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Review

How does climate change influence arctic mercury?

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ABSTRACT

Recent studies have shown that climate change is already having significant impacts on many aspects of transport pathways, speciation and cycling of mercury within Arctic ecosystems. For example, the extensive loss of sea-ice in the Arctic Ocean and the concurrent shift from greater proportions of perennial to annual types have been shown to promote changes in primary productivity, shift foodweb structures, alter mercury methylation and demethylation rates, and influence mercury distribution and transport across the ocean–sea-ice–atmosphere interface (bottom-up processes). In addition, changes in animal social behavior associated with changing sea-ice regimes can affect dietary exposure to mercury (top-down processes). In this review, we address these and other possible ramifications of climate variability on mercury cycling, processes and exposure by applying recent literature to the following nine questions; 1) What impact has climate change had on Arctic physical characteristics and processes? 2) How do rising temperatures affect atmospheric mercury chemistry? 3) Will a decrease in sea-ice coverage have an impact on the amount of atmospheric mercury deposited to or emitted from the Arctic Ocean, and if so, how? 4) Does climate affect air–surface mercury flux, and riverine mercury fluxes, in Arctic freshwater and terrestrial systems, and if so, how? 5) How does climate change affect mercury methylation/demethylation in different compartments in the Arctic Ocean and freshwater systems? 6) How will climate change alter the structure and dynamics of freshwater food webs, and thereby affect the bioaccumulation of mercury? 7) How will climate change alter the structure and dynamics of marine food webs, and thereby affect the bioaccumulation of marine mercury? 8) What are the likely mercury emissions from melting glaciers and thawing permafrost under climate change scenarios? and 9) What can be learned from current mass balance inventories of mercury in the Arctic? The review finishes with several conclusions and recommendations.

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1. Introduction

The entry of contaminants into global biogeochemical cycles produces many opportunities for unexpected outcomes to occur because of climate variability and change (Macdonald, 2005; Macdonald et al., 2005; Wang et al., 2010). The biogeochemical cycle of mercury (Hg) (Fig. 1) is particularly susceptible to global change for a number of reasons:

- the Hg cycle is linked to the organic carbon cycle both by affinity in transport and by methylating processes, and change in the cryosphere will lead to change in the organic carbon cycle;
- the natural Hg cycle is now widely encumbered by direct and indirect emissions from human activities during the past two centuries, which have built up inventories that may become unstable with change in the cryosphere;
- Hg transports within, and/or exchanges between, air, water, soils, sediments and biota;
- Hg switches between chemical forms that exhibit widely differing volatilities, reactivities, bioavailabilities and toxicities; and
- exposure of top predators to Hg can be affected both by bottom-up processes (e.g., supply of Hg and entry into the bottom of the food web) and top-down processes (e.g., foraging behavior of high trophic level animals), most of which are themselves affected by climatic factors.

The Arctic is especially vulnerable to global warming, with models and observations suggesting double the temperature rise compared to temperate or tropical regions of the globe (AMAP/CAFF/IASC, 2005). Accordingly, IPCC (Intergovernmental Panel on Climate Change) global temperature projections of 2 to 3 °C through the latter half of the 21st century would imply 4 to 6 °C for the Arctic. But for the cryosphere, the most significant consequence of warming will occur at the temperature of melting (−2 to 0 °C) where the hydrological and organic carbon cycles undergo whole-scale change. It has long been recognized that large changes are occurring in the Arctic's aquatic systems (Macdonald, 1996; Vörösmarty et al., 2002). These systems are of particular significance as it is within wet environments (wetlands, marine and freshwaters) that most of the subsequent risks to humans and wildlife from Hg exposure are developed through methylation (Macdonald and Loseto, 2010). Furthermore, Arctic change is accelerating (Smol and Douglas, 2007a; Stroeve et al., 2008; Post et al., 2009). This, together with recent work revealing an ever-greater complexity in the biogeochemistry of Hg (Lindberg et al., 2002; Kirk et al., 2006; Poulain et al., 2007; Loseto et al., 2008a; Steffen et al., 2008; Sunderland et al., 2009), makes it clear that climate change will alter human and ecosystem exposure to Hg in many ways some of which we can predict and others of which will be surprises. The complexity of environmental processes and pathways challenges our ability to project exactly how change in the global Hg cycle will manifest in the Arctic.

This review focuses specifically on how the Arctic's Hg cycle has been and is likely to be impacted by climate change. It can be inferred from the detailed schematics of the Hg cycle shown in Fig. 1 that climate-related variables may act on Hg transport, transfer and transformation processes anywhere between global emissions and the accumulation of monomethylmercury (MeHg) in top Arctic predators. Broadly speaking, the Hg cycle can be affected by change in the physical and biological systems or in the carbon cycle. There is better understanding about the physical components of the system and, thus, it is easier to propose how alteration of, for example, temperature, precipitation, and ice cover, would affect the volatility, deposition and air–water exchange of Hg in the Arctic. In contrast, for the biological and carbon systems, there is still insufficient understanding of their coupling with the Hg cycle to construct plausible descriptive or predictive models of climate effects.

This review begins by briefly summarizing the present state of knowledge about change in the physical components of the Arctic.

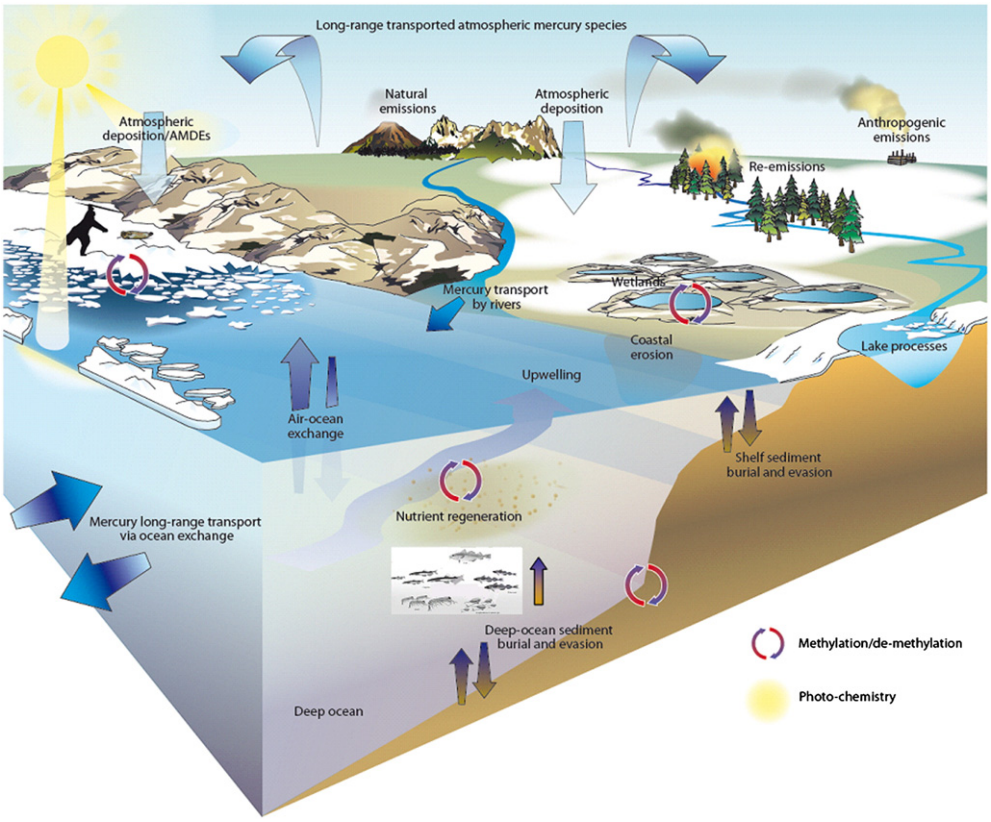


Fig. 1. Cycling of mercury through the Arctic marine and terrestrial ecosystems.

Subsequent sections discuss the connections between these physical changes resulting from climate change and the Arctic Hg cycle.

2. What impact has climate change had on Arctic physical characteristics and processes?

2.1. Atmosphere

Arctic air temperature is increasing (Overland et al., 2008) and the weather becoming less predictable. Indeed, large variation in environmental parameters, frequently alluded to by northerners (Krupnik and Dyanna, 2002), is likely to be an important manifestation of the changing climate. The loss of sea-ice cover for extensive areas of the Arctic Ocean has allowed radiation to penetrate the water during summer, thus storing heat in the upper ocean. This heat later feeds back to the lower atmosphere with the consequence that autumn temperatures in the Arctic have recently been as much as 4 °C above average with an Arctic-wide anomaly above +1 °C. Altering ice cover and heat balance over the Arctic Ocean in this manner then changes atmospheric connections between the Arctic and southern latitudes (Francis et al., 2009; Honda et al., 2009). During the past decade, the Arctic atmospheric pressure pattern has been characterized by anomalously high sea-level pressure on the North American side of the Arctic and low pressure on the Eurasian side (Overland et al., 2008), which has then supported more southerly winds. Altered atmospheric pressure fields imply the possibility of altered patterns of atmospheric transport of Hg into and out of the Arctic (Macdonald et al., 2005). Deposition of Hg within the Arctic, including through AMDE (atmospheric mercury depletion events) chemistry, may also be affected by precipitation and temperature changes (Section 3; Munthe et al., 2011).

2.2. Arctic freshwater and terrestrial systems

Change in terrestrial systems is complex because it may manifest in snow and ice cover, glaciers, permafrost, vegetation, river discharge and timing, moisture balance, incidence of forest fire, migration pathways and invasive species (e.g., Hinzman et al., 2005; Wrona et al., 2005; Prowse and Furgal, 2009). To some degree, all of these system components have been undergoing change, but not at the same rate or in the same way everywhere, and trends are frequently masked by large seasonal and inter-annual variations. This variation will, of course, lead to change in components of the Hg cycle both spatially and temporally. The lower atmospheric warming trends, supported by loss of sea ice (as described in Section 2.3), have led to declines in the length of snow seasons during the past three decades (Peterson et al., 2009), loss of lake ice (Smol and Douglas, 2007b), earlier break-up in rivers (Schindler and Smol, 2006; Prowse and Furgal, 2009) and feedbacks between marine and terrestrial systems (e.g., Lawrence et al., 2008).

Once considered permanent, glaciers and ice fields continue to decline in size; in particular, the Greenland Ice Sheet shows signs of mass wastage (Witze, 2008) as do smaller glaciers in the Arctic (e.g., Sharp et al., 2011). Because snow deposited during the past two centuries and during earlier millennia contains archived materials, freshwater from glacier melt is accompanied by organic matter and dust deposited during the pre-industrial (pre-1800) Holocene (Hood et al., 2009) and Hg from the historical period up to the present (Faïn et al., 2009).

Permafrost temperatures have generally increased (Walker, 2007), with recent observations suggesting that temperatures have risen by 1 to 2 °C during the past three decades (Smith et al., 2005a; Oberman, 2008; Osterkamp, 2008). Thawing leads to the release of old carbon (Guo and Macdonald, 2006; Schuur et al., 2009; Roehm

et al., 2009) and Hg (Klaminder et al., 2008) from organic-rich soils. The process of release during thawing may be particularly pertinent for Hg deposited from the atmosphere and stored at the surface of frozen ground, as this Hg has been shown to 'fast track' to the biota (Harris et al., 2007). Permafrost soils slumping into lakes as a consequence of thaw may also provide a pathway to increase Hg methylation in affected lakes. A widespread desiccation of small Arctic ponds has been observed (Smith et al., 2005b; Riordan et al., 2006; Smol and Douglas, 2007b), and with this the demise of an aquatic food source (zooplankton), which could result in a change in MeHg exposure for animals such as aquatic birds that can switch prey.

Lakes in the Arctic have been losing their ice cover, in some cases for the first time in millennia (Smol and Douglas, 2007b; Schindler and Smol, 2006). Given the collective area of lakes in the Arctic (see Douglas et al., 2011, Section 3.7), changes in lake ecosystems consequent to warming have the leverage to widely alter the systematics of carbon production and metabolism and thereby impact the Hg cycle. It is clear that the earlier opening of lakes to light in spring has changed phytoplankton production, perhaps beyond critical thresholds (Michelutti et al., 2005; Smol and Douglas, 2007a,b). The impacts of these changes have been recorded in Arctic lake sediments, in both the organic carbon and Hg profiles (e.g., Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2010). What these changes mean for biological uptake is less clear. Enhanced productivity could lead to bio-dilution of Hg (e.g., Pickhardt et al., 2002; Larsson et al., 2007), whereas greater light exposure could lead to greater photodemethylation. Conversely, greater productivity and carbon supply could drive higher methylation rates in lake waters as it does in the ocean (Sunderland et al., 2009). Carrie et al. (2010) reported an apparent relationship between warmer temperatures during recent decades and increasing tissue Hg concentrations in burbot (*Lota lota*) in the Mackenzie River, Canada, and suggested that one possible explanation was increased MeHg supply from a warming tributary lake where organic productivity had increased concurrently with fish and sediment Hg concentrations.

A surprising observation has been the speed with which terrestrial vegetation can change in the Arctic (Hinzman et al., 2005). This 'greening of the Arctic' (Jia et al., 2003; Tape et al., 2006) has occurred through a rapid replacement of tundra by shrubs, which then leads to feedback effects on snow cover, soil moisture and temperature. The effect of these sorts of changes on the Hg cycle has not been studied. Not all of the terrestrial change has been toward greening; forest fires and desiccation also have consequences for plant cover (Goetz et al., 2005; Kochtubajda et al., 2006; Verbyla, 2008), which can affect the Hg cycle, including potential to release sequestered Hg (Allen et al., 2005; Biswas et al., 2008).

River discharge from the Arctic's drainage basins has been generally increasing in the Russian Arctic since the 1930s at a rate of about 2 to 3 km^3/y (Peterson et al., 2002; Shiklomanov et al., 2006). For North America, the more limited records suggest that trends are neutral or even declining slightly during recent decades (Déry and Wood, 2005; McClelland et al., 2006). Arctic rivers provide a significant source of particulate and dissolved inorganic Hg and smaller amounts of MeHg to the Arctic Ocean (Coquery et al., 1995; Leitch et al., 2007). An important feature of river hydrology is that the concentration of Hg is positively correlated with discharge (Stanley et al., 2002; Balogh et al., 2004; Leitch et al., 2007). Therefore, projections of altered river flows toward higher frequencies of extreme flow events, imply increased riverine Hg inputs to the Arctic Ocean and lakes even if average flow does not change.

Another global effect of anthropogenic carbon dioxide (CO_2) emissions has been to increase the partial pressure of CO_2 (pCO_2) in the Earth's surface waters through gaseous exchange and thereby reduce pH. Although this problem is becoming widely recognized as a threat to biota in the ocean (Doney et al., 2009), less attention has been paid to lake acidification in remote regions like the Arctic. Two sorts of Hg-related changes are possible: acidification can alter the cycling of organic carbon (Keller et al., 2008) and the rate of Hg methylation (Bates and Mathis, 2009).

2.3. The Arctic Ocean

In October 2009, the United Nations Environment Programme (UNEP) released an updated summary of the 2007 IPCC Assessment report (UNEP, 2009). In this Climate Change Science Compendium, the authors warned that many of the IPCC forecasted changes were underestimated and that the scale and pace of effects such as sea level rise, ocean acidification, freshening ocean waters and sea-ice extent have and will continue to accelerate.

The extensive loss of sea ice which has occurred over recent decades is, undoubtedly, the most obvious recent change witnessed in the Arctic (Serreze et al., 2000; Stroeve et al., 2007, 2008). Between 1979 and 2006, average sea-ice extent in September (the annual sea-ice minimum) declined by about 20% or 1.60 million km^2, which corresponds to about 7.5% per decade (Fig. 2). Remarkably, in September 2007, the minimum sea-ice extent reached a record low of 4.13 million km^2 corresponding to a 30% decrease compared to the September average for the period 1979 to 2000. In subsequent years, sea-ice extent has rebounded somewhat but the average rate of decline has reached 11.2% per decade, and average summer sea-ice cover in 2009 was over 25% below the 1979 to 2000 average (Fig. 2). Of possibly even greater significance is the loss of multi-year (thick) ice, which provides the year-to-year resilience of the permanent pack (Giles et al., 2008; Kwok and Rothrock, 2009). The images shown in Fig. 3 compare ice age (a proxy for ice thickness) in 2007, 2008, 2009, and the 1981 to 2000 average. The amount of multi-year Arctic sea ice in 2009 was the lowest on record even though the overall ice extent was greater than in 2007 and 2008. In autumn 2009, 32% of the ice was 2nd year ice and only 19% was 3rd year ice and older, the lowest in the satellite record (data from National Snow and Ice

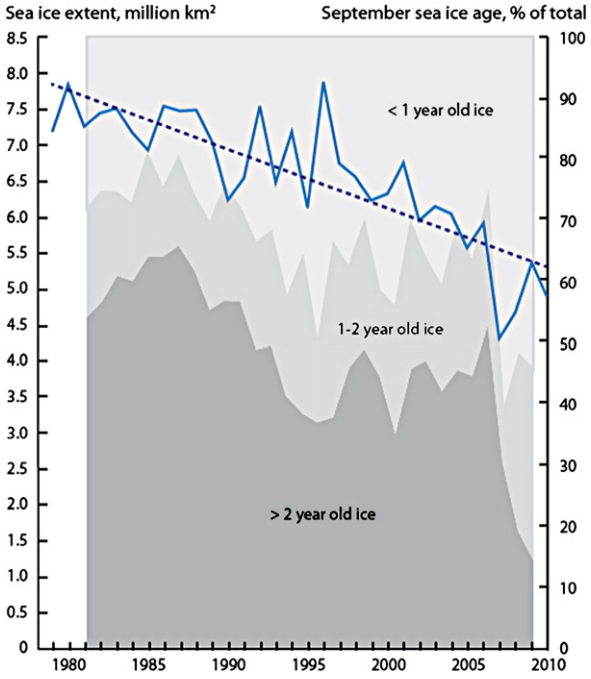


Fig. 2. September sea-ice extent in the Arctic Ocean from 1979 to 2010. The rate of decline since September 1979 has now reached an all time high of 11.2% per decade. The amount of multi-year ice is also declining significantly.
Source: National Snow and Ice Data Center, courtesy of C. Fowler and J. Maslinik, University of Colorado at Boulder.

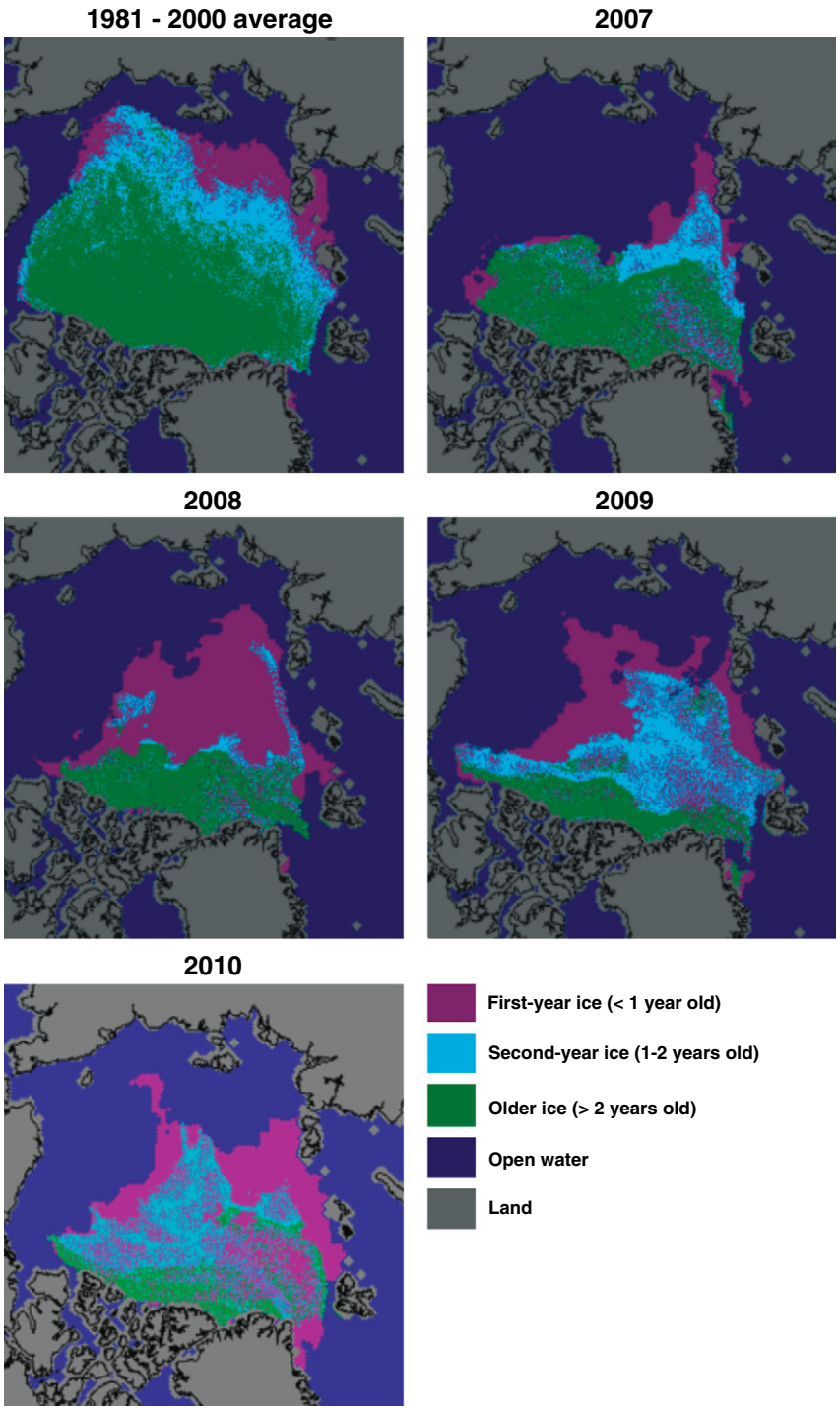


Fig. 3. Arctic sea-ice age at the end of the melt season.
Source: National Snow and Ice Data Center, courtesy of C. Fowler and J. Maslinik, University of Colorado at Boulder.

Data Center, http://nsidc.org/, courtesy of C. Fowler and J. Maslanik, University of Colorado at Boulder). The overall mean winter thickness of the Arctic sea ice, based on submarine data, declined from about 3.6 m in 1980 to 1.9 m in 2007 (Rothrock et al., 2008). Loss of so much permanent ice moves the Arctic Ocean toward a seasonally ice-free state (Lindsay and Zhang, 2005; Maslanik et al., 2007), which will have consequences for light climate, mixing, upwelling, primary production, habitat and range for large animals like bears, walrus and whales and, of course, the Arctic seas as shipping corridors between Asia and Europe. All of these factors have the potential to alter Hg concentrations and geochemistry in the Arctic Ocean and adjoining seas.

Based on the linear regression line shown in Fig. 2, it can be projected that the Arctic Ocean will be ice free in summer by around 2080. However, a quadratic regression model, which could just as easily be applied, projects an ice free summer up to 50 years earlier. Sou and Flato (2009) modeled future change in sea ice in the Canadian Arctic Archipelago and reported that, during the period 2041 to 2060, a 45%

decrease may be expected in summer sea-ice concentrations relative to the period 1950 to 2004. Their model also predicted that ice thickness would decline by 36% and 17% in summer and winter, respectively. Based on the results, the authors projected that the Archipelago may be ice free in summer by about 2050. In comparison, using the Community Climate System Model, version 3 (CCSM3), Holland et al. (2006) project that abrupt changes in the summer Arctic sea ice cover can be expected and ice free summers may occur as early as 2015.

The biogeochemical status of the Arctic Ocean itself is changing, partly due to the loss of sea ice and partly due to change in the properties of water imported from the Atlantic and Pacific Oceans, and discharge from rivers. Recently, the surface waters of the Arctic Ocean have been anomalously fresh, implying greater stratification (McPhee et al., 2009; Proshutinsky et al., 2009). The source of much of the freshening appears to be sea-ice melt, and Arctic Ocean ice shelves (i.e., the marine terminal ends of glaciers) (England et al., 2008; Mueller et al., 2008). Clearly this is not a sustainable freshening as the fresh surface water will be flushed from the Arctic Ocean within years to a decade, and eventually the supply of melting glacier and multi-year ice will run out (Lavoie et al., 2010). The general loss of ice cover within the Arctic Ocean affects wind mixing, up-welling and the light climate. Changes in these parameters then alter the spatial and temporal intensity of primary production (Carmack and Chapman, 2003; Lavoie et al., 2010), and the bacterial remineralization of organic carbon contained in sinking particles. This latter process may be important for Hg in marine food webs considering that Hg methylation is associated with remineralization (Sunderland et al., 2009; Cossa et al., 2009, 2011) and may be a factor in the spatial variation of zooplankton MeHg concentrations within the Beaufort–Chukchi Seas (Stern and Macdonald, 2005). Recently, the loss of ice cover in the Bering Sea has been proposed as a mechanism to reduce MeHg exposure of marine predators due to increased photo-demethylation (Point et al., 2011). Presently, there are very few data with which to assess the importance of these processes in the Arctic or the changes in them that are likely to be occurring. However, a recent study using stable Hg isotopes (Lehnherr et al., 2011) has shown that kinetics involved in the dynamic balance of MeHg are relatively fast compared to transport time scales within watermasses in the Arctic Ocean suggesting that local processes may play a very important role in determining MeHg exposure. We note that local parameters like ice cover, freshwater inflow, and biological activity are clearly subject to climate change.

Global ocean acidification due to anthropogenic CO_2 invasion is becoming a widely-recognized problem (Doney et al., 2009) that may have consequences for many species (e.g., see Cooley and Doney, 2009). From a Hg perspective, acidification may produce profound changes because, as the oceans become more acidic, forams, coccolithophores and other shell makers may become challenged in precipitating their protective shells, for which there has already been produced some evidence (see for example Fabry et al., 2009; Schiermeier, 2011). This would subsequently alter other system components, for example the transfer of carbon from the surface ocean into the deep waters (the so-called 'biological pump'), which would change the cycling of Hg. Presently, it is known that the vertical flux of carbon can affect Hg cycling in two very different ways. First, like many elements, Hg is entrained into the rain of particulate organic carbon (Cossa et al., 2009) and thus Hg can be removed from the mixed layer and delivered to the deep ocean through remineralization and aggregation processes. Second, the remineralization of organic carbon at depth provides the means by which Hg can be methylated (Cossa et al., 2009, 2011; Sunderland et al., 2009), which may well be the critical process in terms of ecosystem exposure to Hg. Low pH environments also favor the production of MeHg. The Arctic Ocean is probably particularly vulnerable because of its cold, relatively fresh surface waters (Bates and Mathis, 2009), which can take up more CO_2 than warmer, saltier oceans. Furthermore, the recent loss of ice cover will allow surface waters to 'catch up' with other regions through enhanced air–sea exchange because the Arctic Ocean historically has lagged behind in the uptake of anthropogenic CO_2 (Anderson et al., 1998; Steinacher et al., 2008). Given that climate change is reducing ice cover (increasing air–sea exchange) and increasing the primary production causing increased regeneration at depth (producing CO_2), accompanying pH declines can be expected. The problem of acidification is manifest in water up-welled over continental shelves (Feely et al., 2008). In the Arctic Ocean, upwelling is also likely to increase systematically in response to withdrawal of the ice edge beyond the shelf (Carmack and Chapman, 2003), thus it might be anticipated that the effects of lowered pH are first seen over the Arctic's shelves (Yamamoto-Kawai et al., 2009).

3. How do rising temperatures affect atmospheric mercury chemistry?

Mercury is transported to the Arctic from lower latitudes via atmospheric pathways largely in the form of gaseous elemental Hg (GEM, or Hg(0)). The deposition of Hg involves the chemical oxidation of GEM to the much more reactive gaseous Hg(II) compounds (RGM) and particle-bound Hg, although particle-bound Hg can also be transported from sub-Arctic sources directly. The oxidation of GEM to RGM is particularly enhanced in episodic AMDEs during polar spring (see Munthe et al., 2011). These are estimated to contribute as much as 10% to 55% of the total atmospheric Hg deposited to the Arctic annually (Ariya et al., 2004; Christensen et al., 2004; Skov et al., 2004; Outridge et al., 2008). Therefore, it is crucial to understand how climate change may affect the frequency, magnitude, timing and locations of AMDEs in the future in order to predict the future inputs of Hg to the Arctic.

3.1. Temperature effects on mercury oxidation reactions

Kinetics experiments (Ariya et al., 2002; Raofie and Ariya, 2003; Pal and Ariya, 2004) and atmospheric models (Ariya et al., 2004; Goodsite et al., 2004; Skov et al., 2004) suggest that the reaction of Hg with atomic bromine (Br) can account for the rapid conversion of GEM that occurs during AMDEs. Bromine also reacts with ozone to form bromine oxide (BrO). Therefore, any temperature effect on the reaction of Hg(0) (GEM) with Br or on the generation of Br would be expected to result in a temperature effect on AMDEs. To date, laboratory studies of the reaction between Hg(0) and Br have only been performed at room temperature (Ariya et al., 2002) and above (Grieg et al., 1970). While experiments in the temperature range of 120 to 175 °C showed no temperature dependence (Grieg et al., 1970), similar studies at the low temperatures seen in Arctic springtime (e.g., −40 to 0 °C) are lacking. However, theoretical calculations of several oxidation reactions of Hg predict that, while the recombination of Hg and Br to HgBr has only a weak negative temperature dependence, subsequent dissociation of HgBr back to Hg(0) and Br increases with temperature, and so the net oxidation of Hg(0) to $HgBr_2$ will be much faster at cold temperatures (Goodsite et al., 2004). Based on these theoretical calculations, it would be expected that rising temperatures in the Arctic would slow down the gas-phase oxidation and deposition of Hg, if concentrations of Br remain unchanged. The potential effects of temperature on reactive Br levels in the Arctic are discussed in the following section. However, it should also be noted that understanding of the reactions leading to Hg oxidation and deposition during AMDEs is not yet complete and that additional gas-phase or heterogeneous reactions may also contribute to the temperature dependence of overall Hg oxidation rates.

3.2. Temperature effects on bromine generation

The source of the high bromine concentrations seen during polar spring is still a topic of intense research (Simpson et al., 2007a), and not yet understood well enough to predict a temperature effect. There are, however, a number of ways in which a changing climate may influence the so-called 'bromine explosion', both direct and indirect. Atomic Br radicals are generated from the photolysis of molecular Br_2 and BrCl after the polar sunrise. The mechanism for maintaining high levels of these molecular halogens is believed to involve heterogeneous reactions with bromide ions (Br^-) in snow, ice, and/or aerosol, where sea salt is the original source of bromide (Fan and Jacob, 1992; Vogt et al., 1996). This heterogeneous generation of Br_2 and BrCl may be affected by temperature in a number of ways. For example, the concentration of bromide ions on the surface of sea-salt aerosol decreases as temperature increases (Koop et al., 2000), leading to less Br^- available for generation of Br_2. In addition, the reaction of HOBr with Br^- is acid-catalyzed, and recent calculations suggest that low temperatures may reduce the buffering capacity of sea-salt aerosol and allow for acidification (Sander et al., 2006), although this effect is not yet confirmed (Morin et al., 2008). An overall negative temperature dependence for Br_2 release from saline ice has been demonstrated in the laboratory (Adams et al., 2002), which would result in a decrease in the release of bromine to the air as temperature increases. However, this does not take into account changes in the concentration or bromide content of the liquid or solid surfaces that are involved in these reactions, and the identity of those surfaces is still under debate.

Temperature may also have indirect effects on bromine activation through changes in the Arctic cryosphere (ice and snow) (Piot and von Glasow, 2008). Frost flowers (intricate ice crystals formed on the surface of new ice) are thought to be a source of halogen-enriched aerosol (Rankin et al., 2000), and areas where they are likely to be present have been linked to high levels of BrO (Kaleschke et al., 2004). However, high BrO events at Barrow, Alaska, were not correlated with air traversing areas of potential frost flowers but rather with air that simply came into contact with first-year sea ice (Simpson et al., 2007b). Either way, if multi-year sea ice in the Arctic Ocean is being replaced by annual ice, as is suggested by decreases in multi-year ice (see Section 2.3), this may provide a mechanism for increased springtime reactive halogen concentrations in the near future. Finally, it also seems that reactions on snow are key to sustaining atmospheric Br levels (Simpson et al., 2005; Piot and von Glasow, 2008). Potential changes to the Arctic snowpack with temperature are likely to be region-specific and are as yet highly uncertain, as are potential impacts on air–snow chemistry. This uncertainty, coupled with the unknown relative contributions of frost flowers and first-year sea ice, makes it difficult to even qualitatively predict how rising average temperatures will impact on reactive bromine levels, and thus atmospheric Hg chemistry, in the future. Further research into the mechanism of the bromine explosion is needed, at which point a modeling study is likely to be necessary to predict the net effect of temperature changes on all the different components.

3.3. Field observations of temperature effects

Field observations can provide an indication of the net result of temperature effects in the underlying processes on atmospheric Hg concentrations. Some field measurements of AMDEs or of associated ozone depletion events (ODEs) have shown that these depletion events are associated with lower temperatures (Brooks et al., 2008; Cole and Steffen, 2010), with one study suggesting that temperatures below −20 °C are required (Tarasick and Bottenheim, 2002). However, others have observed an inconsistent relationship between ODEs and temperature that may be wholly or partially the result of synoptic patterns (Bottenheim et al., 2009; Jones et al., 2010). While the mechanism for the temperature effect on Hg chemistry requires further study, all observations to date have shown that AMDEs (and ODEs) cease at temperatures above freezing (Lu et al., 2001; Lindberg et al., 2001, 2002; Tarasick and Bottenheim, 2002; Steffen et al., 2005; Bottenheim et al., 2009; Cole and Steffen, 2010). If the onset of the spring melt is earlier in a warmer climate, there may therefore be changes in the duration, severity and/or timing of the AMDE season. In fact, Cole and Steffen (2010) reported a statistically significant shift in the peak of the AMDE season to earlier in the spring based on atmospheric Hg concentrations at Alert from 1995 to 2007. Whether this is due to trends in air temperature in the region, changes in sea-ice composition, extent, or break-up, earlier snowmelt on local or regional scales, changes in atmospheric transport patterns, or some combination of the above remains an open question.

4. Will a decrease in sea-ice coverage have an impact on the amount of atmospheric mercury deposited to or emitted from the Arctic Ocean, and if so, how?

At present, the net rate of atmospheric Hg deposition to the surface of the Arctic Ocean has been estimated at 98 t/y (Outridge et al., 2008) using the GRAHM atmospheric Hg model (Dastoor et al., 2008). This net rate was calculated from a total deposition of 243 t/y, a winter/springtime re-emission from the sea ice/snow surface of 133 t/y, and a summer/autumn evasion of 12 t/y from ice-free areas of the ocean. Declining ice cover is likely to have two immediate effects on atmospheric Hg deposition. First, more of the deposited particulate Hg(II) will land directly on the ocean surface instead of onto sea ice. If all other factors remain constant, a reduction of average ocean ice cover from about 80–95% at present to 50% in the future can be projected to reduce re-emission of Hg by about 50 to 60 t/y. Second, the air-sea exchange of Hg(0) will be enhanced. Andersson et al. (2008) have shown there to be a net evasion of Hg(0) from surface water in the Arctic Ocean under current conditions. Based on a measured average evasion rate of 12 pmol/m^2/h (Andersson et al., 2008) and a similar reduction in ice cover to 50%, Hg(0) evasion from ocean to atmosphere would increase by 60 to 90 t/y. Although these estimates are first-order only, and rely on a number of assumptions, they imply that the response of this component of the Arctic Hg cycle to further climate warming might be nearly neutral, with greater net deposition of Hg(II) into the ocean balanced by enhanced reduction to Hg(0) and gaseous evasion.

5. Does climate affect air–surface mercury flux, and riverine mercury fluxes, in Arctic freshwater and terrestrial systems, and if so, how?

There are few Arctic data directly relevant to this question, and those that do exist mainly concern the three processes discussed in the following sections (water discharge, timing of spring freshet, forest fires). However, considerations of the known interactions of the Hg cycle with other freshwater and terrestrial processes or features (such as primary productivity, soil characteristics, permafrost thaw) suggest the potential for significant future changes under a warming climate (Macdonald et al., 2005). For example, the water-column concentrations of nutrients, dissolved organic matter (DOM) and particulate organic matter (POM) in lakes and rivers are expected to increase because of greater export from watersheds (Prowse et al., 2006), partly due to higher rates of microbial decomposition in soils (Xu et al., 2008). In this context, the empirical relationship between catchment-to-lake area ratios and fish Hg levels in Arctic lakes (Gantner et al., 2010) may be suggestive of future climate effects on Hg delivery to freshwater ecosystems. Movement of Hg from catchment soils into receiving waters has been shown to be strongly influenced by soil DOM and POM, which act as Hg carriers (Grigal, 2002; see Section 5.2 for more discussion on this point). Increased nutrient loading may enhance phytoplankton and algal productivity, which

has been shown to affect carbon and Hg dynamics in Arctic lakes (Outridge et al., 2007; Stern et al., 2009). Warmer air temperatures have already increased the active layer depth and period in Arctic permafrost soils, thereby releasing long-retained Hg and carbon (Klaminder et al., 2008), and may tend to increase catchment geochemical weathering rates. Another way that thawing can impact lentic and lotic systems in the Arctic is through the slumping of slopes formerly bonded by permafrost. So-called thaw-slump activity has been accelerating since the 1970s (e.g., see Lantz and Kokelj, 2008), with the consequence that sedimentation and turbidity have increased in affected lakes and rivers. The potential consequences of thaw slumping on the mercury cycle are difficult to project as, on one hand, these slumps may provide the means to scavenge and bury Hg in freshwater sediments, but they also may affect light penetration in lakes and thus reduce photo-reduction of MeHg by UV. Clearly, focused studies of this process are needed.

Long-term changes in terrestrial plant communities, particularly the establishment of grasses and woody species, may also increase organic matter supply to lakes and rivers (Prowse et al., 2006). Rainfall is expected to become a more prominent component of the polar climate, thereby reducing the prominence of spring freshet and altering runoff regimes (Prowse et al., 2006), with consequences for Hg delivery to receiving waters (see the following section). Higher evapotranspiration rates and longer open-water seasons are expected to lower water levels in lakes, ponds and rivers (Prowse et al., 2006). Indeed, widely distributed ponds in the Arctic are already reduced in depth from long-term averages (Smith et al., 2005b; Riordan et al., 2006) with some of the ponds on Ellesmere Island that have been permanent water bodies for millennia now drying out completely during the summer (Smol and Douglas, 2007b).

5.1. Water discharge

The Mackenzie River, Canada, has been intensively studied with respect to its Hg dynamics (Leitch et al., 2007). Water discharge has an amplifying effect on Hg flux in the Mackenzie River with particulate Hg concentrations increasing disproportionately as discharge increases (Fig. 4a). This results in considerably greater Hg flux in high flow years; for example, a 30% increase in discharge produces almost a doubling of particulate Hg concentrations. By contrast, dissolved Hg levels are lower than particulate Hg levels and not strongly related to discharge (Fig. 4b). The correlation between particulate Hg concentration and discharge is due to increased land inundation and bank erosion during high water level years. Therefore, changes in the average discharge or number of extreme flow events of the Mackenzie River are likely to be accompanied by a magnification of Hg flux from the Mackenzie River Basin. On average, the discharge of the Mackenzie River has been increasing at a rate of 0.6 km^3/y over the past 35 years (Peterson et al., 2002), which is predicted to have been accompanied by only a modest increase in Hg flux. However, the strong dependence of Hg flux on discharge indicates that increasing frequency and severity of major storm events would potentially be a more important process than variations of average discharge. The approximate 7% increase in Russian river discharge into the Arctic Ocean since the mid-1930s (Peterson et al., 2009) may also have resulted in an increased Hg flux to the Arctic Ocean. However, as their sediment discharge rates are an order of magnitude less than that of the Mackenzie River (Outridge et al., 2008) a corresponding increase in Hg flux will also be less pronounced.

5.2. Timing of spring freshet

The warming of the Arctic is advancing the dates of snowmelt and spring break-up. Spring break-up on the Mackenzie River has already advanced by an average of three days per decade since 1973 (Woo and Thorne, 2003). Leitch et al. (2007) have shown that the freshet season discharges more than 50% of the total annual Hg flux from the Mackenzie River (see also Fig. 4b). An advance in the freshet season would change the seasonal pattern of the Hg flux, and could potentially better align the peak Hg outflow timing with the season of rapid growth of marine biota in the Mackenzie Delta and Beaufort Sea.

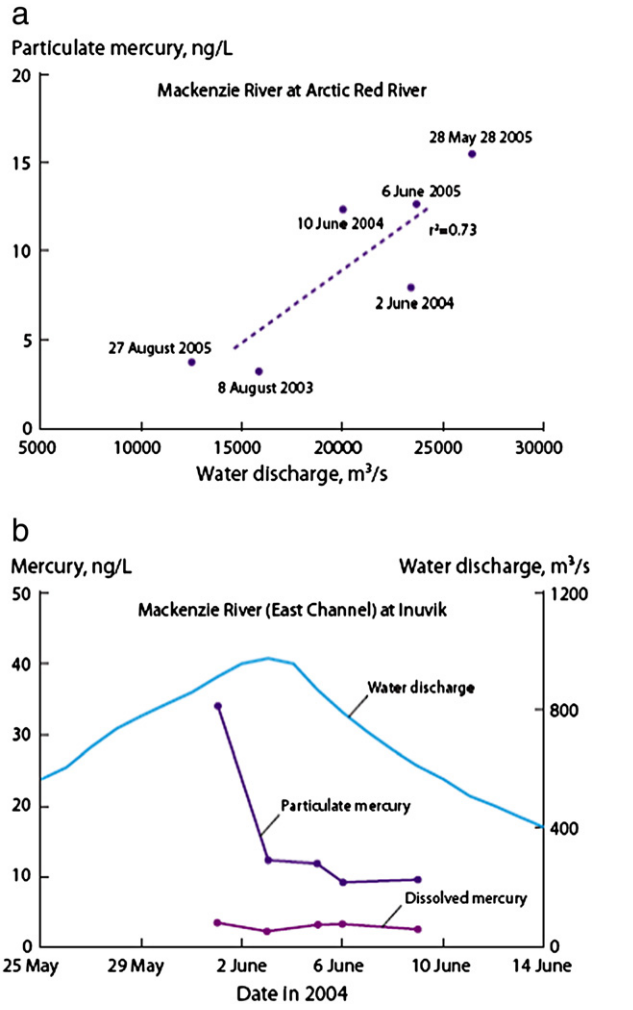


Fig. 4. Relationship between (a) particle mercury concentration and water discharge for the Mackenzie River at the Arctic Red River, and (b) changes in particle and dissolved mercury concentrations and water discharge for the Mackenzie River during the spring freshet 2004.
Source: Leitch et al., 2007.

5.3. Forest fires

Inertinitic carbon fragments (i.e., oxidized or fossilized charcoal) of forest fire origin are commonly present in sediments from the Mackenzie River (Carrie et al., 2009). Enhanced forest and ground fires are likely to be a consequence of climate change in the north partly due to desiccation and partly to increased incidence of convective storms and lightning (Kochtubajda et al., 2006; Wrona et al., 2005). Not only does fire in a drainage basin alter the flow of carbon in rivers and lakes (Czimczik et al., 2003), but it also has the consequence of releasing Hg sequestered in foliage and soil (Biswas et al., 2008). Global forest fires have been estimated to contribute in the order of 675 ± 240 t/y to the global atmosphere (Friedli et al., 2009; Munthe et al., 2011, Section 3.3).

6. How does climate change affect mercury methylation/demethylation in different compartments in the Arctic Ocean and freshwater systems?

One of the potentially most important impacts of climate change may be on net MeHg formation in Arctic aquatic ecosystems (Outridge et al., 2008). While there is some uncertainty about the relative importance of the different sites, sources and processes of MeHg production generally (Munthe et al., 2011; Douglas et al., 2011) it is useful, however, to consider general insights gleaned from research in temperate regions.

6.1. Temperature-related effects

Most of the methylation capacity linked to bacteria is found in sediments. Methylmercury production is highly correlated to anaerobic bacterial activity, which in turn is generally enhanced at elevated temperatures. It is therefore not surprising that higher temperatures often promote sedimentary Hg methylation (Bodaly et al., 1993). Usually, epilimnetic sediments produce more MeHg during warm summer months compared to colder winter months (Canário et al., 2007). However, demethylation in sediments is also clearly a microbial process, and more demethylation is expected at higher temperature. That being said, methylation rates significantly increase with rising temperatures (e.g., by 37% with a temperature increase of about 20 °C) while demethylation rates are already fairly high (often up to 80% per day) regardless of the temperature regime (Canário et al., 2007). Hence, one would expect the net methylation rate in sediments to generally increase with temperature. The impact of climate change on water column MeHg levels, however, can be unpredictable; one example results from the effect of climate-induced changes in the thermocline depths of lakes with anoxic hypolimnia. In temperate lakes, oxygen changes related to climate change may result in a depth reduction of the anoxic hypolimnion, which is critical for the overall produced mass of MeHg in seasonally anoxic lakes. As a consequence, the total mass and concentration of MeHg in epilimnetic waters, and fish MeHg concentrations, decrease because in those lakes a significant proportion of the MeHg is formed in the anoxic hypolimnion and later mobilized into the epilimnion (Rask et al., 2010; Verta et al., 2010). The effect of warmer temperatures on the thermocline depths in Arctic lakes is still uncertain. For example, Arctic lakes often lack an anoxic hypolimnion. However, inputs of more nutrients and DOC as a result of permafrost thawing in combination with stronger thermal stratification through warming of the epilimnion may allow the development of anoxia. This could cause an increase in MeHg production relative to previously completely oxic lakes.

6.2. Watershed chemistry and inputs (mercury, nutrients, dissolved organic matter)

As noted in Section 5, climate change is likely to increase the export of total Hg (Klaminder et al., 2008), DOM and nutrients from watersheds to Arctic lakes and oceans. Considering that DOM is one of the most important factors controlling the bioavailability of Hg(II) (e.g., Gorski et al., 2008; Driscoll et al., 1995), its increased export may have a profound effect on methylation rates. Dissolved organic matter appears to affect MeHg formation in at least three ways: (i) fresh DOM enhances bacterial activity, serving as an organic substrate for microbes (Hammerschmidt and Fitzgerald, 2004; Lambertsson and Nilsson, 2006); (ii) DOM is a carrier of Hg(II) (Skyllberg et al., 2003; Chadwick et al., 2006), delivering it to sites of methylation; and (iii) binding of Hg(II) and MeHg by large DOM molecules decreases Hg(II) bioavailability for methylation, and may reduce the availability of MeHg for bioaccumulation (Barkay et al., 1997; Drexel et al., 2002). However, the overall response is difficult to predict and field measurements are sometimes contradictory (Ravichandran, 2004). There is probably an optimum range of DOM concentrations, at which Hg methylation and MeHg bioavailability peak, but this level is unknown for Arctic systems. Dissolved organic matter also complexes MeHg, making it more mobile and elevating its total concentration in water (Regnell and Hammar, 2004). The relative importance of watershed inputs compared to in situ production depends on the specific ecosystem. The direct export of MeHg from watersheds is often only a minor contribution to MeHg in freshwater lakes, unless the watershed to lake area ratio is very large or the lake is surrounded by wetlands with direct connection to the lake. It can also be a major source for systems with relatively little in situ production, such as large lakes (Rolfhus et al., 2003) or the continental shelf (Hammerschmidt and Fitzgerald, 2006a; Hollweg et al., 2009). Wetlands are often a net source of MeHg and suggested to be its principal source to lakes, in particular when wetland runoff dominates the catchment hydrology (Krabbenhoft et al., 1995; Driscoll et al., 1998; Rudd, 1995; Branfireun et al., 2005; Hall et al., 2008). Arctic lakes with wetlands in their catchments would therefore be expected in general to exhibit increased concentrations of MeHg in lake water compared to those without wetlands (Loseto et al., 2004); MeHg levels may be correlated to the wetland area in the catchment (Lindqvist et al., 1991; Porvari and Verta, 2003). Enhanced formation rates will most certainly lead to higher concentrations of standing pools of MeHg in wetlands but this will only be of importance for aquatic systems if the wetland is also hydrologically connected to a lake, that is, produced MeHg must also be mobilized and exported from the wetland (Watras et al., 2005). Otherwise, MeHg may only undergo fast internal recycling (methylation/demethylation cycle). But even if MeHg is confined to an isolated wetland, it may still expose local wildlife and biota living in the wetland to elevated concentrations of MeHg. This is of concern for Arctic freshwater ecosystems, which often serve as breeding grounds for migratory birds, possibly exposing them to harmful levels of MeHg.

Additionally, weathering of watersheds may liberate sulfate from the mineral phase. In temperate lakes, experimental sulfate additions increased Hg methylation (Gilmour et al., 1992), pointing to sulfate as an important factor affecting MeHg production, especially when microbial sulfate reduction is sulfate-limited (Gilmour and Henry, 1991). However, other bacteria such as iron-reducers (Fleming et al., 2006) may also be important for methylation, but their significance in polar regions is unknown.

6.3. Ice-free season length and methylation/demethylation

Global warming is likely to extend the season for Hg methylation, mostly through earlier onset of thawing and later start of freezing, as methylation will only proceed when soils (wetlands) are not frozen. Prolonging the period during which MeHg can be produced may then lead to enhanced MeHg levels in local biota and even increased export of MeHg into Arctic lakes and other receiving water bodies.

A good analogy to anticipated effects related to enlarged areas of northern wetlands and longer periods of generally 'wet' or submersed soils resulting from early thawing could be the well recognized increase of MeHg in newly flooded reservoirs (Therriault and Schneider, 1998; Tremblay et al., 1998; Montgomery et al., 2000; Hylander et al., 2006). Repeated wetting and flooding of terrestrial soils and vegetation release pulses of easily accessible organic carbon to the aquatic system and bacteria inhabiting the system. Flooded areas of reservoirs typically show higher concentrations of MeHg compared to non-flooded areas or nearby natural lakes (Mailman et al., 2006). Similar effects might be expected when permafrost soils thaw on a large scale or become flooded due to rising water levels. On the other hand, evidence for increased methylation rates in Arctic waterlogged soils is scarce. Methylmercury production was not important in water-logged soils on Devon Island (Oiffer and Siciliano, 2009). Hammerschmidt et al. (2006) found that the contribution of MeHg from tundra watersheds to lakes in Alaska was modest.

In contrast to methylation, the demethylation process is well understood at the molecular level (Silver and Misra, 1988; Walsh et al., 1988; Melnick and Parkin, 2007). The biochemical reaction is characterized in detail, distinguishing between an oxidative pathway producing Hg(II) and CO_2 and a reductive mechanism leading to CH_4 (methane) and Hg(0). The reductive demethylation appears to dominate in marine environments, while oxidative demethylation is more prominent in freshwater sediments (Oremland et al., 1991, 1995). There is no information regarding parameters controlling either demethylation pathway. Hence, it is unclear if and how climate change may affect bacterial demethylation activity.

6.4. Photochemical demethylation

One of the most important degradation processes of MeHg in clear water lakes and the surface of oceans is photo-induced demethylation (Sellers et al., 1996; Sellers and Kelly, 2001; Hammerschmidt et al., 2006). Methylmercury decomposes under ultraviolet (100–400 nm) as well as visible light (400–800 nm) (Gårdfeldt et al., 2001; Chen et al., 2003). The rate of degradation depends on wavelength, with shorter wavelength being more efficient in cleaving the Hg – C bond, and on light intensity. Visible light penetrates deeper into the water column than does UV light and can potentially, therefore, affect a relatively larger volume of dissolved MeHg. UV light, on the other hand, is much more efficient in degrading MeHg than is visible light. Consequently, short and long wavelengths are equally important in clear lakes having relatively little light attenuation. Dark colored lakes; however, have a leveling effect on penetration depth, and thus the more energetic ultraviolet (UV)-light dominates MeHg decomposition. UV-A and UV-B radiation account for about 50% of the overall photo-demethylation in clear water, and for more than 75% in colored lakes (Lehnherr and St. Louis, 2009). If Arctic catchments start to export more DOM due to climate change, it may protect MeHg in receiving water bodies against photo-demethylation. Since ice cover protects dissolved MeHg from photodegradation, enhanced photodecompostion could be expected if global warming increases the number of ice-free days. However, this would mostly affect oceanic surface waters and may not have a large impact on the overall MeHg stored in polar oceans, but could counteract the protective effect of enhanced DOM export in lakes and rivers.

One recently suggested pathway for the formation of MeHg in Arctic environments involves the degassing of volatile DMHg (dimethylmercury) from oceans and its subsequent photo-decomposition (Kirk et al., 2008). For this scenario, it is also necessary to consider climate change effects on DMHg. Unfortunately, little is known about the genesis of DMHg and it is, therefore, not possible to predict if DMHg levels will rise or fall. Presupposing that DMHg is likely to be formed deep in the oceans (where it is normally found at detectable levels, unlike freshwater systems), global warming should have no immediate effect on DMHg production. However, if climate change leads to increased upwelling onto shelves or prolonged ice-free periods in the Arctic, it may lead to more opportunities for DMHg to volatilize into the atmosphere, where it breaks down to MeHg. In addition, levels of DMHg may further increase in the Arctic atmosphere if the degassing occurs before polar sunrise, since DMHg does not degrade in the dark. If the hypothesis regarding DMHg–MeHg interaction holds true, climate change could lead to increased DMHg in air and, in conjunction with long-range atmospheric transport, have the potential to significantly increase overall exposure to MeHg.

Given that [MeHg] is controlled as a dynamic balance between production and loss processes, change in this form of Hg may be effected by alteration of the kinetics in either of these two sorts of pathways. Accordingly, the recent finding that reduced sea-ice cover in the Bering Sea is accompanied by reduced accumulation of MeHg in sea-bird eggs led Point et al. (2011) to propose that greater photodemethylation in the water column was the dominant factor of change in the marine Hg cycle. This study, if confirmed and extended, has strong implications for the Arctic Ocean.

7. How will climate change alter the structure and dynamics of freshwater food webs, and thereby affect the bioaccumulation of mercury?

7.1. Environmental drivers and ecological responses associated with climate warming

Food webs in Arctic freshwaters are likely to be impacted by climate change through three primary environmental drivers: temperature, water chemistry and the hydrological regime (AMAP/CAFF/IASC, 2005). Interactions between these environmental drivers and ecological processes are complex and responses of aquatic food webs in the Arctic may vary regionally depending on the magnitude, rate, and timing of environmental change. Nevertheless, broad effects are expected on the thermal regime, water-column concentrations of nutrients and organic matter, and the hydrology of aquatic ecosystems during the 21st century; in turn, aquatic communities are anticipated to respond through changes in productivity, species composition, and trophic interactions (AMAP/CAFF/IASC, 2005). For example, higher air temperatures will lead to earlier melting of lake and river ice, a longer ice-free period, and higher water temperatures (Prowse et al., 2006). As a consequence, aquatic organisms will experience a longer ice-free growing season. Higher water temperatures may also initiate thermal stratification during summer in high latitude lakes where this physical process presently does not occur (Korhola et al., 2002).

One of the main anticipated ecological responses to these environmental drivers is an increase in aquatic productivity in lakes and rivers. Warmer waters up to 10 to 18 °C by 2100 (Sharma et al., 2007) will stimulate production rates of microorganisms and invertebrates (Shuter and Ing, 1997; Karlsson et al., 2005). Primary production is also likely to be stimulated by greater inputs of nutrients and organic matter (Prowse et al., 2006), although reduced light penetration from DOM fluxes may have a counter effect (Karlsson et al., 2009). Thermal stratification may further increase primary production in high latitude lakes by reducing the mixing depth of phytoplankton and improving their light environment (Korhola et al., 2002).

Shifts in the species composition of aquatic communities will occur as a result of various climate change impacts on the environment. Algal and invertebrate communities have already undergone changes in composition over the past 150 years associated with increases in aquatic productivity and lengthening of the summer growing season (Smol et al., 2005; Michelutti et al., 2005). Future alteration of temperature regimes may affect the distribution of fish, causing extirpation or colonization depending on a species' thermal optimum for growth (Reist et al., 2006a). For example, simulations using a bioenergetic model suggest that a modest warming of lake water in Alaska may increase the energy requirements of lake trout (*Salvelinus namaycush*) beyond the food available to them (McDonald et al., 1996). Climate change will also promote the invasion of exotic species by extending the range of favorable conditions (e.g., temperature, freedom from ice cover) and by increased human presence as the North becomes more easily accessible by sea and ground transportation. Climate change may also alter the migratory behavior of species like birds, fish and whales, thus altering the transport and release of contaminants by the species themselves (Blais et al., 2007). Thawing of permafrost soils will enhance the formation of new aquatic ecosystems such as thermokarst ponds, with their own food web dynamics. The species composition and trophic interactions of aquatic communities in the Arctic are poised for major change during the 21st century.

7.2. Potential mechanisms for climate change impacts on freshwater food webs and mercury bioaccumulation

Empirical evidence is currently lacking for interactions between climate warming and Hg bioaccumulation in Arctic freshwater food webs, with the exception of a small number of studies (see Dietz et al., 2011, Section 7.2.1). In this section, potential mechanisms are presented, based on anticipated changes to food web structure and dynamics that are also key determinants of Hg bioaccumulation in fish: diet resources, growth, and ecosystem productivity. Some impacts on food webs may enhance Hg bioaccumulation while others may reduce it; the net effect is likely to vary geographically due to regional differences in the structure of aquatic food webs and their responses to environmental change.

7.2.1. Dietary changes of fish

Change in available food for fish, such as shifts in the composition or dominance of invertebrate prey species, may affect Hg bioaccumulation in fish if these food sources have altered Hg concentrations. For example, the waterflea (*Daphnia* spp.) has elevated MeHg concentrations compared to other zooplankton species in the High Arctic, and its density in lakes is related to ecosystem productivity (Chételat and Amyot, 2009). An expansion of *Daphnia*'s distribution driven by climate warming could result in a greater transfer of Hg to fish that consume them, similar to temperate lakes where *Daphnia* are a key vector for Hg transfer in pelagic food chains (Pickhardt et al., 2002). *Daphnia* are primary consumer invertebrates that graze on algae and bacteria in the water column (Bertilsson et al., 2003), and therefore, consumption of *Daphnia* by fish could enhance their accumulation of Hg without increasing their trophic level. However, further research is needed to test this hypothesis on enhanced Hg transfer by Daphnia and, more generally, on effects of shifts in species composition on Hg bioaccumulation.

Mercury bioaccumulation is greater in fish that feed at a higher trophic level (Cabana and Rasmussen, 1994), and therefore, fish community composition and food chain length are key determinants of Hg concentrations in top predator species. The length of food chains in temperate lakes is not determined by productivity but rather by ecosystem size, which in turn regulates species diversity and habitat availability (Post et al., 2000). However, factors controlling food chain length in Arctic ecosystems may be different due to their extreme environmental conditions. It is possible, although speculative, that climate warming may increase the length of aquatic food chains in the Arctic through an increase in species diversity or geographic shifts in the distributions of species (Hobbie et al., 1999). There are consequences for Hg bioaccumulation in predatory fish species should an increase in food chain length occur in Arctic lakes and rivers.

Climate change could affect the relative importance of pelagic and benthic energy flow in food webs of Arctic lakes, with possible consequences for Hg bioaccumulation in fish (Reist et al., 2006a). Fish that feed in the open-waters of lakes (i.e., the pelagic food chain) tend to bioaccumulate more Hg than bottom-feeding fish (i.e., those dependent on the benthic food chain) (Power et al., 2002; Gorski et al., 2003; Ethier et al., 2008; Chételat et al., 2011). The conventional view for Arctic lakes is that energy flows primarily through the benthic food chain (Welch and Kalff, 1974; Sierszen et al., 2003; Karlsson and Byström, 2005; Chételat et al., 2010), although there are exceptions such as shallow turbid lakes in the Mackenzie Delta where pelagic carbon is important (Hecky and Hesslein, 1995). An increase in nutrient availability or reductions in light availability to bottom substrates through elevated DOC loading may cause a shift toward greater pelagic primary production (Hansson, 1992; Vadeboncoeur et al., 2003; Karlsson et al., 2009). Likewise, changes in the distribution of forage fish species may increase or decrease the ratio of benthic and pelagic energy flow to predatory fish (Reist et al., 2006a). These shifts in energy flow could, in turn, alter Hg concentrations in fish of Arctic lakes.

Climate change may affect the extent to which fish feed by anadromy (Reist et al., 2006b), which could affect their exposure to and bioaccumulation of Hg. Lakes in the Canadian High Arctic support populations of anadromous and landlocked Arctic char, with higher Hg concentrations generally observed in the latter strain (Lockhart et al., 2005, Dietz et al., 2011, Section 6.2.6). This difference is related to variable growth rates (anadromous individuals tend to grow faster) (Swanson et al., 2011) and may also potentially result from different Hg content of fish diets in lakes versus the ocean. There are other facultative anadromous species in the Arctic (e.g., Dolly Varden (*Salvelinus malma*), brown trout (*Salmo trutta morpha* sp.), brook trout (*Salvelinus fontinalis*) (Reist et al., 2006b)) for which changes in the extent of anadromous feeding could be a relevant factor in Hg bioaccumulation.

7.2.2. Metabolic effects on fish

Long-term warming of fresh waters is likely to alter fish growth rates (Reist et al., 2006a) which may, in turn, affect their bioaccumulation of Hg because fish with higher growth rates tend to have lower Hg concentrations (Simoneau et al., 2005). The effect on Hg bioaccumulation will depend on whether the fish species is near its temperature optimum for growth. Cold-adapted species such as Arctic char and lake trout grow less efficiently in warmer waters (Reist et al., 2006a), which could result in higher Hg concentrations.

Temperature-induced metabolic stress in fish may also enhance Hg bioaccumulation (Reist et al., 2006b). A multi-year study of Arctic char in a High Arctic lake revealed that fish were under greater metabolic stress and had severe glycogen depletion near the end of an abnormally warm summer compared to two colder years (Reist et al., 2006b). If more energy is required to support higher metabolic rates, then fewer resources can be diverted to growth, resulting in higher Hg concentrations in fish tissues. Further research is required to determine the effect of temperature stress on Hg bioaccumulation in cold-adapted fish species.

7.2.3. Bio-dilution of mercury

Climate warming will increase the productivity of freshwater ecosystems which may, in turn, reduce Hg bioaccumulation in fish through growth dilution processes at lower trophic levels in the food web. As phytoplankton production increases, the concentration of Hg per algal cell decreases resulting in less transfer to zooplankton (Pickhardt et al., 2002). A similar reduction in Hg concentration occurs in periphyton that have higher growth rates (Hill and Larsen, 2005). Zooplankton with higher growth rates also have lower Hg concentrations because more biomass is produced per unit of food (and Hg) consumed (Karimi et al., 2007). Bio-dilution effects have been observed in highly productive lakes at temperate latitudes (Chen and Folt, 2005); however, long-term increases of aquatic productivity in the Arctic may be more modest. Bio-dilution effects on Hg bioaccumulation may be limited to regions where more pronounced eutrophication is projected to occur, such as the southern limits of the Arctic.

8. How will climate change alter the structure and dynamics of marine food webs, and thereby affect the bioaccumulation of marine mercury?

Climate-driven changes in the physical environment can both directly and indirectly alter the structure and dynamics of Arctic marine food webs thereby affecting the Hg concentrations of Arctic marine species. Many of the impacts predicted for food webs and Arctic biota are associated with a reduction in sea-ice concentration and thickness, a significant feature of change and a prominent feature defining Arctic marine ecosystems (see Section 2.3).

Moore and Huntington (2008) developed a conceptual model which predicted the impacts of changes in sea ice on marine mammals based on the resilience of ice-obligate, ice-associated and seasonally migrant species. Ice-obligate species are defined as those that depend on sea ice as a platform for hunting, breeding and resting. Reduction in sea-ice extent, for example, will negatively affect polar bears (*Ursus maritimus*) by reducing their opportunities for using ice as a platform from which to prey on ringed seal (*Phoca hispida*), as well as by reducing the survival of the ringed seals themselves as these require sea ice for birthing. These relationships can be very dynamic as the effects of changing sea ice will impact on ecosystem structure and productivity. Similarly, effects on sea-ice associated species such as beluga (*Delphinapterus leucas*), narwhal (*Monodon monoceros*) and bowhead whales (*Balaena mysticetes*) will vary depending on their ability to adapt to ecosystem shifts. Net loss of sea ice, for example, may result in enhanced access and feeding opportunities in previously inaccessible regionally productive areas or by increased foraging opportunities on both prey produced in, or advected to their summer and autumn habitat that may alter Hg exposure. For example, a switch in the diet of polar bears from sympagic-based food webs to pelagic food webs resulted in an increase in Hg levels (Horton et al., 2010). Specific bottom-up and top-down processes (Fig. 5; Braune et al., 2011) are described in the following sections.

8.1. Bottom-up processes: dynamics of energy flow in food webs

Bottom-up processes are described as those which result in changes in the physical environment that will alter the onset, duration, and biomass/quantity and/or quality of primary productivity. These alterations may increase or decrease the amount of energy or carbon available for a species to grow and reproduce and sustain a food web. Overlying the direction of these processes is the potential for changes in trophic transfer of energy across space and time that can lead to food web or predator–prey mismatching. The four Arctic marine food webs described in Braune et al. (2011) (sea ice, shelf, pelagic, benthic) do not exist independently of one another and are directly or indirectly influenced by sea ice and its role in productivity and impacts on carbon sources (Carmack et al., 2006). Thus, changes in sea ice will influence the coupling between food webs which, in turn, will alter food web structure and energy transfer up food webs. Sea ice impacts on the Arctic marine ecosystem may be driven by (i) bottom-up shifts in carbon/energy sources to food webs; (ii) changes at the species level in terms of growth rates and biomass driven by temperature and energy availability/quality; and (iii) change in food web structure and length by the removal or addition of species.

Indirect impacts of sea-ice reduction on the pelagic food webs will be driven by changes in oceanic fluxes/transport from the Atlantic and/or Pacific that carry nutrients and carbon (Macdonald et al., 2005). Changes in sea ice will alter ocean stability, mixing, and thermocline and halocline position. Ocean circulation can affect the amount and timing of the transport of Pacific and Atlantic waters to the Arctic Ocean. Increased primary productivity in the open Arctic Ocean is consistent with summer sea-ice retreat, where phytoplankton blooms are likely to occur further northward in future (Moline et al., 2008). Although this may provide more food for zooplankton and greater energy flow to the pelagic food web, there is the potential for a mismatch between predator and prey interactions. A decoupling of the flow of carbon and energy at lower trophic levels will result in significant impacts on the higher trophic levels, which may then be left without adequate food resources for sustaining healthy populations (Edwards and Richardson, 2004). These processes are likely to differ regionally.

8.1.1. Implications of bottom-up processes on marine mercury

Mercury concentrations in the lowest levels of marine food webs, as well as food web structure, govern Hg concentrations in the higher trophic level species, principally through bioaccumulation and biomagnification processes (Cabana and Rasmussen, 1994). A warming climate will result in reductions in Arctic sea ice that will have a range of bottom-up impacts on Arctic marine food webs. Bottom up impacts will act on the productivity/energy available for food webs that parallel processes of Hg trophic transfer in food webs (Table 1). Methylmercury increases approximately 10^4-fold between water and algae with increases of four to six times at each subsequent trophic level (i.e., algae to zooplankton; invertebrates to small fish; small fish to big fish; and big fish to top predators including man). Uptake is through their food with the fraction of MeHg relative to THg progressively increasing from about 1% to 10% (water to algae), to 30% (invertebrates) and ultimately to 90% in top predator fish and marine mammals (Morel et al., 1998; Lockhart et al., 2005).

Sea-ice brine is the primary habitat for microbial communities responsible for sustaining the food web in the Arctic Ocean. High and seasonally changing Hg concentrations and speciation of Hg in sea-ice brine could have a major impact on Hg uptake in the Arctic marine ecosystem (Chaulk et al., 2011). As perennial sea ice is melting at an alarming rate, the Arctic Ocean will shift to a primarily first-year ice regime. The seasonal increase in first-year sea ice will likely provide more Hg-rich environments (i.e., brine) for primary producers, potentially increasing food web exposure to this contaminant.

A strong understanding of ecosystem dynamics along with a baseline of Hg trends is required in order to test for climate change impacts on food web structure and Hg processes. Food web processes defining Hg levels in higher trophic species have been previously

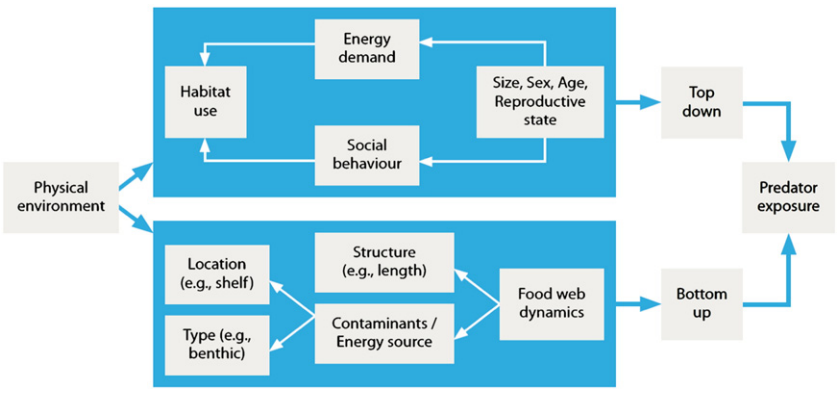


Fig. 5. Mercury levels in Arctc biota reflect the combined effects of a range of top-down and bottom-up processes, many of which are sensitive to the influence of climate change.

Table 1
Types of impacts on Arctic ecosystems expected as a result of bottom-up changes.

Impact level	Impacts on marine Arctic ecosystem	Affected Hg processes
Source	Shifts in carbon/energy/productivity	Hg input at the bottom of the food web
Species	Seasonal ice cover/shift from perennial to first-year	Increasing microbial exposure
Species	Growth rates: bio-dilution, accumulation	Bioaccumulation rates
Food web	Food web size (introduction or loss of species)	Extent of biomagnification

reported by Douglas et al. (2011) and are discussed in Section 8.2 in connection with climate predictions.

8.2. Top down: habitat removal

Changes in the physical environment will alter marine ecosystem habitat resulting in a top-down cascade of trophic effects on food webs. The removal of sea-ice habitat and its associated resources is likely to lead to a deterioration in the health and survival of those species that depend on it. The ice-obligate species will be directly and immediately affected by the removal of a habitat feature required for life functions (hunting, breeding, resting). In contrast, sea-ice associated species will be indirectly affected by the impacts that sea ice loss will have on their food resources and influences related to competition and predation. How high trophic level species respond or show the ability to adapt to such change varies by species (Laidre et al., 2008).

Negative impacts of sea ice habitat loss on the condition and survival of polar bears are well known (Stirling et al., 1999). Reduced sea ice will mean denser seal presence, both among ringed seals but also for the more gregarious species like harp seals (*Phoca groenlandica*), hooded seals (*Cystophora cristata*) and even walruses (*Odobenus rosmarus*). Less space on ice will mean easier access to the seals but also more competition from other bears including interaction and cannibalism as well as easier spread of diseases such as distemper or trichinosis. In contrast, sea-ice reduction and increased plankton productivity may offer better feeding opportunities for bowhead whales. This may in part explain the observed increase of the western Arctic bowhead population (George et al., 2004); however, the increased productivity coupled with sea-ice reduction is anticipated to increase bowhead competition and predation by killer whales (*Orcinus orca*) (Laidre et al., 2008; Moore and Laidre, 2006). These scenarios and recent observations of top-down impacts of sea-ice reduction demonstrate the challenge of understanding climate change and predicting how it will influence Arctic marine fauna.

8.2.1. Implications of top-down processes on marine mercury

As described by Douglas et al. (2011), predators and other high trophic level species exert a top-down influence on food web Hg levels due to their feeding ecology and diet preferences. Social behavior such as habitat selection, dictated to some extent by size, age, sex and reproductive status (Loseto et al., 2008b) will affect dietary exposure to Hg (Loseto et al., 2008a; Gaden et al., 2009; Young et al., 2010). Although most of these studies consider predator behavior in relation to the environment and Hg body burdens only, Gaden et al. (2009) have shown the direct impacts of climate warming-induced sea ice variations on the feeding behavior, diet and thus Hg exposure of ringed seals, an upper trophic level species. Seal muscle Hg levels were found to be significantly higher during periods following relatively short and long sea-ice years, because of ice-induced changes in feeding behavior (Braune et al., 2011, Section 5.3.2, Case Study 8).

9. What are the likely mercury emissions from melting glaciers and thawing permafrost under climate change scenarios?

9.1. Potential release of mercury from melting Arctic glaciers

Glaciers and ice caps represent transient reservoirs for atmospheric contaminants, including Hg. Present-day concentrations of THg measured in snow on Arctic ice caps (including Greenland) are low, of the order of 0.5 to 2 ng/L (Faïn et al., 2008, 2009; Mann et al., 2005; St. Louis et al., 2005; Zdanowicz et al., 2009; Zheng et al., 2009). Depending on the size and turnover time of glaciers, this Hg can remain trapped inside for decades to millennia before being released by melt. However as climate warms and glaciers melt, contaminants that have accumulated over decades or millennia may be prematurely released from ice, adding to contemporary fluxes to aquatic ecosystems (e.g., Blais et al., 2001). This will be more problematic in alpine glacierized catchments at subpolar latitudes than in the polar regions, owing in part to the faster turnover rates and climate response time of alpine glaciers.

Atmospheric Hg deposited in the past on Arctic glaciers and ice caps is only preserved in their net accumulation area, that is, the area where there is a net addition of ice every year (Fig. 6). Many smaller glaciers ($<50\ km^2$) in the Arctic do not, in fact, have an accumulation area: atmospheric Hg deposited in snow on these glaciers is released by melt and runoff in the summer, so there is no net storage. On those Arctic glaciers and ice caps that do accumulate firn and ice, the net accumulation area typically represents 50% to 80% of the total area. Any Hg deposited outside this area, in the ablation zone, is lost in melt and runoff during the same year. This is a seasonal flux that can be estimated from the concentration of Hg in glacial runoff (St. Louis et al., 2005). However, just as in ice-free areas, Hg stored in the supra-glacial snowpack is quickly released in early melt. As summer progresses, the contribution of water from glacial ice wastage becomes proportionally larger and the flux of Hg in snow meltwater is diluted by this comparatively clean glacial water which is largely from old (pre-anthropogenic) ice strata.

An anticipated effect of the current warming trend will be to increase the rate and area of net ablation of circum-Arctic glaciers, leading to an overall enhancement of ice loss (Bahr et al., 2009; Sharp et al., 2011) and release of any stored Hg. This increased ice loss is clearly observable in Greenland (Abdalati and Steffen, 2001; Dahl-Jensen et al., 2009). However, in large polar ice caps like the Greenland Ice Sheet, only a fraction of this ice volume may contain anthropogenic Hg, and the total quantity to be released cannot simply be scaled up from the total ice wastage. This is because "historical" Hg stored in firn and ice is released from a limited area close to the equilibrium line, but also because part of the surface snowmelt percolates down deeper into the firn, rather than being released in runoff.

Predicting the timing of Hg release from melting glaciers is equally difficult. First, the reduction in glacial volume is expected to accelerate over time as rates of meltdown increase. Furthermore, the amount of Hg released will vary over time if the concentrations are greater, for example, in deeper ice layers formed in previous decades when atmospheric Hg levels in the Arctic were higher (e.g., Boutron et al., 1998; Faïn et al., 2009; Zheng et al., 2009). Hence, future Hg fluxes in glacial meltwater are likely to increase, before declining again. When these fluxes will attain their maxima depends on the Hg concentration depth-age profile, turnover time, and wastage rate of individual glaciers. Given the typically low Hg levels measured in glacier snow and firn (a few ng/L), the highly diluted Hg released from large ice caps like Greenland will likely have a limited impact on ecosystems. Somewhat paradoxically, this impact could be greater in smaller glacier-fed watersheds that have lower accumulation/ablation area ratios.

A potentially important, but largely overlooked, consequence of Arctic glacier meltdown is the effect it may have on Hg methylation

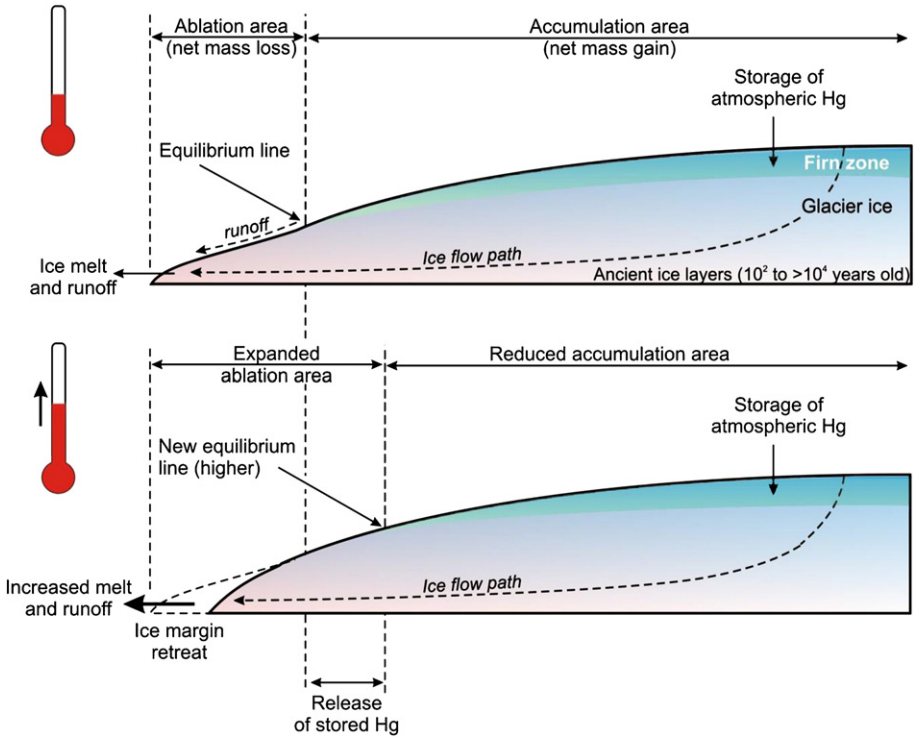


Fig. 6. Schematic illustration of the effect of climate warming on Hg storage and release from an Arctic ice cap or glacier. The impact of "historical" Hg released in melt water-fed streams and lakes depends largely on the accumulation/ablation area ratio of the glacier.

in ice-marginal environments. The ablation zone of glaciers and ice sheets is an area where in summer water flows and pools, and where wind-blown dirt and supraglacial debris accumulate. Bacterial activity takes place in cryoconites (holes in the ice surface filled by microbial mats; Hodson et al., 2008), creating conditions that can promote the methylation of any inorganic Hg present in runoff (St. Louis et al., 2005). The predicted expansion of the ablation area of Arctic glaciers and ice caps is also likely to expand the ice-marginal zone in which these processes can occur, as well as the duration of the seasonal period in which they can take place, and thus the effect could potentially be locally significant in glacially-fed catchments.

9.2. Release of mercury from thawing permafrost

Permafrost is soil, rock, sediment, or other earth material containing ice with a temperature that has remained below 0 °C for two or more consecutive years (AMAP/CAFF/IASC, 2005). Permafrost underlies most of the ground surface in the terrestrial areas of the Arctic as well as some undersea areas (AMAP/CAFF/IASC, 2005). Climate change models predict that the permafrost area in the circumpolar Arctic will decrease by 13% to 28% by 2050 (AMAP/CAFF/IASC, 2005; IPCC, 2007). As a result, thawing permafrost is recognized as a potentially important source of organic carbon and organic carbon-bound trace metals including Hg to Arctic freshwater and marine ecosystems (Macdonald et al., 2005).

The flux of Hg released from thawing permafrost depends on the Hg concentration in permafrost, the thawing rate and the erosion rate. Only limited data are available on permafrost Hg concentrations, which are dependent on the historical atmospheric Hg deposition rates, peat accumulation, and post-depositional change. Givelet et al. (2004) reported Hg concentration profiles in peat cores from two sites on Bathurst Island. Mercury concentrations in the permafrost layer ranged from 20 to 50 ng/g dw, but higher concentrations (20 to 100 ng/g) were reported in five permafrost peat cores along the southern Beaufort Sea coast (Leitch, 2006), probably due to greater amounts of vegetation in this region. The Hg concentration in the surface active layer is typically several-times higher than in the underlying permafrost (Givelet et al., 2004; Leitch, 2006). While this could in part be due to increasing deposition of Hg from the atmosphere over recent decades, the upward movement of Hg released from thawing permafrost is another possible explanation.

A few studies have suggested that the flux of Hg released from thawing permafrost to Arctic lakes (Klaminder et al., 2008) and marine ecosystems (Leitch, 2006; Hare et al., 2008; Outridge et al., 2008) could be significant, even higher than the atmospheric depositional flux. For instance, Klaminder et al. (2008) studied Hg concentrations and fluxes in the surface active layers and sediments from a large palsa mire complex in the Stordalen valley, northern Sweden. The study sites were covered with various types of vegetation along a thermokarst erosion gradient, and results revealed that hummock peat experiencing subsidence and submergence released 40% to 95% of its Hg pool (Fig. 7). The annual average flux of Hg released from the thawing permafrost was estimated to be about 200 $\mu g/m^2/y$ for the period 1970 to 2000, which was about an order of magnitude higher than the estimated atmospheric depositional flux in the region.

For the Arctic Ocean (and associated seas), coastal erosion historically has provided the largest source of particulate matter, higher even than that supplied by rivers (Stein and Macdonald, 2004). The acceleration of coastal erosion in the Arctic in recent years (Forbes, 2011), partly due to permafrost thaw and partly due to sea-level rise and increased open-water fetch permitting stronger wave action, therefore implies that Hg supply and the potential to bury Hg in shelf sediments are both increasing. The present flux of Hg released to the Arctic Ocean from eroding coastal permafrost was estimated to be 47 t/y (range 26 to 47 t/y), half that of the estimated atmospheric flux (Outridge et al., 2008). In Hudson Bay, the best estimate for the erosional Hg input was 0.25 t/y (range 0.25 to 0.38 t/y), compared to 1.5 t/y (range 3.4 to 13.6 t/y) from the atmosphere (Hare et al., 2008). However, unlike the atmospheric deposition, all of the Hg from coastal erosion impinges on the productive shelf regions which are more heavily foraged by migratory and resident species.

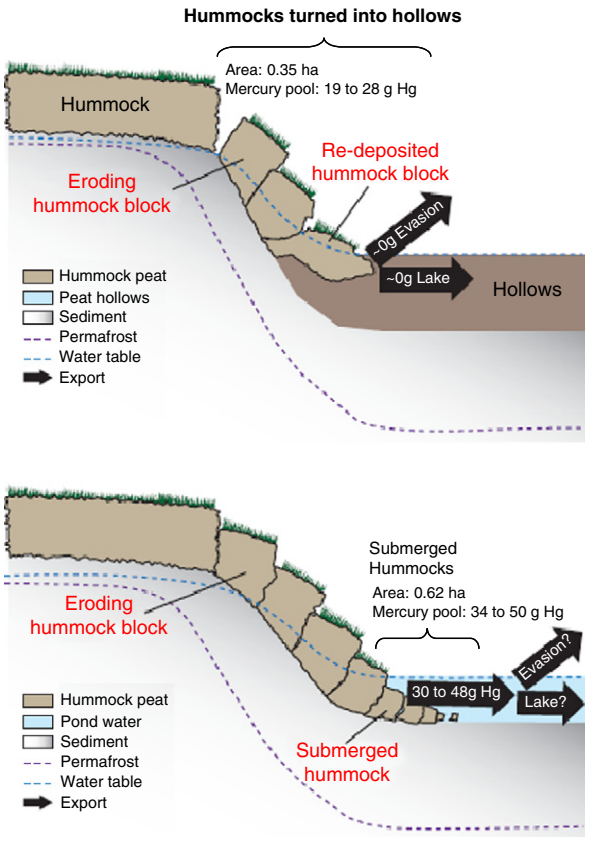


Fig. 7. Conceptual illustration of the collapse of a hummock palsa into (a) peat hollows and (b) pond water. Text in italics indicate the areal change between 1970 and 2000 within the Stordalen palsa mire and the estimated mercury pools affected by this change. Red text indicates eroding peat features, and black arrows the pool of mercury that is estimated to be lost over a period of a few decades.
Source: Klaminder et al., 2008.

The relative importance of thawing permafrost as a Hg source to Arctic freshwater and marine ecosystems is expected to further increase given the projected climate warming (Klaminder et al., 2008). An added risk factor associated with permafrost release of Hg is the concurrent release of labile organic carbon, which may serve as a physical focal point and substrate for enhanced microbial activity and methylation of released inorganic Hg. It should be noted that the freshly created shallow ponds from thawing permafrost appear to be locations of rapid MeHg production (St. Louis et al., 2005), the implications of which have not been studied.

10. What can be learned from current mass balance inventories of mercury in the Arctic?

Mercury mass balance inventories were recently compiled for the marine ecosystems of the Arctic Ocean and Hudson Bay by Outridge et al. (2008) and Hare et al. (2008), respectively. These reviews summarized the best available information on current THg inventories in seawater, sediments and biota, and THg inputs and outputs of the systems together with uncertainty estimates for fluxes expressed as ranges between minimum and maximum possible values. Although data concerning specific features (e.g., biotic Hg mass, total inputs, etc.) of these systems are obviously different, some common conclusions were drawn about the likely effects of climate change on Arctic marine systems in general, and particularly about the potential roles of systemic change as opposed to Hg inputs in driving recent and future Hg trends in marine biota. Unfortunately, MeHg data were too sparse to construct corresponding MeHg budgets.

One of the key findings from these compilations was that, like global oceans in general (Mason and Sheu, 2002; Fitzgerald et al., 2007; Sunderland and Mason, 2007), Arctic marine ecosystems currently contain relatively large total (inorganic) Hg reservoirs in seawater as a result both of significant anthropogenic inputs over the past roughly 200 years as well as large naturally-occurring background Hg inventories. Furthermore, the biologically-unassimilated inorganic Hg reservoir (about 8000 t in the Arctic Ocean, 98 t in Hudson Bay) is at least two orders of magnitude greater than the small inventory contained in Arctic marine biota (comprising less than 0.1% of THg mass in the ocean and about 1% in Hudson Bay). There is no suggestion in these data that the present or future production rates and bio-uptake rates of MeHg by Arctic marine food webs are in general limited by the availability of inorganic Hg in seawater, although additional work in this area is called for. These findings also imply that if the net methylation rate in Arctic marine systems significantly increased/reduced in the future, because of climate-related or other factors, there is a potential for significantly more/less of the large inorganic Hg reservoir to be transferred into the more toxic and bioaccumulative MeHg form, which may translate into higher/lower MeHg levels throughout Arctic marine food webs. It is presently very unclear which of the processes favoring methylation or demethylation will win as a consequence of the sequence of changes now occurring within the Arctic. Based on Lehnherr et al.'s (2011) findings that methylation–demethylation kinetics are relatively rapid, we can propose that change in MeHg exposure may vary widely between locations depending on biogeochemical cycles, something that was strongly hinted at by the organization of Hg into biogeochemical provinces in the Beaufort and Chukchi Seas (Stern and Macdonald, 2005).

As described earlier in this review, climate warming has the potential to alter the rate and geographic extent of a number of environmental, ecological and geochemical processes that can rapidly work on and transform the large abiotic inorganic Hg reservoir presently in seawater to bioavailable MeHg, or otherwise alter the capacity of food webs to assimilate MeHg. On the basis of current understanding, it is difficult to quantitatively predict which processes are likely to be most influential on future biotic Hg trends, or what the overall net effect will be. Table 2 qualitatively summarizes the available evidence on these questions as reviewed by earlier sections in this review and provides direction for future marine Hg research priorities in this area. Possibly a modeling approach incorporating known geophysical, biogeochemical and ecological factors may inform us about the relative importance of the various factors. However, such an ambitious project has not yet been attempted, and would face the

Table 2
Summary of likely impacts of climate warming on Arctic marine biota Hg levels.

Process	Likely process change	Likely impact on biotic Hg levels
Evasion	+	−
Atmospheric mercury depletion events	+	+ (near-term only)
Precipitation	+	+
Riverine inputs	+	+
Coastal erosion	+	+
Methylation	+	+
Demethylation	±	±
Marine primary productivity	+	±
Scavenging/sedimentation	+	−

Source: Outridge et al. (2008), except that marine productivity increases are now believed to promote increased methylation rates and so higher biotic Hg levels (see Sunderland et al., 2009 and Cossa et al., 2009). Likely changes in most processes are summarized from AMAP/CAFF/IASC (2005), for methylation and demethylation (see Section 6). '+' indicates increases in process rates and impact of biotic Hg levels; '−' indicates decreases in rates and impacts; '±' indicates no change.

challenge of the presently limited understanding of some key processes and their relationship to climate factors.

Outridge et al. (2008) tentatively concluded that the overall effect of a warming Arctic Ocean may be a future slow decline in seawater THg concentrations and subsequently of marine food web Hg levels. The recent finding in the Bering Sea, that loss of ice may foster loss of MeHg through enhanced photodemethylation would also indicate future decline of MeHg in marine food webs. However, recent papers by Sunderland et al. (2009) and Cossa et al. (2009, 2011), which related Hg methylation rates in seawater to marine algal organic matter productivity, suggest that a warmer and more productive Arctic Ocean may in fact lead to higher methylation rates of the available inorganic Hg in the water column below the euphotic zone, and thus to higher biotic Hg levels. Simultaneously, increased export rates of organic carbon associated with higher productivity may act to lower inorganic Hg concentrations in surface seawater (see Table 2).

In freshwater systems climate-related effects on Hg fate, methylation and bioaccumulation (e.g., Outridge et al., 2007; Chételat and Amyot, 2009; Chételat et al., 2008; Stern et al., 2009) are likely to be at least as profound as in marine systems. However, there is evidence that atmospheric deposition may assume a more important role simply because freshwater Hg methylation rates often appear to be inorganic Hg-limited, and surface area/volume ratios (i.e., atmospheric inputs relative to volume) are higher than in marine systems. There is abundant evidence for the atmosphere's important role in temperate regions (e.g., Orihel et al., 2007; Hammerschmidt and Fitzgerald, 2006b), and limited evidence from the Arctic. Methylmercury mass balance studies on a series of Alaskan lakes showed that in situ MeHg production (most of which occurred in sediments), was inorganic Hg-limited, thus suggesting that atmospheric Hg(II) loadings provided a major control on methylation rates (Hammerschmidt et al., 2006). The findings also highlighted the importance of Hg loading from watershed soil during summer. Therefore, climate change impacts on soil and permafrost seem highly relevant in settings like these. Photo-decomposition was the major MeHg loss process, accounting for about 75% of annual MeHg production. Climate warming is predicted to reduce photo-demethylation and enhance methylation rates due to increased organic carbon and inorganic Hg loadings from catchments, and higher temperatures and autochthonous productivity (Hammerschmidt et al., 2006).

A THg mass balance study on Amituk Lake, Cornwallis Island, by Semkin et al. (2005) found that the transport and retention of THg was determined by unique environmental characteristics in the Arctic (e.g., snowmelt-dominated transport, limited mixing of melt waters in the lake). Catchment snowmelt water was the main transfer step for atmospheric Hg to lake waters, but 59% of the springtime Hg inflow was flushed into the ocean because ice cover limited mixing of incoming water with the lake's water column. This mass balance makes it clear that climate warming is likely to have a large impact on how Hg is delivered to High Arctic lakes because of changes to the cryosphere. Warmer spring temperatures recently have increased the rate of Hg sedimentation in Amituk and other northern lakes because of parallel increases in algal productivity and Hg scavenging by POM (Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2009). This increased rate of THg transfer to sediments, together with associated organic carbon, may be another mechanism by which methylation rates are enhanced by warming trends in northern lakes.

11. Conclusions and recommendations

Conclusions (in numbered bullets) are organized under section headings, followed by recommendations (in italics) when appropriate.

What impact has climate change had on Arctic physical characteristics and processes?

1. Because of the intimate associations between climatic variables and many environmental processes and characteristics, the effects of recent climate warming on the Arctic's physical environment have been profound. From a Hg perspective, the most important impacts have occurred in precipitation rates and type (rain *vs* snow); riverine discharge and seasonality; lake ice and sea-ice seasonality, thickness and extent; declining length and depth of snow cover; increasing active layer depth in permafrost soils, altered vegetation in drainage basins, and changing atmospheric connectivity between the Arctic and southern latitudes.

How do rising temperatures affect atmospheric mercury chemistry?

2. Rising average air temperatures in the Arctic are predicted to slow the net oxidation rate of atmospheric gaseous Hg (0) to aerosol Hg(II) during AMDEs, because of an increased rate of $HgBr_2$ dissociation and a reduction in the release of Br radicals from sea ice. This effect would tend to decrease the rate of Hg deposition associated with AMDEs. Conversely, a continuation of the upward temperature trend may lead to increases in halogen-rich first-year sea ice and, by extension, increases in reactive Br release into the marine boundary layer, which would act to increase the rate of AMDE Hg deposition.

The uncertainty about the net effect of temperature increases on AMDE chemistry and Hg deposition, coupled with the unknown relative contributions of frost flowers and first-year sea ice to atmospheric Br chemistry, makes it impossible to even qualitatively predict how rising average temperatures will impact Br levels, and atmospheric Hg chemistry, in the future. Given the important role AMDEs may play in THg inputs to the Arctic, additional laboratory and field investigations of temperature effects are warranted.

Will a decrease in sea-ice coverage have an impact on the amount of atmospheric mercury deposited to or emitted from the Arctic Ocean, and if so, how?

3. Reductions in sea ice are likely to affect Hg dynamics across the air–seawater interface in two ways: first, more of the Hg (II) aerosol deposited during AMDEs and by other processes will land directly on seawater rather than on sea ice and so will be less likely to be immediately revolatilized; and second, the rates of bi-directional exchange of gaseous Hg(0) will be enhanced with possibly an increased net Hg loss from the ocean. The overall combined effect may be nearly neutral.

Because the evasion of dissolved gaseous Hg from the ocean could become a major loss process in the overall Hg budget of a warmer Arctic, further efforts to constrain the rate of marine Hg evasion should be undertaken.

Does climate affect air–surface mercury flux, and riverine mercury fluxes, in Arctic freshwater and terrestrial systems, and if so, how?

4. The best empirical information on this question concerns three processes: riverine Hg fluxes, timing of the spring freshet, and forest fires. River flows have increased in recent decades in Canada and Russia, which are likely to have also increased riverine Hg fluxes. Earlier freshets in spring may better align the flush of riverine Hg with the season of rapid biological growth and productivity in river estuaries and deltas. Enhanced frequency and temperatures of forest and ground fires in the North may play an important role in mobilizing Hg and carbon stored in soils into the air and local water bodies.

Additional research is warranted on these processes, as well as other processes which could be important: release of Hg, nutrients and labile carbon into lakes and the ocean as a result of thawing of permafrost

soils and peatlands; the 'greening' of the Arctic tundra with grasses and woody plants which may add more carbon to aquatic systems; and altered hydrological regimes which will probably see reduced lake water levels, lower snowpacks and so reduced spring freshets.

How does climate change affect mercury methylation/demethylation in different compartments in the Arctic Ocean and freshwater systems?

5. Several processes may theoretically elevate the overall net Hg methylation rate in Arctic aquatic systems: warmer, longer ice-free seasons as well as enhanced inputs of catchment soil nutrients, sulfate and carbon to water bodies, are likely to increase overall aquatic primary productivity and promote more bacterial activity in sediments and wetlands; increased inputs of inorganic Hg resulting from permafrost thaw, coastal erosion or riverine fluxes resulting from climate change would provide more of the necessary inorganic Hg substrate required for methylation. However, some effects, such as increased MeHg–DOM binding in waters or elevated photo-demethylation rates, may act to reduce levels of MeHg or its uptake by aquatic food webs.

Most of the insights into possible climate–Hg methylation linkages are gleaned from temperate locations and extrapolated to the Arctic. Bacterial demethylation and its relationship to climate variables are poorly understood. As net methylation rate is the key rate-limiting step link between the inorganic Hg forms which dominate the environment and toxic MeHg which biomagnifies in food webs, research into this area should be a priority.

How will climate change alter the structure and dynamics of freshwater food webs, and thereby affect the bioaccumulation of mercury?

6. Food webs in Arctic freshwaters are likely to be affected by climate change through three main environmental drivers: temperature, water chemistry and the hydrological regime. The main impacts on Hg bioaccumulation from changes to foodwebs will probably occur via effects on dietary resources and trophic position, growth, and ecosystem productivity. Some impacts may enhance Hg bioaccumulation while others may reduce it; the net effect is likely to vary geographically and by species, due to regional differences in the structure of aquatic food webs and their responses to environmental change.

Empirical evidence is largely lacking for interactions between climate warming and Hg bioaccumulation in Arctic freshwater food webs, which limits predictive ability.

How will climate change alter the structure and dynamics of marine food webs, and thereby affect the bioaccumulation of marine mercury?

7. Many of the impacts predicted for Arctic marine food webs and biota are associated with reductions in sea-ice concentration and thickness. These impacts are mediated through energy and carbon flows, increased primary productivity, nutrient and carbon transport from rivers and other oceans, high animal growth rates, and altered food chain length, all of which will probably affect marine biotic Hg levels but in variable ways and directions. In sea-ice dependent marine mammals such as beluga and seals, ice extent-related changes in habitat selection and feeding behavior are known to significantly affect dietary exposure to Hg.

The number and scope of studies examining marine biotic Hg–climate relationships needs to be expanded in terms of numbers of species and time span; sea-ice obligate marine mammals and fish may be most affected by climate change.

What are the likely mercury emissions from melting glaciers and thawing permafrost under climate change scenarios?

8. Future trends in Hg fluxes from glaciers will increase under a warming climate, before ultimately declining as archived pollutant Hg in upper ice layers is flushed out. In comparison to permafrost; however, the overall fluxes will be insignificant except possibly in ice-margin environments. Thawing permafrost is already releasing significant masses of largely inorganic Hg to lakes and the Arctic Ocean which approach or even exceed atmospheric inputs depending on the setting. Concurrent release of ancient organic matter which may serve as a substrate and physical focus for bacterial methylation activity will increase the risk to ecosystems. On the other hand, the associated particulate loads into aquatic systems also provide the potential to scavenge and bury Hg and/or alter light climate and thus alter photo-demethylation.

Owing to its growing importance as a major source of inorganic Hg and carbon to aquatic environments, the role of permafrost in the Arctic Hg cycle should become a priority research issue.

What can be learned from current mass balance inventories of mercury in the Arctic?

9. The Arctic Ocean and Hudson Bay contain large total (inorganic) Hg inventories in seawater as a result of anthropogenic inputs over the past roughly 200 years as well as even larger natural background Hg masses. The biologically-unassimilated fraction of Hg is at least two orders of magnitude greater than the small amount (0.1% to 1% of total mass) in marine biota. In Alaskan lakes, in situ sedimentary MeHg production was inorganic Hg-limited, suggesting the importance of atmospheric and watershed Hg(II) loadings for methylation rates. Photo-decomposition was the major Hg loss process in these lakes. The transport and retention of THg in Arctic lakes are determined by environmental features (e.g., snowmelt-dominated transport, limited mixing of melt waters in lakes, very low primary productivity and Hg trapping) that are characteristic of these environments. The above observations strongly imply that conversions between inorganic and organic Hg forms are key to understanding Hg trends in animals and projecting the effects of climate change on Hg exposure in ecosystems.

Mass balance budgets for MeHg in Arctic marine systems may be as revealing as they were for lakes, but first require significantly greater efforts aimed at measuring MeHg masses and transformation rates in different environmental compartments.

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