukon (Selwyn Basin, zone 3; 113 vs. 96 ng g^{-1}) and west Yukon (zone 2: 43 vs. 37 ng g^{-1}). This trend can be explained by upland sediments being closer to geogenic Hg sources. As a result, Hg concentrations would likely decrease towards the more distant lowlands on account of gradual Hg volatilization as well as en-route filtration and settling of Hg-carrying particles.

Average atmospheric Hg deposition rates for survey zones based on GRAHM modeled estimates varied from 6 to 12 μg m^{-2} y^{-1}. Within each survey zone, local concentrations of sediment THg did not correlate with the large-scale GRAHM projections (grid cells of 25 × 25 km). Likewise, modeled atmospheric deposition rates did not correlate with average sediment THg concentrations among survey zones. The disconnection between atmospheric Hg deposition and THg concentrations in bulk sediment may be due to: (i) the importance of watershed transport processes that occur following deposition; (ii) the 1970 to 1990 GSC THg data predate the 2005 model for atmospheric THg deposition; (iii) the sediment sampling depth of up to 30 cm, which weakens

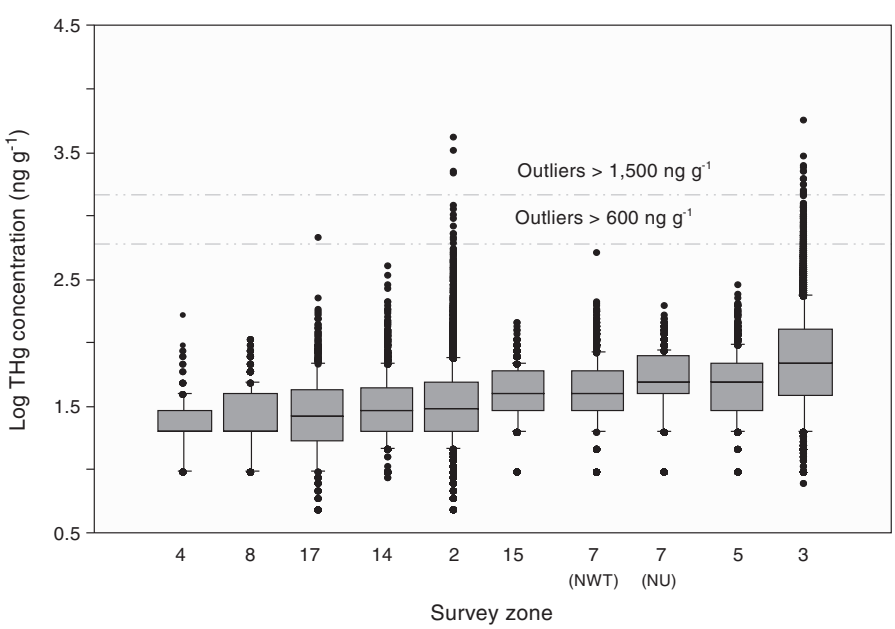

Fig. 5. Box plots of THg concentration (on a logarithmic scale; ng g^{-1}) in stream and lake sediments across northern Canada by survey zone (see Fig. 4 for locations; Nasr et al., 2011). The line inside each box is the median, the upper and lower edges of the box are the 75th and 25th percentiles, and the upper and lower error bars are the 90th and 10th percentiles. Highly elevated outliers for the entire dataset are presented with dashed horizontal lines.

detection of accelerated atmospheric Hg deposition over recent times; and (iv) the relatively narrow range of net atmospheric Hg deposition and sediment THg flux rates across the Arctic region (section 3.2).

A detailed analysis was conducted on the influence of landscape features and sediment characteristics on sediment THg concentrations in streams and lakes from the Yukon (Nasr et al., 2011). Higher sediment THg was found in streams within certain terrain types including swamps, flood plains, hills, and mature mountainous terrain. Sediment THg was also slightly but significantly higher in streams flowing through alluvial and organic soils than in streams flowing over bare rock and through outwash and till deposits. Within Yukon's Selwyn Basin, sediment THg was positively correlated with organic matter content, suggesting the role of organic matter in capturing and retaining Hg. In this survey zone, sediment THg concentrations were also negatively correlated with the wet-area to catchment-area ratio. This correlation was consistent with the trend of higher THg in sediments from upland to lowland locations in the Selwyn Basin.

Overall, bulk concentrations of THg in lake and stream sediments across northern Canada were related to geogenic Hg sources and local transport processes, as influenced by local climate, vegetation cover, and topography (Nasr et al., 2011). Colder, generally frozen areas had lower sediment THg concentrations, while catchments with greater vegetation cover and water bodies with enhanced organic matter accumulation displayed a greater degree of Hg sequestration. These factors suggest potential long-term impacts from changes in vegetation cover and climate on sediment Hg levels in streams and lakes.

3.2. Mercury fluxes to Arctic lake sediments

Lake sediments provide environmental archives for estimating historical Hg fluxes to lakes (Biester et al., 2007; Goodsite et al., 2013; Lindberg et al., 2007; Lockhart et al., 2000). These studies involve the collection of cores from deep points in lakes, followed by metal analysis and dating of extruded core slices. The NCP supported much of the sediment research conducted in the 1990s on Hg deposition to lake sediments in the Canadian Arctic, which was summarized in Macdonald et al. (2000). Landers et al. (1998) assembled a large dataset of Hg fluxes to Arctic freshwater sediments in Canada and Alaska, as well as the European Arctic, which included fluxes from pre-industrial (before ~1850) and recent periods (~1950 to 1995) for ten Canadian Arctic or sub-Arctic lakes north of 54° latitude. Since then, studies by Bindler et al. (2001), Fitzgerald et al. (2005), Outridge et al. (2007), Landers et al. (2008), Muir et al. (2009), Stern et al. (2009), Carrie et al. (2010), and Cooke et al. (2010) have reported on Hg in sediments from 40 lakes in Alaska, northern Canada, and West Greenland. The following is an assessment of latitudinal and longitudinal trends in Hg fluxes to these 40 lakes, the majority (28) of which are located in northern Canada.

3.2.1. Spatial and temporal trends of Hg fluxes inferred from lake sediments

Sediment Hg fluxes (μg m^{-2} y^{-1}) were determined for each dated core slice by multiplying the measured THg concentration (μg g^{-1}) by the estimated sedimentation rate (g m^{-2} y^{-1}) for that slice. Anthropogenic Hg fluxes (ΔHgF, μg m^{-2} y^{-1}) were calculated as the difference in the core between the recent flux and the pre-industrial flux. For most cores, the Hg flux in the pre-industrial era was estimated with sediment horizons dated to the 1820 to 1870s and the recent flux to the period of 1990 to 2005, typically represented by the top 1–2 cm of most Arctic and sub-Arctic cores. Results were, in most cases, corrected for particle focusing, changing sedimentation rates, and/or erosional inputs (Carrie et al., 2010; Fitzgerald et al., 2005; Muir et al., 2009). In post-2000 studies, ΔHgF ranged from −2.6 to 16 μg m^{-2} y^{-1} (geometric mean: 3.6 μg m^{-2} y^{-1}). The negative values reflect higher estimated Hg fluxes in pre-industrial horizons, which were observed in only 2 of 40 lakes. Omitting one very high flux for Lake AX–AJ (Muir et al., 2009), ΔHgF declined weakly with increasing latitude ($r^2 = 0.27$, $p < 0.001$, $n = 39$) but was not significantly correlated with longitude (Fig. 6).

In earlier studies, Landers et al. (1998) and Lockhart et al. (1998) reported similar fluxes and latitudinal trends for ΔHgF in a combined total of 23 Arctic and sub-Arctic lakes north of 54° in Canada and Alaska. They corrected for focusing but not for erosional inputs or increasing sedimentation. These pre-2000 results are also shown in Fig. 6 where ΔHgF ranged from −14 to 19 μg m^{-2} y^{-1} (geometric mean: 3.0 μg m^{-2} y^{-1}). A steeper decline in ΔHgF with latitude was found in the earlier studies after omitting one negative result (Feniak Lake; Landers et al., 1998) ($r^2 = 0.34$, $p = 0.005$, $n = 22$), which reflects higher fluxes in two sub-Arctic cores (Fig. 6). Overall, the combined results of earlier and more recent studies show quite uniform Hg fluxes across the Canadian Arctic above 65° N.

Mercury profiles in almost all dated sediment cores show increases in ΔHgF post-1900 for 14 sub-Arctic and 18 Arctic lakes studied by Muir et al. (2009) (Fig. 7). Fitzgerald et al. (2005) reported a similar trend in five lakes in northern Alaska. The increase, particularly during the first half of the 20th century, coincides with other reports of increasing Hg in the Arctic such as trends in hard tissues of marine animals

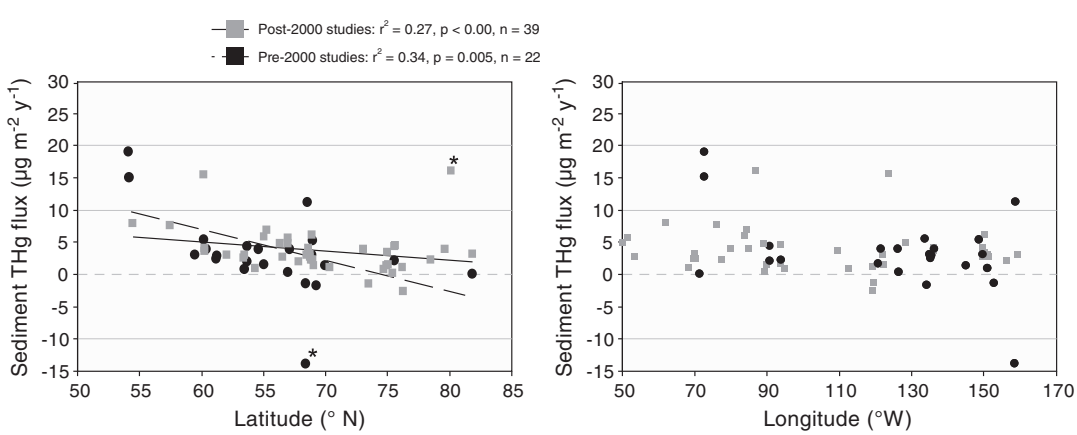

Fig. 6. Anthropogenic fluxes of THg (ΔHgF) in dated sediment cores from Arctic and sub-Arctic lakes in Canada, Alaska, and West Greenland. Two results with asterisks were omitted from the regressions. Data are separated for cores reported (and in most cases sampled) post-2000 (references in text) and pre-2000 cores reported by Landers et al. (1998) and Lockhart et al. (1998).

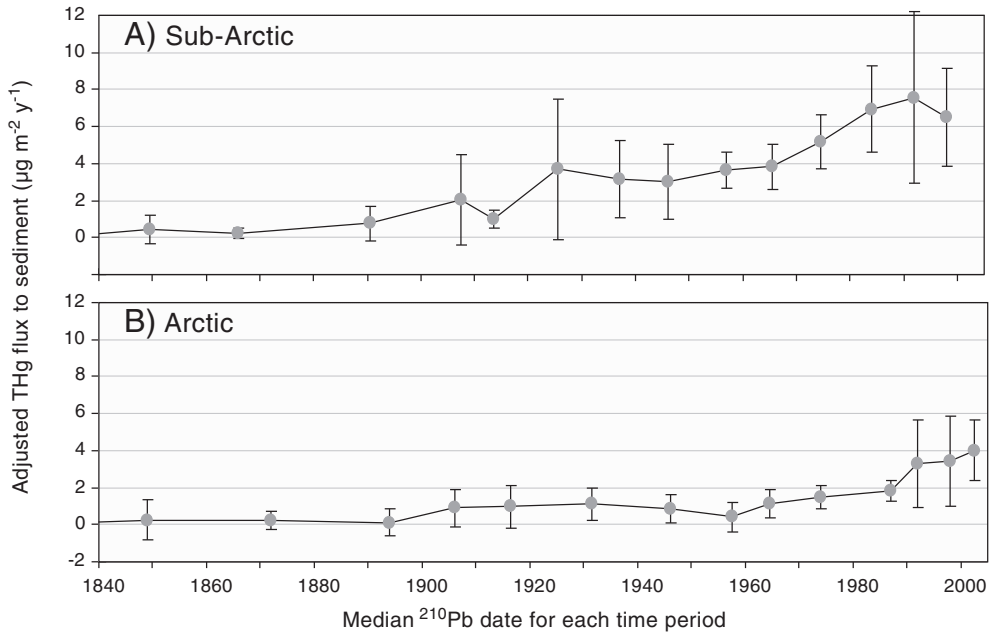

Fig. 7. Average historical profiles of anthropogenic Hg deposition fluxes adjusted for changes in particle focusing and sedimentation (ΔHgF_{adj}, µg m^{-2} y^{-1}, ±95% confidence limits) in sub-Arctic ($n = 14$, 51–64° N) and Arctic ($n = 18$, 65–83° N) sediment cores over time intervals of 5–20 years.
Data from Muir et al. (2009).

(Dietz et al., 2009). The sub-Arctic cores, as well as those from northern Alaska, show a leveling off of Hg fluxes starting in the 1980s. Lindberg et al. (2007) noted that while there was good evidence from lake sediment records for large (30–50%) declines in Hg deposition in urban areas in the Northern Hemisphere due to local reductions in Hg(II) emissions, reductions in anthropogenic inputs at remote locations would be much less pronounced because of a dominant input from the global Hg pool. This pattern is less apparent in the High Arctic cores presented here (Fig. 7) and in other studies at the same latitude by Cooke et al. (2010) and Outridge et al. (2007) which show continued increases in Hg fluxes.

3.2.2. Agreement of Hg fluxes inferred from lake sediment with modeled deposition

Atmospheric deposition fluxes were estimated with the GRAHM model, which ranged from about 2.2–9.5 µg m^{-2} y^{-1} over the area from 60° N to 83° N in the Canadian Arctic (Durnford et al., 2010; Muir et al., 2009). The Danish Eulerian Hemispheric Model (DEHM) predicted annual Hg deposition, including AMDEs, that ranged from 6 to 12 µg m^{-2} y^{-1} in the Canadian Arctic Archipelago (Christensen et al., 2004). Thus, there was relatively good agreement between modeled atmospheric deposition fluxes and measured anthropogenic fluxes to fresh waters.

3.2.3. Interpretation of Hg fluxes to lake sediments

While all evidence points to increasing Hg fluxes, especially in High Arctic lakes, there is much debate on whether this implies that Hg from anthropogenic sources, such as from recent increases in Asian Hg emissions, is entering the lakes in greater amounts or whether other factors such as increased sedimentation and higher primary productivity driven by climate change are attenuating Hg inputs from the atmosphere or the lake catchment (e.g., Kirk et al., 2011a; Outridge et al., 2011). A detailed review of Arctic lake sediments and their use as environmental archives of atmospheric Hg deposition is found in Goodsite et al. (2013). A brief overview of the various factors influencing Hg profiles in Arctic lake sediments is provided here.

Much focus has been on historical variations in sedimentation rates estimated from ^{210}Pb dating of the cores, which may be affected by erosion (Fitzgerald et al., 2005; Outridge et al., 2005), aeolian inputs (Lindeberg et al., 2006), or by artifacts related to the dating technique (Cooke et al., 2010). Fitzgerald et al. (2005) measured pre-industrial (pre-1850) sedimentation rates that were one to five times lower than late 20th century rates in five Alaskan Arctic lakes north of the treeline. They concluded that 11–64% of Hg in recent sediments was from soil erosion. In a core from Lake DV-09 (Devon Island, Nunavut), Outridge et al. (2005) found significant correlations between aluminum and zinc, as well as between aluminum and Hg, and attributed a significant fraction of Hg input to local geological sources via weathering and runoff from melting snow. Cooke et al. (2010) have argued that the ^{210}Pb dating method has overestimated sedimentation rates for horizons in the mid-19th century and earlier. Using a composite age–depth model incorporating ^{210}Pb and ^{14}C dates, they estimated that pre-industrial Hg fluxes were 0.25–0.30 µg m^{-2} y^{-1} in two High Arctic lakes, or about five times lower than most other estimates. It is worth noting that ^{210}Pb activities in Arctic sediments are very low in high-latitude lake sediments. Frozen soil retards the release of the parent isotope radon-222, and lake-ice cover limits the efficiency with which atmospheric ^{210}Pb is transferred to lake sediments (Wolfe et al., 2004). These studies highlight the challenges in accurately estimating sedimentation rates.

The role of aquatic productivity in modifying Hg fluxes into lake sediments has recently been investigated because of its potential implications for interpreting anthropogenic Hg deposition to Arctic aquatic ecosystems. Climate change in the Arctic has increased algal productivity in lakes over recent decades, as indicated by greater accumulation of algal biomass in sediments (Michelutti et al., 2005). Outridge et al. (2005, 2007) proposed that algal scavenging of Hg from the water column may enhance the rate of Hg transfer into lake sediments, and strong correlations have been observed between fluxes or concentrations of Hg and algal carbon in sediments from a number of Canadian Arctic lakes (Carrie et al., 2010; Outridge et al., 2007; Stern et al., 2009). Evidence for the algal Hg scavenging hypothesis is based on a detailed characterization of organic carbon compounds and their profiles in lake sediment cores as well as profiles of diatoms (a type of algae that produces silica valves). Total organic carbon by itself may be a poor measure of the labile, thiol-rich algal organic matter that is believed to be involved in Hg scavenging (Sanei et al., 2010). Outridge et al. (2005, 2007) reported increasing total organic carbon in Amituk

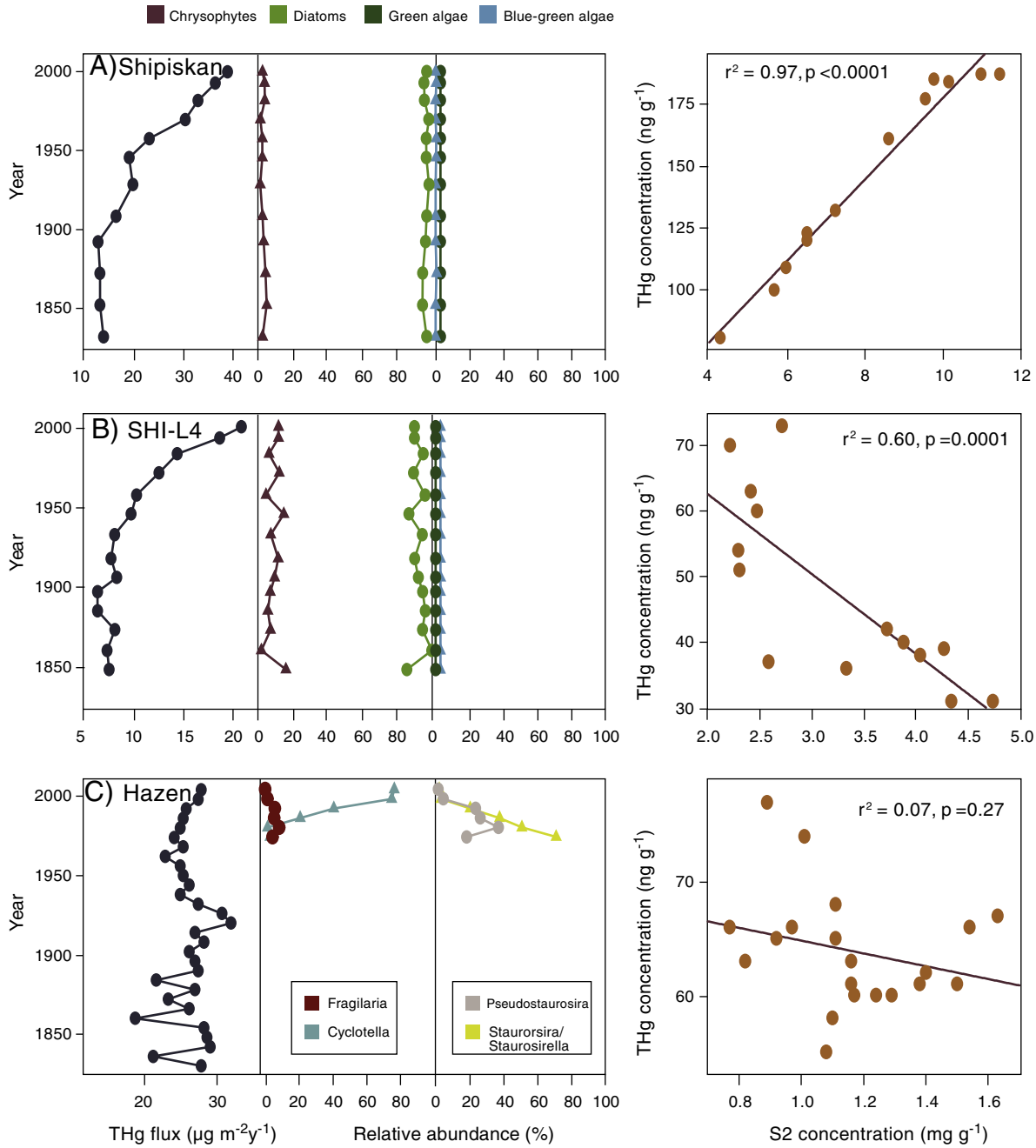

Fig. 8. Examples of different Hg and algal profiles in dated sediment cores from 3 of 14 Canadian Arctic lakes (Shipiskan, SHI-L4, Hazen). For each lake, sediment THg fluxes adjusted for particle focusing (ΔHgF), relative abundance (%) of microfossils—including either diatoms, chrysophytes, green algae and blue-green algae or predominant diatom species—and the relationship between THg and S2 carbon concentrations (ng g^{-1}) are presented.
Reprinted with permission from Kirk et al. (2011b). © American Chemical Society.

Lake and Lake DV-09, but the relative increase in algal-derived carbon, estimated using a kerogen carbon parameter (S2), was markedly greater (760% since 1854).

However, associations between sediment profiles of Hg and algal carbon have not been found in other Canadian Arctic lakes (Fig. 8; Kirk et al., 2011b) nor in pre-industrial sediments (Cooke et al., 2012). Kirk et al. (2011b) compared profiles of Hg with those for algal carbon and species composition in dated sediment cores from 14 lakes spanning latitudinal and longitudinal gradients across the Canadian Arctic. Fluxes of THg to sediments increased during the Industrial Era (approximately post-1850) in 11 of the 14 lakes (post-industrial Hg fluxes corrected for particle focusing, ΔHgF = 2–24 μg m^{-2} y^{-1}) (Fig. 8; Kirk et al., 2011b). After adjustment of fluxes for post-industrial changes in sedimentation rate (ΔHgF_{adj}) as in Muir et al. (2009b), THg fluxes increased since industrialization in all 14 lakes (ΔHgF_{adj} = 0.3–16 μg m^{-2} y^{-1}) suggesting that THg originating from catchment-independent factors, such as atmospheric deposition increased in all systems examined (Kirk et al., 2011b). Several of these lakes also showed post-industrial shifts in algal assemblages consistent with climate-induced changes (Fig. 8). For example, in three lakes where species-level diatom analysis was carried out, the benthic *Fragilaria* spp.—typical of ice-dominated, oligotrophic High Arctic lakes—was replaced by planktonic, epiphytic or other benthic species characteristic of longer ice-free seasons. In 11 lakes, sediment profiles showed post-1850 increases in algal carbon

flux (ΔS2, corrected for particle focusing), suggesting that lake primary productivity has recently increased at the majority of the sampled sites ($\Delta S2 = 0.1–4\ g\ m^{-2}\ y^{-1}$) (Kirk et al., 2011b). However, in six of the 14 lakes surveyed by Kirk et al. (2011b), no relationship was observed between THg and S2 concentrations, and in one lake, a significant negative relationship was observed due to increased THg and decreased S2 carbon deposition during the Industrial Era (Fig. 8). In two of the seven lakes where a significant THg:S2 correlation was observed, the relationship was interpreted as an artifact of post-depositional S2 degradation. In six of the seven lakes where a significant positive THg:S2 correlation was observed, algal assemblages either did not change through time or the timing of the shifts did not correspond to changes in Hg deposition. Kirk et al. (2011b) suggested that, although Arctic lakes are experiencing a myriad of changes including increased Hg and S2 deposition or shifting algal assemblages, increased lake primary productivity may not be driving changes in Hg fluxes to sediments.

While the scientific literature is divided over the explanation for increased Hg fluxes in Arctic lake sediment cores, there is consensus that climate change, which is occurring rapidly in the Arctic, is having a major influence on sedimentation rates. Mean annual snowfall has increased in the central Canadian Archipelago where most of the High Arctic cores have been collected (Michelutti et al., 2003), suggesting more snowmelt runoff is leading to greater erosion inputs in some catchments. The disappearance of shallow ponds on islands of the Canadian Arctic Archipelago has been attributed to increased evaporation to precipitation ratios (Smol and Douglas, 2007), and more rapid drying of lake catchments could result in greater aeolian inputs for some lakes. Thus, additional studies are needed to explain increasing Hg fluxes in Arctic lakes.

3.3. Impact of permafrost thawing on Hg transport to Arctic lakes

Thawing permafrost is already changing the Arctic landscape and will likely accelerate in coming decades (ACIA, 2005; Lantz and Kokelj, 2008). Consequent to thaw, significant changes in hydrology, organic carbon pathways, and freshwater resources are also expected (ACIA, 2005). Currently, nearly half of the land surface in Canada is underlain by some form of permafrost (Smith and Burgess, 1999). The extent to which thawing permafrost will change the amount of Hg entering fresh waters in the Canadian Arctic is a significant gap in our knowledge of how ecosystems will respond to climate warming.

Recent studies show that the influx of slump material from degrading permafrost into freshwater systems will introduce a variety of materials that were previously trapped in the frozen ice and soil (Kokelj and Burn, 2005; Kokelj et al., 2005). As the active layer deepens and more hydrological flow pathways develop in the permafrost, greater geochemical weathering from drainages is expected (Kokelj et al., 2005; Prowse et al., 2006). The inputs will result in changes to freshwater chemistry. In the case of retrogressive thaw slump development as seen in the Mackenzie Delta uplands region, higher concentrations of major ions and decreases in DOC are associated with the presence of thaw slumps on shorelines (Kokelj et al., 2005). In addition, studies of permafrost peatlands in northern Sweden indicate that thawing and erosion of thermokarst can release significant amounts of Hg to sub-Arctic lakes (Klaminder et al., 2008; Rydberg et al., 2010).

Since 2008, the transport of Hg from thawing permafrost has been investigated in the Mackenzie Delta region near Inuvik, where thaw slumping is occurring on a large scale (Deison et al., 2012). A series of lakes with catchments disturbed by permafrost melting were paired to undisturbed lakes of similar size in adjacent catchments. This paired-lake design allowed for a case–control analysis of lakes where retrogressive thaw slumps were present and absent.

Thaw slump development increased inorganic sedimentation rates in impacted lakes while decreasing concentrations of total organic carbon, THg, and MeHg in sediments (Deison et al., 2012). Sediment cores drawn from four lakes with permafrost thaw slump development on their shorelines had higher sedimentation rates (of largely inorganic material) and lower concentrations of THg, MeHg, and organic carbon in surface sediments compared to four lakes where thaw slumps were absent. Concentrations of THg and MeHg were positively correlated with total organic carbon and labile algal-derived (S2) carbon due to an association between the movement of organic matter and Hg accumulation in lake sediments. Thus, the large inputs of inorganic material from thaw slumps did not increase Hg concentrations in lake surface sediments. However, retrogressive thaw slumps of clay-rich tills in the Mackenzie Delta uplands region represent only one type of thermokarst, and different outcomes of permafrost degradation may be expected for other thermokarst structures such as polygon and runnel ponds.

4. Biogeochemical transformations of Hg

4.1. Microbial transformations of Hg

Microbes actively alter Hg speciation in the environment. It is thought that two main reactions compete for the inorganic divalent Hg substrate: 1) reduction of Hg(II) to elemental Hg(0); and 2) methylation of Hg(II) to MeHg. Methylmercury can also be demethylated via microbial pathways. Molecular tools allowing the quantification of intracellular Hg, such as luminescent biosensors hosted by bacteria, suggest that a fraction of the Hg deposited by AMDEs in the Arctic is bioavailable (Larose et al., 2010, 2011; Lindberg et al., 2002; Scott, 2001). In this context, bioavailable Hg is the inorganic form accessible and internalized by microbes and potentially used as substrate for MeHg production. The link between bioavailable Hg deposited during AMDEs and its methylation in fresh waters remains unclear (Dommergue et al., 2009). Recent evidence suggests that wet deposition may contribute a higher proportion of bioavailable Hg to Arctic snow packs than AMDEs (Larose et al., 2011). Water DOC concentrations in Arctic lakes can enhance the bioavailability of Hg up to a threshold of ~8.5 mg L^{-1}, above which higher concentrations of DOC inhibit biological uptake of Hg (Chiasson-Gould et al., 2014; French et al., 2014). Whether it is in snow, water, sediments, or in littoral or pelagic zones, the predominant location(s) in freshwater ecosystems where methylation occurs have not been identified.

In temperate environments, Hg methylation is mostly a microbial process driven by the activity of sulfate- and iron-reducing bacteria (Fleming et al., 2006; Gilmour et al., 1992) as well as methanogens (Hamelin et al., 2011). Currently for the Arctic, further investigation is required on both the chemical speciation of Hg and the physiology of psychrophilic microbes, which are adapted to cold environments. Sulfate-reducing bacteria are present and active in sediments of polar desert lakes and are likely involved in Hg methylation (Drevnick et al., 2010; A. Poulain, University of Ottawa, unpublished data).

Few estimates of MeHg production rates are available for aquatic ecosystems in the Canadian Arctic. Warm, organic rich ponds on Ellesmere Island can methylate Hg at rates comparable to temperate wetlands (Lehnherr et al., 2012b). Laboratory incubations of Arctic wetland soils indicate that methylation can occur (Loseto et al., 2004b; Oiffer and Siciliano, 2009). Elevated MeHg concentrations in High Arctic pond waters provide further evidence that shallow water bodies can be important methylation sites (Lehnherr et al., 2012b; St. Louis et al., 2005). Sediment methylation rates were measured in Alaskan lakes and found to be the primary source of MeHg to those ecosystems (Hammerschmidt et al., 2006).

Little research has been conducted on microbial-mediated processes of Hg oxidation and reduction in Arctic fresh waters. Poulain et al. (2007a) showed that on Cornwallis Island, filtration of microbes from snowmelt samples did not alter the rate of Hg(II) reduction when exposed to sunlight or kept in the dark. This result was in stark contrast with important microbial redox processing of Hg on Arctic sea ice (Poulain et al., 2007b). Møller et al. (2014) found mercury reductase genes in snow over a Greenland lake, suggesting the presence of mercury-reducing microbes. At lower latitudes, Hg(0) production in

lake surface waters is mostly photomediated (Poulain et al., 2004). More recently, Brazeau et al. (2013) found that Hg(0) production in sediments of sub-Arctic lakes was microbially-mediated, although production occurred at a low rate. Further work is required to evaluate the contribution of microbes to the redox cycling of Hg in Arctic fresh waters.

4.2. Photochemical transformations of Hg

Photochemical transformations of Hg play a key role in modifying the mobility and toxicity of Hg in air, snow, and fresh water. These transformations are mediated through a variety of direct and indirect processes that can be grouped in two categories: processes affecting the formation of volatile Hg(0) (i.e. redox processes) and processes affecting the balance between methylation and demethylation. Most studies on the photochemistry of Hg have been conducted at field sites in temperate regions or in the laboratory, and some recent reviews provide a good overview of the results (Ariya et al., 2009; Vost et al., 2011; Zhang, 2006).

4.2.1. Photoreduction and photooxidation

Species of Hg(II) are generally soluble and reactive in water, whereas elemental Hg(0) is volatile. As a result, photoreduction of Hg(II) species into Hg(0) will promote Hg evasion from Arctic freshwater ecosystems and Hg(0) oxidation leads to its retention. Only two studies have directly evaluated photochemical reaction rates for Hg reduction and oxidation in polar fresh waters (Table 2). In those studies, elemental Hg(0) was not directly measured. Instead, all volatile Hg species dissolved in water were purged and analyzed. The resulting operationally defined fraction is referred to as dissolved gaseous Hg (DGM), which is often assumed to be mainly composed of Hg(0) in fresh water. In Amyot et al. (1997), formation rates of DGM in waters of three Arctic lakes and one wetland on Cornwallis Island were controlled by: 1) the intensity of solar radiation, particularly in the ultraviolet (UV) range of the spectrum; and, by 2) the concentration of available photoreducible Hg(II) complexes. In Poulain et al. (2007a), the authors measured in situ net reduction rates during spring and summer in a series of streams and ponds along a salinity gradient covering four orders of magnitude. Production of DGM, normalized for the amount of photons received, declined dramatically with increasing salinity. These authors further provided evidence that biogenic organic materials produced by algae favored the oxidation of Hg(0) in marine lagoons, but not in freshwater ponds. Overall, the Arctic data from Poulain et al. (2007a) indicate that aqueous Hg in inland fresh waters is more prone to photoreduction—and therefore to loss by evasion—than in nearby marine systems.

In addition to these field experiments, freshwater concentrations of DGM have only been measured at two Arctic locations, specifically in lakes near the Toolik Field Station (Alaska, USA) and in lakes, ponds, and streams on Cornwallis Island (Table 2). In a set of ten lakes located on the tundra of Alaska's North Slope near Toolik, DGM concentrations ranged from 0.015 to 0.078 ng L^{-1} with a mean of 0.040 ± 0.017 ng L^{-1} (Fitzgerald et al., 2005; Tseng et al., 2004). These lakes exhibited supersaturation—exceeding 100% saturation—with Hg(0) ranging from 234 to 1220% under all conditions. Light attenuation and hence DOC were the best predictors of surface DGM levels. This suggests that DGM production was dominated by photochemical processes (Tseng et al., 2004). Surface DGM levels in lakes on Cornwallis Island ranged from 0.032 to 0.124 ng L^{-1} and exhibited supersaturation with values typically between 100 and 200% (Amyot et al., 1997). The lower supersaturation of Cornwallis lakes is partly due to the colder temperatures encountered in these systems (1–3 °C) compared to Alaskan lakes in mid-summer (12–15 °C).

4.2.2. Photodemethylation

Photodemethylation of MeHg is a significant, although often ignored, mechanism affecting MeHg pools in temperate lakes (Lehnherr and St. Louis, 2009; Sellers et al., 1996). In polar regions, only a few studies have been published on in situ measurements of this phenomenon. Hammerschmidt and Fitzgerald (2006) conducted field experiments in Toolik Lake (Alaska, USA) during which they incubated filtered and unfiltered water samples amended with MeHg chloride (final concentration: 3 ng L^{-1}) under epilimnetic conditions. The decomposition of MeHg was shown to be exclusively abiotic and mediated by light. Photodecomposition rates were related to MeHg concentrations and to the intensity of photosynthetically active radiation (PAR). The estimated loss of MeHg to photodecomposition in this lake accounted for about 80% of the MeHg mobilized annually from in situ sedimentary production—the main source to Toolik Lake. The estimated photodecomposition flux of MeHg was 1.3 μg m^{-2} y^{-1} over an ice-free period of 100 days. In their flux calculations, Hammerschmidt and Fitzgerald (2006) assumed that PAR was responsible for photodemethylation. More recently, Lehnherr and St. Louis (2009) revisited this dataset and calculated a photodecomposition flux of 0.57 μg m^{-2} y^{-1}, assuming that the bulk of photodemethylation is caused by UV radiation rather than PAR. A lower estimate of photodecomposition flux was obtained by Lehnherr and St. Louis (2009) because UV light is more rapidly attenuated in the water column compared to PAR. Measurements of

Table 2
Water concentrations and production rates of DGM in Arctic freshwater ecosystems.

Location	Date of sampling	*n*	pH	DOC (mg L^{-1})	DGM concentration (ng L^{-1})	Production rate of DGM (ng L^{-1} h^{-1})	Source
Lakes							
Cornwallis Island (Nunavut)	1994–1995	5					1
Amituk Lake	08/03/1994		8.2	1.6	0.032 ± 0.003	0	
Amituk Lake	08/05/1994		8.2	1.6	0.041 ± 0.004	0	
Merretta Lake	08/14/1994		8.0	2.3	0.061 ± 0.001	0.003	
North Lake	08/15/1994		8.3	1.1	0.058 ± 0.006	0.003	
North Lake	07/27/1994		8.3	1.1	0.124 ± 0.007	0.005	
Toolik Field Station (Alaska)	2000	9	7.9–8.3	2.7–5.8	0.036		2
Toolik Field Station (Alaska)	2000–2002	27	8.0–8.3	2.7–4.3	0.040 ± 0.017		3
Wetlands							
Cornwallis Island (Nunavut)	1994–1995	1	8.1–8.2	1.8	0.048	0.006	1
Freshwater ponds, streams, snowmelt, and coastal water							
Cornwallis Island (Nunavut)	2004	12	7.5–8.5			0.050[a]	4

n = number of sites sampled, DOC = dissolved organic carbon.
Sources: 1 = Amyot et al. (1997); 2 = Tseng et al. (2004); 3 = Fitzgerald et al. (2005); and 4 = Poulain et al. (2007a).
[a] Units in ng mol_{photon}^{-1} m^{-2}.

photodemethylation rates in two Ellesmere Island ponds yielded relatively similar values to those from Alaska (Lehnherr et al., 2012a). Further work by Hammerschmidt and Fitzgerald (2010) suggests that iron also plays an important role in the photochemical decomposition of MeHg in Alaskan lakes.

4.3. Mass balance of MeHg in High Arctic ponds

Information on MeHg budgets and mass balances are currently lacking for lakes in the Canadian Arctic although Lehnherr et al. (2012a) recently quantified the production of MeHg in two wetland ponds in the Lake Hazen region using a mass-balance approach over three separate years during the ice-free season. Wetland and pond waters in the Canadian High Arctic tend to have higher concentrations of MeHg compared to larger lakes (St. Louis et al., 2005; Fig. 1), and can be sites for MeHg production.

The Lake Hazen region, located on northern Ellesmere Island within Quttinirpaaq National Park, experiences anomalously warm summer conditions for its latitude (Soper and Powell, 1985), but receives very little precipitation, approximately 95 mm annually (Thompson, 1994). Wetland sites there are characterized by a wet sedge-grass meadow that surrounds a central pond containing aquatic mosses and emergent vegetation. The two study sites (Ponds 1 and 2) lacked inflow and outflow streams, with the exception of Pond 1 in 2008 which was flooded by rising water levels in nearby Lake Hazen. Their hydrological isolation allowed for the calculation of a simple mass balance budget of MeHg by quantifying MeHg inputs from wet atmospheric precipitation, MeHg removal by photodemethylation, and MeHg storage in the water column compartment.

Concentrations of MeHg in unfiltered water ranged from 0.30 to 1.8 ng L^{-1} in Pond 1 and 0.04 to 0.30 ng L^{-1} in Pond 2, and were comparable to the range of MeHg concentrations reported in surveys of Ellesmere Island wetlands and ponds (Table 1; Loseto et al., 2004a; St. Louis et al., 2005). In both ponds, the proportion of THg in the MeHg form typically peaked in mid-July, reaching up to a remarkable 62% in Pond 1 and 34% in Pond 2. MeHg concentrations in zooplankton from both ponds (800 ng g^{-1} dw in Ponds 1 and 100 ng g^{-1} dw in Pond 2) reflected the difference in water MeHg concentrations between the two sites and were generally high compared to what has been reported for most other freshwater ecosystems, to the extent that sometimes up to 12% of all the MeHg in the water column was stored in zooplankton. MeHg concentrations in precipitation ranged from below detection (<0.015 ng L^{-1}) to 0.25 ng L^{-1}; however due to low precipitation rates typical of this region of the High Arctic, precipitation represented an input of only 0.026–0.051 ng MeHg m^{-2} d^{-1}. No other estimates of MeHg inputs from rainfall currently exist for the Canadian Arctic. The average fluxes quantified for the Lake Hazen region during July were significantly lower than the long-term average of 0.11 ng m^{-2} d^{-1} reported for wet deposition in the more southern boreal forest of northwestern Ontario (Graydon et al., 2008). Loss by photodemethylation was greater in Pond 1 (14–33 ng m^{-2} d^{-1}) than in Pond 2 (2 ng m^{-2} d^{-1}) due to higher concentrations of MeHg in Pond 1, which led to higher photodemethylation rates (Lehnherr et al., 2012a). Furthermore because Pond 1 was shallower than Pond 2 on average, the water column in Pond 1 was exposed to higher levels of solar radiation.

The in-pond production of MeHg—roughly equivalent to the net diffusion of MeHg to the water column from sediments where Hg(II) is methylated—was calculated as the quantity of MeHg required to balance the MeHg budget and took into account net water column accumulation over the study period (ΔMeHg), inputs, and sinks as follows:

$$\text{MeHg production} = \Delta\text{MeHg} - \text{inputs(precipitation)} + \text{sinks(photodemethylation)}.$$

For a given site, there was almost no difference in areal MeHg production between 2005 and 2007, but MeHg production was an order of magnitude higher in Pond 1 (14–19 ng m^{-2} d^{-1}) than in Pond 2 (1.8–1.9 ng m^{-2} d^{-1}). For both sites, the input from precipitation was a much smaller MeHg source (<2%) than in-pond Hg(II) methylation. Although the influx of Lake Hazen water during the flooding of the Pond 1 wetland in 2008 contributed very little MeHg (0.3 ng m^{-2} d^{-1}) to Pond 1, it had the indirect effect of stimulating rates of Hg(II) methylation. As a result, MeHg production in 2008 was twice as high (40 ng m^{-2} d^{-1}) as the other two years. It is known that the flooding of wetland vegetation can increase MeHg production by releasing organic carbon, nutrients and Hg(II) from flooded soils and vegetation, thereby stimulating microbial Hg(II) methylation (St. Louis et al., 2004). Despite the large MeHg production rates measured in both ponds, MeHg concentrations in pond waters did not consistently increase over time because photodemethylation was an effective sink for newly produced MeHg.

This study demonstrates that High Arctic wetlands can be important sources of MeHg. MeHg yields reported for wetlands in polar deserts have been more modest (Loseto et al., 2004a), highlighting that MeHg production varies on large spatial scales in response to differences in temperature and primary productivity.

The large difference in MeHg production rates between Ponds 1 and 2, two systems that are on the surface very similar, points to important biogeochemical controls on Hg(II) methylation and MeHg production. In a survey of ponds from the same region, Lehnherr et al. (2012b) showed that MeHg concentrations in pond waters were positively correlated to MeHg concentrations in surface sediments as well as proxies of anaerobic microbial activity (e.g., methane concentrations and the NH_4^+:NO_3^- ratio) but negatively correlated to UV-A exposure. MeHg concentrations in surface sediments were in turn dependent on Hg(II) concentrations in sediments as well as the potential rate of methylation, as determined using sediment core incubation experiments. These findings are consistent with the mass-balance results, which suggest that Hg(II) microbial methylation in pond sediments is the primary MeHg source to pond waters, while UV-A driven photodemethylation is an important sink for MeHg.

5. Trophic transfer in food webs

5.1. Trophic transfer of Hg in coastal Arctic lakes with and without anadromous Arctic char

Anadromous fish transport nutrients and contaminants from the ocean into freshwater environments, a process termed biotransport (Gregory-Eaves et al., 2007; Krümmel et al., 2003). The effect of anadromous Arctic char on Hg biomagnification through lake food webs was investigated in six Arctic lakes in the West Kitikmeot region of Nunavut (Swanson and Kidd, 2010). Three lakes contained anadromous populations of Arctic char whereas the other three lakes contained no Arctic char. All lakes contained lake trout as a top predator in addition to a similar suite of forage fishes. Lake trout had THg concentrations ranging from 0.01 to 1.40 μg g^{-1} wet weight (ww) and size-corrected concentrations were significantly lower in lakes that contained anadromous Arctic char. Lower THg in lake trout from lakes with anadromous Arctic char resulted from increased lake trout condition and not among-system differences in biomagnification rates. Fish Hg concentrations are often negatively related to fish condition (an index of how heavy a fish is at a given length) (e.g., Dittman and Driscoll, 2009), and lake trout were in significantly better condition in lakes where anadromous Arctic char were present (Swanson and Kidd, 2010). This effect could be due to greater prey availability for lake trout in lakes with anadromous Arctic char, but further research is required. Overall, it appeared that either the mass of Hg biotransported by anadromous Arctic char to lakes was negligible, or that the effect of increased Hg loading via anadromous char was counteracted by increased fish growth in lakes where anadromous char were present (Swanson and Kidd, 2010).

5.2. Trophic transfer of Hg in lakes with landlocked Arctic char

Lakes in the Canadian Arctic Archipelago are very unproductive and have simple food chains. Arctic char are often the only fish species present and are thus the apex predator. Pelagic zooplankton communities typically consist of few species at low abundance. The benthic environment of lakes is typically dominated by chironomids, although central and sub-Arctic systems may host a more diverse invertebrate community. Several recent studies have investigated the bioaccumulation of Hg in these lake food webs containing landlocked Arctic char. These studies either included investigations of the entire food web including Arctic char (Gantner et al., 2010a,b), or focussed on Hg uptake in aquatic invertebrates such as zooplankton and chironomids (Chételat and Amyot, 2009; Chételat et al., 2008).

A food web study in 18 lakes along a latitudinal gradient from 61 to 82° N included sampling of Arctic char, pelagic zooplankton, benthic invertebrates and, where present, ninespine stickleback (Gantner et al., 2010b). Benthic invertebrates were typically higher in Hg than pelagic zooplankton. Trophic characterization using $\delta^{15}N$ and $\delta^{13}C$ showed that benthic invertebrates—mainly chironomid larvae and pupae—were the primary source of food and thus, also of MeHg for landlocked Arctic char. Further, cannibalism commonly occurs in landlocked populations of Arctic char and results in greater bioaccumulation of Hg in cannibalistic fish (Gantner et al., 2010a; Muir et al., 2005). Trophic magnification factors, which were estimated by the slope of MeHg concentration versus trophic level for all food web organisms in a lake, did not explain among-lake variation of Hg concentrations in adult Arctic char. Among-lake differences in Arctic char THg concentrations were not

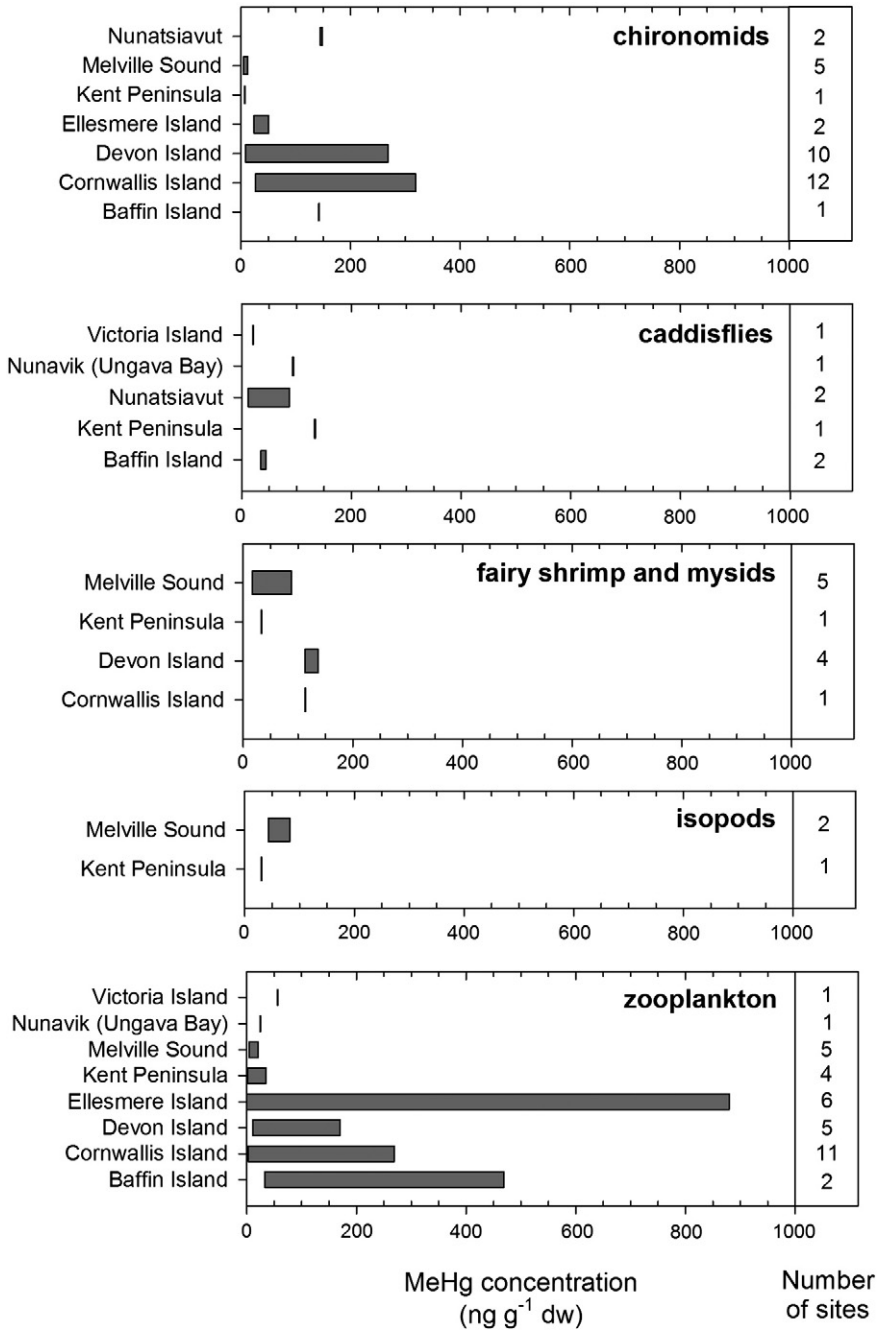

Fig. 9. Ranges of MeHg concentrations in invertebrates from lakes and ponds in different regions of the Canadian Arctic. The number of water bodies sampled per region is identified in the right-hand column.
Data are from Chételat et al. (2008), *Chételat and Amyot (2009)*, Gantner et al. (2010b), Swanson and Kidd (2010), Lehnherr et al., 2012a, and van der Velden et al. (2013a).

related to THg in surface water and sediment or to latitude and longitude. Catchment-to-lake area ratios were correlated with THg concentrations in landlocked Arctic char, which emphasizes the importance of loadings from the surrounding landscape on Hg cycling in lakes. More recent study of Arctic char lakes on Cornwallis Island has found correlations between lake catchment area, water chemistry, and food web Hg bioaccumulation (Lescord et al., 2015-in this issue).

5.3. Factors affecting Hg bioaccumulation in Arctic invertebrates

Aquatic invertebrates have been recently investigated in several Arctic regions for Hg bioaccumulation (Fig. 9). Order-of-magnitude variation in MeHg concentrations was reported for invertebrate groups, particularly chironomids and zooplankton. Maximum concentrations in chironomids were measured on Cornwallis and Devon Islands, while zooplankton MeHg concentrations were higher on several islands in the eastern Arctic compared to other study areas. The highest invertebrate MeHg concentrations were in zooplankton from ponds on Ellesmere Island (up to 880 ng g^{-1} dw), where high mercury methylation rates were measured in sediment (Lehnherr et al., 2012a). The concentration of MeHg in aquatic invertebrates is affected by their trophic level, feeding behavior, Hg supply to the food web, taxonomic variation, and developmental processes (Chételat et al., 2012, 2008; Clayden et al., 2014; Cremona et al., 2008; Watras et al., 1998).

In the Canadian High Arctic, taxonomic composition is an important determinant of MeHg bioaccumulation in zooplankton communities, and different species can vary several-fold in their MeHg concentrations despite low levels of Hg in the water (Chételat and Amyot, 2009). In a study of 16 lakes and ponds, zooplankton communities containing *Daphnia* (mainly *Daphnia middendorffiana*) had, on average, five times the MeHg content of copepod-dominated communities. Metamorphosis is also a significant factor affecting Hg bioaccumulation in chironomids (Chételat et al., 2008), which is the main invertebrate consumed by landlocked Arctic char in many high-latitude lakes. Passing through four developmental stages (eggs, larvae, pupae, adults), these benthic invertebrates undergo complete metamorphosis and have a life cycle of at least two to three years in the Arctic (Welch, 1976). A study of 22 ponds and lakes in the Arctic Archipelago showed that adult chironomids had 1.7–2.9 times higher MeHg than immature stages (Chételat et al., 2008). Adults had higher MeHg concentrations than pupae because of a reduction in body weight during emergence and mating with no associated loss in MeHg burden. Larvae were least concentrated with MeHg because they were still growing and had the lowest burdens.

5.4. Tracing the source(s) of Hg in lake food webs using Hg stable isotopes

Investigations of Hg stable isotopes in environmental samples have pursued the question of whether their ratios may be specific to a source (e.g., coal combustion) or a process (e.g., methylation, photochemical reduction), with the intention of using the ratios as an isotopic tracer similar to other elements such as carbon, nitrogen, oxygen, and lead. If a unique source *signature* could be identified, this information would be particularly useful in the Arctic, which has few local pollution sources and receives anthropogenic Hg via atmospheric transport from multiple regions (Durnford et al., 2010). Recent studies have shown that there can be significant variations in Hg isotope composition in environmental samples (Bergquist and Blum, 2009; Ridley and Stetson, 2006). However, while much progress has been made, a full understanding of Hg isotope fractionation and its application to trace sources and processes has not been achieved (Hintelmann, 2012; Yin et al., 2010).

Mercury's seven stable isotopes (196, 198, 199, 200, 201, 202 and 204 amu) span a relative mass difference of 4%. Isotopes ^{200}Hg and ^{202}Hg are the most abundant (23.1% and 29.7%). Mass-dependent fractionation (MDF) of Hg, or fractionation as a function of isotope mass, can occur during processes such as volatilization from water, microbial reduction, and bioaccumulation (Bergquist and Blum, 2009). Mass-dependent fractionation is reported in delta notation (δ), which is the per mil (‰) deviation from a reference material and usually reported relative to ^{198}Hg (Blum and Bergquist, 2007). A wide range of MDF values have been reported (Fig. 10A). Mercury isotopes can also undergo mass-independent fractionation (MIF). Mass-independent fractionation is the difference between the measured δ^{xxx}Hg ratio and the theoretically predicted δ^{xxx}Hg ratio and denoted by a Δ^{xxx}Hg notation usually relative to the most abundant ^{202}Hg isotope. The range of MIFs in geological media is low but large values (>0.3‰) have been observed for odd-numbered Hg isotopes during photochemical reduction (Bergquist and Blum, 2007), and a wide range of values has been reported in Arctic media (Fig. 10B). The processes that cause MIF are not fully understood but are thought to involve slight differences in reactivity of odd and even Hg isotopes due to their nuclear structure (Bergquist and Blum, 2009; Jackson et al., 2008). Although there is still debate, most investigators now accept that MIF is mainly induced by photochemical reactions of Hg and MeHg, and that biochemical MIF is unlikely. This implies that Hg MIF variations may provide information about the source of Hg to aquatic food webs.

Sherman et al. (2010) found that Hg deposited on the surface of Arctic snow at Barrow (Alaska) underwent MIF from sunlight-induced reactions during AMDEs, wherein the odd-mass number isotopes of Hg

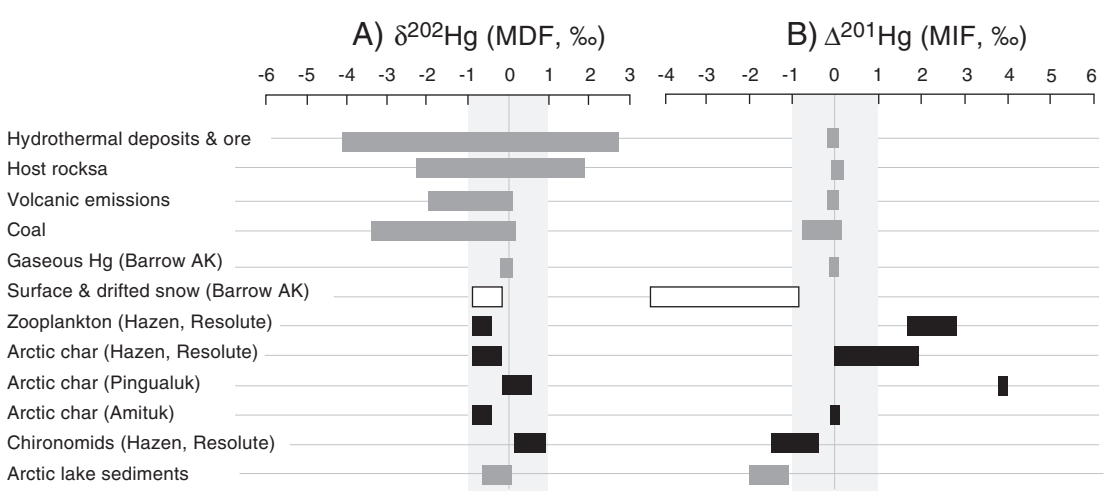

Fig. 10. Mercury isotope results for selected geological sources and for samples from the Arctic. The horizontal bars represent the range in (A) mass-dependent fractionation (MDF) expressed as δ^{202}Hg, and (B) mass-independent fractionation (MIF) expressed as Δ^{201}Hg. The pale gray vertical bars represent estimates of crust- and mantle-derived Hg isotope ratios. Geological data are from Bergquist and Blum (2009), results for snow and gaseous Hg are from Sherman et al. (2010), and biota and sediments are from Gantner et al. (2009).

were preferentially reduced and emitted. This depletion resulted in negative values of Δ^{201}Hg (Fig. 10B). This distinctive MIF for Hg in snow was also found in Arctic lake sediments that had similar negative MIF values (Fig. 10B; Gantner et al., 2009). As of 2010, the values of Δ^{201}Hg reported by Gantner et al. (2009) are the most negative MIFs ever reported for lake sediments. Jackson et al. (2004) also noted more negative MDF values of δ^{202}Hg in more recent horizons of a core from Romulus Lake near Eureka on Ellesmere Island—see Ridley and Stetson (2006) for replotting of Jackson's original data. Jackson et al. (2008) found similar negative δ^{202}Hg values in Cli Lake in the Northwest Territories and Shipiskan Lake in Labrador. It is not known whether this negative Hg signature represents a distinct long-range transport signal or is due to isotopic fractionation related to biological activity within the lake such as Hg methylation in sediments (Ridley and Stetson, 2006).

The negative Δ^{201}Hg isotope signature in lake sediments also appeared in benthic chironomids from the same lakes (Gantner et al., 2009) thereby suggesting transfer of this signature to sediment dwelling organisms. However, this negative MIF source was not evident in pelagic organisms in Arctic lakes. Zooplankton and Arctic char samples had much different values of Δ^{201}Hg compared to chironomids. Results for Arctic char in Hazen and Resolute lakes ranged from −0.02 to 1.7‰ for Δ^{201}Hg (Fig. 10B) and char from most other lakes analyzed by Gantner et al. (2009) were also within this range. These results are in agreement with those for lake trout from sub-Arctic lakes (Cli and Shipiskan), which showed large positive Δ^{201}Hg values (Jackson et al., 2008). However char from Amituk Lake differed by having lower Δ^{201}Hg values (−0.11–0.16‰) while Pingualuk char had the highest values (3.67–3.89‰). Pingualuk Lake serves as an interesting site to investigate atmospheric inputs of Hg because it has no inflow, no outflow, minimal catchment area, and it receives its water mainly through direct precipitation. Although no zooplankton were analyzed for Hg isotopes in Pingualuk Lake, the large positive Δ^{201}Hg is consistent with char feeding on zooplankton. The low Δ^{201}Hg for char in Amituk Lake may be due to the large catchment area of Amituk which could contribute to an isotope signature resembling that of snow Hg which has undergone a greater degree of photochemical transformation.

Gantner et al. (2009) found a negative correlation of δ^{202}Hg in Arctic char with latitude, which may be related to degree of MDF of Hg during atmospheric transport to the Arctic from various source regions or because of differences in terrestrial Hg sources. Those authors did not observe a latitudinal gradient in Δ^{201}Hg (in contrast to research on seabirds in Alaska by Point et al., 2011) but found that it was related to the size of the lake catchment.

6. Fish

6.1. Geographic and species variation in fish Hg concentrations

Broad-scale patterns of Hg concentrations in freshwater fish species common to the Canadian Arctic were examined using the Canadian Fish Mercury Database (Depew et al., 2013). Fish THg concentrations for a total of 85 Arctic sites were available from NCP and other government

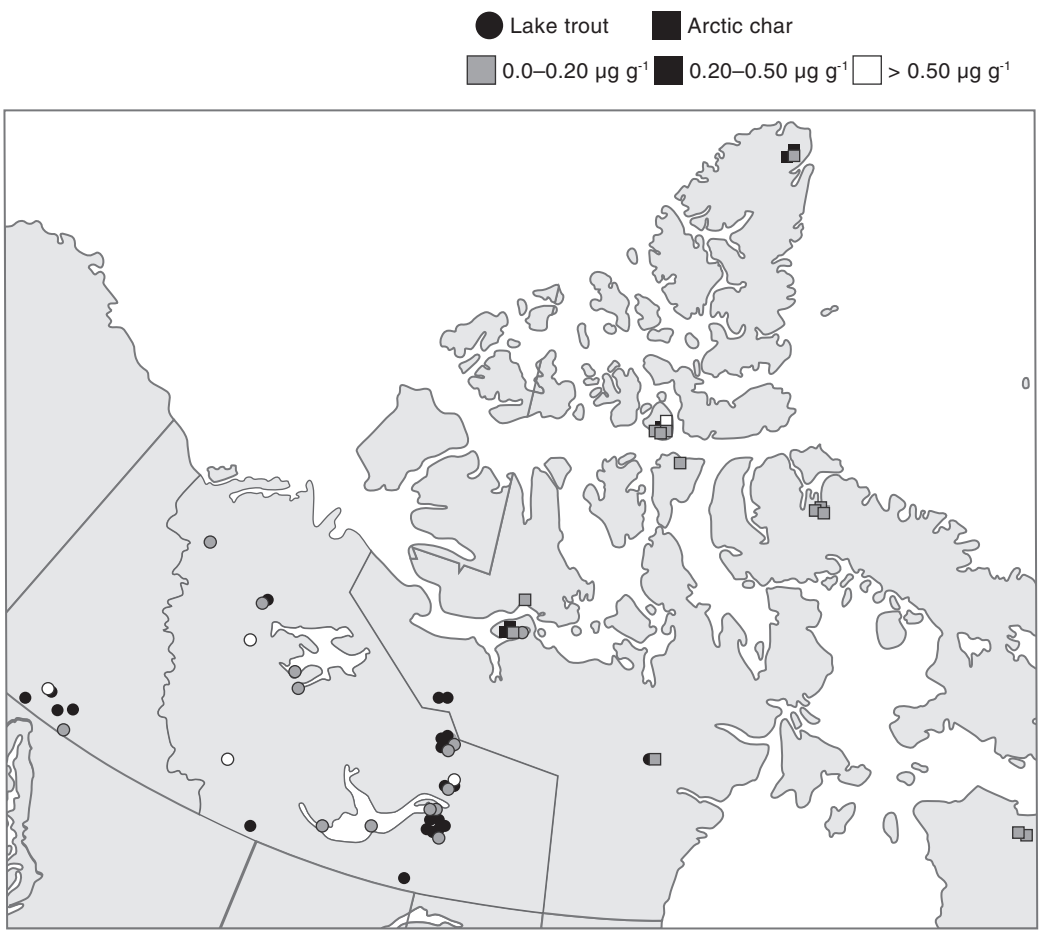

Fig. 11. Length-adjusted THg concentrations in lake trout and Arctic char muscle measured between 2002 and 2009 in freshwater ecosystems in the Canadian Arctic. Site-average concentrations are sorted into three categories with the highest concentration category (>0.5 μg g^{-1} ww) representing the Health Canada consumption guideline for commercial sale of fish. Concentrations were standardized to lengths of 544 mm and 377 mm for lake trout and Arctic char, respectively.
Data are from Depew et al. (2013).

monitoring programs as well as private-sector environmental monitoring reports (see Annex Table A2.2 in NCP, 2012 for specific data sources). Data for six species of fish—lake trout, lake-dwelling Arctic char, northern pike, burbot, lake whitefish, and round whitefish—were compiled from multiple lakes and rivers sampled between 2002 and 2009. Older data on Hg in Arctic fish are summarized elsewhere (Fisk et al., 2003; Lockhart et al., 2005). Fish muscle concentrations of THg were length-adjusted by regression of fish THg vs. length (where the standard length was the mean length of all individuals for a species). Adjusted THg values were then sorted into three concentration categories: <0.2 μg g^{-1} ww, 0.2–0.5 μg g^{-1} ww, and >0.5 μg g^{-1} ww. The Health Canada consumption guideline for commercial sale of fish is 0.5 μg g^{-1} ww (Health Canada, 2011). Lake trout was the most widely sampled species (46 sites), followed by whitefish (round or lake whitefish in 32 sites), Arctic char (25 sites), northern pike (9 sites) and burbot (7 sites).

Average length-adjusted THg concentrations in lake trout were mainly between 0.2 and 0.5 μg g^{-1} (52% of sites) or less than 0.2 μg g^{-1} (39%) (Fig. 11). Only four lakes among those surveyed contained lake trout with mean length-adjusted THg concentrations greater than 0.5 μg g^{-1}. Average THg concentrations in lake-dwelling Arctic char were predominately less than 0.2 μg g^{-1} (68%) or between 0.2 and 0.5 μg g^{-1} (28%), with only one site greater than 0.5 μg g^{-1} (Amituk Lake on Cornwallis Island). At the majority of sites (91%), whitefish had average THg concentrations of less than 0.2 μg g^{-1} (Fig. 12). Few data were available for northern pike or burbot, but average Hg concentrations for these species were less than 0.5 μg g^{-1} at most sites (Fig. 12).

No geographic patterns or regional hotspots for Hg were evident for freshwater fish in the 2002 to 2009 dataset (Figs. 11, 12). This finding is consistent with Lockhart et al. (2005) who also found no strong geographic patterns in the Canadian Arctic using an older, larger dataset of fish collected over 30 years since 1971. Intensive lake surveys in the Mackenzie River Basin and the High Arctic suggest that differences in fish Hg concentrations among lakes are related to lake-specific characteristics such as lake and watershed size or DOC concentration that influence local transport and/or methylation of Hg (Evans et al., 2005a; Gantner et al., 2010a). Although the majority of water bodies in the 2002 to 2009 dataset were undisturbed, a few sites were included where local human activities could have affected fish Hg concentrations.

6.2. Arctic char

6.2.1. Comparison of Hg bioaccumulation in sea-run and lake-dwelling Arctic char

Previous investigations have noted that sea-run Arctic char have much lower Hg concentrations than lake-dwelling populations (Lockhart et al., 2005; Muir et al., 1997). It is unclear why Hg concentrations are so much lower, given that sea-run char spend only a few weeks feeding in the ocean during the summer, and spend the remainder of the year in freshwater. A recent study examined this question by comparing THg concentrations in nine paired sea-run and lake-dwelling Arctic char populations along a latitudinal gradient in eastern Canada from Rivière de la Trinité, Québec (49° 25′ N, 67° 18′ W) in the south to Heintzelman Lake (81° 42′ N, 66° 56′ W), Ellesmere Island in the north (van der Velden et al., 2013b, 2012). The study included comparisons of Hg levels in Arctic char as well as in marine and lake food webs (van der Velden et al., 2013a).

The results confirmed that lake-dwelling Arctic char were distinctly smaller than sea-run conspecifics and had substantially higher THg concentrations (Fig. 13). Similar differences in fish size and THg

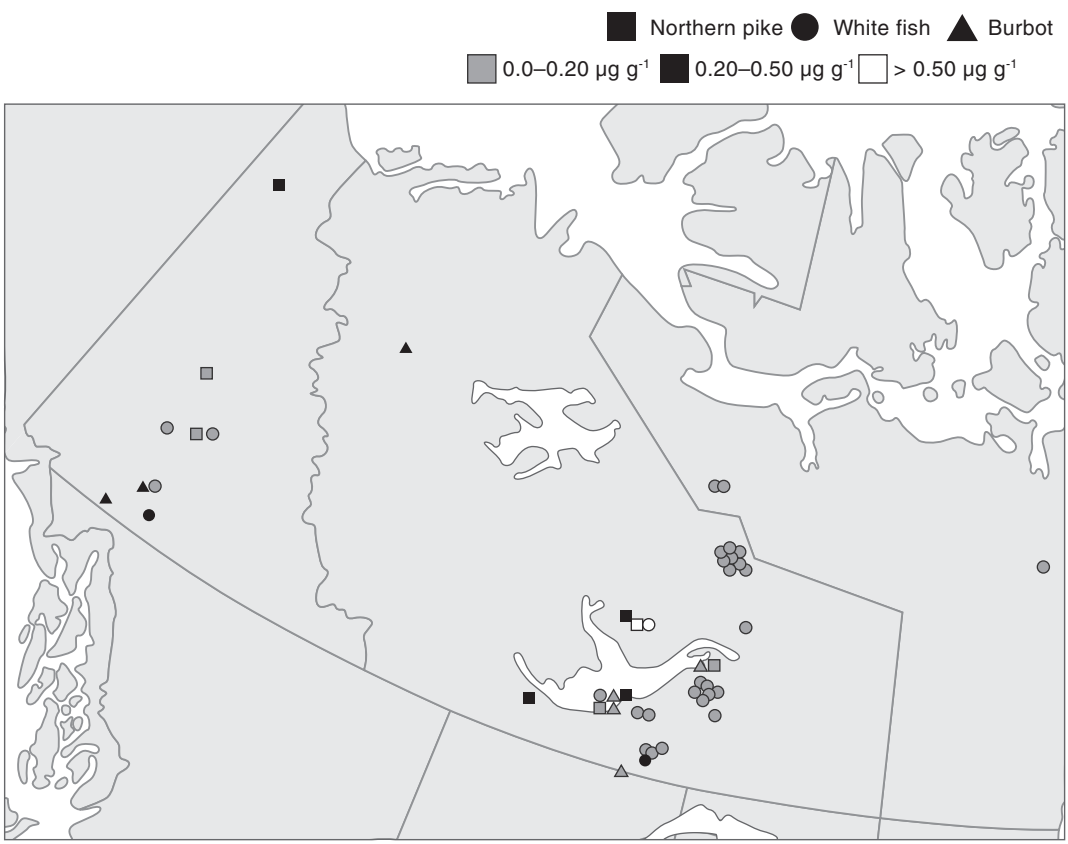

Fig. 12. Length-adjusted THg concentrations in northern pike, burbot, and lake or round whitefish measured between 2002 and 2009 in freshwater ecosystems in the Canadian Arctic. Site-average concentrations are sorted into three categories with the highest concentration category (>0.5 μg g^{-1} ww) representing the Health Canada consumption guideline for commercial sale of fish. Concentrations were standardized to a length of 599 mm for pike, 595 mm for burbot, 327 mm for round whitefish, and 395 mm for lake whitefish.
Data are from Depew et al. (2013).

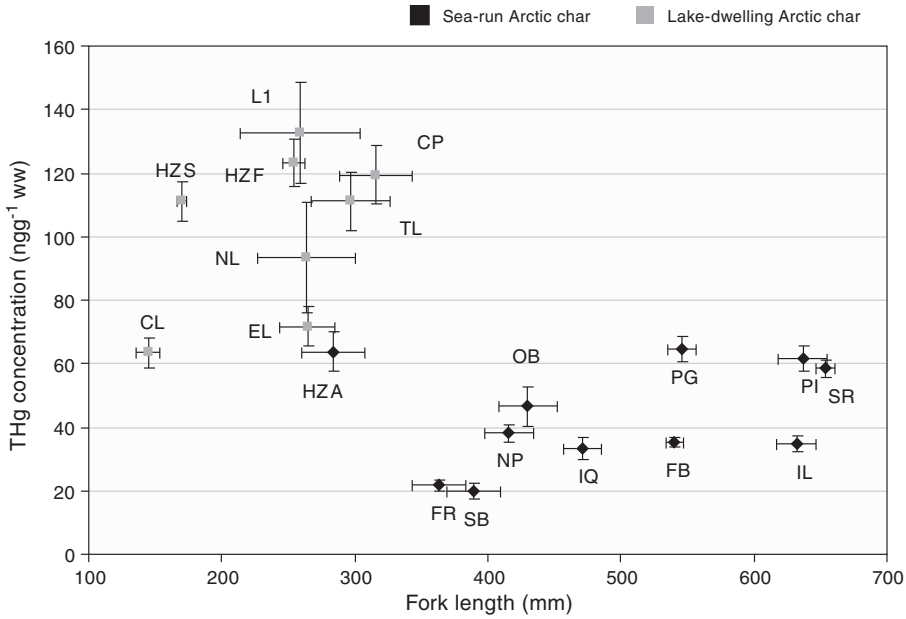

Fig. 13. Relationship between mean (±standard error) fork length and THg concentration in sea-run (anadromous) and non-piscivorous, lake-dwelling populations of Arctic char from the eastern Canadian Arctic (van der Velden et al., 2012, 2013b). Labels identify the sites: Heintzelman Lake, anadromous fish—HZ A; Fraser River (Nain Bay)—FR; Saglek Bay—SB; Okak Bay—OB; Iqalugaarjuit Lake (Pangnirtung)—IL; Pangnirtung Fiord—PG; Iqaluit—IQ; Pond Inlet—PI; Nepihjee River (Dry Bay)—NP; Frobisher Bay (Iqaluit)—FB; Salmon River (Pond Inlet)—SR; Heintzelman Lake, fast-growing fish—HZ F; Heintzelman Lake, slow-growing fish—HZ S; Coady's Pond #2—CP; Upper Nakvak Lake—NL; Esker Lake—EL; Tasiapik Lake—TL; Crazy Lake—CL; unnamed lake 1—L1 (see van der Velden et al., 2013b for site locations and sample sizes).

concentrations were observed between sea-run and landlocked Arctic char in the West Kitikmeot region (Swanson et al., 2011). In that study, the authors found that sea-run and resident (with access to the sea, but not migrating) Arctic char had significantly lower THg (0.04 μg g^{-1} ww) than landlocked char (0.19 μg g^{-1} ww) at a standardized fork length of 500 mm. At all latitudes in the eastern Arctic, THg concentrations were higher in lake-dwelling than in sea-run Arctic char, and latitudinal gradients were not obvious (Fig. 14; van der Velden et al., 2013a,b). Similarly, Gantner et al. (2010a) found no evidence of a latitudinal gradient in THg in landlocked Arctic char once concentrations were adjusted for length.

In the eastern Canadian Arctic, differences in THg concentrations between sea-run and lake-dwelling Arctic char could not be explained by differences in fish age, fork-length, length-at-age, or trophic position (van der Velden et al., 2013b). Rather, the difference in Arctic char THg concentration with feeding habitat was related to differential THg concentrations in prey items, due to lower mercury concentrations at the base of marine, relative to freshwater food webs (van der Velden

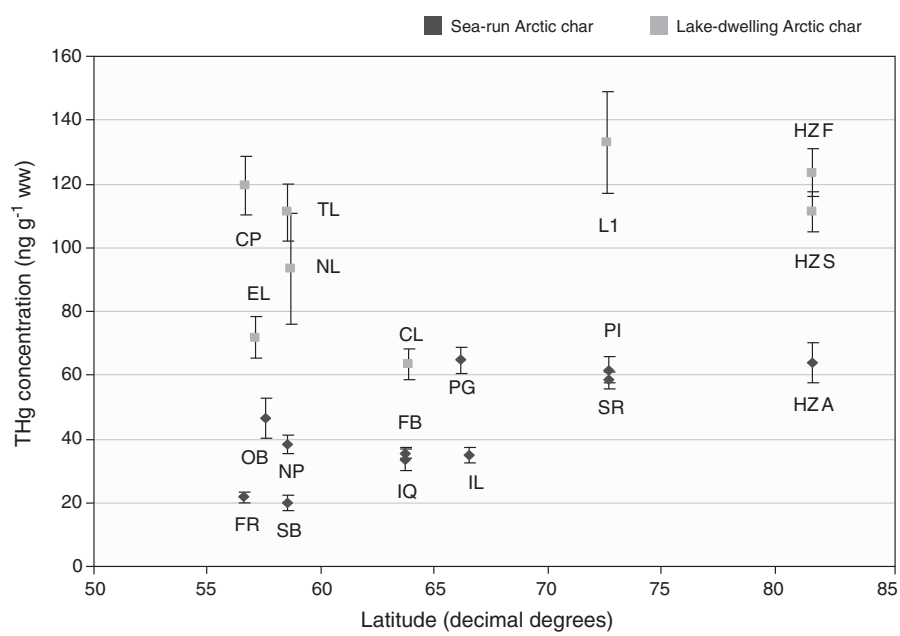

Fig. 14. Relationship between mean (±standard error) THg concentration and site latitude for sea-run and non-piscivorous, lake-dwelling populations of Arctic char from the eastern Canadian Arctic (van der Velden et al., 2013b). Labels identify the sites as described in Fig. 13. Data are not length or age adjusted.

et al., 2013a). Consistent with the results from eastern Canada, Swanson et al. (2011) concluded that trophic position could not explain differences in THg concentrations among life history types of Arctic char in the West Kitikmeot. In contrast, fish age and carbon to nitrogen ratios—an estimate of lipid content—were statistically related to higher THg concentrations in landlocked relative to sea-run char. Those findings suggest that slower growth rates and poorer body condition in landlocked char resulted in greater Hg bioaccumulation in the West Kitikmeot.

6.3. Lake trout

6.3.1. Anadromous lake trout in the West Kitikmeot

Although lake trout are generally thought to be a wholly freshwater fish species, recent research in the West Kitikmeot region has shown that there are actually three life history types: 1) landlocked (no access to the sea, wholly freshwater); 2) resident (access to the sea, exist in sympatry with anadromous individuals but wholly freshwater); and 3) anadromous (Swanson et al., 2010). The geographic extent of anadromous lake trout is not currently known. However, it is possible that anadromous populations exist across the entire mainland Arctic coast (Swanson et al., 2010).

Life history was found to have a significant effect on Hg bioaccumulation in lake trout from the West Kitikmeot (Swanson et al., 2011; Swanson and Kidd, 2010). In four coastal lakes where both anadromous and resident lake trout were present, anadromous fish had significantly lower THg concentrations (0.19 μg g^{-1} ww) than resident fish (0.31 μg g^{-1} ww) at a standardized fork length of 650 mm (Swanson and Kidd, 2010). Landlocked trout in two nearby inland lakes had an average, length-adjusted THg concentration similar to the coastal, resident trout (Swanson et al., 2011). Differences among life history types appear to be related to muscle lipid content, which can result from varying energy costs for foraging or diet type and abundance (Swanson et al., 2011). Other studies have reported less Hg in fish with higher lipid content (Wiener et al., 2003), which may reflect growth dilution or a dilution effect by the lipid. The lower THg concentrations in anadromous lake trout may also be due to lower Hg concentrations in marine prey compared with prey in freshwater environments in the Arctic (van der Velden et al., 2013a).

6.3.2. Lake trout in the Mackenzie River Basin

Concentrations of THg in lake trout of the Northwest Territories have been summarized by Lockhart et al. (2005), who synthesized many years of fish inspection records with more recent measurements made during stock assessments in lakes along the Mackenzie River. Lake trout in this area can have THg concentrations that exceed Health Canada's 0.5 μg g^{-1} ww guideline for commercial sale of fish (Lockhart et al., 2005). Since 2005, contaminant trend monitoring of lake trout under the NCP has focused on Great Slave Lake, with additional periodic assessment of a series of lakes along the Mackenzie River for which historic records of lake trout Hg levels exist (Evans et al., 2005a; Evans and Muir, 2010; Lockhart et al., 2005). From 2004 to 2009, the sampling of two lakes per year in the Mackenzie River Basin revealed that THg concentrations in lake trout followed earlier patterns reported in Evans et al. (2005a)—higher THg concentrations were more commonly associated with smaller lakes having larger watersheds (NCP, 2012). Lake trout inhabiting smaller lake ecosystems are more likely to have high Hg levels than fish living in large lake ecosystems such as Great Bear and Great Slave Lakes. This difference is thought to be due to a combination of higher temperatures, lake productivity, and wetland and littoral zone influences on Hg methylation rates in small rather than large lake ecosystems (Evans et al., 2005a). Furthermore, small lakes have less dilution capacity than large lakes, and lakes with larger watershed to lake area ratios would receive greater Hg loads from the catchment.

6.4. Temporal trends of Hg in Arctic fish populations

Several fish populations have been monitored over the last two decades in the Canadian Arctic for their muscle concentrations of THg (Table 3). The 21 populations include landlocked Arctic char, lake trout, burbot or northern pike, and the sampling effort ranged from periodic (2–3 years) to intensive (9–18 years), in most cases since the early 1990s. Table 3 summarizes the temporal trend observations as reported by the authors of each study.

Table 3
Summary of temporal trends for THg concentrations in muscle of freshwater fish monitored in the Canadian Arctic.

Region	Water body	Fish species	Time period	Number of sampling years	Trend[a]	Reference
Nunavut	Amituk Lake	Arctic char (landlocked)	1989–2009	10	No trend	NCP (2012)
	Char Lake	Arctic char (landlocked)	1993–2010	9	No trend	NCP (2012)
	Lake Hazen	Arctic char (landlocked)	1990–2010	10	No trend	NCP (2012)
	Resolute Lake	Arctic char (landlocked)	1993–2010	14	No trend	NCP (2012)
Labrador	Esker Lake	Arctic char (lake-dwelling)	1978–2008	2	Significant decrease[b]	van der Velden et al. (in this issue)
	Tasialuk Lake	Arctic char (lake-dwelling)	1978–2007	2	Significant increase	van der Velden et al. (in this issue)
Yukon	Kusawa Lake	Lake trout	1993–2009	11	Significant non-linear trend	NCP (2012)
	Lake Laberge	Lake trout	1993–2009	12	No trend	NCP (2012)
Northwest Territories	Lac Belot	Lake trout	1999–2005	2	No trend	NCP (2012)
	Cli Lake	Lake trout	1996–2009	3	No trend	NCP (2012)
	Colville Lake	Lake trout	1999–2009	3	No trend	NCP (2012)
	Great Bear Lake	Lake trout	1979–2007	3	Significant increase	NCP (2012)
	Great Slave Lake					
	West Basin	Lake trout	1990–2012	14	Significant increase	Evans et al. (2013)
	West Basin	Burbot	1992–2012	18	Significant increase	Evans et al. (2013)
	West Basin	Northern pike	1992–2012	12	No trend	Evans et al. (2013)
	East Arm	Lake trout (<590 mm FL)	1993–2012	15	No trend	Evans et al. (2013)
	East Arm	Lake trout (>590 mm FL)	1993–2012	14	Significant increase	Evans et al. (2013)
	East Arm	Burbot	1999–2012	11	Significant increase	Evans et al. (2013)
	Kelly Lake	Lake trout	1998–2007	2	Significant increase	NCP (2012)
	Lac St. Therese	Lake trout	2003–2008	2	Significant increase	NCP (2012)
	Mackenzie River	Burbot	1985–2009	14	Significant increase	Stern et al. (2010)[c]
	Trout Lake	Lake trout	1991–2008	3	Significant increase	NCP (2012)

FL = fork length.
[a] Trend significance according to author(s) of the study.
[b] The authors reported a significant decline in age-adjusted but not length-adjusted THg concentration.
[c] See also Carrie et al. (2010).

No statistically significant trends were found for landlocked Arctic char from three lakes on Cornwallis Island and one lake on Ellesmere Island in Nunavut (Table 3). Among those four lakes, the dataset for Resolute Lake, with 14 sampling years, had the highest power (65%) to detect a log-linear trend of 5% change in THg concentration, according to an analysis using PIA software (Bignert, 2007). The temporal trends in the Canadian Arctic contrast with changes in THg observed in a single population of landlocked char from a small lake in southwest Greenland (Rigét et al., 2010) where length-adjusted concentrations increased significantly over the period from 1994 to 2008. This trend was tentatively linked to increasing mean monthly air temperatures during May to August although correlations were not statistically significant due to the small number of sampling years ($n = 6$). In the eastern Canadian Arctic (Labrador), no overall temporal trend in THg concentration was observed for lake-dwelling or anadromous Arctic char despite warming temperatures in the region over the last thirty years (van der Velden et al., 2015-in this issue).

In the Yukon, no significant temporal trend in THg was observed for Lake Laberge lake trout over a 16 year period from 1993 to 2009. In Kusuwa Lake, lake trout THg concentrations showed a non-linear trend from 1993 to 2009, with a significant decline in the last two years of the measurement period (NCP, 2012).

In contrast, the Mackenzie River Basin in the Northwest Territories is an Arctic region undergoing increases in fish Hg bioaccumulation (Table 3). In Great Slave Lake, THg concentrations of lake trout and burbot from both the West Basin and East Arm increased significantly at a rate of 2–5% y^{-1} since the 1990s (Evans et al., 2013; Table 3). Long-term monitoring of Hg in burbot of the Mackenzie River near Fort Good Hope showed that, over a 25-year period from 1985 to 2009, concentrations of THg in muscle and liver increased approximately two-fold (Stern et al., 2010; Table 3). An investigation of THg temporal trends in lake trout from lakes in the Mackenzie River Basin was conducted although the survey was limited to periodic sampling at most sites over the last two decades. Nevertheless, trends of THg increase were observed in four of seven lakes (Table 3), with greater increases in the smaller lakes (NCP, 2012). Because lake trout THg concentrations exceeded the 0.5 μg g^{-1} ww guideline for commercial sale of fish, consumption advisories were issued for Cli, Trout, and Kelly Lakes, and Lac Ste. Therese in the summer of 2010 (NWT HSS, 2010). Given that strong increases were associated with smaller and/or shallower lakes, it is probable that other small- to medium-size lakes in the Northwest Territories are showing similar Hg increases. It is unclear what environmental factors are driving these recent trends in Hg bioaccumulation, and additional study is needed to examine the role of climate change in the region as well as potential changes in deposition patterns of atmospheric Hg.

6.4.1. Temporal trends of Hg in Mackenzie River burbot

Additional study was conducted to investigate environmental drivers of greater Hg bioaccumulation in burbot from the Mackenzie River (Carrie et al., 2010). This temporal increase could not be explained by differing physiological characteristics or changes in feeding behavior, as suggested by no relationships between THg concentrations and $\delta^{15}N$ and $\delta^{13}C$ ratios, length and weight of fish. The authors also concluded that changes in atmospheric deposition could not account for the increasing trend in burbot THg concentration because atmospheric Hg concentrations have been stable or falling in the Arctic over the last 25 years (AMAP, 2011; Cole et al., 2013). However, other environmental factors in addition to atmospheric Hg concentration can determine the net deposition of Hg to terrestrial surfaces (Dastoor et al., 2008).

To examine historical trends in sediment Hg fluxes in the watershed, a dated sediment core was collected from Hare Indian Lake, a tributary lake near the Mackenzie River sampling site. Carrie et al. (2010) showed a striking temporal correlation between THg concentrations in burbot

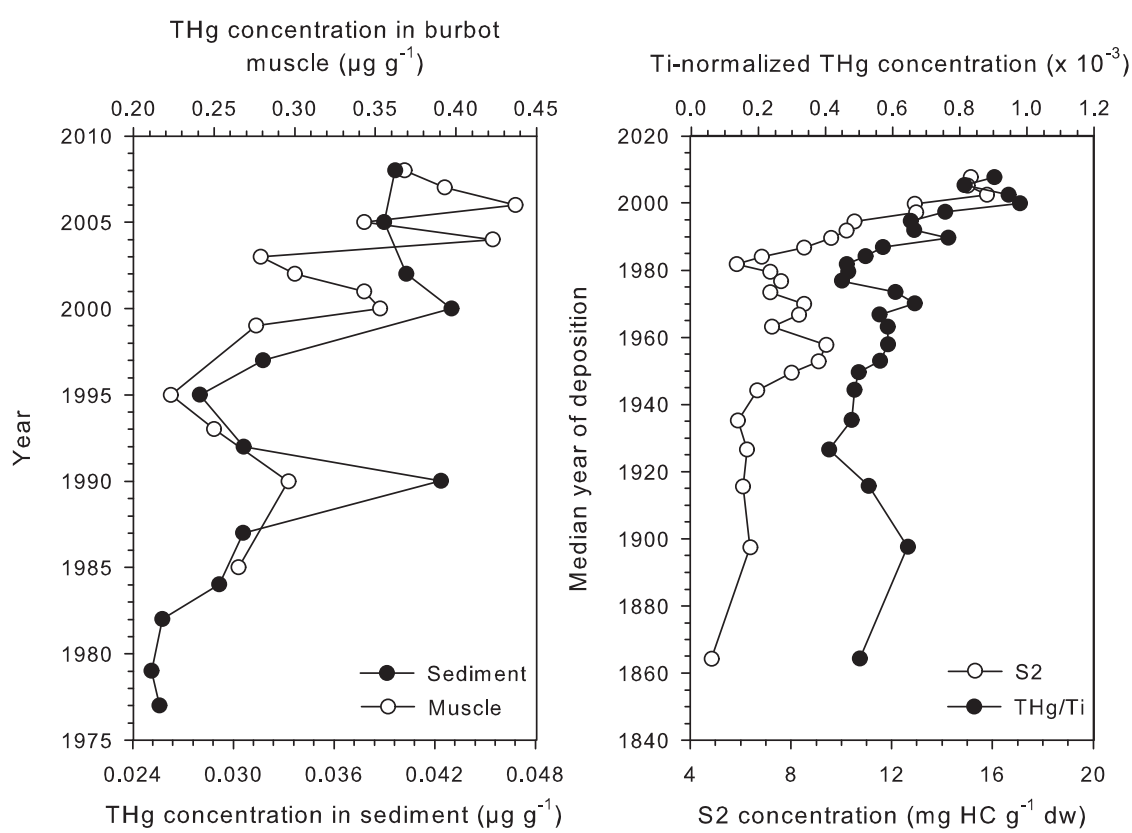

Fig. 15. Chronological variation of THg concentrations in burbot from the Mackenzie River and in a sediment core from nearby Hare Indian Lake (left panel) as well as a comparison between THg concentrations—normalized for geogenic inputs using Ti—and algal (S2) carbon concentrations in the same sediment core (right panel).
Reprinted with permission from Carrie et al. (2010). © American Chemical Society.

muscle and in sediment core slices when plotted against year of fish collection and median year of sediment deposition, respectively (Fig. 15). Furthermore, the sediment core showed strong co-variation over the last 150 years between concentrations of THg and labile, algal-derived organic matter (measured as S2 carbon by Rock-Eval pyrolysis; Sanei and Goodarzi, 2006) (Fig. 15). Concentrations of THg in the sediment core were normalized against the conservative element titanium (Ti) to correct for potential geogenic inputs of Hg.

The association between THg and algal organic matter may reflect Hg scavenging by primary producers, similar to what has been reported in other Arctic lakes (Section 3.2). The increase in sediment accumulation of algal-derived organic matter since the 1980s is consistent with the climate record of the Mackenzie River Basin. The mean annual air temperature for nearby Norman Wells, for instance, has increased significantly by approximately 1.9 °C since the early 1970s. This region has also seen a significant decrease in snow cover over the same time period. Reduction in the period of ice cover and consequent improvement in the light regime for algal growth is thus a plausible explanation for the influence of rising air temperature on algal productivity. The striking increase in burbot THg concentration, coincident with the temporal trends in lake algal productivity and sediment Hg fluxes, suggest that climate warming may mobilize Hg, which, in turn, results in increased exposure for Arctic fish.

6.4.2. A multi-species assessment of temporal Hg trends in Great Slave Lake

Beginning in 1999, a long-term monitoring program of contaminants in fish was initiated for Great Slave Lake as part of the NCP, focusing on three top predator species: lake trout, burbot, and northern pike (Evans et al., 2013). Fish were collected in two general regions of the lake: 1) the West Basin which is more shallow (mean depth = 41 m), relatively warmer and more productive, and strongly influenced by the Slave River inflow; and 2) the East Arm, including Christie Bay, which is deeper (mean depth = 199 m), colder and less productive (Evans, 2000; Fee et al., 1985; Rawson, 1955). Data collected before 1999 also exist from other NCP studies in Great Slave Lake and periodic monitoring of the commercial fishery which operates out of Hay River in the West Basin. Only length and weight were measured in earlier fish collections and the sample number was often small. More recent sampling under the NCP includes measurements of age, carbon and nitrogen stable isotopes, and percent lipid.

Overall, there is compelling evidence of a Hg increase in lake trout and burbot in the two regions of Great Slave Lake (Evans et al., 2013), which is consistent with the observed trend of Hg increase occurring in burbot at Fort Good Hope downstream on the Mackenzie River (Carrie et al., 2010). Air temperatures showed a similar long-term (1975 to 2012) trend of increase as at Fort Good Hope although on the shorter term (1990 to 2012), the trend was not significant. Wind speed and precipitation also have varied over the long-term and short-term, and potentially could be affecting Hg trends in Great Slave Lake fish (Evans et al., 2013). When multivariate analyses were conducted to investigate the role of climate in affecting THg trends in West Basin burbot and lake trout, temperature emerged as a significant influencing factor, although the coefficient was negative indicating that higher Hg concentrations in fish occurred during the cooler years over the measurement periods. Moreover, annual temperature means explained more of the variance than May to September means (the presumed growing season), suggesting that trends were driven by events occurring during the cooler months of the year. The Pacific North American oscillation also improved explanatory power of the factors affecting Hg trends in lake trout. Evans et al. (2013) proposed that this factor may operate through high pressure ridges over the west coast mountains, the oxidation of rising atmospheric Hg at higher altitudes, and its deposition through sinking air masses and precipitation on the east side of these mountains.

Sediment cores were collected from three locations in Great Slave Lake in 2009 to assess historical trends in Hg fluxes: two locations in the West Basin and a third in the East Arm (Evans et al., 2013). Average sediment THg concentrations ranged from 32 to 83 ng g^{-1}, and there were no obvious temporal trends in concentrations at the three sites (Fig. 16). Rates of THg flux to sediments showed a long-term trend of increase in the East Arm while the trend was more variable for the West Basin sites (Fig. 16). Trends in THg flux largely reflected trends in sedimentation rate (Evans et al., 2013). Algal (S2) carbon in sediments showed a pronounced trend of increasing concentration since the 1990s. However, this trend did not mirror trends in sedimentation rates and sediment THg concentrations, in contrast to the findings at Fort Good Hope (Carrie et al., 2010). Moreover, there was a poor correspondence between S2 and air temperatures (as annual means and running 4-year averages), particularly over the past 20 years when S2 concentration showed a steady increase in all three cores. Thus, there is little evidence from the sediment cores that increases in THg concentrations over the three and a half decades for lake trout and two decades for burbot from the West Basin are associated with increasing air temperatures and greater aquatic productivity. Rather, higher Hg concentrations in lake trout and burbot occurred during the colder years (Fig. 16), and for reasons which are under investigation but could involve changes in atmospheric sources of reactive mercury.

7. Wildlife in freshwater ecosystems

7.1. Waterfowl

Waterfowl harvested by northern hunters, specifically ducks and geese, generally have low body burdens of Hg. From the late 1980s to mid-1990s, an extensive survey of contaminants in waterfowl was conducted across Canada that measured THg in the muscle of waterfowl captured at 28 locations in the Arctic (Braune and Malone, 2006b; Muir et al., 1997). Bird species that feed mainly on terrestrial grasses and aquatic plants such as geese and dabbling ducks had muscle THg concentrations <0.35 μg g^{-1} ww (Braune and Malone, 2006b). Diving ducks, which also feed extensively on aquatic invertebrates, had similarly low THg concentrations (Braune and Malone, 2006b). Piscivorous mergansers had higher muscle concentrations of THg up to 1.5 μg g^{-1} ww due to their higher trophic level (Braune and Malone, 2006b). Liver concentrations of THg in dabbling and diving duck species were also measured and were <1.5 μg g^{-1} ww (Braune et al., 2005; Braune and Malone, 2006a).

7.2. Small mammals

Overall, little information is available on Hg bioaccumulation in small mammals that feed in Arctic freshwater ecosystems although two recent studies were conducted in the Yukon on muskrat and mink. Muskrat muscle tissue from the Old Crow flats averaged 1 ng THg g^{-1} dw (M. Humphries, McGill University, unpublished data). This low level is typical of an Arctic herbivore that feeds on vascular plants. Reflecting their carnivorous diet of fish and small mammals, mink sampled in the Yukon had hepatic THg concentrations of 0.92 ± 0.90 μg g^{-1} ww, similar to those found in Arctic fox (Gamberg et al., 2005; Hoekstra et al., 2003). Female mink had higher concentrations of THg and MeHg in all tissues than their male counterparts, likely because they ingest proportionally more food (and more Hg) due to their smaller body size and their greater energy requirements for reproduction.

8. Summary

Some of the most significant advances highlighted in this review have been made in the area of Hg cycling in the Arctic environment. Large amounts of new data are now available for water and sediment, which provide more information on the concentrations, fluxes, and transformations of Hg in these abiotic matrices. This information was virtually absent for the Arctic a decade ago. Investigations of Hg

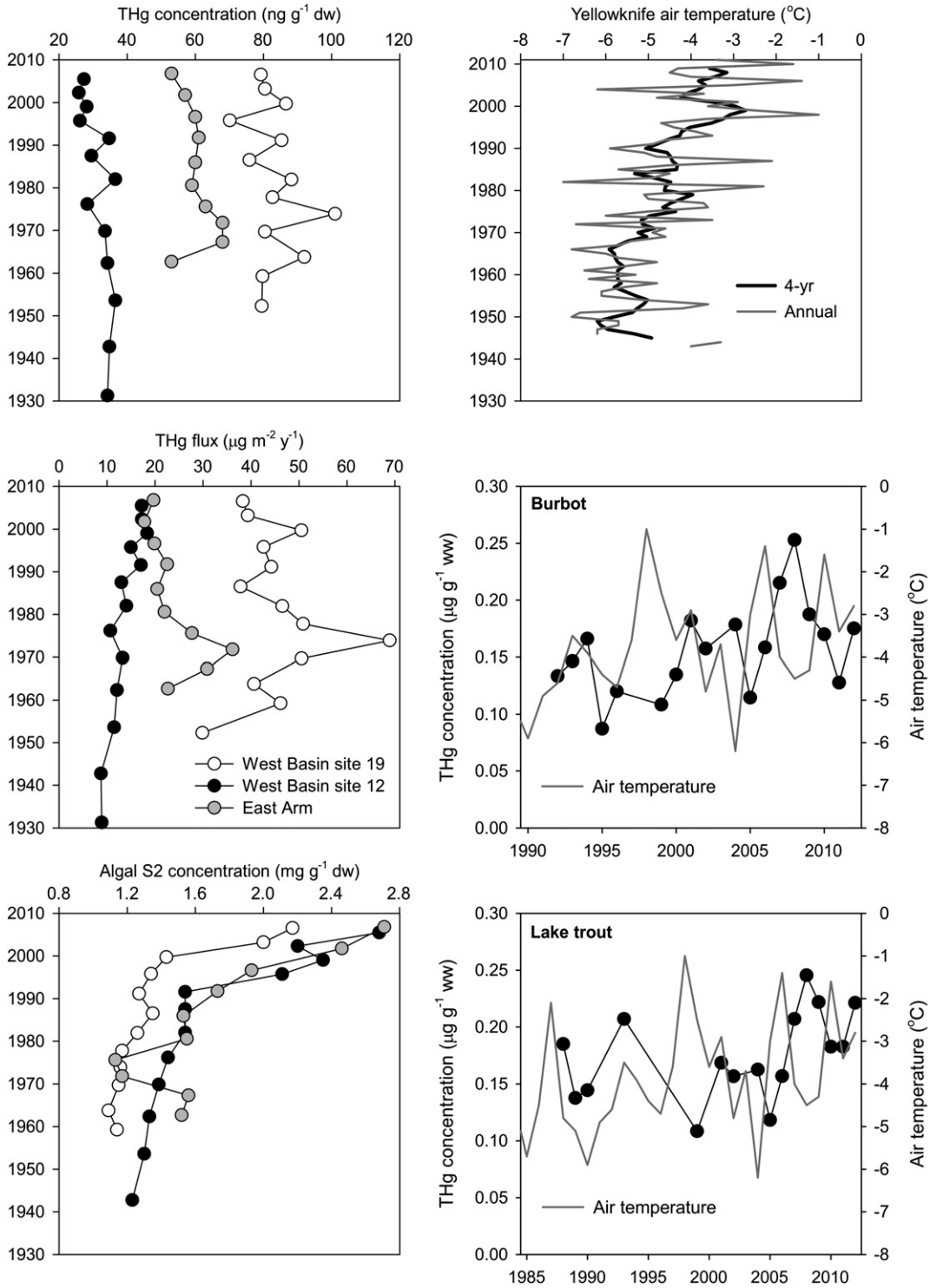

Fig. 16. Temporal trends of THg concentration and flux as well as algal (S2) carbon concentration in two sediment cores from the West Basin (sites 19 and 12) and one from the East Arm of Great Slave Lake. Also shown are long-term variations in air temperature at Yellowknife (annual and 4-year rolling annual means), and measured THg concentrations in West Basin lake trout and burbot with mean annual air temperature.
Reprinted with permission from Evans et al. (2013). © American Chemical Society.

biogeochemistry have focussed on a range of freshwater environments including lakes, rivers, and ponds in polar desert, tundra and sub-Arctic taiga in northern Canada.

In the High Arctic, snowmelt was found to be an important source of Hg to lake waters. Higher levels of water MeHg were found in some fresh waters, such as shallow ponds, where conditions are probably more suitable for in situ methylation. Little information currently exists on Hg methylation sites and rates in freshwater environments in the Canadian Arctic, although estimates from Ellesmere Island ponds suggest that Hg methylation rates can be comparable to temperate aquatic ecosystems. It is also unclear what processes lead to the occurrence of MeHg in the snow that enters fresh waters. More fundamental research is recommended on mechanistic aspects of Hg methylation and degradation, as well as the bioavailability of Hg (as divalent inorganic Hg

and as MeHg), to better understand the processes regulating MeHg production and entry into Arctic freshwater food webs.

Mercury fluxes to lake sediments have increased several-fold since the onset of the Industrial Era at a large number of sub-Arctic and Arctic sites. While all evidence points to increasing Hg fluxes in the lakes, it is unclear to what extent Hg from anthropogenic sources is being deposited in greater amounts or whether other factors, such as higher algal productivity or increased sedimentation, are attenuating Hg inputs from the atmosphere and lake catchment. Further research is recommended to explain increasing Hg fluxes to Arctic lake sediments, specifically the roles of anthropogenic Hg inputs and other processes in the lakes and their catchments.

An important advancement under the NCP was the establishment of more frequent monitoring for key Arctic indicator species, which provided greater statistical power to detect changes in biotic Hg levels. Over the last two to four decades, Hg concentrations have increased in some populations of freshwater fish in the Mackenzie River Basin while other populations from Yukon and Nunavut showed no change or a slight decline. The different Hg trends indicate that the drivers of temporal change may be regional or habitat-specific. Further research is required to identify the underlying processes leading to changes over time in fish Hg concentrations, particularly at sites where increases have been observed. Multiple factors may be implicated and should be assessed, including the roles of Hg delivery (e.g., atmospheric deposition, Hg methylation), shifts in food web structure, and climate change.

No geographic patterns or regional hotspots were evident for Hg in common freshwater fish species that were sampled across the Canadian Arctic between 2002 and 2009. Site average Hg concentrations in fish muscle did not exceed the Health Canada consumption guideline for commercial sale of fish (0.5 $\mu g\ g^{-1}$ ww) at the majority of sites surveyed. Lake-dwelling Arctic char are distinctly smaller than sea-run conspecifics and have substantially higher THg concentrations. The difference in THg level between sea-run and lake-dwelling Arctic char from eastern Canada was related to lower THg concentrations in organisms at the base of marine relative to lacustrine food webs. Food web processes as well as Hg supply from the catchment both affect the bioaccumulation of Hg by Arctic fish. Preliminary work in the emerging field of Hg stable isotopes shows a future potential for differentiating sources of Hg to aquatic biota.

Widespread evidence indicates that Arctic fresh waters are undergoing profound change at a rapid rate. Preliminary research indicates that this environmental change is altering the cycling and bioaccumulation of Hg through effects on Hg fluxes and food webs. In the Mackenzie River Basin, slumping of permafrost soils has increased the transport of inorganic material to lakes, but these large inputs have not increased Hg concentrations in sediment. Recent increases in algal primary production and catchment inputs may be enhancing Hg fluxes to Arctic lakes. Climate warming may be affecting the local biogeochemical processing of Hg and its resulting mobilization may have increased exposure to fish in the Mackenzie River. Large uncertainties remain in this emerging and complex field. Many environmental changes are occurring in the Arctic and detailed, process-focussed investigations are needed to more precisely identify how these changes will alter the fate of Hg. Several aspects of the Hg cycle may be impacted including how Hg is delivered to aquatic ecosystems, its biogeochemical transformations, and its trophic transfer in food webs.

Acknowledgments

The authors wish to thank the Northern Contaminants Program (NCP) of Aboriginal Affairs and Northern Development Canada, as well as ArcticNet and International Polar Year, for their funding support which made possible the generation of much of the data presented in this review. In particular, we thank Russell Shearer for his continued support and enthusiasm for the NCP, and Scott Tomlinson and Jason Stow of the NCP for their support in the preparation of the assessment report from which this review originates as well as the preparation of this manuscript. Rami Yassine kindly assisted with the preparation of figures. We also extend our appreciation to the Arctic Monitoring and Assessment Programme (AMAP) for use of text from their 2011 report on mercury in the circumpolar Arctic. The authors gratefully acknowledge the Aboriginal organizations in the Yukon, Northwest Territories, Nunavut, Nunavik, and Nunatsiavut for their support of the NCP and their active participation in monitoring and research activities. We thank two reviewers for their constructive comments on an earlier version of this manuscript.

References

ACIAArctic climate impact assessment. New York: Cambridge University Press; 2005. p. 1042.

AMAPAMAP assessment 2011: mercury in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway; 2011. p. xiv+193.

Amyot M, Lean D, Mierle G. Photochemical formation of volatile mercury in high Arctic lakes. Environ Toxicol Chem 1997;16:2054–63.

Ariya PA, Peterson K, Snider G, Amyot M. Chapter 15 — mercury chemical transformation in the gas, aqueous and heterogeneous phases: state-of-the-art science and uncertainties. In: Pirrone N, Mason RP, editors. Mercury fate and transport in the global atmosphere: emissions, measurements and models. Springer; 2009. p. 720.

Benoit JM, Gilmour CC, Mason RP, Riedel GS, Riedel GF. Behavior of mercury in the Patuxent river estuary. Biogeochemistry 1998;40:249–65.

Bergquist BA, Blum JD. Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. Science 2007;318:417–20.

Bergquist BA, Blum JD. The odds and evens of mercury isotopes: applications of mass-dependent and mass-independent isotope fractionation. Elements 2009;5:353–7.

Biester H, Bindler R, Martinez-Cortizas A, Engstrom DR. Modeling the past atmospheric deposition of mercury using natural archives. Environ Sci Technol 2007;41:4851–60.

Bignert A. PIA statistical application developed for use by the Arctic Monitoring and Assessment Programme. Arctic Monitoring and Assessment Programme; 2007. p. 13 [available from www.amap.no, Oslo, Norway].

Bindler R, Renberg I, Appleby PG, Anderson NJ, Rose NL. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: a coast to ice margin transect. Environ Sci Technol 2001;35:1736–41.

Blum JD, Bergquist BA. Reporting of variations in the natural isotopic composition of mercury. Anal Bioanal Chem 2007;388:353–9.

Braune BM, Malone BJ. Mercury and selenium in livers of waterfowl harvested in northern Canada. Arch Environ Contam Toxicol 2006a;50:284–9.

Braune BM, Malone BJ. Organochlorines and trace elements in upland game birds harvested in Canada. Sci Total Environ 2006b;363:60–9.

Braune BM, Hobson KA, Malone BJ. Regional differences in collagen stable isotope and tissue trace element profiles in populations of long-tailed duck breeding in the Canadian Arctic. Sci Total Environ 2005;346:156–68.

Brazeau ML, Blais JM, Paterson AM, Keller W, Poulain AJ. Evidence for microbially mediated production of elemental mercury (Hg0) in subarctic lake sediments. Appl Geochem 2013;37:142–8.

Carrie J, Wang F, Sanei H, Macdonald RW, Outridge PM, Stern GA. Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate. Environ Sci Technol 2010;44:316–22.

Carrie J, Stern GA, Sanei H, Macdonald RW, Wang F. Determination of mercury biogeochemical fluxes in the remote Mackenzie River Basin, northwest Canada, using speciation of sulfur and organic carbon. Appl Geochem 2012;27:815–24.

Chételat J, Amyot M. Elevated methylmercury in High Arctic *Daphnia* and the role of productivity in controlling their distribution. Glob Chang Biol 2009;15:706–18.

Chételat J, Amyot M, Cloutier L, Poulain A. Metamorphosis in chironomids, more than mercury supply, controls methylmercury transfer to fish in High Arctic lakes. Environ Sci Technol 2008;42:9110–5.

Chételat J, Amyot M, Cloutier L. Shifts in elemental composition, methylmercury content and $\delta^{15}N$ ratio during growth of a High Arctic copepod. Freshw Biol 2012;57:1228–40.

Chiasson-Gould SA, Blais JM, Poulain A. Dissolved organic matter kinetically controls mercury bioavailability to bacteria. Environ Sci Technol 2014;48:3153–61.

Christensen JH, Brandt J, Frohn LM, Skov H. Modelling of mercury in the Arctic with the Danish Eulerian Hemispheric Model. Atmos Chem Phys 2004;4:2251–7.

Clayden M, Kidd K, Chetelat J, Hall BD, Garcia E. Environmental, geographic and trophic influences on methylmercury concentrations in macroinvertebrates from lakes and wetlands across Canada. Ecotoxicology 2014;23:273–84.

Cole AS, Steffen A, Pfaffhuber KA, Berg T, Pilote M, Poissant L, et al. Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude sites. Atmos Chem Phys 2013;13:1535–45.

Cooke CA, Hobbs WO, Michelutti N, Wolfe AP. Reliance on ^{210}Pb chronology can compromise the inference of preindustrial Hg flux to lake sediments. Environ Sci Technol 2010;44:1998–2003.

Cooke CA, Wolfe AP, Michelutti N, Balcom PH, Briner JP. A holocene perspective on algal mercury scavenging to sediments of an Arctic lake. Environ Sci Technol 2012;46:7135–41.

Cremona F, Planas D, Lucotte M. Assessing the importance of macroinvertebrate trophic dead ends in the lower transfer of methylmercury in littoral food webs. Can J Fish Aquat Sci 2008;65:2043–52.

Dastoor AP, Davignon D, Theys N, Van Roozendael M, Steffen A, Ariya PA. Modeling dynamic exchange of gaseous elemental mercury at polar sunrise. Environ Sci Technol 2008;42:5183–8.
Deison R, Smol JP, Kokelj SV, Pisaric MFJ, Kimpe LE, Poulain AJ, et al. Spatial and temporal assessment of mercury and organic matter in thermokarst affected lakes of the Mackenzie Delta uplands, NT, Canada. Environ Sci Technol 2012;46:8748–55.
Depew DC, Burgess NM, Anderson MR, Baker R, Bhavsar SP, Bodaly RAD, et al. An overview of mercury concentrations in freshwater fish species: a national fish mercury dataset for Canada. Can J Fish Aquat Sci 2013;70:436–51.
Dietz R, Outridge PM, Hobson KA. Anthropogenic contributions to mercury levels in present-day Arctic animals — a review. Sci Total Environ 2009;407:6120–31.
Dittman JA, Driscoll CT. Factors influencing changes in mercury concentrations in lake water and yellow perch (*Perca flavescens*) in Adirondack lakes. Biogeochemistry 2009;93:179–96.
Dommergue A, Ferrari CP, Gauchard PA, Boutron CF, Poissant L, Pilote M, et al. The fate of mercury species in a sub-arctic snowpack during snowmelt. Geophys Res Lett 2003; 30:1621. http://dx.doi.org/10.1029/2003GL017308.
Dommergue A, Ferrari CP, Amyot M, Brooks S, Sprovieri F, Steffen A. Chapter 10. Spatial coverage and temporal trends of atmospheric mercury measurements in Polar Regions. In: Pirrone N, Mason R, editors. Mercury fate and transport in the global atmosphere. New York: Springer Science + Business Media; 2009. p. 293–321.
Douglas TA, Loseto LL, MacDonald RW, Outridge P, Dommergue A, Poulain A, et al. The fate of mercury in Arctic terrestrial and aquatic ecosystems, a review. Environ Chem 2012;9:321–55.
Drevnick PE, Muir DCG, Lamborg CH, Horgan MJ, Canfield DE, Boyle JF, et al. Increased accumulation of sulfur in lake sediments of the High Arctic. Environ Sci Technol 2010; 44:8415–21.
Durnford D, Dastoor A, Figueras-Nieto D, Ryjkov A. Long range transport of mercury to the Arctic and across Canada. Atmos Chem Phys 2010;10:6063–86.
Emmerton CA, Graydon JA, Gareis JAL, St. Louis VL, Lesack LFW, Banack JKA, et al. Mercury export to the Arctic Ocean from the Mackenzie River, Canada. Environ Sci Technol 2013;47:7644–54.
Evans MS. The large lake ecosystems of northern Canada. Aquat Ecosyst Health Manag 2000;3:65–79.
Evans MS, Muir DCG. Spatial and long-term trends in persistent organic contaminants and metals in lake trout and burbot from the Northwest Territories. Synopsis of research conducted under the 2009–2010 Northern Contaminants Program. Canada, Ottawa: Indian and Northern Affairs; 2010. p. 160–9.
Evans MS, Lockhart L, Doetzel L, Low G, Muir D, Kidd KA, et al. Elevated mercury concentrations in fish in lakes in the Mackenzie River Basin: the role of physical, chemical, and biological factors. Sci Total Environ 2005a;351–352:479–500.
Evans MS, Muir D, Lockhart L, Stern G, Ryan M, Roach P. Persistent organic pollutants and metals in the freshwater biota of the Canadian Subarctic and Arctic: an overview. Sci Total Environ 2005b;351–352:94–147.
Evans M, Muir D, Brua RB, Keating J, Wang X. Mercury trends in predatory fish in Great Slave Lake: the influence of temperature and other climate drivers. Environ Sci Technol 2013;47:12793–801.
Fee EJ, Stainton MP, Kling HJ. Primary production and related limnological data from some lakes in the Yellowknife, N.W.T. area. Canadian Technical Report of Fisheries and Aquatic Sciences, 1409. ; 1985. p. 55.
Fisk A, Hobbs KE, Muir DCG. Contaminant levels and trends in the biological environment. Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada, Ottawa; 2003. [pp. xix + 175].
Fitzgerald WF, Engstrom DR, Lamborg CH, Tseng C-M, Balcom PH, Hammerschmidt CR. Modern and historic atmospheric mercury fluxes in northern Alaska: global sources and Arctic depletion. Environ Sci Technol 2005;39:557–68.
Fleming EJ, Mack EE, Green PG, Nelson DC. Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. Appl Environ Microbiol 2006;72:457–64.
French TD, Houben AJ, Desforges J-PW, Kimpe LE, Kokelj SV, Poulain AJ, et al. Dissolved organic carbon thresholds affect mercury bioaccumulation in Arctic lakes. Environ Sci Technol 2014;48:3162–8.
Gamberg M, Boila G, Stern G, Roach P. Cadmium, mercury and selenium concentrations in mink (*Mustela vison*) from Yukon, Canada. Sci Total Environ 2005; 351–352:523–9.
Gantner N, Hintelmann H, Zheng W, Muir DC. Variations in stable isotope fractionation of Hg in food webs of Arctic lakes. Environ Sci Technol 2009;43:9148–54.
Gantner N, Muir DC, Power M, Iqaluk D, Reist JD, Babaluk JA, et al. Mercury concentrations in landlocked Arctic char (*Salvelinus alpinus*) from the Canadian Arctic. Part I: influence of lake biotic and abiotic characteristics on geographic trends in 27 populations. Environ Toxicol Chem 2010a;29:633–43.
Gantner N, Power M, Iqaluk D, Meili M, Borg H, Sundbom M, et al. Mercury concentrations in landlocked Arctic char (*Salvelinus alpinus*) from the Canadian Arctic. Part I: insights from trophic relationships in 18 lakes. Environ Toxicol Chem 2010b;29:621–32.
Gantner N, Veillette J, Michaud WK, Bajno R, Muir D, Vincent WF, et al. Physical and biological factors affecting mercury and perfluorinated contaminants in arctic char (*Salvelinus alpinus*) of Pingualuit Crater Lake (Nunavik, Canada). Arctic 2012;65:195–206.
Gilmour CC, Henry EA, Mitchell R. Sulfate stimulation of mercury methylation in freshwater sediments. Environ Sci Technol 1992;26:2281–7.
Goodsite ME, Outridge PM, Christensen JH, Dastoor A, Muir D, Travnikov O, et al. How well do environmental archives of atmospheric mercury deposition in the Arctic reproduce rates and trends depicted by atmospheric models and measurements? Sci Total Environ 2013;452–453:196–207.
Graydon JA, St. Louis VL, Hintelmann H, Lindberg SE, Sandilands KA, Rudd JWM, et al. Long-term wet and dry deposition of total and methyl mercury in the remote boreal ecoregion of Canada. Environ Sci Technol 2008;42:8345–51.
Graydon JA, Emmerton CA, Lesack LFW, Kelly EN. Mercury in the Mackenzie River delta and estuary: concentrations and fluxes during open-water conditions. Sci Total Environ 2009;407:2980–8.
Gregory-Eaves I, Demers MJ, Kimpe L, Krümmel EM, Macdonald RW, Finney BP, et al. Tracing salmon-derived nutrients and contaminants in freshwater food webs across a pronounced spawner density gradient. Environ Toxicol Chem 2007;26: 1100–8.
GSCNational geochemical reconnaissance (NGR). Geological Survey of Canada (GSC), Natural Resources Canada; 2008.
Guo L, Macdonald RW. Source and transport of terrigenous organic matter in the upper Yukon River: evidence from isotope ($\delta^{13}C$, $\Delta^{14}C$, and $\delta^{15}N$) composition of dissolved, colloidal, and particulate phases. Glob Biogeochem Cycles 2006;20:GB2011. http://dx.doi.org/10.1029/2005GB002593.
Halm DR, Dornblaser MM. Water and sediment quality in the Yukon River and its tributaries between Atlin, British Columbia, Canada, and Eagle, Alaska, USA: 2004. U.S. Geological Survey open-file report 2007-1197; 2007. p. 120.
Hamelin S, Amyot M, Barkay T, Wang Y, Planas D. Methanogens: principal methylators of mercury in lake periphyton. Environ Sci Technol 2011;45:7693–700.
Hammerschmidt CR, Fitzgerald WF. Photodecomposition of methylmercury in an Arctic Alaskan lake. Environ Sci Technol 2006;40:1212–6.
Hammerschmidt CR, Fitzgerald WF. Iron-mediated photochemical decomposition of methylmercury in an Arctic Alaskan lake. Environ Sci Technol 2010;44:6138–43.
Hammerschmidt CR, Fitzgerald WF, Lamborg CH, Balcom PH, Tseng CM. Biogeochemical cycling of methylmercury in lakes and tundra watersheds of Arctic Alaska. Environ Sci Technol 2006;40:1204–11.
Hare A, Stern GA, Macdonald RW, Kuzyk ZZ, Wang FY. Contemporary and preindustrial mass budgets of mercury in the Hudson Bay Marine System: The role of sediment recycling.". Sci Total Environ 2008;406:190–204.
Health Canada, Canadian standards ("maximum levels") for various chemical contaminants in foods. Health Canada; 2011 [available online at http://www.hc-sc.gc.ca/fn-an/securit/chem-chim/contaminants-guidelines-directives-eng.php].
Hintelmann H. Use of stable isotopes in mercury research. In: Bank M, editor. Mercury in the environment. University of California Press; 2012.
Hoekstra PF, Braune BM, Elkin B, Armstrong FA, Muir DC. Concentrations of selected essential and non-essential elements in arctic fox (*Alopex lagopus*) and wolverines (*Gulo gulo*) from the Canadian Arctic. Sci Total Environ 2003;309:81–92.
Jackson TA, Muir DCG, Vincent WF. Historical variations in the stable isotope composition of mercury in Arctic lake sediments. Environ Sci Technol 2004;38:2813–21.
Jackson TA, Whittle DM, Evans MS, Muir DCG. Evidence for mass-independent and mass-dependent fractionation of the stable isotopes of mercury by natural processes in aquatic ecosystems. Appl Geochem 2008;23:547–71.
Kirk JL, St. Louis VL. Multiyear total and methyl mercury exports from two major sub-Arctic rivers draining into Hudson Bay, Canada. Environ Sci Technol 2009;43:2254–61.
Kirk JL, Muir DCG, Antoniades D, Douglas MSV, Evans MS, Jackson TA, et al. Response to comment on climate change and mercury accumulation in Canadian high and subarctic lakes. Environ Sci Technol 2011a;45:6705–6.
Kirk JL, Muir DCM, Antoniades D, Douglas MSV, Evans MS, Jackson TA, et al. Climate change and mercury accumulation in Canadian high and subarctic lakes. Environ Sci Technol 2011b;45:964–70.
Klaminder J, Yoo K, Rydberg J, Giesler R. An explorative study of mercury export from a thawing palsa mire. J Geophys Res 2008;113:G04034. http://dx.doi.org/10.1029/2008JG000776.
Kokelj SV, Burn CR. Near-surface ground ice in sediments of the Mackenzie Delta, Northwest Territories, Canada. Permafr Periglac Process 2005;16:291–303.
Kokelj SV, Jenkins RE, Milburn D, Burn CR, Snow N. The influence of thermokarst disturbance on the water quality of small upland lakes, Mackenzie Delta region, Northwest Territories, Canada. Permafr Periglac Process 2005;16:343–53.
Krümmel EM, Macdonald RW, Kimpe LE, Gregory-Eaves I, Demers MJ, Smol JP, et al. Delivery of pollutants by spawning salmon. Nature 2003;425:255–6.
Lahoutifard N, Sparling M, Lean D. Total and methyl mercury patterns in Arctic snow during springtime at Resolute, Nunavut, Canada. Atmos Environ 2005;39: 7597–606.
Landers DH, Gubala C, Verta M, Lucotte M, Johansson K, Vlasova T, et al. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. Atmos Environ 1998;32:919–28.
Landers DH, Simonich SL, Jaffe DA, Geiser LH, Campbell DH, Schwindt AR, et alThe fate, transport, and ecological impacts of airborne contaminants in western national parks (USA). Corvallis, OR: United States Environmental Protection Agency, Office of Research and Development, NHEERL, Western Ecology Division; 2008 [EPA/600/R-07/138].
Lantz TC, Kokelj SV. Increasing rates of retrogressive thaw slump activity in the Mackenzie Delta region, N.W.T., Canada. Geophys Res Lett 2008;35:L06502.
Larose C, Dommergue A, De Angelis M, Cossa D, Averty B, Marusczak N, et al. Springtime changes in snow chemistry lead to new insights into mercury methylation in the Arctic. Geochim Cosmochim Acta 2010;74:6263–75.
Larose C, Dommergue A, Marusczak N, Coves J, Ferrari CP, Schneider D. Bioavailable mercury cycling in polar snowpacks. Environ Sci Technol 2011;45:2150–6.
Lehnherr I, St. Louis VL. Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. Environ Sci Technol 2009;43:5692–8.
Lehnherr I, St. Louis VL, Emmerton CA, Barker JD, Kirk JL. Methylmercury cycling in high arctic wetland ponds: sources and sinks. Environ Sci Technol 2012a;46:10514–22.
Lehnherr I, St. Louis VL, Kirk JL. Methylmercury cycling in high arctic wetland ponds: controls on sedimentary production. Environ Sci Technol 2012b;46:10523–31.
Leitch DR, Carrie J, Lean DRS, Macdonald R, Stern AG, Wang F. The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. Sci Total Environ 2007; 373:178–95.

Lescord GL, Kidd KA, Kirk JL, O'Driscoll NJ, Wang X, Muir DCG. Factors affecting biotic mercury concentrations and biomagnification through lake food webs in the Canadian high Arctic. Sci Total Environ 2015;509–510:195–205. [in this issue].
Lindberg S, Brooks S, Lin C-J, Scott K, Landis M, Stevens R, et al. Dynamic oxidation and gaseous mercury in the Arctic troposphere at polar sunrise. Environ Sci Technol 2002;36:1245–56.
Lindberg S, Bullock R, Ebinghaus R, Engstrom D, Feng XB, Fitzgerald W, et al. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio 2007;36:19–32.
Lindeberg C, Bindler R, Renberg I, Emteryd O, Karlsson E, Anderson NJ. Natural fluctuations of mercury and lead in Greenland lake sediments. Environ Sci Technol 2006;40:90–5.
Lockhart WL, Wilkinson P, Billeck BN, Danell RA, Hunt RV, Brunskill GJ, et al. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. Biogeochemistry 1998;40:163–73.
Lockhart WL, Macdonald RW, Outridge PM, Wilkinson P, DeLaronde JB, Rudd JWM. Tests of the fidelity of lake sediment core records of mercury deposition to known histories of mercury contamination. Sci Total Environ 2000;260:171–80.
Lockhart WL, Stern GA, Low G, Hendzel M, Boila G, Roach P, et al. A history of total mercury in edible muscle of fish from lakes in northern Canada. Sci Total Environ 2005; 351:427–63.
Loseto LL, Lean DRS, Siciliano SD. Snowmelt sources of methylmercury to high arctic ecosystems. Environ Sci Technol 2004a;38:3004–10.
Loseto LL, Siciliano SD, Lean DRS. Methylmercury production in high arctic wetlands. Environ Toxicol Chem 2004b;23:17–23.
Macdonald RW, Barrie LA, Bidleman TF, Diamond ML, Gregor DJ, Semkin RG, et al. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Sci Total Environ 2000;254:93–234.
Michelutti N, Douglas MSV, Smol JP. Diatom response to recent climatic change in a High Arctic lake (Char Lake, Cornwallis Island, Nunavut). Glob Planet Chang 2003;38: 257–71.
Michelutti N, Wolfe AP, Vinebrooke RD, Rivard B, Briner JP. Recent primary production increases in Arctic lakes. Geophys Res Lett 2005;32:1–4.
Møller AK, Barkay T, Hansen MA, Norman A, Hansen LH, Sørensen SJ, et al. Mercuric reductase genes (merA) and mercury resistance plasmids in High Arctic snow, freshwater and sea-ice brine. FEMS Microbiol Ecol 2014;87:52–63.
Muir DCG, Braune BM, DeMarch B, Norstrom R, Wagemann R, Gamberg M, et al. Chapter 3. Ecosystem uptake and effects. In: Jensen J, Adare K, Shearer R, editors. Canadian Arctic Contaminants Assessment Report. Ottawa: Indian and Northern Affairs Canada; 1997. p. 191–294.
Muir DCG, Wang XW, Bright D, Lockhart L, Kock G. Spatial and temporal trends of mercury and other metals in landlocked char from lakes in the Canadian Arctic archipelago. Sci Total Environ 2005;351:464–78.
Muir DCG, Wang X, Yang F, Nguyen N, Jackson TA, Evans MS, et al. Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. Environ Sci Technol 2009;43:4802–9.
Murphy PNC, Ogilvie J, Arp P. Topographic modelling of soil moisture conditions: a comparison and verification of two models. Eur J Soil Sci 2009;60:94–109.
Nasr M, Ogilvie J, Castonguay M, Rencz A, Arp PA. Total Hg concentrations in stream and lake sediments: discerning geospatial patterns and controls across Canada. Appl Geochem 2011;26:1818–31.
NCP Canadian Arctic Contaminants Assessment Report. Northern Contaminants Program (NCP). Ottawa: Indian and Northern Affairs Canada; 1997. p. 460.
NCP Canadian Arctic Contaminants Assessment Report II. Northern Contaminants Program (NCP). Ottawa: Indian and Northern Affairs Canada; 2003.
NCP Canadian Arctic Contaminants Assessment Report III: Mercury in Canada's North. Northern Contaminants Program (NCP). Canada, Ottawa: Aboriginal Affairs and Northern Development; 2012. p. xxiii+276.
NRCan Canada3D — digital elevation model of the Canadian landmass. Natural Resources Canada (NRCan); 2007.
NWT HSS. Increase in mercury levels in Trout Lake, Cli Lake, Ste Therese and Kelly Lake. Consumption advisory released by the NWT Health and Social Services (HSS) on June 16, 2010. [Available online at] http://www.hss.gov.nt.ca/health/environment-and-your-health/mercury-levels-fish, 2010.
Oiffer L, Siciliano SD. Methyl mercury production and loss in Arctic soil. Sci Total Environ 2009;407:1691–700.
Outridge PM, Stern GA, Hamilton PB, Percival JB, McNeely R, Lockhart WL. Trace metal profiles in the varved sediment of an Arctic lake. Geochim Cosmochim Acta 2005; 69:4881–94.
Outridge PM, Sanei H, Stern GA, Hamilton PB, Goodarzi F. Evidence for control of mercury accumulation rates in Canadian High Arctic lake sediments by variations of aquatic primary productivity. Environ Sci Technol 2007;41:5259–65.
Outridge PM, Sanei H, Stern GA, Goodsite M, Hamilton PB, Carrie J, et al. Comment on climate change and mercury accumulation in Canadian high and subarctic lakes. Environ Sci Technol 2011;45:6703–4.
Point D, Sonke JE, Day RD, Roseneau DG, Hobson KA, Vander Pol SS, et al. Methylmercury photodegradation influenced by sea-ice cover in Arctic marine ecosystems. Nat Geosci 2011;4:188–94.
Poulain AJ, Amyot M, Findlay D, Telor S, Barkay T, Hintelmann H. Biological and photochemical production of dissolved gaseous mercury in a boreal lake. Limnol Oceanogr 2004;49:2265–75.
Poulain AJ, Garcia E, Amyot M, Campbell PGC, Raofie F, Ariya PA. Biological and chemical redox transformations of mercury in fresh and salt waters of the High Arctic during spring and summer. Environ Sci Technol 2007a;41:1883–8.
Poulain AJ, Ni Chadhain SM, Ariya PA, Amyot M, Garcia E, Campbell PGC, et al. Potential for mercury reduction by microbes in the High Arctic. Appl Environ Microbiol 2007b;73:2230–8.
Prowse TD, Wrona FJ, Reist JD, Gibson JJ, Hobbie JE, Lévesque LMJ, et al. Climate change effects on hydroecology of arctic freshwater ecosystems. Ambio 2006;35:347–58.
Prowse TD, Furgal C, Bonsal BR, Peters DL. Climate impacts on northern Canada: regional background. Ambio 2009;38:248–56.
Rawson DS. Morphometry as a dominant factor in the productivity of large lakes. Verh Int Ver Theor Angew Limnol 1955:164–75.
Ridley WI, Stetson SJ. A review of isotopic composition as an indicator of the natural and anthropogenic behavior of mercury. Appl Geochem 2006;21:1889–99.
Rigét F, Vorkamp K, Muir D. Temporal trends of contaminants in Arctic char (*Salvelinus alpinus*) from a small lake, southwest Greenland during a warming climate. J Environ Monit 2010;12:2252–8.
Rydberg J, Klaminder J, Rosén P, Bindler R. Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes. Sci Total Environ 2010;408:4778–83.
Sanei H, Goodarzi F. Relationship between organic matter and mercury in recent lake sediment: the physical–geochemical aspects. Appl Geochem 2006;21:1900–12.
Sanei H, Outridge PM, Dallimore A, Hamilton PB. Mercury–organic matter relationships in pre-pollution sediments of thermokarst lakes from the Mackenzie River Delta, Canada: the role of depositional environment. Biogeochemistry 2010:1–16.
Schroeder WH, Anlauf KG, Barrie LA, Lu JY, Steffen A, Schneeberger DR, et al. Arctic springtime depletion of mercury. Nature 1998;394:331–2.
Schuster PF, Striegl RG, Aiken GR, Krabbenhoft DP, Dewild JF, Butler K, et al. Mercury export from the Yukon River Basin and potential response to a changing climate. Environ Sci Technol 2011;45:9262–7.
Scott KJ. Bioavailable mercury in arctic snow determined by a light-emitting mer-lux bioreporter. Arctic 2001;54:92–5.
Sellers P, Kelly CA, Rudd JWM, MacHutchon AR. Photodegradation of methylmercury in lakes. Nature 1996;380:694–7.
Semkin RG, Mierle G, Neureuther RJ. Hydrochemistry and mercury cycling in a High Arctic watershed. Sci Total Environ 2005;342:199–221.
Sherman LS, Blum JD, Johnson KP, Keeler GJ, Barres JA, Douglas TA. Mass-independent fractionation of mercury isotopes in Arctic snow driven by sunlight. Nat Geosci 2010;3:173–7.
Smith SL, Burgess MM. Mapping the sensitivity of Canadian permafrost to climate warming. Interactions between the cryosphere, climate and greenhouse gases. Proceedings of IUGG 99 symposium HS2. Birmingham: IAHS Publication; 1999. p. 71–80.
Smol JP, Douglas MSV. Crossing the final ecological threshold in high Arctic ponds. Proc Natl Acad Sci U S A 2007;104:12395–7.
Soper JH, Powell JMBotanical studies in the Lake Hazen region, northern Ellesmere Island, Northwest Territories, Canada. Ottawa: National Museums of Canada; 1985. p. 67.
Spencer RGM, Aiken GR, Wickland KP, Striegl RG, Hernes PJ. Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. Glob Biogeochem Cycles 2008;22:GB4002. http://dx.doi.org/10.1029/2008GB003231.
St. Louis VL, Rudd JWM, Kelly CA, Bodaly RA, Paterson MJ, Beaty KG, et al. The rise and fall of mercury methylation in an experimental reservoir. Environ Sci Technol 2004;38: 1348–58.
St. Louis VL, Sharp MJ, Steffen A, May A, Barker J, Kirk JL, et al. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere island in the Canadian high Arctic. Environ Sci Technol 2005;39:2686–701.
Stern GA, Sanei H, Roach P, Dalaronde J, Outridge PM. Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a Subarctic lake in Yukon, Canada: further evidence toward the algal-mercury scavenging hypothesis. Environ Sci Technol 2009;43:7684–90.
Stern GA, Roach P, Tomy G, Dickson C. Trace metals and organohalogen contaminants in fish from selected Yukon lakes: a temporal and spatial study. Synopsis of research conducted under the 2009–2010 Northern Contaminants Program. Canada, Ottawa: Indian and Northern Affairs; 2010. p. 179–85.
Swanson HK, Kidd KA. Mercury concentrations in arctic food fishes reflect the presence of anadromous arctic charr (*Salvelinus alpinus*), species, and life history. Environ Sci Technol 2010;44:3286–92.
Swanson HK, Kidd KA, Babaluk JA, Wastle RJ, Yang PP, Halden NM, et al. Anadromy in Arctic populations of lake trout (*Salvelinus namaycush*): otolith microchemistry, stable isotopes, and comparisons with Arctic char (*Salvelinus alpinus*). Can J Fish Aquat Sci 2010;67:842–53.
Swanson HK, Gantner N, Kidd KA, Muir DCG, Reist JD. Comparison of mercury concentrations in landlocked, resident, and sea-run fishes (*Salvelinus* spp.) from Nunavut, Canada. Environ Toxicol Chem 2011;30:1459–67.
Thompson W. Climate. Resource description and analysis: Ellesmere Island, National Park Reserve. National Resource Conservation Selection, Prairie and Northern Region, Parks Canada, Department of Canadian Heritage, Winnipeg, Manitoba; 1994. p. 78.
Tseng CM, Lamborg C, Fitzgerald WF, Engstrom DR. Cycling of dissolved elemental mercury in Arctic Alaskan lakes. Geochim Cosmochim Acta 2004;68:1173–84.
van der Velden S, Reist JD, Babaluk JA, Power M. Biological and life-history factors affecting total mercury concentrations in Arctic charr from Heintzelman Lake, Ellesmere Island, Nunavut. Sci Total Environ 2012;433:309–17.
van der Velden S, Dempson JB, Evans MS, Muir DCG, Power M. Basal mercury concentrations and biomagnification rates in freshwater and marine food webs: effects on Arctic charr (*Salvelinus alpinus*) from eastern Canada. Sci Total Environ 2013a;444: 531–42.
van der Velden S, Evans MS, Dempson JB, Muir DCG, Power M. Comparative analysis of total mercury concentrations in anadromous and non-anadromous Arctic charr (*Salvelinus alpinus*) from eastern Canada. Sci Total Environ 2013b;447:438–49.
van der Velden S, Dempson JB, Power M. Comparing mercury concentrations across a thirty year time span in anadromous and non-anadromous Arctic charr from Labrador, Canada. Sci Total Environ 2015;509–510:165–74. [in this issue].

Vost EE, Amyot M, O'Driscoll NJ. Chapter 5. Photoreactions of mercury in aquatic systems. In: Cai Y, Liu N, O'Driscoll NJ, editors. Advances in environmental chemistry and toxicology of mercury. John Wiley and Sons; 2011. p. 586.
Watras CJ, Back RC, Halvorsen S, Hudson RJM, Morrison KA, Wente SP. Bioaccumulation of mercury in pelagic freshwater food webs. Sci Total Environ 1998;219:183–208.
Welch HE. Ecology of Chironomidae (Diptera) in a polar lake. J Fish Res Board Can 1976; 33:227–47.
Wiener JG, Krabbenhoft DP, Heinz GH, Scheuhammer AM. Ecotoxicology of mercury. In: Hoffman DJ, Rattner BA, Burton GA, Cairns J, editors. Handbook of ecotoxicology. Boca Raton: Lewis Publishers; 2003. p. 409–63.
Wolfe AP, Miller GH, Olsen CA, Forman SL, Doran PT, Holmgren SU. Geochronology of high latitude lake sediments. In: Pienitz R, Douglas MSV, Smol JP, editors. Developments in paleoenvironmental research, vol. 8. New York: Springer; 2004. p. 19–52.
Woo MK. Hydrology of a drainage basin in the Canadian High Arctic. Ann Assoc Am Geogr 1983;73:577–96.
Yin R, Feng X, Shi W. Application of the stable-isotope system to the study of sources and fate of Hg in the environment: a review. Appl Geochem 2010;25:1467–77.
Zhang H. Photochemical redox reactions of mercury. Struct Bond 2006;120:37–79.