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Review

Mercury in the marine environment of the Canadian Arctic: Review of recent findings

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HIGHLIGHTS

- The water column in Arctic marine waters is important for mercury methylation.
- Mercury deposited on marine snow pack is rapidly re-emitted to the atmosphere.
- Rates of mercury biomagnification were similar across Arctic marine food webs.
- Mercury is higher in Beaufort Sea biota than in other Canadian Arctic areas.
- Mercury in some marine biota has increased in recent decades.

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ABSTRACT

This review summarizes data and information which have been generated on mercury (Hg) in the marine environment of the Canadian Arctic since the previous Canadian Arctic Contaminants Assessment Report (CACAR) was released in 2003. Much new information has been collected on Hg concentrations in marine water, snow and ice in the Canadian Arctic. The first measurements of methylation rates in Arctic seawater indicate that the water column is an important site for Hg methylation. Arctic marine waters were also found to be a substantial source of gaseous Hg to the atmosphere during the ice-free season. High Hg concentrations have been found in marine snow as a result of deposition following atmospheric mercury depletion events, although much of this Hg is photoreduced and re-emitted back to the atmosphere. The most extensive sampling of marine sediments in the Canadian Arctic was carried out in Hudson Bay where sediment total Hg (THg) concentrations were low compared with other marine regions in the circumpolar Arctic. Mass balance models have been developed to provide quantitative estimates of THg fluxes into and out of the Arctic Ocean and Hudson Bay.
Several recent studies on Hg biomagnification have improved our understanding of trophic transfer of Hg through marine food webs. Over the past several decades, Hg concentrations have increased in some marine biota, while other populations showed no temporal change. Marine biota also exhibited considerable geographic

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variation in Hg concentrations with ringed seals, beluga and polar bears from the Beaufort Sea region having higher Hg concentrations compared with other parts of the Canadian Arctic. The drivers of these variable patterns of Hg bioaccumulation, both regionally and temporally, within the Canadian Arctic remain unclear. Further research is needed to identify the underlying processes including the interplay between biogeochemical and food web processes and climate change.

Contents

1. Introduction

The marine environment in the Canadian Arctic is truly vast and diverse. It includes deep basins and large shelves of the Arctic Ocean, many fjords, channels and straits in the Arctic Archipelago, Hudson Bay (the largest northern inland sea) and large, productive polynyas such as the North Water Polynya in Baffin Bay and the Bathurst Polynya in the Beaufort Sea. Over the last two decades, investigations of mercury (Hg) in these marine ecosystems have largely focussed on marine mammals and birds because of their dietary and cultural importance for northern Aboriginal peoples and the presence of elevated Hg concentrations in some animals. Marine mammals such as seals, beluga (*Delphinapterus leucas*), and polar bears (*Ursus maritimus*) generally have higher concentrations of Hg than terrestrial mammals and

freshwater fish, and this is related (at least in part) to their higher trophic position in marine food webs (Fisk et al., 2003; Muir et al., 1999). The potential health effects of environmental contaminants in human consumers of marine and other species in the Canadian Arctic have been previously reviewed (Donaldson et al., 2010) and will not be discussed further here.

Previous studies under Canada's Northern Contaminants Program (NCP) identified geographic variation in Hg bioaccumulation among populations of marine species, although the factors driving these differences remain poorly resolved. Annual monitoring of key marine species during Phase III (2002 to 2009) of the NCP has strengthened the temporal trend datasets for the marine environment. Those datasets have shown recent increases in Hg concentrations in some Arctic animals but not in others. The reasons for these varying trends among Arctic species and populations are unclear but are likely related, at least in part, to changes in Hg deposition and, in part, to changes in the Hg cycle after deposition. Research conducted since the last *Canadian Arctic Contaminants Assessment Report* (*CACAR II*) (Fisk et al., 2003) suggests that climate change may be affecting marine food webs with consequences for Hg bioaccumulation in seabirds and seals. In this review, we summarize recent data and information for Hg in both abiotic and biotic compartments of the marine environment in the Canadian Arctic. Recent progress on our understanding of the biological effects of Hg in fish and wildlife in the Canadian Arctic is reviewed by Scheuhammer et al. (2015-in this issue).

2. Overview of the mercury cycle in the Arctic marine environment

The movement of Hg through the marine environment is complex because of the sheer size and open-nature of the system, the multiple pathways and transformations that deliver and export Hg, and the diverse habitats, which include estuaries, continental shelves, deep ocean basins, and sea ice, each of which possesses different conditions for Hg processing. In addition, it is likely that Hg cycling in the Arctic is strongly affected by environmental characteristics such as seasonality in primary production and light (ranging from 24-hour darkness to 24-hour sunlight), the extent of ocean ice cover, the intensity and timing of atmospheric mercury depletion events (AMDEs), and proximity of large river inputs (Douglas et al., 2012). There has long been limited empirical information on Hg cycling in the Arctic marine environment (Macdonald and Loseto, 2010), with the result that concepts of its cycle have been extrapolated from knowledge developed through studies in other oceans (e.g. Fitzgerald et al., 2007; Morel et al., 1998; Sunderland and Mason, 2007). Recently, significant progress has been made in understanding sources of methylmercury (MeHg), the form of greatest toxicological concern, following the discovery that it is produced from inorganic Hg within the oxic water column. Profiles of total Hg and MeHg collected in the Mediterranean Sea, the North Pacific Ocean and the Southern Ocean (Cossa et al., 2009, 2011; Sunderland et al., 2009) all show a strong connection between MeHg and organic regeneration indicated by nutrient maxima/oxygen minima. We now know that methylation processes take place within the water column of the Arctic Ocean and its marginal seas, and that the resultant concentrations of MeHg depend greatly on local processes including organic matter remineralization, which favors methylation, and solar radiation which favors demethylation (Kirk et al., 2008, 2012; Lehnherr et al., 2011; St. Louis et al., 2007; Wang et al., 2012).

Atmospheric, terrestrial, and oceanic pathways deliver Hg to Arctic marine waters, primarily as divalent inorganic Hg [Hg(II)] (Fig. 1). In marine waters, Hg(II) is sequestered, transformed, or removed from the system by: 1) reduction to elemental Hg [Hg(0)] and evasion to the atmosphere; 2) sedimentation of particulate-bound Hg; 3) transformation to monomethylmercury (MeHg) and dimethylmercury (Me_2Hg); and, 4) export to the Atlantic Ocean via ocean currents and ice. The production of MeHg and Me_2Hg may also occur in anoxic sediments (Fitzgerald et al., 2007; Mason et al., 2006). Methylmercury in the ocean water column can be broken down to Hg(II) by photodemethylation or by biotic demethylation (Lehnherr et al., 2011). Although it is impeded by ice cover during the long Arctic winter, evasion of Hg(0) from surface waters to the atmosphere is an important

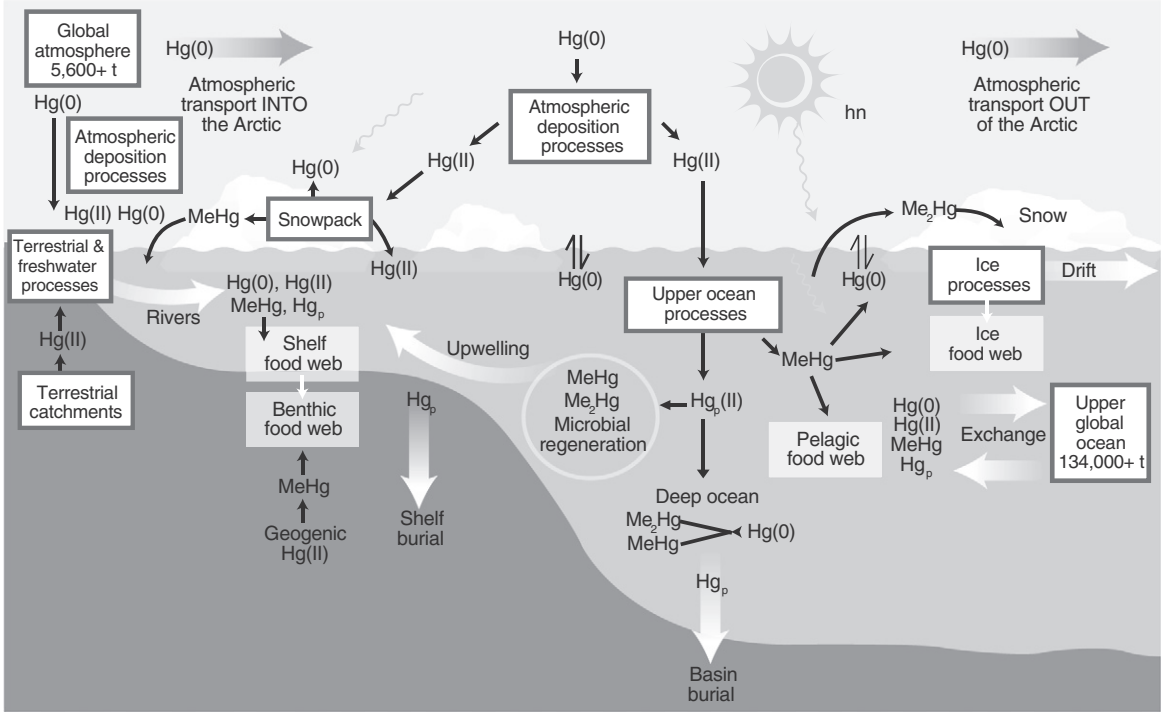

Fig. 1. Schematic diagram of major pathways and transformations in the Hg cycle for Arctic marine ecosystems. Large shaded arrows refer to atmospheric or oceanic transport pathways that exchange Hg with the global environment and move Hg between reservoirs within the Arctic Ocean. Small black arrows refer to biogeochemical processes that transform Hg into different species.
Source: AMAP (2011).

flux driven by microbial or light-induced processes (Andersson et al., 2008; Fitzgerald et al., 2007; Sommar et al., 2010; Sunderland and Mason, 2007). It has been proposed that sea ice may be important habitat for Hg cycling in the Arctic marine environment (Chaulk et al., 2011; Macdonald and Loseto, 2010; Poulain et al., 2007a).

Algae and bacteria are the main entry points for uptake of aqueous MeHg in marine food webs (Atwell et al., 1998; Campbell et al., 2005). These microorganisms transfer MeHg to zooplankton in the water column, to benthic invertebrates on sediment and rock substrates, and to crustaceans such as amphipods and copepods that are associated with sea ice. Methylmercury is then further biomagnified to higher trophic level consumers, namely fish, marine mammals, and seabirds.

3. Speciation of mercury in Arctic marine waters

An extensive survey was recently conducted of water-column concentrations of total Hg (THg), gaseous elemental Hg (GEM), and methylated Hg (both MeHg and Me_2Hg) throughout the Canadian Arctic Archipelago and Hudson Bay to examine potential zones of production and/or destruction of different Hg species (Kirk et al., 2008). Concentrations of THg were low throughout the water column in both the Arctic Archipelago and Hudson Bay (mean ± standard deviation: 0.39 ± 0.40 and 0.42 ± 0.53 ng L^{-1}, respectively). Concentrations of GEM were low in surface waters and varied little among sites, averaging 25.4 ± 10.2 pg L^{-1} in the Arctic Archipelago and 29.6 ± 5.0 pg L^{-1} in Hudson Bay. In deeper regions of the water column, concentrations of GEM were variable, ranging from below the method detection limit to 133 pg L^{-1}, and averaging 34.3 ± 29.7 pg L^{-1} in the Arctic Archipelago and 26.5 ± 24.5 pg L^{-1} in Hudson Bay. In addition, concentrations of GEM at different depths within the same site often varied greatly. Therefore, biotic and/or abiotic processes responsible for net GEM production varied both geographically and with depth in the water column. Although reduction of Hg(II) is likely the dominant source of GEM in marine waters, photodegradation of MeHg (Chen et al., 2003) and Me_2Hg at the surface as well as biotic and/or abiotic reductive demethylation may also produce GEM deep in the water column (Mason et al., 1998).

Throughout both the Arctic Archipelago and Hudson Bay, concentrations of methylated Hg and Me_2Hg were generally low in surface waters (23.8 ± 9.9 and 4.7 ± 4.4 pg L^{-1}, respectively) but increased with depth (maximum: 178 and 170 pg L^{-1}, respectively; mean: 70.3 ± 37.3 and 56.8 ± 37.8 pg L^{-1}, respectively) (Kirk et al., 2008). This suggests that methylated Hg species are produced in intermediate Arctic marine waters and/or sediments. In addition, the percent of THg in a methylated form was high (maximum: 66%; mean: 28 ± 16%) and was associated with extremely low concentrations of THg at mid and bottom depths. Similarly high percentages of THg as MeHg were observed in deep waters of the Southern Ocean (Cossa et al., 2011). For the Arctic Ocean, oceanographic processes, such as water regeneration and vertical mixing, were shown to affect Hg distribution in marine waters (Kirk et al., 2008). In particular, the rapid kinetics measured for methylation and demethylation of Hg(II) (Lehnherr et al., 2011) strongly suggests that local processes likely drive MeHg concentrations and exposure, and THg and MeHg profiles collected in the southern Beaufort Sea support this hypothesis (Wang et al., 2012). Production of MeHg in intermediate waters where organic matter is regenerated may, therefore, be an important source of MeHg to organisms like zooplankton which feed in the surface mixed layer, where primary production is generally greatest (Michel et al., 2006). Me_2Hg may also evade to the atmosphere to be deposited on land, undergoing decomposition by sunlight (Fig. 1) (Niki et al., 1983a,b; St. Louis et al., 2007).

Instantaneous fluxes of gaseous Hg species from the ocean to the atmosphere were calculated to determine if Arctic marine waters are a source for atmospheric Hg. Ocean–atmosphere fluxes of both GEM and Me_2Hg were high (range: 2.6–388 and 0.2–176 ng m^{-2} day^{-1}, respectively; average: 130 ± 138 and 27.3 ± 47.8 ng m^{-2} day^{-1}, respectively), demonstrating that marine waters of the Arctic Archipelago and Hudson Bay region are a substantial source of gaseous Hg to the atmosphere during the ice-free season (Kirk et al., 2008). Likewise, waters of the western Arctic Ocean in summer tend to be in a state of over-saturation, with sea-ice at times inhibiting the evasion of Hg(0) to the atmosphere (Andersson et al., 2008). These authors also showed that the Mackenzie River plume exhibits high dissolved Hg(0), consistent with recent model estimates showing that Arctic rivers are major sources of Hg to coastal regions (Fisher et al., 2012). Reduction of this riverine Hg may, therefore, provide the means to evade a portion to the atmosphere, thus reducing the input of Hg from land to ocean. Interestingly, average ocean–atmosphere GEM fluxes in these regions of the Arctic were higher than those calculated previously for the North Atlantic, Mediterranean, and Baltic waters (2.8–94.7 ng m^{-2} day^{-1}) (Cossa et al., 1997; Kuss and Schneider, 2007; Mason et al., 2001). Average ocean–atmosphere Me_2Hg fluxes for the Arctic Archipelago and Hudson Bay were also higher than previous estimates for the Arctic, Antarctic, and Atlantic Oceans (2.8–4.9 ng m^{-2} day^{-1}) (Pongratz and Heumann, 1998a). Further, the Arctic ocean–atmosphere fluxes of GEM and Me_2Hg were determined during the open-water season and are likely lower than fluxes directly after ice-out when substantial degassing may occur of gaseous Hg species trapped under the sea ice throughout winter (St. Louis et al., 2007). In fact, concentrations of Me_2Hg (11.1 ± 4.1 pg L^{-1}) and GEM (129 ± 36 pg L^{-1}) measured by St. Louis et al. (2007) under the sea ice near Resolute Bay (Nunavut) were higher than those measured in ice-free surface waters of the Arctic Archipelago and Hudson Bay.

4. Sea ice and snowpack

4.1. Mercury in Arctic marine snow

Recent investigations of snow on sea ice and in Arctic coastal areas suggest that inorganic Hg accumulation is enhanced in marine snow relative to the terrestrial environment (Poulain et al., 2007b; St. Louis et al., 2007). Concentrations of THg in excess of 50 ng L^{-1} have been commonly reported for snow on sea ice (Kirk et al., 2006; Lu et al., 2001; St. Louis et al., 2007) but are rare for inland snowpack and have not been observed in glacier ice or snow in the Canadian Arctic (see Gamberg et al., in this issue). Higher snow THg concentrations may occur in the marine environment because of AMDEs which are a result of atmospheric photochemical reactions involving marine halogens (Ariya et al., 2004; Lindberg et al., 2002; Simpson et al., 2007). Marine halogens, particularly chloride, may also affect Hg transformations in the snowpack by limiting Hg evasion through the formation of chloride–Hg complexes that are less susceptible to photoreduction (Bartels-Rausch et al., 2011; Poulain et al., 2007c; St. Louis et al., 2007) or by favoring the photooxidation of GEM (Amyot et al., 2003; Lalonde et al., 2004). In an extensive snow survey in the Canadian High Arctic, St. Louis et al. (2007) found a strong positive correlation between snow chloride and THg concentrations consistent with experimental observations of a chloride effect on Hg(II) retention. Interestingly, MeHg concentrations in snowpacks were not related to chloride concentration (St. Louis et al., 2007).

In a laboratory-based study, Mann et al. (in this issue) determined that Hg photoreduction rate constants in snow from Resolute Bay, NU, ranged between 0.07–0.55 h^{-1} for snow that was irradiated with 1.26–5.78 W m^{-2} of constant ultra violet (UV) irradiation (280–400 nm) while frozen, and 0.03–0.57 h^{-1} for snow that was melted before being irradiated, assuming pseudo-first order reaction kinetics. It was further determined that Hg reduction rate constants in Arctic snow do not have a simple linear relationship with increasing UV intensity, but rather that the highest rates of Hg photoreduction are found at low and high UV intensities, with a minimum located between 3 and 4 W m^{-2}. The total amount of Hg photoreduced in snow does, however, increase linearly with increasing UV intensity. The

chemical composition of the snow appears to influence both the rate constant and the proportion of Hg in snow that is photoreducible. Snow with higher chloride concentrations had a lower percentage of photoreduced Hg, while the rate constant for photochemical oxidation of Hg(0) was higher in snow with the highest chloride content. Rate constants for Hg(0) photooxidation in melted snow exposed to 5.78 W m^{-2} UV radiation ranged between 0.09 and 0.17 h^{-1}. It was further noted that melting the snow appeared to influence the proportion of Hg that was photoreducible. In addition, when comparing frozen and melted snow samples, frozen snow generally had a greater overall photoreducible Hg amount compared to melted snow of the same composition. The photochemical dynamics of mercury in snow are further discussed in a recent review by Mann et al. (2014).

While THg is often most concentrated in the surface layer, the middle stratum and depth hoar—a layer of large crystals at the base of the snowpack—can also be dominant Hg reservoirs in marine snow (Table 1). High THg in lower snowpack layers may be due to Hg(II) deposited during AMDEs which penetrates into snowpacks (St. Louis et al., 2005). Strong winds may also cause wind pumping and enhance the transfer of reactive gaseous Hg (RGM) and particulate Hg (PHg) into deeper snow layers. Burial through snow accumulation, sublimation, condensation, and ice-layer formation are other processes that promote Hg retention in the snowpack (Douglas et al., 2008, 2012). In contrast with THg, average MeHg concentrations were generally low (<0.1 ng L^{-1}) in both surface and deeper layers of marine snowpack on Hudson Bay and in the Canadian High Arctic (Kirk et al., 2006; St. Louis et al., 2007).

Areal loads of THg and MeHg in snow were estimated to determine their importance as a source of Hg to Arctic marine waters during spring melt. In the High Arctic, median loads in snowpacks were estimated at 5.2 mg THg ha^{-1} and 0.03 mg MeHg ha^{-1} (St. Louis et al., 2007), while in Hudson Bay, the average snow THg loading was 2.1 mg ha^{-1} (Kirk et al., 2006). These areal loads from snow were relatively low in comparison to annual wet deposition rates at lower North American latitudes which range from 22 to 200 mg THg ha^{-1} (Mercury Deposition Network data, as cited in St. Louis et al., 2007). These authors concluded that, overall, snow likely contributes low amounts to the marine pools of Hg in the Arctic Archipelago and Hudson Bay (Kirk et al., 2006; St. Louis et al., 2007).

4.2. Rapid re-emission of mercury from snow following Atmospheric Mercury Depletion Events (AMDEs)

Due to the deposition of atmospheric Hg(II) to snowpacks during AMDEs, average THg concentrations in surface snow collected 1 km offshore on Hudson Bay sea ice near Churchill, Manitoba, in the spring of 2003 and 2004, as well as THg measured in snow samples from different layers of snowpacks at sites located 2.5, 5, and 7 km from the shoreline in the spring of 2004, were quite high and variable in both years (in 2003: 111.4 ± 161.2 ng L^{-1}, n = 23; in 2004: 40.7 ± 69.7 ng L^{-1}, n = 59) (Kirk et al., 2006).

In spring of 2004, atmospheric Hg species were continuously monitored in surface snow at the site 1 km offshore on Hudson Bay sea ice (Kirk et al., 2006). At this site, concentrations of THg in snow averaged 67.7 ± 97.7 ng L^{-1} during AMDEs. However, following the end of each AMDE, average concentrations of THg in surface snow declined dramatically and, by four or more days after AMDEs, were only 4.25 ± 1.85 ng L^{-1}. Total Hg concentrations in meltwater collected at spring snowmelt were low in both years. In 2003, THg concentrations in two meltwater samples were only 7.54 and 3.49 ng L^{-1} respectively ($n = 2$), and in 2004, THg concentrations in meltwater averaged 3.31 ± 1.35 ng L^{-1} ($n = 4$). Although AMDEs resulted in deposition of Hg(II) into the upper layers of the snowpack, they did not alter MeHg concentrations in snow because GEM is not transformed directly to MeHg. In fact, MeHg concentrations in snow were often below the method detection limit of 0.015 ng L^{-1}. On several days following snowfall events, wet precipitation appeared to increase MeHg concentrations in surface snow to between approximately 0.06–0.11 ng L^{-1} ($n = 30$).

4.3. Distribution of mercury in Arctic sea ice

A detailed study of Hg dynamics in Arctic sea ice conducted in the Beaufort Sea by Chaulk et al. (2011) sampled a range of ice types: newly formed ice, first year ice (both drifting and landfast), and multiyear ice. Despite the variation of ice types, ice characteristics (thickness, stage of ice formation, extent of snow cover) and ambient air temperatures, THg in ice was consistently low (0.5–4 ng L^{-1}), with the highest concentrations found in the surface layer. Local AMDEs observed at the time of sampling did not appear to strongly impact THg concentrations in new ice or surface seawater. However, brine in the sea ice was substantially more concentrated in THg (2.6–71.2 ng L^{-1}), with higher concentrations found in more saline brines. The formation of brine pockets and channels was found to be an important process for Hg movement within the ice pack.

Sea-ice accumulation of Hg may potentially be driven by three major processes: 1) freeze rejection of Hg from seawater; 2) scavenging of atmospheric Hg by exposed ice surfaces; or, 3) leaching of Hg from overlying snow (Chaulk et al., 2011). Evidence collected from the ice survey in the Beaufort Sea suggested that freeze rejection from seawater

Table 1
Comparison of THg concentrations in different layers of the snowpack (surface [S], middle stratum [M], depth hoar [D]) at various sea ice locations in the Canadian Arctic. Observations are presented in order of increasing concentrations (mean ± 1 standard deviation, *n* in parentheses) in the surface layer.
Modified from AMAP (2011).

Location	Date	Snow THg concentration (ng L^{-1})			Rank of snow strata	Reference
		Surface	Middle stratum	Depth hoar		
Resolute, NU	June 9, 2004	1.8 ± 0.6 (3)	4.9 ± 0.5 (3)	45.2 ± 13.1 (3)	D > M > S	Poulain et al. (2007b)
Allman Bay, NU	May 10, 2004	3.6 (1)	0.3 (1)	0.6 (1)	S > D > M	St. Louis et al. (2007)
Talbot Inlet, NU	May 10, 2004	4.5 (1)	0.4 (1)	7.9 (1)	D > S > M	St. Louis et al. (2007)
Alert, NU	April 12, 2002	5.7 (1)	0.4 (1)	2.5 (1)	S > D > M	St. Louis et al. (2005)
Buchannan Bay, NU	May 10, 2004	6.1 (1)	1.3 (1)	5.4 (1)	S > D > M	St. Louis et al. (2007)
Norwegian Bay, NU	May 16, 2004	8.0 (1)	8.1 (1)	1.2 (1)	M > S > D	St. Louis et al. (2007)
Alert, NU	April 22, 2002	11.1 (1)	21.1 (1)	1.3 (1)	M > S > D	St. Louis et al. (2005)
Eureka Sound, NU	May 16, 2004	15.9 (1)	1.4 (1)	9.8 (1)	S > D > M	St. Louis et al. (2007)
Bay Fiord, NU	May 16, 2004	19.8 (1)	18.1 (1)	48.6 (1)	D > S > M	St. Louis et al. (2007)
Churchill, MB	March 31, April 16, May 22–23, 2004	21.4 ± 27.2 (9)	15.2 ± 13.8 (9)	10.6 ± 9.6 (9)	S > M > D	Kirk et al. (2006)
Wellington Channel, NU	May 16, 2004	66.4 (1)	3.3 (1)	2.3 (1)	S > M > D	St. Louis et al. (2007)
Jones Sound, NU	May 11, 2004	78.2 (1)	8.0 (1)	17.1 (1)	S > D > M	St. Louis et al. (2007)
Makinson Inlet, NU	May 10, 2004	150 (1)	253 (1)	281 (1)	D > M > S	St. Louis et al. (2007)

Note: Concentrations in each layer were measured in the same snowpack on a single sampling date except observations at Churchill which are means of multiple sampling dates and/or snowpacks.

and, in some cases, leaching from the overlying snow contributed to the observed Hg concentrations. Surface enrichment of sea ice was a ubiquitous phenomenon, probably due to the enrichment of brine and particles in surface frazil ice. No evidence was found for efficient scavenging of atmospheric Hg in newly formed frazel ice, although Douglas et al. (2008) observed very high THg concentrations in ice crystal formations (surface hoar, frost flowers, diamond dust) on the Alaskan coast. Brine pockets and channels, which concentrate Hg, are also important microbial niches in sea ice. It has been proposed that these Hg-rich environments may be key sites for microbial transformation and uptake of Hg into the pelagic, ice-based food web (Chaulk et al., 2011; Macdonald and Loseto, 2010; Poulain et al., 2007a).

5. Marine sediments

Little information exists on Hg concentrations in marine sediments from the Canadian Arctic, and the largest dataset currently available is for Hudson Bay. The first sediment investigations in Hudson Bay were conducted by Lockhart et al. (1998) and Stewart and Lockhart (2005) who reported THg concentrations in three cores taken from the southeastern region in 1992 and 1993. An additional 13 cores were collected in 2005 by Hare et al. (2008, 2010) (Fig. 2).

In Hudson Bay, sediment THg ranged from 8 to 58 ng g^{-1} dry weight (dw) with a mean of 26 ng g^{-1} ($n = 325$) (Hare et al., 2008, 2010; Lockhart et al., 1998; Stewart and Lockhart, 2005). These values were at the low end of concentrations observed in other sediment studies on the Arctic Ocean, the Beaufort Shelf, and along the Greenland coast (Fig. 3). The Hudson Bay values were also low compared to THg concentrations in freshwater sediments observed across the Canadian Arctic (see Chételat et al., in this issue). Such low concentrations of sediment Hg in Hudson Bay likely reflect low geological inputs from the watershed and low concentrations of incoming particulate matter accumulating in the sediments.

Spatial variation of THg in Hudson Bay sediments appears to be largely controlled by the sorting of Hg-bearing particles from the water column. Surface THg concentrations were positively related to the fraction of surficial silt and clay (percent < 63 μm) and to water depth, but not distance offshore. Two deepwater cores from depths >400 m in the Hudson Strait were exceptions and had low silt and clay content and low sediment Hg concentrations for their depth. Sediments in the Hudson Strait may receive particles from a different source such as ice-rafted particulate matter from the shallow Foxe Basin (Kuzyk et al., 2008).

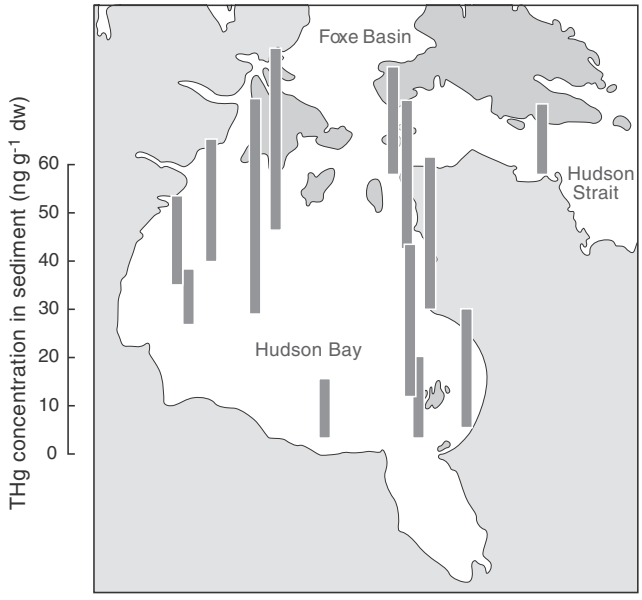

Fig. 2. Concentrations of THg (ng g^{-1} dw) in surface sediment cores sampled from various locations in Hudson Bay and Hudson Strait.
Data from Hare et al. (2010).

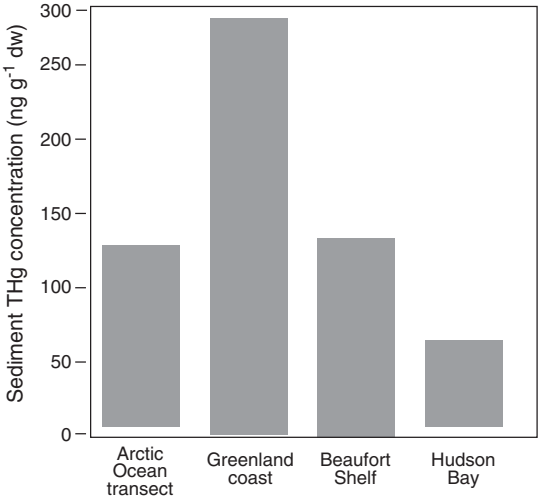

Fig. 3. Ranges of sediment THg concentrations in Hudson Bay (Hare et al., 2010) and other marine regions in the circumpolar Arctic, specifically the Arctic Ocean (Gobeil et al., 1999), the Beaufort Shelf (Macdonald and Thomas, 1991), and the Greenland coast (Asmund and Nielsen, 2000).

Vertical profiles of THg in Hudson Bay sediments were examined for historical changes related to atmospheric deposition of anthropogenic Hg (Hare et al., 2010). Sediment mixing processes were modeled to determine the simplest chronology of Hg inputs that could explain the observed vertical THg profiles in Hudson Bay sediments. The model assumed steady sedimentation and mixing rates over time, and negligible diagenetic alteration of Hg relative to biomixing. These assumptions were supported by several recent geochemical studies of the same core set (Kuzyk et al., 2008, 2009). The modeled chronologies demonstrated that stable Hg concentrations existed in most cores at sediment depths accumulated before the industrial age (circa 150 years ago). In these cores, sediment THg fluxes increased during the early years of the Industrial Era—1870 to 1930—followed by stable or declining Hg inputs toward the end of the 20th Century. The flux patterns were consistent with general historical patterns of anthropogenic Hg emissions in North America. Several other cores in Hudson Bay displayed consistent increases in THg concentration in deep sediment accumulated before the Industrial Era. Concomitant increases in the proportion of marine carbon in some of the latter cores suggest that natural changes in the materials incorporated into sediments can increase THg concentrations by as much as those increases sustained by anthropogenic loading. Based on differences between background and surface THg concentrations, Hare et al. (2010) estimated that Hudson Bay has accumulated 52–80 t of anthropogenic Hg in its sediments since the onset of the Industrial Era, an amount deemed small relative to recent annual rates of anthropogenic Hg emissions in North America.

6. Mass balance models

To date, two mass balance mercury budgets have been proposed for the Arctic Ocean (Fisher et al., 2012; Outridge et al., 2008) and one for Hudson Bay (Hare et al., 2008).

6.1. Mass balance estimates of mercury for the Arctic Ocean

Outridge et al. (2008) calculated a Hg budget using an inventory of THg in the Arctic Ocean based on a reasonably well-balanced sediment and water budget (Stein and Macdonald, 2004), fluxes for various

pathways estimated from THg concentrations, fluxes of media obtained through a comprehensive literature survey, and a modified version of the Global/Regional Atmospheric Heavy Metal (GRAHM) model (Dastoor and Larocque, 2004) to estimate the net atmospheric flux of THg into the Arctic Ocean. They concluded that atmospheric deposition and coastal erosion were the two largest sources of Hg to the Arctic Ocean, contributing 48% (98 t y^{-1}) and 23% (47 t y^{-1}), respectively, of the total annual Hg input. The GRAHM model incorporated a re-emission term of 133 t y^{-1} (volatilization of Hg from snowpack, snowmelt, and runoff, equivalent to 55% of gross deposition) and evasion term of 12 t y^{-1}. Rivers were a minor source, collectively contributing only 6% (13 t y^{-1}) of the total annual Hg input. Sedimentation was the largest Hg sink, removing 59% (182 t y^{-1}) from the Arctic Ocean by all processes.

In contrast, computations made by Fisher et al. (2012) using a coupled ocean–atmosphere model (GEOS-Chem) suggested that rivers (80 t y^{-1}) were the most important source of Hg to the Arctic Ocean (70°–90° N), followed by the atmosphere (45 t y^{-1} net deposition [25 t y^{-1} through direct deposition and 20 t y^{-1} through meltwater inputs of atmospheric Hg deposited on snow/ice surfaces]) and coastal erosion (15 t y^{-1}). Further, Fisher et al. (2012) reported that evasion of Hg from the surface ocean (90 t y^{-1}) and particle settling (43 t y^{-1}) were the most important processes removing Hg from surface ocean waters. However, it is important to understand that because of a lack of data for vast regions of the Arctic, these estimates cannot yet be validated using field measurements and represent an evolving understanding of the various Hg sources and sinks to the Arctic Ocean. Further, the large difference between model results and field measurements of atmospheric inputs in these budgets underscores what is widely regarded as one of the central uncertainties in marine Arctic Hg science—what is the actual net deposition from the atmosphere that accumulates in the water? More work using a variety of methodological approaches is essential to resolve the uncertainty in the atmospheric Hg contribution to Arctic ecosystems, especially since this flux should be most immediately affected by emission controls.

6.2. Mercury budget for Hudson Bay

Mass balances of THg were modeled for Hudson Bay to investigate pre-industrial and contemporary sources and pathways of THg and their sensitivity to projected climate change (Hare et al., 2008). Estimates of atmospheric deposition, mass exchange of marine water, river inputs, and sedimentation of THg were primarily based on measurements taken within the Hudson Bay system by Hare et al. (2008), Kirk et al. (2006), and Sanei et al. (2010), while estimates of Hg fluxes from coastal erosion and surface water evasion were modeled from measurements taken in similar marine environments (Hare et al., 2008).

The net Hg influx to and flux out of Hudson Bay in pre-industrial times were both estimated at 3.4 t y^{-1} and appear to have been in a steady state over decades to centuries based on post-glacial sediment cores showing consistent THg concentrations in depths not reached by contemporary inputs (Hare et al., 2008, 2010). Pre-industrial Hg fluxes appear to have been dominated by the resuspension of shallow coastal sediments in the south (<2 t y^{-1}) and relatively low inputs from rivers and marine water masses (<1 t y^{-1} each). Primary Hg losses from the system occurred through sedimentation and mass export of marine water (~2 and 1 t y^{-1}, respectively). The net exchange of Hg between the ocean and atmosphere estimated by Hare et al. (2008) was the least-constrained flux because models and field data range widely, but most likely contributed a negligible net amount of Hg during the pre-Industrial Era (0.1 t y^{-1}).

The total contemporary Hg influx and outflux, estimated at 6.3 t y^{-1} each, represent a two-fold increase from pre-industrial fluxes. The most notable change was increased Hg burial in recent sediments (4.5 t y^{-1}), implying that much of the modern Hg load entering this system is buried in the sediments (Hare et al., 2008). Higher river inputs (1.9 t y^{-1}) and a larger net gain from the atmosphere (1.5 t y^{-1}) may reflect increased contemporary atmospheric deposition to Hudson Bay and its watershed. The contemporary THg inventory in the Hudson Bay water column was estimated at 98 t, about 1% of which is present in marine organisms and the remainder in abiotic forms (Hare et al., 2008).

While the THg mass balances for Hudson Bay indicate recent human impact, information on MeHg fluxes may be more relevant to concerns of bioaccumulation in food webs and would prove useful in determining the relative contribution of potential sources including coastal shelf sediments, river watersheds, and the Hudson Bay water column. Kirk and St. Louis (2009) examined the importance of MeHg fluxes from two large rivers as sources to Hudson Bay and suggested that internal MeHg production in the bay may be significant. These measurements are also particularly relevant given the potential for increased MeHg loadings from the vast wetlands of the southern Hudson Bay watershed under warming climate conditions (Macdonald et al., 2005).

7. Biogeochemical cycling of mercury

7.1. Methylation and demethylation

Until recently, the main sites of MeHg production in the Canadian Arctic had not yet been identified, although it was known that inorganic Hg(II) is methylated in marine environments (Fitzgerald et al., 2007). Based on studies from other regions, methylation of Hg(II) may potentially occur in sediments (particularly in shallow coastal shelves), in the water column, or on snow and sea ice (Macdonald and Loseto, 2010). The breakdown of Me_2Hg in the water column or in the air after its evasion may also be a source of MeHg for biological uptake (Kirk et al., 2008; St. Louis et al., 2005, 2007). It has been suggested that open polynyas are important sites for Me_2Hg evasion (St. Louis et al., 2005, 2007), bringing up the possibility of biotic Hg(II) methylation in surface waters with elevated phytoplankton biomass (Pongratz and Heumann, 1998a). Production of Me_2Hg has been determined for pure cultures of marine bacteria collected from Antarctic surface waters and in macroalgae isolated from an Arctic fjord (Pongratz and Heumann, 1998b, 1999). However, recent work in the Arctic Ocean suggests that Me_2Hg can also be produced in deep waters (Section 3; Kirk et al., 2008). A possible mechanism for phytoplankton-associated methylation was proposed by Larose et al. (2010) implicating transmethylation reactions (Bentley and Chasteen, 2002) that are involved in the degradation of the phytoplankton osmolyte dimethylsulfoniopropionate (DMSP). Other studies in lower-latitude oceans have also challenged the current paradigm that only anaerobic conditions support significant MeHg production or net rates of methylation (Cossa et al., 2011; Heimbürger et al., 2010; Mason and Fitzgerald, 1990; Sunderland et al., 2009) and underscore the need for more fundamental research examining mechanistic aspects of Hg methylation in polar regions.

The first estimates of Hg methylation rates in coastal sediments of the Arctic Archipelago were determined by laboratory incubations of Hg isotopes in sediment slurries from Allen Bay, Cornwallis Island (St. Pierre et al., 2014). The methylation and demethylation potentials were low, suggesting that those organic-poor coastal sediments are likely not an important source of MeHg to the water column. However, the results may not be representative of organic-rich sediment in more productive Arctic coastal areas, and additional research is needed to examine the influence of spatial heterogeneity in sediment characteristics on Hg methylation in the Arctic. In the incubation experiments, the rate of Hg methylation was stimulated by a temperature increase from 4 to 12 °C, without a compensatory increase in demethylation. Climate warming may, therefore, increase the potential for MeHg production in coastal sediments.

The first measurements of methylation rates in marine waters of the Canadian Arctic are consistent with the notion that the water column is

an important site for MeHg production (Lehnherr et al., 2011). Seawater samples were amended with isotopically labeled Hg(II) and MeHg, and incubated to quantify rates of methylation and demethylation. The results of these experiments demonstrated that both MeHg and Me_2Hg are produced in polar marine waters by methylation of Hg(II). Additionally, Me_2Hg can also be formed from methylation of MeHg, but in general, Me_2Hg production was slower than MeHg production. Methylmercury can be demethylated under both light and dark conditions as a result of photodemethylation and microbial demethylation, respectively.

A numerical model using the rate constants of MeHg production and degradation measured during these incubations estimated that, on average, Hg(II) methylation in the water column accounted for about half (47 ± 62%) of the MeHg present in marine waters of the Canadian Arctic Archipelago and is therefore the single largest source of MeHg to Arctic marine waters and food webs (Lehnherr et al., 2011). Furthermore, the model estimates indicated that MeHg demethylation in the water column limits how far MeHg can be transported by ocean currents. For example, 90% of the MeHg in a particular water mass is likely demethylated in the time it takes for that water to travel 20–200 km. Therefore, the majority of MeHg occurring in Arctic marine waters probably does not originate from distant sources, highlighting the importance of Hg(II) methylation in the water column. The model results also indicated that some sites appear to be net sources of MeHg (methylation hotspots) while others can be net sinks for MeHg, depending on the availability of Hg(II), which limits MeHg production. The implication of this finding is that if concentrations of Hg(II) in Arctic marine waters were to increase as a result of either increased anthropogenic inputs or environmental change, the production of MeHg in the water column from Hg(II) methylation is also likely to increase.

Recent work in the Bathurst Polynya (Beaufort Sea) has shown a MeHg maximum associated with the widespread nutrient maximum in the Western Arctic Ocean (Wang et al., 2012). Based on kinetic rate constants reported by Lehnherr et al. (2011), Wang et al. (2012) dismissed transport from the Chukchi Sea, where the nutrient maximum is formed, as a plausible source of the MeHg. Other potential sources of MeHg to the study site, including the Mackenzie River (Leitch et al., 2007) or diffusion out of shelf bottom sediments, were also found to be unlikely. Estimates of primary production for the polynya and the resultant rate of organic matter remineralization occurring locally in the nutrient maximum, however, were shown to provide the only plausible mechanism to produce MeHg at the observed concentrations. This result may provide, at least partially, an answer as to why there is such wide regional variation in Hg uptake by apex marine predators in the Arctic marine environment. However, the rapid dynamics of MeHg production and destruction make it difficult to link the Hg cycle within the ocean to the MeHg accumulation in the food web.

While limited information currently exists on photodemethylation in polar seawater, this loss process likely occurs near the water-column surface where UV light can penetrate (e.g., Lehnherr et al., 2011; Monperrus et al., 2007). Experimental work suggests that MeHg–chloride complexes, which are the dominant form in seawater, are more resistant to photodemethylation, particularly in comparison to aqueous MeHg complexes in fresh water (Zhang and Hsu-Kim, 2010). Sea ice and snow cover strongly reduce light penetration and, hence, photodemethylation in the Arctic Ocean for much of the year. Reductions in summer sea-ice extent associated with climate change will most probably increase photodemethylation in the marine Hg cycle and possibly decrease MeHg concentrations. Using new techniques, Point et al. (2011) measured the stable isotope composition of Hg in seabird eggs along a latitudinal gradient extending across the Bering and Chukchi Seas and found evidence that less photodemethylation occurs at the northern, more ice-covered sites. Photodemethylation of aqueous MeHg produces distinct Hg isotope fractionation patterns (Bergquist and Blum, 2007, 2009), and the extent of this fractionation in Hg bioaccumulated by seabirds was significantly correlated to the percent of sea-ice cover. Accordingly, the authors proposed that the loss of seasonal ice in the Arctic as a consequence of climate change might actually enhance the breakdown of MeHg and lead to a decline in Hg uptake at the top of marine food webs (Point et al., 2011). Clearly, we do not yet know how widely the findings from the Bering and Chukchi Seas can be extended, but it seems likely that for any given region, climate change will alter the dynamic balance between processes destroying MeHg (e.g., photodemethylation) and processes producing it (organic matter remineralization) leading to opposing trends depending on the setting.

7.2. Reduction and oxidation

Reduction–oxidation (redox) reactions of Hg can be driven by photochemical or microbial processes. While photochemical reactions appear to dominate the redox cycle in fresh waters, recent evidence from the Arctic suggests that microbes may be key players in altering Hg redox chemistry in salt water.

7.2.1. Microbial redox processes

Microbes are well known for their capacity to form the neurotoxin MeHg, but they also have the capacity to detoxify this metal via Hg resistance enzymes (Barkay et al., 2003). Some types of bacteria have a mercuric reductase enzyme (called merA) that reduces Hg(II) to volatile Hg(0), and some also have an enzyme (merB) that decomposes organomercurial species (Barkay et al., 2003). In a study of Arctic microbial communities associated with seawater, microbial mats and macroalgae, Poulain et al. (2007a) found evidence from messenger RNA detection that marine, cold-adapted microbes expressed diverse forms of the merA gene coding for the mercuric reductase enzyme. This discovery of expressed Hg resistance genes suggests that microbial populations in the Arctic marine environment are sensitive to Hg contamination. However, THg concentrations were low in water and sediments from which these microbial populations were sampled. Therefore, the induction of Hg resistance may reflect: 1) the existence of environmental conditions that enhance Hg bioavailability due to microbe physiology or to the physical and chemical properties of the Arctic environment, and/or 2) the presence of micro-niches with high Hg concentrations, such as those encountered in snow and frost flowers (Douglas et al., 2008). Investigations in northeastern Greenland have recently found that mercury-resistant bacteria occur in snow and to a lesser extent in brine associated with Arctic sea ice (Møller et al., 2011).

Poulain et al. (2007a) modeled the potential for microbes to reduce Hg in the High Arctic. Results of their kinetic redox model suggest that microbially mediated reduction of Hg(II) could account for most of the Hg(0) present in the surface waters of the Arctic Ocean. Studies conducted in the circumpolar Arctic show ranges of dissolved gaseous Hg (DGM) concentrations in seawater that broadly overlap with those of freshwater systems (60–643 fM; Table 2). Virtually nothing is known about Hg redox chemistry deeper in the ocean water column or in sediments. Elevated GEM concentrations were measured in deep ocean water beyond light penetration (see Section 3), suggesting that microbes may be important mediators of Hg redox transformations in that environment. The production of GEM in seawater collected from the aphotic zone and incubated in the absence of light supports this notion (Lehnherr et al., 2011). In addition, elevated concentrations of DGM were recorded under sea ice in the Canadian Arctic Ocean (Andersson et al., 2008; St. Louis et al., 2007), suggesting that DGM builds up under sea ice. This DGM is likely composed of a mixture of Me_2Hg and Hg(0), both of which are volatile and may be of microbial origin. The rate of microbial metabolism is dictated by temperature, and the Arctic is undergoing climate warming. Therefore, it is critical that further research be conducted at the cellular level on microbial contributions to Hg transformations in the polar marine environment. Investigations should focus on microbial species currently adapted to

Table 2
Water concentrations of DGM in surface waters of Arctic marine ecosystems.

Location	Sampling date	*n*	DGM concentration (fM)	Reference
North Atlantic and Arctic oceans (near the Fram Strait)	2004	>400	54–174	Temme et al. (2005)
Arctic Ocean (Griffith Island and Resolute Passage, NU)	2004–2005	8	643 ± 179[a]	St. Louis et al. (2007)
Canadian Arctic Archipelago[b]	2005	11	127 ± 51[a]	Kirk et al. (2008)
Hudson Bay region[b]	2005	13	148 ± 25[a]	Kirk et al. (2008)
Arctic Ocean (including the Canadian Archipelago, Beaufort Sea, Chukchi Sea and Central Basin)	2005	Continuous measures[c]	220 ± 110	Andersson et al. (2008)
Arctic Ocean (near Kongsfjorden, Norway)	2002	5	60–349	Sommar et al. (2007)

n = number of sites sampled, fM = femtomoles L^{-1} (i.e. 10^{-15} M).
[a] GEM measurements.
[b] Only surface water data are presented here.
[c] I.e. every 10 min over a 3-month period.

the Arctic and species likely to arise and become dominant with climate change.

7.2.2. Photochemical redox processes

Halogens such as chlorine and bromine and their reactive derivatives are involved in photooxidation of Hg(0) to Hg(II). This process has been documented in the atmosphere (Ariya et al., 2008), in snow (Dommergue et al., 2003; Lalonde et al., 2003; Mann et al., 2014, in this issue; Poulain et al., 2004; Steffen et al., 2008) as well as in surface waters of the St. Lawrence River (Lalonde et al., 2001) and the coastal Atlantic Ocean (Whalin and Mason, 2006). In the presence of solar radiation, elemental Hg is more likely to be oxidized back to divalent Hg in marine systems than in fresh waters. During bottle incubation experiments conducted with coastal waters near Cornwallis Island, Poulain et al. (2007c) showed that the light-induced production of elemental Hg greatly decreased with increasing salinity, reaching virtually no net production in natural coastal seawater. Using controlled experiments and kinetic modeling, Qureshi et al. (2010) determined that photooxidized Hg forms a stable complex with chloride in North Atlantic Ocean water that is less available for photoreduction reactions. These results predict a decrease in the photoreduction of Hg in marine waters and, therefore, more retention of Hg(II) as compared to fresh waters. Altogether these data suggest that conditions encountered in coastal and marine systems tend to increase the retention of inorganic Hg(II) by favoring oxidation reactions.

8. Bioaccumulation and biomagnification of mercury

The exact mechanisms by which Hg enters the food chain are not fully understood. Fish and wildlife are exposed to Hg mainly through their diet because typically low concentrations in air and water result in minimal transfer through inhalation, gill or dermal exposure (Duffy et al., 2001; Hall et al., 1997; Rodgers, 1994). Methylmercury is the main species of Hg absorbed by fish and wildlife. Bioaccumulation occurs because MeHg is efficiently assimilated into tissues following absorption in the gut but is slowly eliminated from the body. Once MeHg is absorbed in the gut, it enters the blood stream and is distributed to tissues and organs in the body. In fish, MeHg first accumulates in the viscera (kidney, spleen, liver) and is only later redistributed to the muscle and brain tissue (Oliveira et al., 1999). Mammals and birds are capable of detoxifying their MeHg burden through demethylation (Wagemann et al., 1998; Wiener et al., 2003). As a result, a large and variable portion of the Hg in liver and kidney is inorganic (Wagemann et al., 1998; Wiener et al., 2003). Mercury in the skeletal muscle and brain is predominately in the form of MeHg (Basu et al., 2009; Scheuhammer et al., 1998; Wagemann et al., 1998). Mercury concentrations are often higher in older and larger individuals of an animal population because those individuals tend to eat larger types of prey that are at a higher trophic position and are more contaminated.

Mercury is one of the few metals that is known to accumulate through food webs to concentrations that are much higher in upper trophic level organisms than those in primary producers or consumers (Kidd et al., 2012). In the Canadian Arctic, MeHg is found in marine waters at ultra-low levels, yet concentrations are orders of magnitude higher in predatory animals such as beluga and polar bears. This phenomenon occurs because MeHg is biomagnified through a food web; that is, it first concentrates in microbes (algae and bacteria) and then is further amplified in dietary transfers between consumers. The greatest biomagnification occurs at the base of food webs where MeHg is approximately 105 times more concentrated in microbes than in water (Watras et al., 1998). Biomagnification then occurs at each additional trophic level, by a factor calculated to be about 6.0 ± 3.7 times in polar marine food webs (Lavoie et al., 2013).

9. Food webs

9.1. Trophic transfer of mercury through marine food webs in the Canadian Arctic

The first investigations of Hg biomagnification in marine food webs focused on Lancaster Sound (Atwell et al., 1998) and the North Water Polynya (Campbell et al., 2005). Those studies indicated that Hg concentrations increase several-fold from ice algae (North Water Polynya) and particulate organic matter (Lancaster Sound) up through invertebrates and fish to seabirds and marine mammals. Since then, Hg biomagnification in marine food webs has been investigated in Cumberland Sound, in Hudson Bay, in Queens Channel, and in the eastern Beaufort Sea and Amundsen Gulf.

9.1.1. Cumberland Sound

In Cumberland Sound, located on the east coast of Baffin Island, THg concentrations in biota (log-transformed, μg g^{-1} dw) sampled from 2007 to 2009 increased significantly with trophic position, estimated by their $\delta^{15}N$ ratios (McMeans et al., 2015-in this issue). Concentrations increased from invertebrates (clams (*Hiatella arctica*) and zooplankton) to mid-trophic position fishes (e.g. *Salvelinus alpinus*) and seals (*Phoca hispida*, *Phoca groenlandica*) to the top predator, Greenland shark (*Somniosus microcephalus*). Of the known benthic and pelagic Greenland shark prey sampled, those with the highest THg concentrations were Arctic skate (*Amblyraja hyperborea*) and harp seal (*P. groenlandica*). However, neither total body length, sex, nor trophic position or diet (as inferred from $\delta^{15}N$, $\delta^{13}C$ and fatty acids), except for a weak, positive relationship between THg and the fatty acid 18:1n − 9, were able to significantly explain THg variability among individual Greenland sharks. The high THg concentration in Greenland sharks, however, was consistent with their high trophic position and with significant biomagnification of THg through this seasonally ice-covered ecosystem.

9.1.2. Hudson Bay

Mercury biomagnification was investigated in a marine food web of Hudson Bay using THg concentrations in the muscle of three species of seals sampled from western Hudson Bay (Young et al., 2010) and one

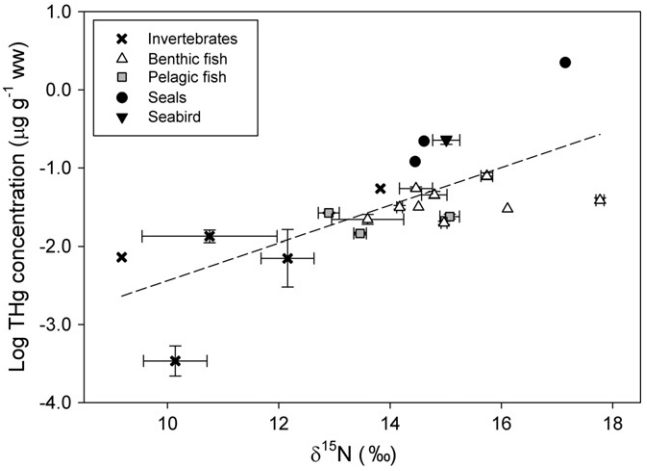

Fig. 4. Relationship between $\delta^{15}N$ ratios (‰) and log-transformed THg concentrations ($\mu g\ g^{-1}$ ww) in a marine food web of Hudson Bay (linear regression model: log THg = $4.84 + 0.240 * \delta^{15}N$, $r^2 = 0.49$, $p < 0.001$, $n = 21$). Invertebrates (sea angel (*Clione limacina*), jellyfish (mixed species), squid (*Gonatus* sp.), amphipods (gammarid and hyperiid), euphausiids (Euphausiacea), pelagic fish (Arctic cod (*Boreogadus saida*)), capelin (*Mallotus villosus*), sandlance (*Ammodytes* spp.), and benthic fish (sculpins (*Gymnocanthus tricuspis*, *Triglops* spp.), banded gunnels (*Pholis fasciata*), Arctic and daubed shannies (*Stichaeus punctatus* and *Leptoclinus maculatus*, respectively), eelpout (*Gymnelis viridis*), Atlantic poacher (*Leptagonus decagonus*), fourline snake blennies (*Eumesogrammus praecisus*), snailfish (*Liparis* sp.)) were sampled from 2007 to 2009. Seabirds (thick-billed murre) were sampled in 2007. Ringed seals were sampled in 2006, bearded seals (*Erignathus barbatus*) in 2005, and harbor seals (*Phoca vitulina*) from 1999 to 2006.
Fish data are from Braune et al. (2014a). Invertebrate and seabird data are from Braune (Environment Canada, unpublished data). Seal data are from Young et al. (2010).

seabird species—the thick-billed murre (*Uria lomvia*)—sampled from Coats Island in northern Hudson Bay. Whole fish and invertebrates delivered by thick-billed murres to nestlings on the ledges of cliffs on Coats Island were collected and supplemented by invertebrates sampled from plankton tows near the Nuvuk Islands for THg analysis. A significant positive relationship was found between log THg concentrations and $\delta^{15}N$ ratios in the biota sampled from Hudson Bay (Fig. 4). Concentrations of THg increased from invertebrates through fish to the top trophic consumers, seabirds and seals. The mean muscle $\delta^{15}N$ ratio and THg concentration for thick-billed murres were very similar to that found in the muscle of adult ringed seals. In a recent paper, Foster et al. (2012) analyzed a large Hg database focusing exclusively on zooplankton in Hudson Bay, including THg and MeHg determinations at the species level. They found that even at the lower trophic levels of the food web, MeHg uptake and transfer varied significantly, thus providing an important source of variance in the exposure of higher trophic level feeders.

9.1.3. Queens Channel

Mercury biomagnification was studied in invertebrates, fish and seabird chicks sampled opportunistically in the summer of 2011 from a small, tidally-driven polynya near Nasaruvaalik Island in Queens Channel (Clayden et al., 2015-in this issue). The biomagnification rate of MeHg (based on $\delta^{15}N$) was slightly higher (0.256) than in the much larger North Water Polynya (0.223, in Campbell et al., 2005). The trophic magnification factor of MeHg from invertebrates through fish (3.4) was comparable to estimates from eastern Canadian Arctic and sub-Arctic food webs (van der Velden et al., 2013a). Concentrations of MeHg from the Queens Channel polynya were measured in two previously uncharacterized taxa, jellyfish (Medusozoa) and Arctic alligatorfish (*Ulcina olrikii*). Jellyfish had lower MeHg concentrations than expected given their trophic position, possibly because they differ markedly in their biochemistry from other organisms in this study. Since this is one of the few studies on Hg biomagnification in polynyas, further research might help to identify whether the physical, chemical or biological characteristics of these ecosystems influence Hg bioaccumulation or biomagnification, as shown for other systems (Lavoie et al., 2013). Small polynyas are broadly distributed and are key habitats for marine wildlife in the Arctic (Stirling, 1997), so it is important to understand what roles they play in the broader dynamics of Hg in Arctic environments.

9.1.4. Eastern Beaufort Sea and Amundsen Gulf

The Beaufort Sea beluga whale population is one of Canada's largest, estimated at a minimum of 40,000 individuals (COSEWIC, 2004). Concern over high Hg concentrations measured in this population of beluga whales (Lockhart et al., 2005a) led to studies designed to evaluate food web processes driving Hg concentrations in this region. Satellite telemetry data from tagged beluga provided the information to characterize habitat use, while studies on local food webs were used to estimate Hg exposure in beluga whales (Loseto, 2007; Loseto et al., 2006, 2008a, 2008b, 2009). Based on beluga habitat preference, three different sex and size defined habitat use groups were observed (Loseto et al., 2006). It is likely that differential habitat use by different segments of the population influenced their feeding ecology and thus their Hg exposure. Therefore, using the habitat use groups, belugas were hypothesized to feed locally as follows: 1) small males (<3.8 m) and females (with and without calves) using shallow open water near the mainland were hypothesized to feed within the estuarine-shelf food web; 2) medium length males (3.8–4.2 m) and females (>3.7 m) without calves using the sea ice edge were hypothesized to feed on Arctic cod (*Boreogadus saida*) associated with sea ice (Gradinger and Bluhm, 2004) in the pelagic food web; and, 3) the largest males (≥4.2 m) using heavy sea-ice concentrations in deep, offshore waters were hypothesized to feed in the benthic and epibenthic food web (Loseto et al., 2008a) due to their known diving ability; e.g. up to 800 m (Citta et al., 2013; Richard et al., 1997).

Food webs were designed for each ecozone to support the hypothesized feeding preference of beluga in the eastern Beaufort Sea and Amundsen Gulf region (Loseto et al., 2008a). Biomagnification rates were estimated using the slopes of THg concentrations versus trophic position of invertebrates, fish, and beluga sampled from the different food webs (Loseto et al., 2008a). The slopes for THg ranged from 0.23 to 0.26 and did not differ significantly between the estuarine, pelagic, and epibenthic food webs. Biomagnification slopes were similar to those calculated for THg in Hudson Bay (slope of 0.24) and Cumberland Sound (slope of 0.23; McMeans et al., 2015-in this issue), and slightly higher but still comparable to values calculated for the North Water Polynya near Baffin Bay (slope of 0.20; Campbell et al., 2005), and West Greenland waters (slope of 0.18; Rigét et al., 2007b). A recent review reported a mean biomagnification slope of 0.21 ± 0.07 for THg in polar marine food webs (Lavoie et al., 2013) which supports earlier observations of similar Hg biomagnification slopes among disparate Arctic marine habitats (Rigét et al., 2007b).

Although biomagnification slopes were similar among beluga feeding habitats, the Hg concentrations observed among the beluga feeding groups differed, suggesting that biomagnification rates remained constant and were not driving differences among groups. Despite the high influx of inorganic Hg and MeHg to the Mackenzie River Delta (Leitch et al., 2007), Hg concentrations in prey associated with the shallow estuarine food web were among the lowest (Fig. 5) and the beluga whale habitat group thought to feed there also had the lowest THg concentrations (muscle: 2.6 $\mu g\ g^{-1}$ dw) (Loseto et al., 2008a). Potential prey from the offshore and benthic habitats had THg concentrations that were generally higher than prey from Amundsen Gulf and the estuarine shelf, including Arctic cod found in both areas (Fig. 5). Among the benthic fish species, THg concentrations in fourhorn sculpin (*Myoxocephalus quadricornis*) were the highest (Fig. 5). These differences in THg concentrations in prey were consistent with the differences in THg concentrations between beluga using nearshore and offshore habitats. Beluga using the nearshore/shelf habitat had lower THg concentrations than those hypothesized to be feeding at the ice

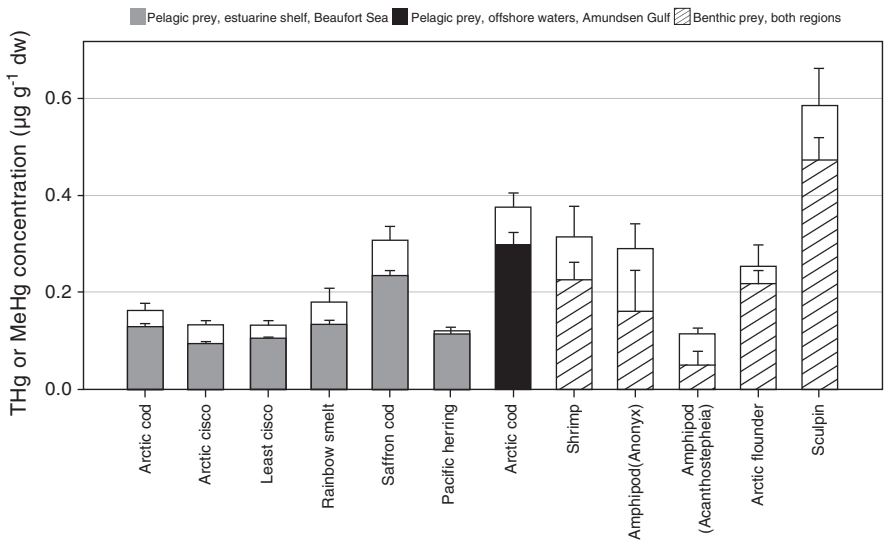

Fig. 5. Concentrations of THg and MeHg (µg g^{-1} dw) (white and shaded/patterned bars, respectively) in potential prey species collected from different habitats of the Beaufort Sea and Amundsen Gulf. Pelagic and benthic prey species were collected from the shallow estuarine shelf of the Beaufort Sea and offshore waters in the Amundsen Gulf. Muscle was analyzed for fish while invertebrates were analyzed whole.
Data are from Loseto et al. (2008a).

edge and deeper offshore habitats whose THg concentrations did not significantly differ from one another (muscle: 6.0 and 4.4 µg g^{-1} dw, respectively). While the assigned beluga feeding groups were an oversimplification of temporal and spatial complexities of beluga movement and seasonal feeding, the exercise was valuable for a general understanding trophic transfer of Hg in the different food webs.

10. Marine fish

10.1. Sea-run Arctic char

Arctic char (Salvelinus *alpinus*) is a member of the salmonid family, which also includes lake trout (*Salvelinus namayush*) and Dolly Varden (*Salvelinus malma malma*), and has the most northern distribution of the three species. Dolly Varden is considered to have a limited distribution within the Canadian Arctic and occurs primarily west of the Mackenzie River Delta while Arctic char extend to the east (Reist and Sawatzky, 2010). Arctic char and Dolly Varden are freshwater species that either reside entirely in lakes and rivers or are anadromous and migrate to the ocean for several weeks during the Arctic summer to feed on marine invertebrates and small fish.

10.1.1. Spatial patterns

Mercury concentrations in sea-run char were measured periodically in small samples (generally five fish per sample) during the 1970s–1990s and those results were summarized in Lockhart et al. (2005b). More recently, 2004–2012, a systematic survey of THg concentrations in sea-run char was made at 20 locations across northern Canada including the western Arctic, central Arctic, northern Baffin Island area, and Labrador (Evans et al., in this issue). Char muscle had extremely low concentrations of THg with site averages ranging from 0.014 ± 0.002 µg g^{-1} wet weight (ww) at Cape Dorset ($n = 10$) to 0.097 ± 0.015 µg g^{-1} ww for Vittrekwa River char ($n = 7$). In general, THg concentrations increased with fish length and weight at individual sites. Concentrations of THg were also often negatively correlated with condition factor; i.e. fish with low condition factors had higher THg concentrations. Evans et al. (in this issue) hypothesized that lower Hg concentrations in fish with high condition factors were associated with greater growth dilution, and since condition factor was not related to $\delta^{15}N$ ratios, trophic feeding level was not a factor. Mercury concentrations were substantially lower in sea-run char than in resident and land-locked char possibly due to lower Hg concentrations in the marine diet of the sea-run char (van der Velden et al., 2013a, 2013b). Sea-run Dolly Varden in the western Canadian Arctic also had relatively low THg concentrations with means from 10 sites ranging from 0.029 ± 0.007 µg g^{-1} ww to 0.161 ± 0.037 µg g^{-1} ww (Tran et al., 2015-in this issue). Site-specific differences in Hg in sea-run char likely reflect variation in the Hg content of their prey, which may be related to localized inputs of Hg from large watersheds (e.g., the Mackenzie River), Hg methylation rates in the marine environment, and the types of prey available, in addition to char growth rates.

10.1.2. Temporal trends

Fourteen of the 20 sites investigated by Evans et al. (in this issue) were sampled more than once although various factors limited the power of the statistical analyses including small sample sizes prior to 2002, substantial differences in the sizes of fish caught in successive years from some locations, and a low number of sampling years. The best records were for sea-run char at Cambridge Bay (central Arctic), Pangnirtung (eastern Baffin Island), Pond Inlet (northern Baffin Island), and Nain Labrador (Nunatsiavut) where trend analyses were based on earlier collections (Lockhart et al., 2005b) combined with sampling conducted from 2004 to 2012 (Evans et al., in this issue). The factors affecting log-transformed THg concentrations were explored using a general linear model with length, year, and a length-by-year interaction as independent variables. Cambridge Bay char showed a significant increase ($p < 0.02$) in THg concentrations from 1977 to 2012 as did Pangnirtung char from 1990 to 2009 ($p < 0.001$) (Fig. 6). Pond Inlet char (2005 to 2012) showed no trend in THg concentrations (Fig. 6) with variations related only to fish length. The inability to detect a trend in these fish may have been limited to the shorter time record. Total Hg was measured in char from Nain in 1998 and 1999 and again from 2007 to 2010; these records were extended by including char caught from Voisey Bay in 1978 (Bruce et al., 1979). Log THg concentrations showed a significant decrease ($p = 0.003$) over 1978–2010 and 1999–2010 but no trend was detected over 2007 to 2010 (Fig. 6). Trends of increasing THg were also detected at Paulatuk in the western Arctic (1984–2007), Hall Beach west of Fox Basin (1978–2007), Arviat in western Hudson Bay (2005–2008) and Hopedale off the Labrador coast (1999–2007). The only decreasing trend, in addition to Nain, was noted at Iqaluit on southern Baffin Island (1992–2009). A study including sea-run char sampled from four locations along the Labrador

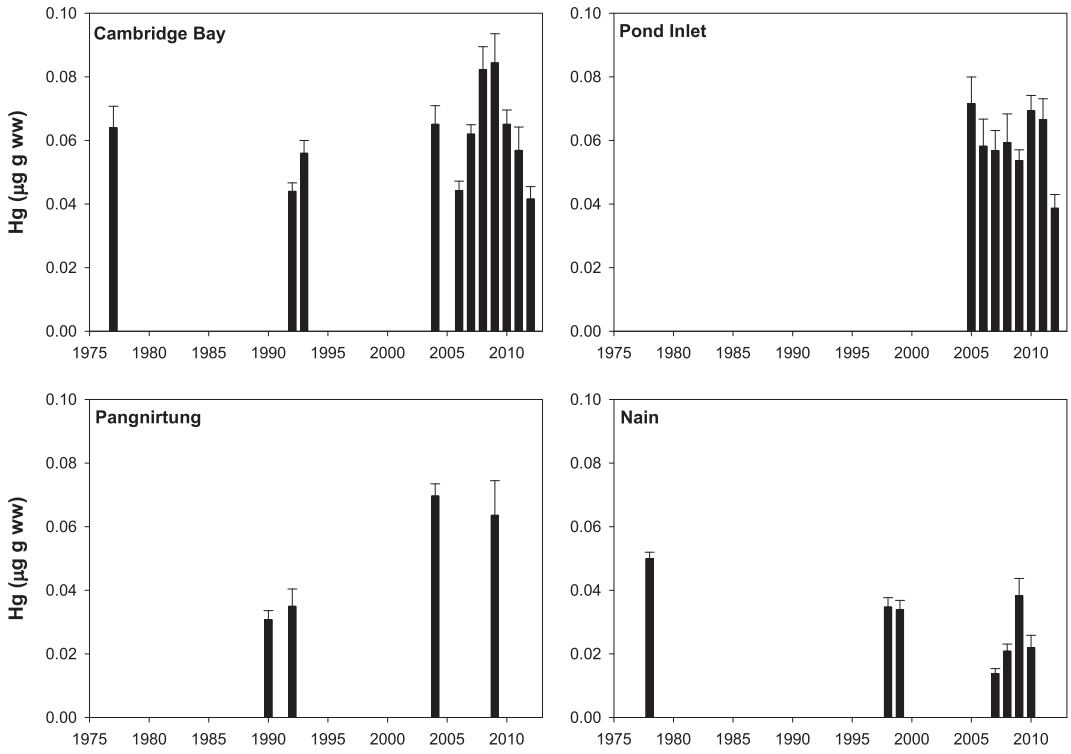

Fig. 6. Temporal variation in mean (±standard deviation) THg concentrations in sea-run char from Cambridge Bay (1977–2012), Pangnirtung (1990–2009), Pond Inlet (2005–2012), and Nain (1978–2010). Statistical results are described in the text.
Based on data from Bruce et al. (1979), Evans et al. (in this issue) and Lockhart et al. (2005b).

coast in 1977/1978 and again in 2007/2008 showed a significant increase in THg concentrations at one site (Hebron Fiord) and no significant changes at the other three sites (Okak Bay, Tikkoatokay Bay, Voisey Bay) between the two time periods (van der Velden et al., 2015–in this issue); with only two years of study for each site, the ability to detect trends was limited. However, a more comprehensive study of sea-run char by Evans et al. (in this issue) suggests a recent trend of increasing Hg across the Arctic when compared with concentrations observed in previous decades. These results should, however, be interpreted with some caution given the limited number of years sampled for most sites.

10.2. Other marine fish

There is limited information on Hg concentrations in other species of marine fish in the Canadian Arctic including those that may be important sources of dietary Hg for seabirds and marine mammals. Arctic cod is a keystone species which has been sampled in several food web studies; e.g. the Beaufort Sea and Amundsen Gulf (Loseto et al., 2008a), the central basin of the Arctic Ocean (Stern and Macdonald, 2005), Lancaster Sound (Atwell et al., 1998), and the North Water Polynya (Campbell et al., 2005). Arctic cod captured in offshore waters had higher THg concentrations than those from an estuarine shelf (Loseto et al., 2008a) (Fig. 5), and spatial variation in cod THg was also observed between deep basins in the Arctic Ocean (Stern and Macdonald, 2005). In addition, several species of deep-water demersal fish were found to have higher THg concentrations relative to fish from an estuarine shelf (Loseto et al., 2008a). Notably high THg concentrations were also observed in Cumberland Sound Arctic skate muscle (0.42 ± 0.18 µg g^{-1} ww) compared to Arctic char, Greenland halibut (*Reinhardtius hippoglossoides*) and shorthorn sculpin (*Myoxocephalus scorpius*) (McMeans et al., -2015-in this issue). The factors that determine geographic and habitat variation of Hg bioaccumulation in marine fish remain unresolved and warrant future investigation to better understand Hg transfer to top predator animals in the marine environment.

Greenland sharks are the largest predatory fish found in Arctic waters. In Cumberland Sound, Greenland sharks had high THg concentrations in muscle (1.62 ± 0.52 µg g^{-1} ww), consistent with their top trophic position (McMeans et al., 2015-in this issue) and within the range reported for beluga whales (see Section 12.3). As large, long-lived, and abundant consumers of fishes and marine mammals, Greenland sharks are likely a significant reservoir for THg which has been transferred through a variety of trophic pathways in Arctic waters. Therefore, including Greenland sharks in future THg mass balance and trophic transfer models is warranted.

11. Marine birds

Seabirds feed at relatively high trophic positions in Arctic marine food webs (Hobson et al., 2002) and dietary Hg is efficiently transferred to avian eggs in a dose-dependent manner (Wolfe et al., 1998). Nearly 100% of the THg transferred to eggs is in the form of MeHg (Wiener et al., 2003). Therefore, although liver and kidney are the most common tissues monitored for Hg exposure in wildlife (Shore et al., 2011), eggs of seabirds are often used to monitor environmental contaminants, including Hg, due to ease of sampling.

11.1. Interspecies comparisons

Eggs of thick-billed murres, northern fulmars (*Fulmarus glacialis*), black-legged kittiwakes (*Rissa tridactyla*), black guillemots (*Cepphus grylle*), and glaucous gulls (*Larus hyperboreus*) were sampled from Prince Leopold Island in Lancaster Sound from 2003 to 2004 and again in 2008. Concentrations of THg varied significantly among the five seabird species sampled, with glaucous gull eggs having the highest concentrations and those of black-legged kittiwakes, the lowest (Fig. 7). In a study including seabird species sampled from the North

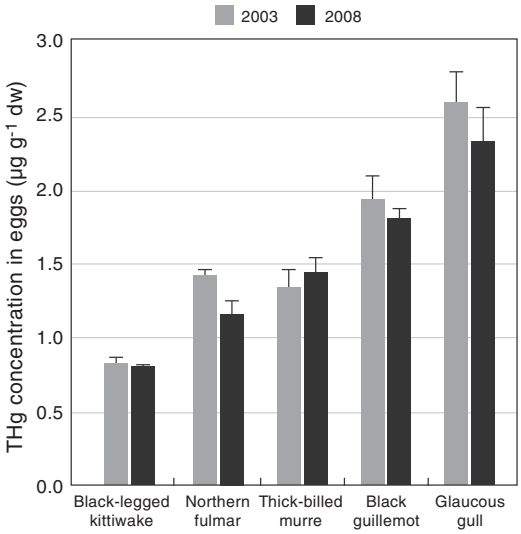

Fig. 7. Mean concentrations (±standard error) of THg (µg g^{-1} dw) in eggs of five seabird species collected from Prince Leopold Island from 2003 to 2004 and again in 2008 (Braune, 2009).

Water Polynya in 1998, Campbell et al. (2005) attributed differences found among seabird species to trophic position with glaucous gulls feeding almost a full trophic level higher than kittiwakes. Many Arctic seabirds overwinter in areas far from their breeding colonies, thus diet in overwintering areas will also contribute to their exposure to contaminants.

Eggs of Arctic terns (*Sterna paradisaea*) sampled in 2008 from a colony just north of Cornwallis Island in the High Arctic had a mean THg concentration of 2.1 ± 0.13 µg g^{-1} dw (Akearok et al., 2010), very similar to those found in some glaucous gull and black guillemot eggs. However, THg concentrations in eggs of ivory gulls (*Pagophilus eburnea*) from Seymour Island in the Canadian High Arctic in 2004 (mean of 6.4 ± 5.17 µg g^{-1} dw) were among the highest ever recorded in Arctic seabird eggs (Braune et al., 2006).

11.2. Spatial patterns

In 2007 and 2008, livers of adult thick-billed murres were sampled at five colonies in the eastern Canadian Arctic (Fig. 8). A comparison of hepatic THg concentrations from those five colonies found no significant differences among the three lower latitude colonies—Coats Island, Digges Island, and Akpatok Island—in the northern Hudson Bay and Hudson Strait region, nor were there significant differences between the two higher latitude colonies at Prince Leopold Island and the Minarets (Braune et al., 2014b). However, hepatic THg concentrations in murres from the two higher latitude colonies were significantly higher than from the three lower latitude colonies (Fig. 8) (Braune et al., 2014b). These results were similar to those from a spatial survey of Hg in Canadian Arctic seabird eggs carried out in 1993 which showed that concentrations of THg were significantly higher in murre eggs from

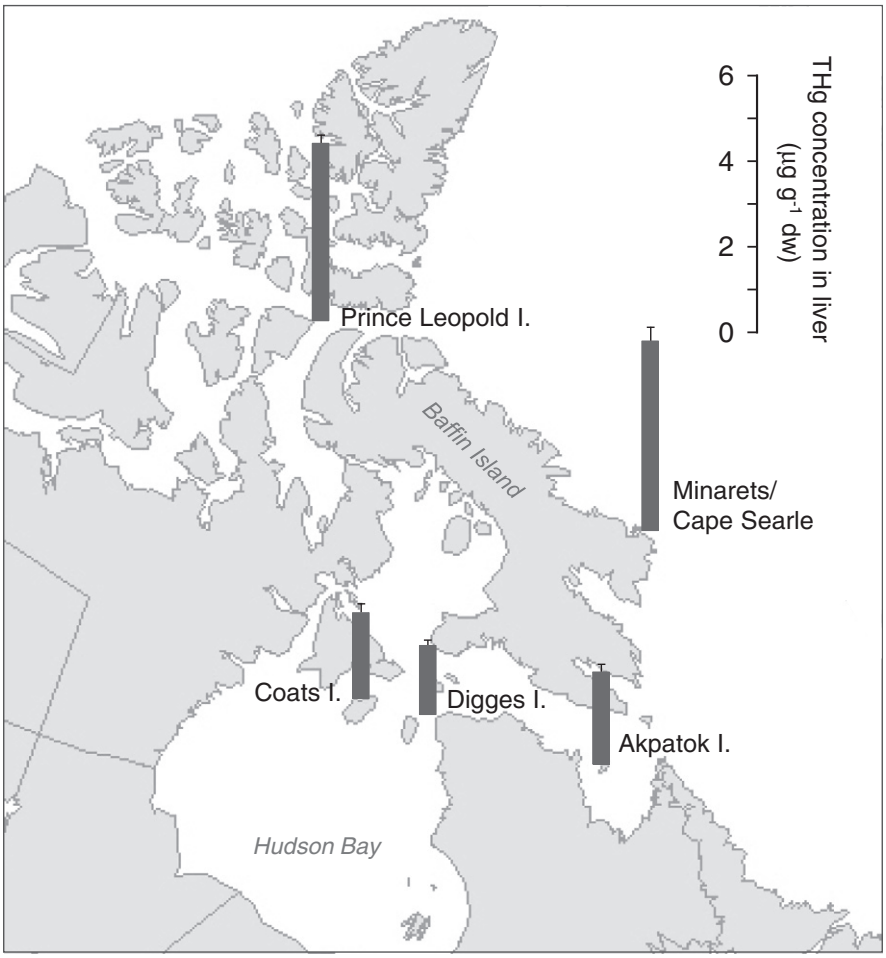

Fig. 8. Mean concentrations (±standard error) of THg (µg g^{-1} dw) in livers of adult thick-billed murres collected from five colonies in 2007–2008 ($n = 10$ for each colony except Coats Island where $n = 5$).
Based on data from Braune et al. (2014b).

the High Arctic sites—Prince Leopold Island, Coburg Island—compared with the lower Arctic murre colonies sampled—Coats Island, Digges Island—and there were no significant differences found for THg in eggs between the two Low Arctic colonies (Braune et al., 2002).

These results suggest that there are latitudinal differences in the factors determining Hg exposure, with birds breeding at the higher latitude colonies accumulating more Hg. Similar latitudinal differences have been observed by Dietz et al. (1996) for Greenland species and Braune et al. (2002) in the Canadian Arctic. Akearok et al. (2010) also found that THg concentrations in common eider (*Somateria mollissima*) eggs were higher from a High Arctic colony just north of Cornwallis Island compared with eider eggs sampled from the sub-Arctic Southampton Island in 2008. However, Mallory et al. (2004) found the opposite pattern for common eiders, with higher hepatic THg concentrations in eiders from Hudson Bay locations relative to birds sampled elsewhere throughout the Canadian Arctic. No spatial pattern was evident for hepatic concentrations of THg in long-tailed ducks (*Clangula hyemalis*) sampled from nine locations throughout the Canadian Arctic (Braune et al., 2005). Both eiders and long-tailed ducks are benthic feeders, however, and may be exposed to different Hg patterns via their prey than pelagic feeders (Chen et al., 2014) such as murres and other seabirds.

11.3. Temporal trends

Seabird eggs from Prince Leopold Island on Lancaster Sound have been monitored for THg since 1975 (Braune, 2007). Interpretation of temporal trends may be confounded if birds vary their diet among trophic levels through time (Hebert et al., 2000). Therefore, regression analyses used to analyze temporal trends of THg in the seabird eggs included $\delta^{15}N$ as a covariate to control for potential inter-year trophic changes in diet. Significant increases in THg concentrations occurred between 1975 and 2012 in eggs of thick-billed murres ($n = 70$, $p < 0.001$) and northern fulmars ($n = 71$, $p < 0.001$), and between 1975 and 2008 in eggs of black-legged kittiwakes ($n = 26$, $p < 0.03$) (Fig. 9). Since 2003, however, THg concentrations in fulmars no longer appear to be increasing (Fig. 9). Concentrations of THg in eggs of ivory gulls collected from Seymour Island also increased between 1976 and 2004, although the increase was not statistically significant (Braune et al., 2006). Recent increases in Hg bioaccumulation in Canadian Arctic seabirds are consistent with a broader geographic analysis of temporal Hg trends in Arctic biota that showed a west-to-east circumpolar gradient in the occurrence of recently increasing Hg trends (Rigét et al., 2011). This gradient was due to a higher proportion of marine time series showing significant Hg increases in the Canadian and Greenland regions of the Arctic compared to the North Atlantic Arctic. The reasons for recent Hg increases in seabirds are unclear but may involve changes in atmospheric Hg deposition associated with anthropogenic and natural emissions, coupled with environmental and biological (e.g., food web) processes which may also be affected by climate change.

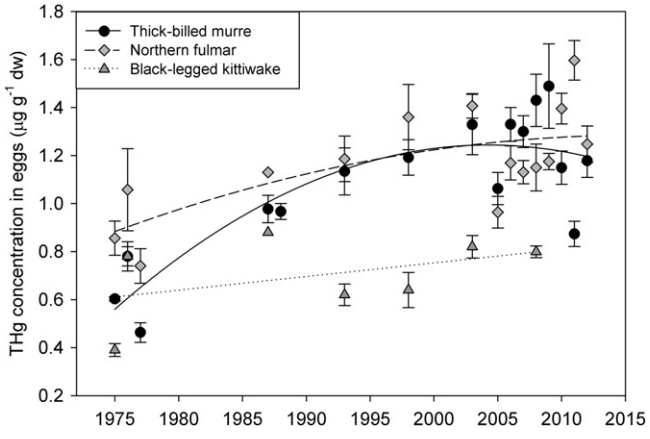

Fig. 9. Mean concentrations (±standard error) of THg in eggs of thick-billed murres, northern fulmars and black-legged kittiwakes from Prince Leopold Island, 1975 to 2012 (Braune, Environment Canada, unpublished data).

12. Marine mammals

12.1. Historical trends of mercury in marine mammals

Calcified hard tissues such as teeth can be used to estimate the extent to which global anthropogenic Hg emissions have increased Hg concentrations in Arctic biota since the pre-industrial period. Total Hg concentrations in teeth of Canadian Arctic beluga whales, walruses (*Odobenus rosmarus rosmarus*), and ringed seals have been examined from pre-industrial, historical (19th and early- to mid-20th Century) and present-day populations by Outridge et al. (2002, 2005, 2009). Teeth from modern ringed seals sampled in Amundsen Gulf, and from beluga sampled in the Beaufort Sea and near Somerset Island, had significantly higher THg concentrations than historical teeth (Outridge et al., 2002, 2005, 2009). In the Beaufort Sea and Amundsen Gulf region, THg concentrations in marine biota increased after the late 19th Century, with the most substantial increases occurring in the mid-20th Century. Beluga teeth collected around Somerset Island from the late 19th Century to 1998 showed THg increases of 1.2- to 5.5-fold, but the change did not begin until the 1920s to 1940s, which indicates that most, or all, of the increase took place after the early 20th Century (Dietz et al., 2009; Outridge et al., 2005). This historical trend in the Canadian Arctic is consistent with observations from Greenland on the Hg content of calcified and keratinaceous hard tissues such as teeth, hair and feathers (Dietz et al., 2009).

12.2. Ringed seal

The ringed seal is the most abundant Arctic pinniped, and its circumpolar distribution, makes it an ideal candidate for examining spatial patterns of contaminants. Because of their high abundance, ubiquitous distribution, and central position in the food web, ringed seals play an important role in the ecology of Arctic marine ecosystems (Smith et al., 1991). The ringed seal diet consists of fish, mainly Arctic cod, polar cod (*Arctogadus glacialis*), and crustaceans such as amphipods, mysids and euphausids (Reeves, 1998).

12.2.1. Tissue selection and data adjustment

Elevated THg concentrations have been observed in ringed seal liver and kidney since the 1970s (Muir et al., 1992; Smith and Armstrong, 1978; Wagemann and Muir, 1984). Early assessments found concentrations that were two- to three-fold higher in ringed seals in the southern Beaufort Sea—Sachs Harbour and Ulukhaktok—than in the eastern Canadian Arctic Archipelago (Muir et al., 1992; Wagemann et al., 1996), and higher in the Hudson Strait/Labrador region than in southern Hudson Bay (Dietz et al., 1998; Muir et al., 1999).

Comparisons of average concentrations in ringed seal liver are challenging because Hg varies with age (Rigét et al., 2012). The relationship of THg in liver and muscle with age was examined for seals collected from Arviat, Resolute, and Sachs Harbour in 2005 to 2007 (Fig. 10). Liver THg concentrations increased exponentially with age for seals less than five years and appeared to be relatively stable beyond that age. Adjusting for age is not always straightforward because the relationship between liver THg and age can also vary among locations. Thus, for this review of spatial patterns, only data for seals aged five years or older were used. Seal muscle concentrations of THg showed no overall trend with age (Fig. 10). Atwell et al. (1998) also found no correlation between muscle THg concentrations and age in ringed seals from Resolute. The lack of a relationship between muscle THg and age for seals and beluga is thought to be related to the more rapid elimination of the predominately MeHg in muscle, while for liver, the increase with age implies longer term storage of inorganic Hg (Dehn

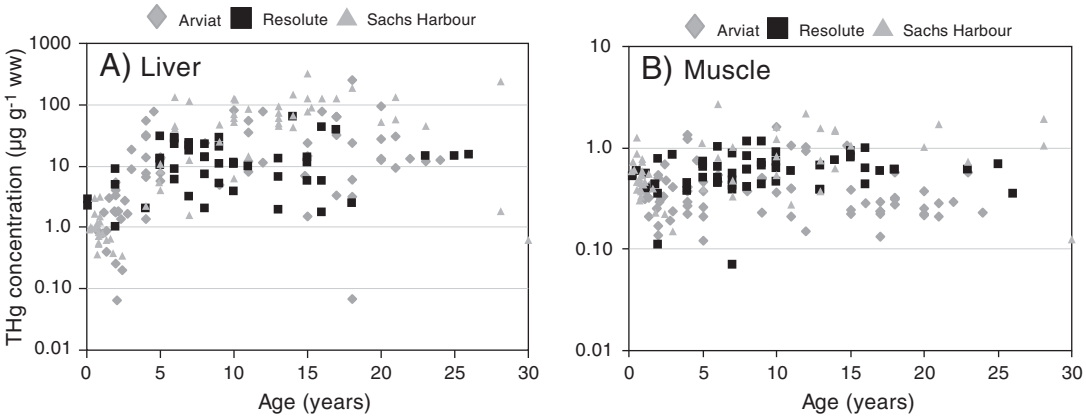

Fig. 10. Influence of age on log-transformed THg concentrations (µg g^{-1} ww) in (A) liver and (B) muscle of ringed seals collected from Arviat, Resolute, and Sachs Harbour in 2005 to 2007 (Muir, Environment Canada, unpublished data).

et al., 2005; Loseto et al., 2008b). Measurements of Hg elimination rates in seal muscle and liver would help to evaluate the appropriateness of these tissues for the long-term monitoring of Hg trends.

On average, THg concentrations in seal muscle were 32 times lower than in liver for tissues collected from the same location, and similar ratios have been reported elsewhere (Dehn et al., 2005; Wagemann et al., 1996). Most of the THg in liver is in the form of non-toxic, inorganic Hg-selenides (Wagemann et al., 2000). Dehn et al. (2005) showed that the proportion of THg as MeHg in ringed seal liver from Ulukhaktok ranged from 1 to 12% with lower proportions in animals greater than five years old, while Wagemann et al. (2000) reported an average MeHg fraction of 2% for ringed seals from the Canadian Arctic. In contrast, Dehn et al. (2005) showed that 81% of THg in muscle was in the form of MeHg.

12.2.2. Spatial patterns

Spatial patterns of THg in ringed seal liver were examined using geometric means (±95% confidence intervals) for each of 12 communities across the Canadian Arctic for which data were available post 2000 (Fig. 11). Data for males and females were combined because, in general, THg concentrations in ringed seal liver are not influenced by sex (Dehn et al., 2005). No statistical analysis was conducted because different THg–age relationships among populations complicate age-adjustment of liver THg concentrations. However, only individuals aged five years or older were included, as discussed earlier. Unadjusted THg concentrations in seal liver were higher in Sachs Harbour and Ulukhaktok in the western Arctic compared to most sampling locations in the eastern Arctic including Arctic Bay, Arviat, Inukjuaq, Nain, Pangnirtung, Pond Inlet, Qikiqtarjuaq, and Resolute. A similar geographic pattern for THg in seal liver was reported by Wagemann et al. (1996) and Rigét et al. (2005).

In order to remain consistent with the analysis of spatial patterns in liver, spatial patterns of THg in muscle of adult ringed seals ≥5 years or >100 cm length, if age was not available, were examined using geometric means for each of 12 communities across the Canadian Arctic for which data were available post-1999 (Fig. 12). Muscle THg concentrations varied significantly among locations in the eastern and western Arctic, and were significantly higher in Sachs Harbour, Ulukhaktok (Gaden et al., 2009), Resolute, and Qikiqtarjuaq compared with other communities sampled. Similar to results for liver, higher concentrations in ringed seal muscle were found in the western Arctic—Sachs Harbour,

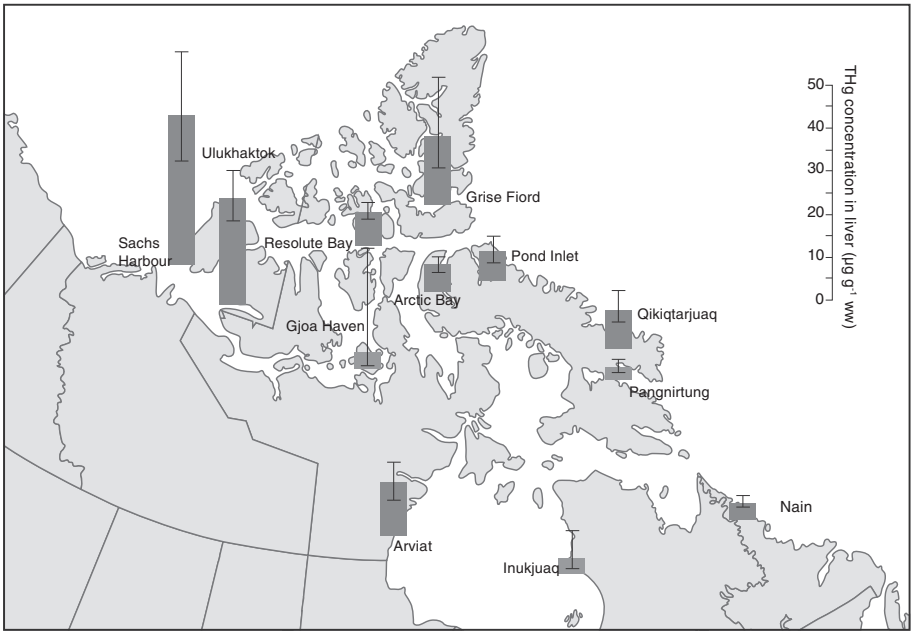

Fig. 11. Concentrations of THg (geometric means ± 95% confidence intervals) in ringed seal liver from 12 communities sampled between 2000 and 2008. Only individuals aged five years or older were included (Muir, Environment Canada, unpublished data). Sample sizes ranged from $n = 6$ (Inukjuaq) to $n = 72$ (Resolute).

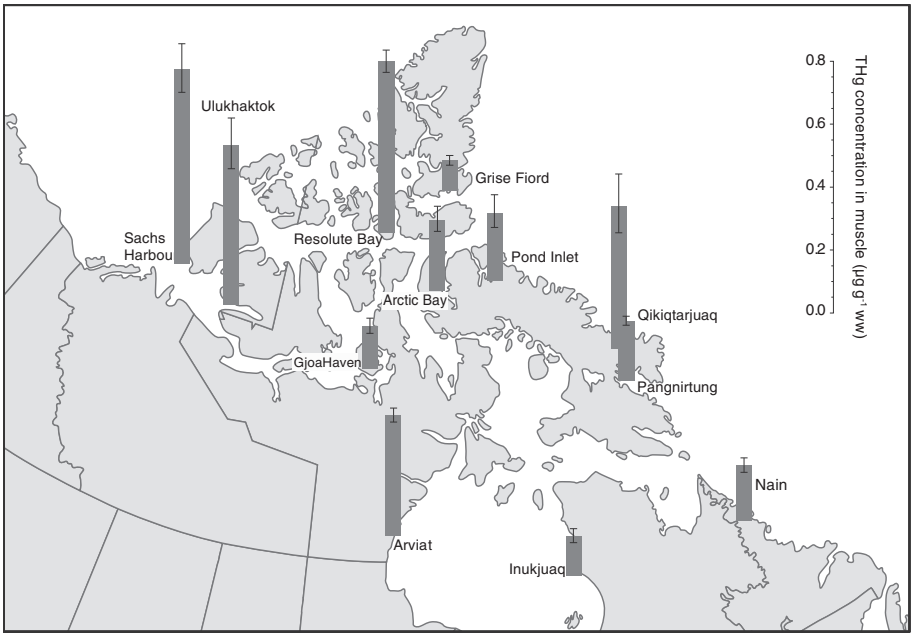

Fig. 12. Concentrations of THg (geometric means ± 95% confidence intervals) in ringed seal muscle from 12 communities sampled between 1999 and 2009. Only individuals ≥5 years or >100 cm length, if age was not available, were included (Muir, Environment Canada, unpublished data).

Ulukhaktok—but in addition, two other High Arctic sites—Resolute, Qikiqtarjuaq—showed elevated THg concentrations. It is unclear what factors are driving these geographic trends.

In a separate investigation in Nunatsiavut (northern Labrador), ringed seals were collected in 2008 and 2009 from the Nachvak, Saglek, Okak, and Anaktalak fjords (Brown, Fisheries and Oceans Canada, and Reimer, Royal Military College of Canada, Unpublished data). Average THg concentrations in ringed seal muscle were low and ranged from 0.128 to 0.230 μg g^{-1} ww among the four fjords. Overall, these results show relatively little spatial variation among Labrador fjords and are consistent with low muscle concentrations of THg measured in ringed seals at two other sites in the region (see Fig. 12).

12.2.3. Comparison of mercury concentrations in ringed seal with other seal species

Ringed seals, harbor seals, and bearded seals were sampled near communities in western Hudson Bay to examine differences in diet and THg concentrations among size classes (Young et al., 2010). Age-specific differences in foraging, muscle THg concentrations and $\delta^{15}N$ ratios varied among pups, juveniles, and adults of ringed and bearded seals. Ringed and bearded seals had similar THg concentrations in muscle, but harbor seals were an order of magnitude higher. Ringed seals had lower THg concentrations in liver than both bearded and harbor seals. Based on $\delta^{13}C$ ratios, bearded seals appeared to feed more in the benthic food web. Elevated liver and muscle THg concentrations in harbor seals compared to the other two species were likely due to harbor seals feeding at a higher trophic level.

12.2.4. Temporal trends

No significant trends in THg concentrations in ringed seal muscle were found in the communities of Arviat, Resolute, Sachs Harbour, or Pangnirtung from 1999 to 2009 (Fig. 13). While declines were observed in seals from Arviat and Resolute, the trends were not statistically significant, perhaps due to low sample sizes and relatively high within-year

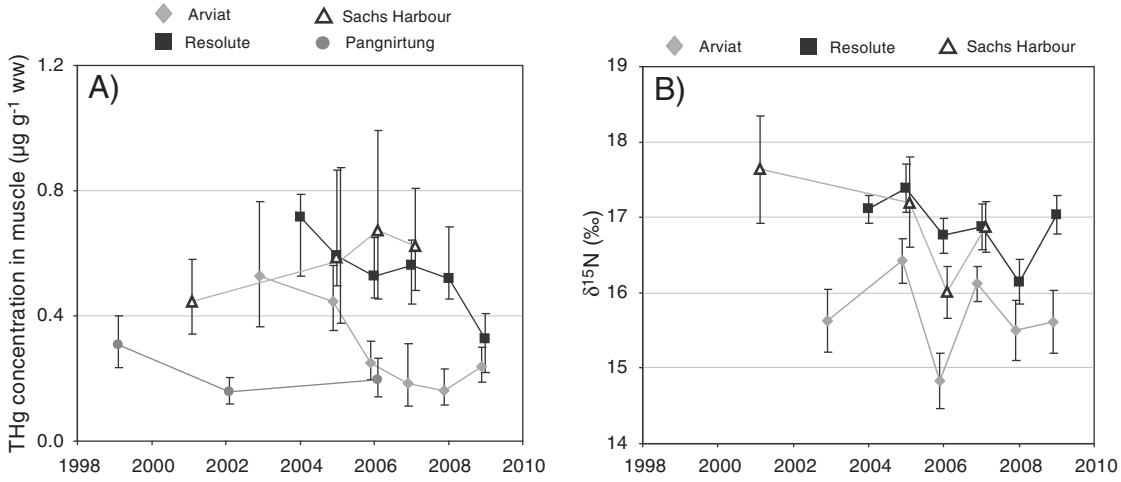

Fig. 13. Temporal trends of (A) THg concentrations from 1999 to 2009 and (B) $\delta^{15}N$ ratios from 2001 to 2009 in ringed seal muscle from Arviat, Resolute Bay, Sachs Harbour, and Pangnirtung. Values are geometric means ± 95% confidence limits. $\delta^{15}N$ ratios were not available for Pangnirtung (Muir, Environment Canada, unpublished data).

variance. This overall finding is in general agreement with results for THg in ringed seal muscle from Ulukhaktok where no significant trends were observed during 2002 to 2007 (Gaden et al., 2009).

Average $\delta^{15}N$ ratios for ringed seal muscle from Arviat, Resolute, and Sachs Harbour changed little (±1‰) over the study period (Fig. 13) suggesting that seals continued to feed at the same trophic level. Earlier measurements of $\delta^{15}N$ in ringed seal muscle collected in Resolute from 1988 to 1990 averaged 16.4 ± 0.2‰ (Atwell et al., 1998), which is within the range observed for samples collected between 2004 and 2009. Gaden et al. (2009) also found only minor shifts in average $\delta^{15}N$ of <1‰ in seals from Ulukhaktok over a 14-year period.

Gaden et al. (2009) examined the relationship of THg concentrations in ringed seals with the length of the ice-free season in the eastern Amundsen Gulf. Muscle tissue of male and female adult ringed seals (aged ≥7 years) were sampled at Ulukhaktok (Holman) from 1973 to 2007. Age influenced the THg concentrations but there was no significant difference between concentrations in males and females. Age-adjusted THg concentrations displayed a second-order polynomial relationship with the length of the ice-free season in the year prior to seal collection. Seal THg concentrations were higher for years with short (~60 days) and long (greater than ~140 days) ice-free seasons. Gaden et al. (2009) hypothesized that THg concentrations in ringed seals were influenced by the environmental conditions of the previous year on their prey; i.e. variation in the length of the ice-free season may have affected the population of Arctic cod—the preferred prey of ringed seals in winter (Smith, 1987). Additional field studies are necessary to understand the reasons for this apparent trend.

12.3. Beluga

Mercury in liver is largely inorganic and bound to selenium, rendering it biologically unavailable following demethylation, whereas Hg in muscle is largely in the form of MeHg and better reflects recent diet exposure related to beluga size and habitat use (Loseto et al., 2008b). Therefore, both liver and muscle are often analyzed for THg in beluga.

12.3.1. Beluga in Hudson Bay

Gaden and Stern (2010) examined temporal trends of THg in the liver and muscle of beluga sampled in Hudson Bay from Arviat on the west coast (1984 to 2008) and Sanikiluaq on the east coast (1994 to 2008). Mean annual concentrations of THg were between 5–21 μg g^{-1} ww in liver and 0.68–1.3 μg g^{-1} ww in muscle at Arviat, and between 5–43 μg g^{-1} ww in liver and 0.49–1.8 μg g^{-1} ww in muscle at Sanikiluaq. Age was correlated with THg concentrations in both the liver and muscle at both sampling locations. Age-adjusted THg concentrations varied significantly with time only in female beluga from Arviat, increasing in the liver and decreasing in the muscle (Fig. 14). The lack of a significant temporal trend in males from Arviat suggests differences in habitat and prey selection between sexes as discussed in Section 9.1.4 (Loseto et al., 2006, 2008a). The increase in THg concentrations in beluga liver over the study period may have resulted partly from the accumulation of inorganic Hg which has a slow elimination rate in mammalian livers (Friberg et al., 1979).

Stable isotope indicators of diet ($\delta^{15}N$ and $\delta^{13}C$) measured in beluga liver generally did not explain THg trends in the liver or muscle of beluga at Arviat and Sanikiluaq (Gaden and Stern, 2010). Only $\delta^{13}C$ ratios in Arviat beluga showed a significant temporal trend, becoming more depleted between 1984 and 2008 ($p = 0.02$). The observed decrease in muscle THg and depletion in $\delta^{13}C$ ratios in beluga from Arviat suggest that these whales may have shifted toward a more pelagic diet containing less THg (Cherel and Hobson, 2007; Ohizumi and Miyazaki, 2010). Interestingly, polar bears in western Hudson Bay have also shown a negative shift in $\delta^{13}C$ ratios from 1991 to 2007 (McKinney et al., 2009). The lack of significant trends in $\delta^{15}N$ ratios suggests that beluga in Hudson Bay have not changed the trophic level at which they feed over time (Hobson and Welch, 1992). The decrease in dietary exposure to THg in some Hudson Bay beluga may be affected by a longer ice-free season in Hudson Bay (Ford et al., 2009; Gagnon and Gough, 2005; Hochheim et al., 2010; Rodrigues, 2009).

12.3.2. Beluga in the western Arctic

Age-adjusted concentrations of THg in the liver of beluga whales from the western Arctic increased from the 1980s to the 1990s followed by stable, high concentrations in the early 2000s (Lockhart et al., 2005a). A recent analysis of the beluga data used average THg concentrations in the liver and muscle for specific age or size classes, respectively. Two age groups were examined for temporal trends in liver THg concentrations. Age was estimated based on one growth layer group of dentine in longitudinally-sectioned teeth (Stewart et al., 2006). The mean THg concentration in livers of whales from 16 to 35 years of age was 18.84 ± 1.1 μg g^{-1} ww across years (1981–2012), and whales from 36 to 55 years had significantly higher ($p < 0.0001$) concentrations which averaged 53.38 ± 3.9 μg g^{-1} ww.

Given the physiological differences in how THg accumulates in liver and muscle, temporal trends were also examined in muscle. For this analysis, male beluga were grouped by size, medium-sized males (3.8–4.2 m) and large-sized males (>4.2 m), according to habitat use and relationships found with diet as described in Section 9.1.4 (Loseto et al., 2006, 2008a, 2009). When averaged over all years (1981–2012), THg concentrations were significantly higher in the large males (1.60 ± 0.06 μg g^{-1} ww) than in the medium-sized males (1.18 ± 0.05 μg g^{-1} ww) ($p < 0.0001$).

Concentrations of THg increased in liver and muscle of beluga from 1981 to 2002 which was consistent with the findings of Lockhart et al.

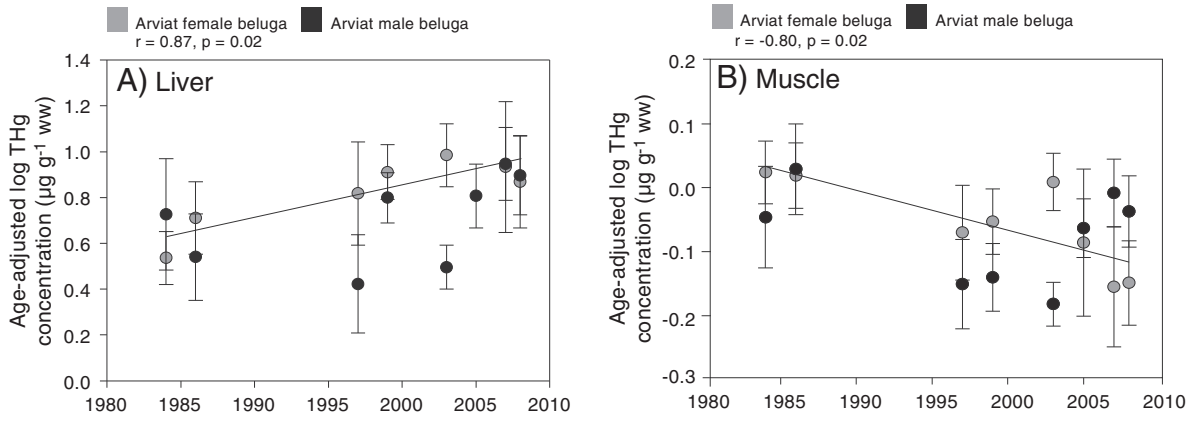

Fig. 14. Annual mean THg concentrations (±standard error) in (A) liver and (B) muscle of beluga sampled at Arviat from 1984 to 2008 (Gaden and Stern, 2010). Data have been log-transformed and age-adjusted.

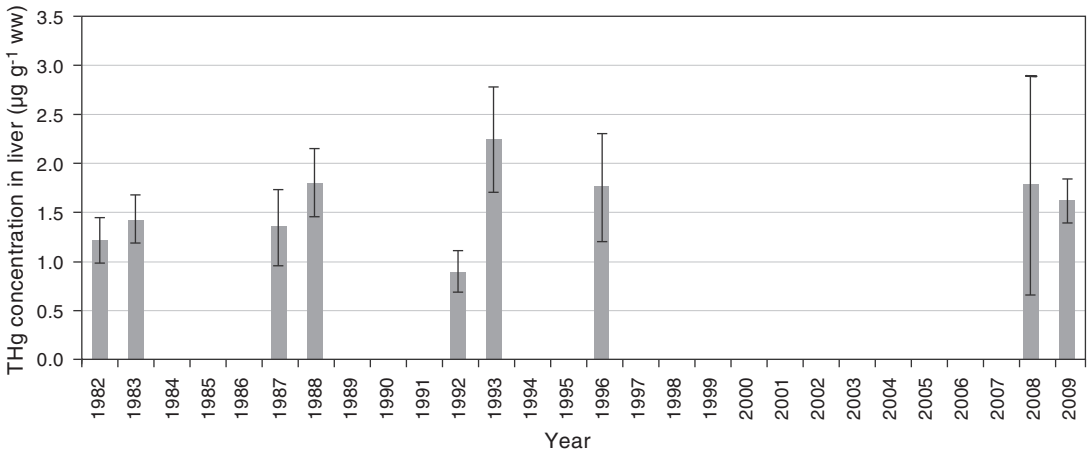

Fig. 15. Temporal variation in concentrations of THg (mean ± standard error) in liver of walruses ranging in age from 8 to 20 years sampled from 1982 to 2009 near Igloolik (Stern, Fisheries and Oceans Canada, unpublished results).

(2005a). For the data spanning 2002 to 2012, no significant linear decline was observed for liver THg concentrations in younger beluga, however in older beluga, THg decreased significantly (r = -0.33, p = 0.02, n = 48). Muscle THg concentrations showed a significant linear decrease in the large size class (r = -0.22, p = 0.05, n = 85). Further investigation as to what factors may be reducing Hg exposure in western Arctic beluga is described in Loseto et al. (2015-in this issue).

12.4. Walrus

Walruses were sampled occasionally between 1982 and 2009 in the Foxe Basin near Igloolik. Liver THg concentrations were generally <3 µg g^{-1} ww (Fig. 15) and, for the most part, were considerably lower than in other marine mammals. No temporal trends were observed for walruses between 1982 and 2009, although the number of monitoring years (n = 9) was relatively low during that period. Liver THg concentrations of walruses were not related to age.

12.5. Narwhal

Narwhals (*Monodon monocerus*) were sampled periodically between 1978 and 2004 off Baffin Island near Pond Inlet. Liver THg concentrations ranged from 6.7 to 17 µg g^{-1} ww (Fig. 16). No temporal trends were evident for liver THg concentrations of narwhals between 1978 and 2004, although the number of monitoring years (n = 8) was again relatively low (Fig. 16). Liver THg concentrations of narwhals were not related to length for animals of 350 to 485 cm.

12.6. Polar bear

The polar bear is a top predator in the Arctic marine ecosystem and, as such, THg concentrations in the polar bear are among the highest observed in the Arctic (Dietz et al., 2009; Muir et al., 1999). Polar bears are distributed throughout the circumpolar region and, thus, are an ideal species for monitoring contaminants.

12.6.1. Spatial patterns

Spatial patterns of THg in polar bears were investigated during 2005–2008 in Alaska (Chukchi and Bering Seas), Canada, and Greenland (Routti et al., 2011). Liver concentrations of THg in polar bears from the northern and southern Beaufort Sea were higher than in all other areas, except for Lancaster/Jones Sound and Gulf of Boothia (Fig. 17). Previous studies of polar bears from the Canadian Arctic similarly reported Hg concentrations being highest in the Beaufort Sea population and lowest in the Hudson Bay population (Braune et al., 1991; Norstrom et al., 1986; Rush et al., 2008). Bears from the Hudson Bay area had lower concentrations of THg compared to other areas except the adjacent Davis Strait. Concentrations of THg in bears from Alaska (Chukchi and Bering

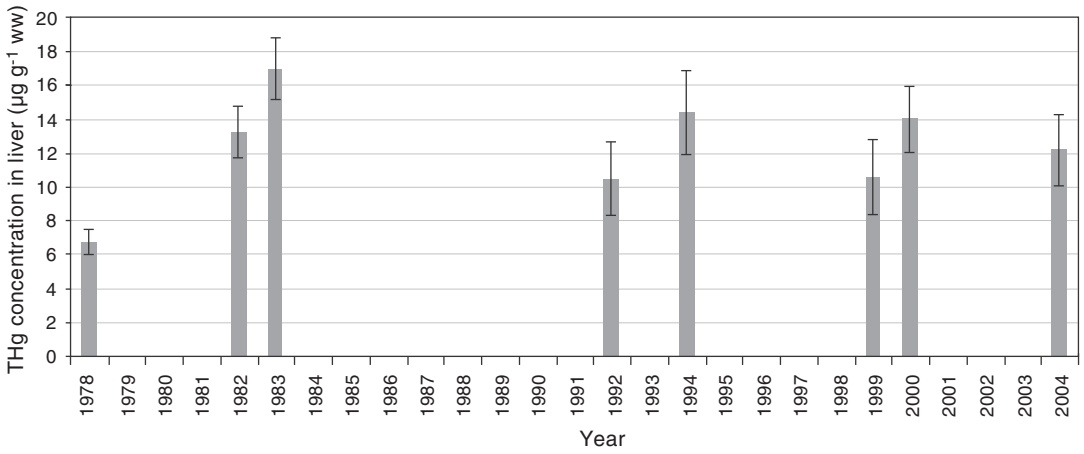

Fig. 16. Temporal variation in liver concentrations of THg (mean ± standard error) of narwhals ranging in length from 350 to 485 cm sampled from 1978 to 2004 near Pond Inlet (Stern, Fisheries and Oceans Canada, unpublished results).

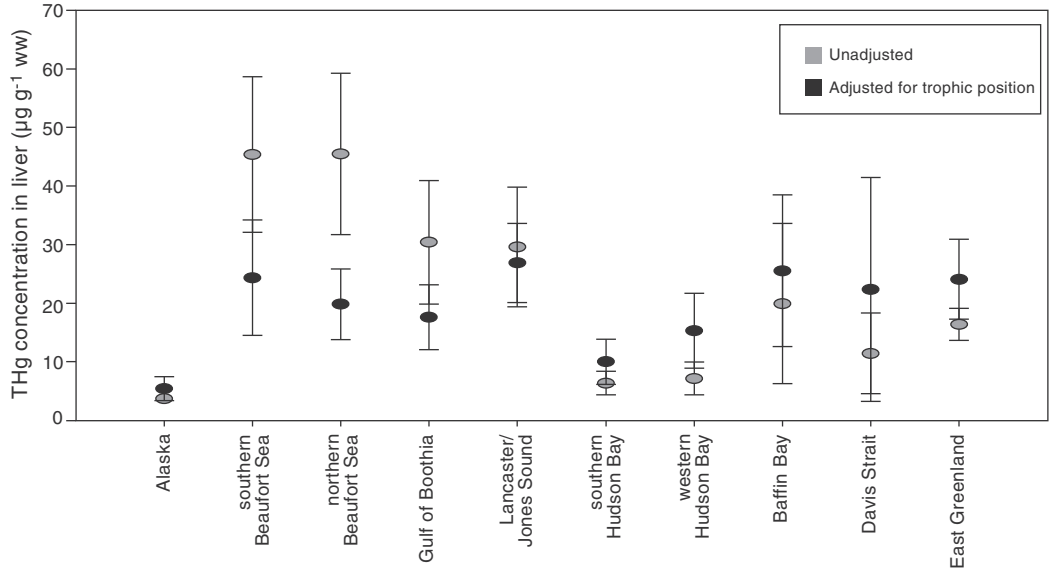

Fig. 17. Geometric mean concentrations of THg (µg g^{-1} ww; ±95% confidence intervals) in polar bear liver from 10 subpopulations in Alaska (Chukchi and Bering Seas), Canada, and Greenland collected from 2005 to 2008. All concentrations were adjusted for sex and age. In addition, THg concentrations were adjusted for trophic position using muscle $\delta^{15}N$ and compared to unadjusted concentrations.
Based on data from Routti et al. (2012).

Seas) were as low as those from Hudson Bay, which is consistent with the generally low concentrations of THg found in marine and terrestrial mammals from Alaska compared to other Arctic regions (Dehn et al., 2006).

The observed geographic pattern of Hg concentrations in these polar bear studies may be related to both abiotic and biotic factors. High Hg concentrations in marine mammals from the eastern Beaufort Sea may potentially be a consequence of Hg transported from the Mackenzie River (Leitch et al., 2007). However, geographic patterns in Hg concentrations of beluga, narwhals, and ringed seals have also been related to geological formations (Rigét et al., 2005; Wagemann et al., 1996). In addition, recent studies have pointed to the influence of food web structure and feeding behavior on Hg concentrations in polar bears (Cardona-Marek et al., 2009; Horton et al., 2009) and other marine mammals including beluga whales (Loseto et al., 2008a) and various seal species (Young et al., 2010).

Liver THg concentrations for a subset of the same Alaskan, Canadian, and East Greenland bears collected from 2005 to 2008 were investigated in relation to differences in food web structure among the subpopulations (estimated using $\delta^{15}N$, $\delta^{13}C$ and fatty acid tracers in muscle) (Routti et al., 2012). Regardless of subpopulation, liver THg concentrations were positively related to $\delta^{15}N$ ratios indicating that polar bears feeding at a higher trophic level accumulate more THg compared to polar bears feeding at a lower trophic level. This finding is consistent with previous studies that reported trophic biomagnification of Hg for other Arctic fish and wildlife (Gaden et al., 2009; Loseto et al., 2008b; Muir et al., 2005). Adjustment for trophic position reduced the geographic variability of liver THg concentrations among polar bear subpopulations (Fig. 17) (Routti et al., 2012). Liver THg concentrations were negatively correlated with muscle $\delta^{13}C$ ratios, which suggest that polar bears that feed in areas with higher river inputs of terrestrial carbon may accumulate more Hg than bears feeding in areas with lower freshwater input. Liver THg concentrations were also positively related to a fatty acid (20:1n − 9) which is biosynthesized in large amounts in *Calanus* copepods. It was hypothesized that *Calanus* may be an important link in the uptake of Hg in the food web and ultimately in polar bears (Routti et al., 2012). The findings of Routti et al. (2012) indicate that food web structure and dietary exposure have a significant influence on geographic trends of THg in liver of polar bears.

St. Louis et al. (2011) similarly found that food web structure explained, in part, geographic variation in Hg bioaccumulation in polar bears. In that study, THg concentrations and $\delta^{15}N$ isotope ratios in polar bear hair indicated that southern Beaufort Sea bears bioaccumulated more Hg because they fed at a higher trophic position than bears from western Hudson Bay. $\delta^{13}C$ ratios suggested that Beaufort Sea bears fed more on pelagic than benthic carbon compared to Hudson Bay bears. McKinney et al. (2011) found $\delta^{13}C$ evidence which showed that, compared to other polar bear subpopulations, the diet of Hudson Bay polar bears may be more dependent on freshwater associated prey such as seals that inhabit rivers or estuaries. However, regional differences in polar bear Hg concentrations were also likely due to the pool of MeHg available for uptake into the food web because concentrations of methylated Hg mid-depth in the pelagic water column of the Canadian Arctic Archipelago were, on average, twice as high as in Hudson Bay (St. Louis et al., 2011). These findings indicate that food web length and structure combined with MeHg bioavailability are important factors in the interpretation of spatial Hg trends in polar bears, particularly in a changing Arctic.

12.6.2. Temporal trends

Recent temporal trends of THg concentrations in the livers of polar bears differed among populations in the circumpolar Arctic. In polar bears from the Beaufort Sea area, a slight increase in liver THg concentrations was observed between the 1980s and 2002 (Fig. 18) (Rush et al., 2008). However, Routti et al. (2011) reported that no further changes in THg concentrations were observed from 2002 to 2007 and 2008 for polar bears from the same Beaufort Sea subpopulations (Fig. 18). Results reported by Rush et al. (2008) indicated that a slight increase in THg concentrations occurred in bears from other subpopulations and areas of the Canadian Arctic sampled in 2002 relative to the 1980s. Concentrations of THg in polar bears from Alaska (Chukchi Sea) and Canadian Arctic subpopulations (except the Beaufort Sea) were lower in 2007–2008 relative to concentrations in 2002 (Fig. 18). In contrast, concentrations of THg in polar bear liver from East Greenland increased significantly in 2006 relative to measurements from 1999 and 2000 ($p < 0.05$) (Fig. 18). This finding was in agreement with increasing THg concentrations in polar bear hair from Northwest Greenland between 1992 and 2008 (Dietz et al., 2011), ringed seal

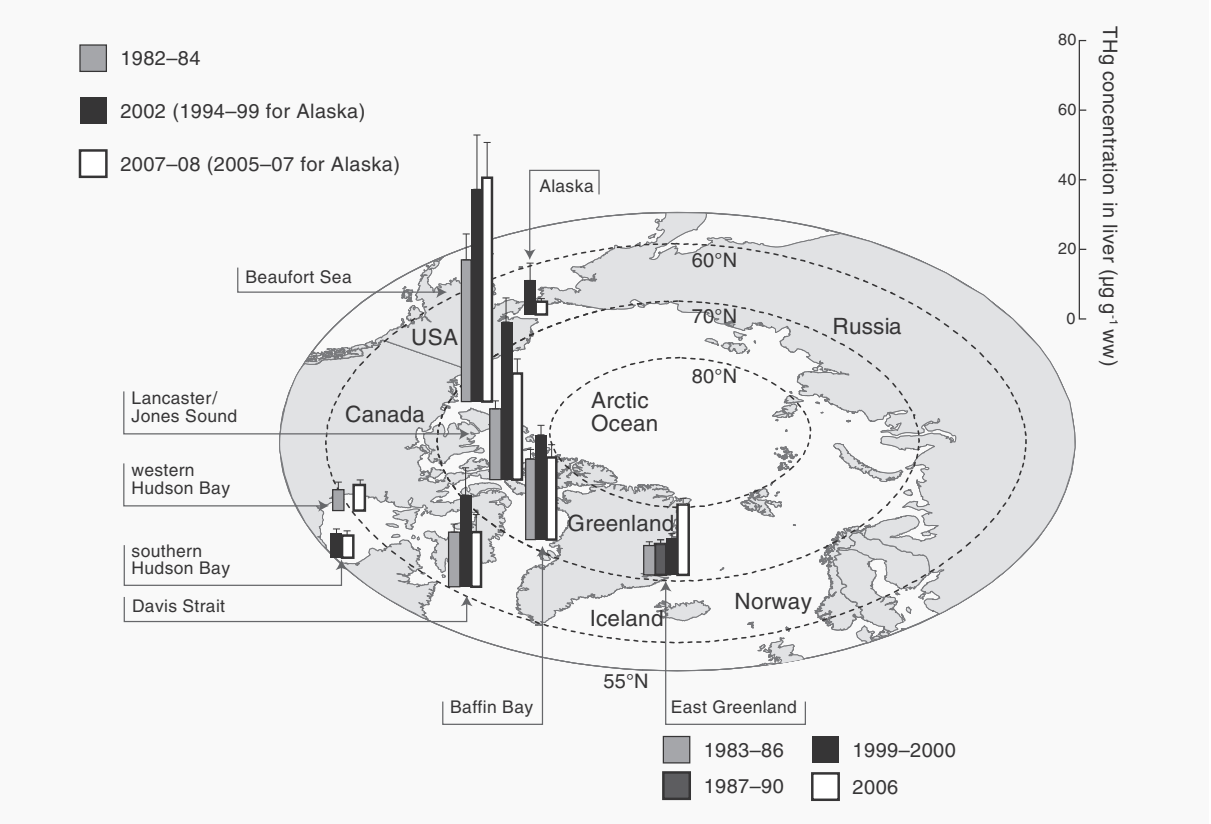

Fig. 18. Concentrations (µg g^{-1} ww; geometric mean ± standard error) of THg in polar bear liver from Alaska (Chukchi and Bering Seas) in 1994 to 2007, Canada in 1982 to 2008, and East Greenland in 1983 to 2006.
Data from Routti et al. (2011) and the references therein.

teeth from Central, West, and East Greenland between 1994 and 2006 (Aubail et al., 2010), and ringed seal liver from central West Greenland during 1999 to 2004 (Rigét et al., 2007a). In contrast, Dietz et al. (2006) reported a decline in THg in polar bear hair from East Greenland between 1973 and 2001.

Overall, geographic trends of THg in polar bears appear to be related to Hg sources—potentially atmospheric deposition, river inputs, and/or local geology—and to polar bear diet. Temporal trends suggest that Hg concentrations in East and Northwest Greenland polar bears have recently increased. Future studies should focus on the role of changing climate and anthropogenic emissions on geographic and temporal trends of Hg in polar bears.

13. Summary

Some of the most significant advances in Arctic Hg science over the last decade were made in the area of biogeochemical cycling, although the mechanisms linking these processes to MeHg entry into Arctic marine food webs are still poorly understood. Much new information has been collected on Hg concentrations in marine water, snow, and ice. Concentrations of methylated Hg in seawater were shown to increase with depth, suggesting that methylated Hg species are produced in intermediate Arctic marine waters and/or sediments. Ocean–atmosphere fluxes of GEM and Me_2Hg were high, and Arctic marine waters have been shown to be a substantial source of gaseous Hg to the atmosphere during the ice-free season. As a result of AMDEs, inorganic Hg accumulation in marine snow was enhanced relative to the terrestrial environment. However, THg concentrations in surface snow declined rapidly within days of an AMDE as a result of re-emission of Hg to the atmosphere. Estimates of areal loads of THg in snow suggest that snowmelt is likely a small flux of Hg to Arctic marine waters during spring.

The most extensive sampling of marine sediments in the Canadian Arctic has been done in Hudson Bay where sediment THg concentrations were low compared to other marine regions in the circumpolar Arctic. In most sediment cores, vertical profiles of sediment Hg fluxes increased during the early years of the Industrial Era (1870 to 1930), followed by stable or declining Hg inputs toward the end of the 20th Century.

Mass balance models were developed for the Arctic Ocean and Hudson Bay to provide quantitative estimates of THg fluxes into and out of these ecosystems. Depending on the model used for the Arctic Ocean, either net atmospheric deposition or rivers constituted the most important source of Hg to the system. For Hudson Bay, rivers were identified as the largest single source followed in importance by the atmosphere and ocean inflow Hg fluxes. More work using a variety of methodological approaches is essential to resolve the uncertainties in the riverine and atmospheric Hg contributions to Arctic ecosystems, especially since the atmospheric flux would be most immediately affected by emission controls.

Despite recent advances, biogeochemical processing of Hg in the Arctic marine environment still remains poorly characterized. The first measurements of methylation rates in Arctic seawater suggest that the water column is an important site for MeHg formation from inorganic Hg. This observation challenges the paradigm that only anaerobic conditions support significant MeHg production. Production of Me_2Hg may occur in deep waters as suggested by recent water-column profiles in the Arctic Ocean, and its breakdown in the water column may be a source of MeHg for biological uptake. Recent evidence from the Arctic suggests that microbes may be key players in altering Hg redox chemistry in salt water. The discovery of expressed Hg resistance genes suggests that microbial populations in the Arctic marine environment are sensitive to THg contamination and may be actively reducing this

metal to its elemental form. These findings underscore the need for more fundamental research examining mechanistic aspects of Hg methylation and redox reactions in polar regions.

Although the exact mechanisms by which Hg enters the food chain are not fully understood, biomagnification of Hg has been observed in several marine food webs. Concentrations of THg in muscle of sea-run Arctic char were consistently very low at various locations across the Canadian Arctic. However, little information exists for obligate marine fish species that may be important sources of Hg for seabirds and marine mammals. The factors that determine geographic and habitat variation of Hg bioaccumulation in marine fish remain unresolved and more studies are needed to better understand Hg transfer through marine food webs.

Spatial analyses of THg concentrations in marine biota found that ringed seals, beluga, and polar bears had higher Hg concentrations in the eastern Beaufort Sea region than in other parts of the Canadian Arctic, particularly in comparison to Hudson Bay, Nunavik (northern Quebec), and Nunatsiavut. Recent evidence indicates that higher THg in Beaufort Sea polar bears is due to their higher trophic position and higher concentrations of MeHg in water available for entry into the food web. Although the eastern Beaufort Sea was consistently a region of high Hg bioaccumulation, additional geographic variability was observed among species. A latitudinal difference in THg concentrations was found among colonies of thick-billed murres, with birds breeding at the higher latitude colonies having higher THg concentrations than those breeding at sub-Arctic colonies. Further research is needed to link biogeochemical and food web processes with geographic variation in Hg concentrations of Arctic biota.

More frequent monitoring of key Arctic biota over the past decade has resulted in more powerful datasets and a better ability to detect changes in Hg concentrations. Temporal trends of Hg in marine biota differed among species and locations in the Canadian Arctic. Populations of ringed seals near five Arctic communities, narwhals from the Baffin Island region, and walruses from Igloolik showed no temporal change in THg concentration, whereas Hg concentrations in muscle of beluga from the western Canadian Arctic appear to have declined since the 1990s. Increases in THg concentrations were observed in recent years for sea-run char near two Arctic communities, and since 1975, in eggs of three Arctic-breeding seabird species at Prince Leopold Island. Recent temporal trends of THg in polar bears varied among populations in the circumpolar Arctic, and inter-annual variation in ice conditions may be affecting the dietary exposure of seals to Hg. Overall, the different Hg trends reported for Arctic marine biota indicate that the drivers may be regional or habitat-specific. Particularly at sites where increases were observed, further research is required to identify the underlying processes leading to changes over time in marine biota Hg bioaccumulation.

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