Chapter 3

What is the Fate of Mercury Entering the Arctic Environment?

Coordinating author: Thomas Douglas

Co-authors: Marc Amyot, Tamar Barkay, Torunn Berg, John Chételat, Philippe Constant, Aurélien Dommergue, Marlene Evans, Christophe Ferrari, Klaus Gantner, Matthew Johnson, Jane Kirk, Niels Kroer, Catherine Larose, David Lean, Lisa Loseto, Robie Macdonald, Derek Muir, Torkel Gissel Nielsen, Peter Outridge, Alexandre Poulain, Laurier Poissant, Sigurd Rognerud, Henrik Skov, Søren Sørensen, Feiyue Wang, Christian Zdanowicz

3.1. Introduction

This chapter focuses on the environmental fate of mercury (Hg), that is, the movements, transformations and bioaccumulation of Hg following its entry into the Arctic surface environment via the oceanic, atmospheric and terrestrial pathways described in Chapter 2. The chapter emphasizes those processes that are most relevant to biological Hg uptake and the consequent development of risk from Hg exposure in wildlife and human health, which will be explored in Chapters 5, 6, and 8.

The chapter begins with a discussion of the chemical transformations of net deposited atmospheric Hg in aquatic and terrestrial environments and their associated snow and ice (Section 3.2). This is followed by a discussion of the movement of Hg from the abiotic environment into food webs (Section 3.3). Methylation, a key process controlling the fate of Hg in most ecosystems, is the focus of Section 3.4 while Section 3.5 addresses how trophic processes control Hg in higher order animals. Case studies on Eastern Beaufort Sea beluga (*Delphinapterus leucas*) and landlocked Arctic char (*Salvelinus alpinus*) provide salient examples of the relationship between ecosystem trophic processes and biological Hg levels. Section 3.6 explores whether atmospheric mercury depletion events (AMDEs) contribute to increased Hg levels in Arctic biota. The effects of organic carbon on Hg speciation, dynamics, and bioavailability are explored in Section 3.7. Finally, Section 3.8 focuses on long-term sequestration of Hg into non-biological archives.

Mercury and its various chemical forms are discussed by reference either to chemically-defined species (e.g., gaseous elemental Hg, and monomethyl Hg) or to operationally-defined species based on laboratory analytical schemes (e.g., total Hg, reactive Hg; Mason et al., 1998; Fitzgerald et al., 2007; Strode et al., 2007). Following these conventions, the following terminology and symbols are used: Hg(0) – elemental Hg either dissolved in water (DGM) or as a gas-phase vapor in air or snowpack interstitial air (GEM); Hg(II) – inorganic divalent Hg; MeHg – monomethyl Hg (CH_3Hg^+); DMHg – dimethyl Hg ($(CH_3)_2Hg$); Hg_C – colloidal Hg; THg – total Hg; and Hg_R – reactive Hg (about equivalent to the THg(II) pool including colloids and ligands).

3.1.1. The Arctic as a unique location

The terrestrial Arctic surrounds the Arctic Ocean, and many of the unique aspects of this region as a whole are the result of the interplay of physical, chemical, and biological processes between the land and the sea. With respect to the inputs and cycling of Hg, the Arctic, and particularly the Arctic Ocean, has a number of features that set it apart from all other regions. As a consequence, while many Hg processes (e.g., photochemical reactions, methylation) can be inferred from studies in temperate locations, the Hg cycle within the Arctic cannot due to its unique aspects. It has been argued that these features confer to Arctic Ocean ecosystems a particular sensitivity to the global Hg cycle, brought about by an array of post-depositional processes promoting Hg methylation (Macdonald and Loseto, 2010).

First, the Arctic has an exceptional seasonality going from 24 hours of darkness in winter to 24 hours of sunlight in summer. This seasonality is synchronous around the Arctic so that spring freshet, biological production and photo-active processes all have a parallel cadence that is unique to polar environments. On land there are extreme shifts from a snow-covered to a green (vegetated) landscape every spring and then back to snow in the autumn. The short growing season is utilized by aquatic and terrestrial vegetation that receives almost continuous sunlight. Given that Hg undergoes photolytic reactions and is also entrained into the Arctic carbon cycle, then the Hg cycle will also exhibit exceptional seasonality.

Second, sea ice is a defining feature of the Arctic Ocean. Sea ice provides a semi-permeable, seasonally variable interface between air and water with consequences for exchange of contaminants (e.g., Hg), heat, and gases. Sea ice also provides a habitat for a food web that includes almost everything from viruses to polar bears. The formation of sea ice during winter contributes brine to the ocean, thereby fostering mixing (the winter polar mixed layer) and convection (the Arctic haloclines). Halogen aerosols emitted from sea ice, together with the seasonality of sunlight, are key factors underpinning AMDEs which are unique to polar regions. At present one of the most visible changes in the Arctic Ocean is the loss of multi-year sea ice and its replacement by seasonal sea ice. This transition toward younger, more saline ice will have wide-ranging but poorly understood, effects on Hg biogeochemical cycling.

Third, the Arctic Ocean is a semi-enclosed sea, which restricts seawater exchange with the Pacific and Atlantic Oceans and thereby controls the residence time and sources of seawater within the ocean. The semi-enclosed setting of the Arctic Ocean also presents unique opportunities to construct material budgets. In terms of atmospheric connections, the Arctic receives and mixes air masses and their associated contaminants from all the major northern hemisphere continents (Europe, Asia, North America), and redistributes that air back to temperate latitudes.

Fourth, the Arctic Ocean receives an exceptional input of freshwater runoff, thereby physically linking the land and sea. Comprising about 3% of the world's oceans by area, the Arctic receives 11% of global runoff. Much of this runoff is from locations underlain by permafrost that is degrading in response to climate warming. The consequence of all this runoff is that the upper Arctic Ocean is strongly stratified, which limits immediate exchange with the atmosphere to the top 50 m of the water column in most places. Stratification by runoff is augmented in summer by widespread sea-ice melt, again restricting the depth (volume) of water that can exchange heat, moisture and chemical constituents with the atmosphere. Stratification together with sea-ice formation over the shelves leads to the production of haloclines in the Arctic Ocean. These underlie the polar mixed layer and separate this from the deeper water in the basins which has arrived from the Atlantic Ocean via Fram Strait. The haloclines tend to contain nutrient maxima, which indicate biological regeneration of organic matter. This regeneration may occur partly by vertical flux of labile carbon (plankton, fecal pellets, aggregates) within the Arctic Ocean and partly by imported regenerated products, especially those contained within Pacific water entering through Bering Strait and passing over the Chukchi Shelf.

Fifth, the Arctic generally has a low sloping topography. Much of the land area consists of broad, low lying plains, while the Arctic Ocean contains the largest proportion of continental shelves (fully 50% of the ocean area) of all oceans. The shelves tend to be the location of active biogeochemical cycling because they have higher primary production and are the locations of recurrent flaw leads in winter. The leads provide important oases for the production of food, and are the immediate recipients of the enormous dissolved and particulate terrigenous inputs. The sediments accumulating on the shelves provide important locations where organic carbon metabolism can reduce or eliminate dissolved oxygen leading to a series of redox reactions, which affect the cycling of many elements including Hg. Particulate inputs to shelves include suspended sediments from rivers and even more sediment from coastal erosion, which is likely to be accelerating due to sea-level rise and permafrost thaw.

Last, the interior area of the Arctic Ocean has an exceptionally low particulate export ('biological pump') because it is oligotrophic, which may mean that bio-active elements like Hg tend to recycle within the stratified polar mixed layer rather than transfer to deeper waters through particle flux. All of these processes are described in greater detail here and in Chapter 4.

3.2. What is the fate of net deposited atmospheric mercury in the various environmental media?

The net deposition of atmospheric Hg to the Arctic is the product of multiple processes: the total amount of Hg deposited onto snow and ice during springtime AMDEs, plus Hg added by other atmospheric deposition processes to the snow pack, land, or aquatic surfaces (i.e., wet or dry deposition outside the AMDE season), minus gaseous Hg(0) re-emitted from snow and ice surfaces due to microbial and photochemical reduction of Hg(II), minus the evasion of DGM (which includes all readily volatilized forms of Hg but dominated by Hg(0)) from freshwater or seawater.

The bulk of the Hg remaining subsequent to these processes is mostly in the form of inorganic particulate Hg(II) species, dominated by uncharged or negatively charged complexes with OH^-, Cl^- and Br^- (Poulain et al., 2007a). A small increase in MeHg concentration in the snowpack has been shown to occur just prior to snowmelt (Constant et al., 2007), but it is not known how much of this is produced in the snowpack compared to that falling in snow. The impact of this net deposited Hg on Hg concentrations in receiving waters (rivers, lakes, ocean) is the subject of ongoing research. Recent studies (St. Louis et al., 2005, 2007; Dommergue et al., 2010) which focused on the fate in marine systems of Hg from snowpacks during and following snowmelt determined that melt runoff was not a substantial contributor to the THg or MeHg budgets of Arctic seawater. In freshwaters, however, significant increases in THg flux to sediments during the 20th century indicate that deposited atmospheric Hg has had an impact on Hg levels in lake sediments and, by extension, on freshwater Hg budgets in the Arctic (Fitzgerald et al., 2005; Semkin et al., 2005; Muir et al., 2009).

Deposited Hg either enters aquatic environments (marine systems, melt ponds, lakes, rivers) or remains in multi-year snow and ice. The fate of Hg deposited onto freshwater and marine environments is considered separately. After entering seawater, Hg(II) can be photo- or microbially-reduced and lost due to evasion of DGM. This has been inferred from elevated GEM concentrations in air above Arctic seawater (Sommar et al., 2004, 2010) and melt ponds on sea ice (Aspmo et al., 2006). Andersson et al. (2008) determined DGM concentrations along an extensive transect crossing the North American boundary of the Arctic Ocean and the interior ocean (Figure 3.1), and showed clearly that ice-covered regions tended to have high levels of DGM in the water beneath the ice. These data suggest that the reduction of Hg(II) to Hg(0) occurs widely in seawater, but that sea-ice cover prevents evasion of the Hg(0) back into the atmosphere. Mercury photo-reduction and evasion from aquatic systems also occurs at lower latitudes, and the air-sea exchange of Hg in aquatic systems has been explored in detail by Strode et al. (2007) and Whalin et al. (2007), among others. The production of DGM in Arctic coastal streams and ponds, estuaries, and in marine waters is strongly affected by chloride, with lower DGM formation observed at higher salinities (Poulain et al., 2007b). Halogens in general, and chloride ions in particular, have been shown to enhance Hg(0) photo-oxidation to Hg(II) and hence hamper evasion (Lalonde et al., 2001; Whalin et al., 2007). On the other hand, rivers provide a significant source of THg, including dissolved and particulate forms, to Arctic coasts (Coquery et al., 1995; Leitch et al., 2007; Outridge et al., 2008). In the case of the Mackenzie River, as it enters the coast during ice-free conditions (late July), processes leading to high levels of DGM in the water appear to prevail as there is a strong increase in DGM associated with plume water (Figure 3.2; Andersson et al., 2008). Andersson et al. (2008) proposed that the high levels of DGM might either be supplied directly by the Mackenzie River or be a sign of enhanced DGM production facilitated by riverine dissolved organic carbon (DOC). Clearly, more seasonal measurements are required to determine the annual balance between supply of Hg to

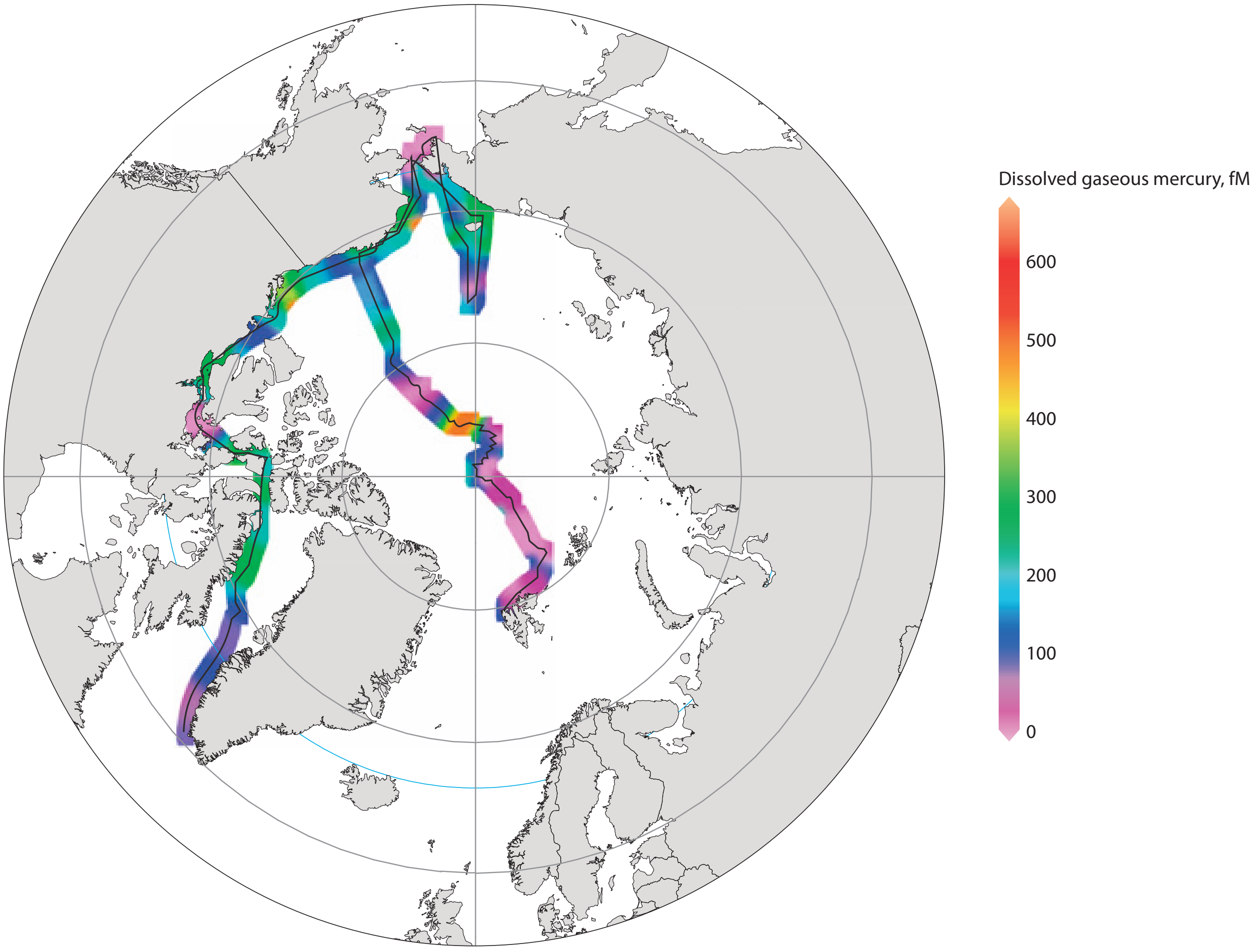

Figure 3.1. Dissolved gaseous mercury (DGM) in surface water along the *Beringia* 2005 cruise track showing predominant supersaturation in the water, with generally higher DGM concentrations found under locations covered with sea ice. Modified from Andersson et al. (2008).

coastal regions, loss of Hg through evasion, burial or advection, and entry of Hg into shelf food webs. The suppression of Hg reduction due to chloride is also partly counterbalanced by the presence of particles (possibly particulate iron oxides), which favor the conversion of oxidized Hg to its elemental form, although the exact mechanisms have not been elucidated.

There are three other important mechanisms by which the net deposited Hg may be lost to the surface Arctic Ocean: export of ice and snow to the Atlantic Ocean; outflow of water to the Atlantic Ocean; and vertical particle flux into the deep ocean. Net deposited Hg contained in the ocean or sea ice is actively removed from the Arctic Ocean on time scales set by the export rates of ice, particles and water. Sea ice is exported at a rate of about 2500 km^3/y which, if a 3 m layer of sea ice is assumed, implies the export of about 0.8 × 10^6 km^2/y of snow/ice and its burden of deposited Hg. The time required for sea ice to leave the Arctic Ocean varies from one to six years depending on where it has been produced (Macdonald et al., 2005). This sets an upper limit of six years for net Hg deposition to be held on or within sea ice and associated snow. Seasonal ice formation and melting almost certainly reduce this ice residence time. Mass balance calculations indicate that sea-ice export was a minor loss process, amounting to only about 7 t/y, because of very low ice Hg concentrations (Outridge et al., 2008). Seawater in the upper Arctic Ocean has residence times varying from one to three years on the shelves, about ten years in the polar mixed layer and roughly 30 years in halocline waters beneath the mixed layer (Macdonald and Bewers, 1996;

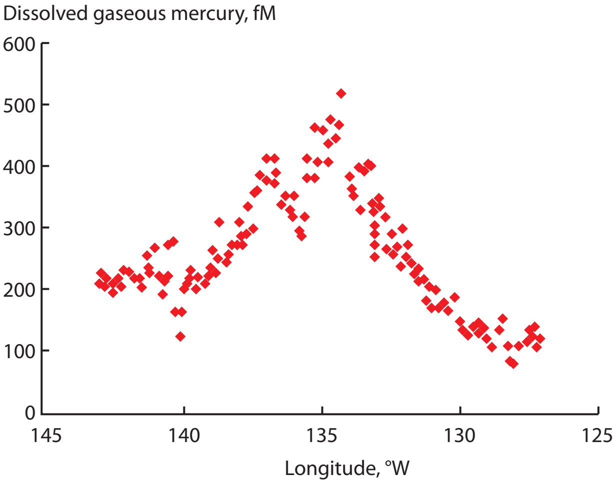

Figure 3.2. Dissolved gaseous mercury (DGM) in surface water along the *Beringia* 2005 cruise track as it crossed the Mackenzie River plume. The high DGM concentrations in plume waters may indicate direct supply from the river, or enhanced production of DGM facilitated by riverine dissolved organic carbon. Modified from Andersson et al. (2008).

Macdonald et al., 2005). Deeper in the ocean, the residence times are up to several centuries based on ^{14}C and other tracers (e.g., Macdonald et al., 1993; Schlosser et al., 1994). Again, this sets the time scale over which deposited Hg can be held in this reservoir. Seawater export accounted for 68 t/y (range of estimates 22 to 113 t/y) total Hg from the Arctic Ocean, or about a third of total losses of Hg annually (Outridge et al., 2008). Finally, Hg may be scavenged by algae- and microbe-derived particulate organic matter (POM) and exported to the deep ocean (Mason and Fitzgerald, 1993; Sunderland et al., 2009). How important this process is in the Arctic is not known with precision, but globally, it appears to account for almost half of the contaminant Hg deposited into the ocean (Sunderland and Mason, 2007). First-order estimates currently suggest that over half (108 t/y, range 13 to 200 t/y) of the total Hg losses from the Arctic Ocean occur via this route (Outridge et al., 2008). The effect of particle flux will be to reduce the residence time of deposited Hg in surface water to a period shorter than the residence time of the water.

Freshwater systems (lakes and rivers) provide another ecosystem receptor for Hg deposition to the Arctic. Watershed transport of deposited inorganic Hg to lakes appears to vary among different Arctic regions with differences largely driven by physiographic conditions. In Amituk Lake in the Canadian High Arctic, snowmelt delivered the most THg during spring in June and early July (Loseto et al., 2004a; Semkin et al., 2005). The spring freshet is the critical period of discharge from High Arctic watersheds because up to 80% of the total annual precipitation is deposited as snow during the long polar winter (Woo, 1983). The snow-associated Hg, which is largely of atmospheric origin, flows in meltwater over soils early in the season when they are largely still frozen, and is eventually transported to lakes (Semkin et al., 2005). Thus the integration of this atmospheric Hg into ecosystem soils and vegetation may be limited. Erosion of thawed soils during summer provides an important source of inorganic Hg to lakes in Alaska (Fitzgerald et al., 2005) and possibly elsewhere in the Arctic. Soil loadings of Hg to Alaskan lakes were associated primarily with silt (Fitzgerald et al., 2005) and were greater in lakes with higher watershed/lake area ratios (Hammerschmidt et al., 2006).

Mercury reaching Arctic lakes from snowmelt runoff and throughout the remainder of the open water season can be recycled back to the atmosphere before entering food webs, through sunlight- or microbially-mediated reduction of Hg(II) (Costa and Liss, 1999; O'Driscoll et al., 2006), as it can in Arctic seawater. Arctic lakes generally contain supersaturated surface water concentrations of DGM (Amyot et al., 1997; Tseng et al., 2004). The latter studies reported average DGM concentrations of the order of 200 fM (40 pg/L), representing about 3% of the total dissolved Hg in lake waters. In Arctic Alaskan lakes, the DGM evasion flux was similar to the atmospheric input of Hg in summer precipitation (Tseng et al., 2004). DGM concentrations in lakes typically vary both daily and seasonally and its formation in surface waters is believed to be dominated by photochemical processes. At depth, other processes likely to be associated with microbial activity dominate (Vandal et al., 1991; Mason et al., 1995; Poulain et al., 2004). The relative importance of photochemical *vs* biological processes in controlling the reduction rate of Hg(II) in Arctic freshwaters remains to be elucidated. According to Amyot et al. (1997), the rate is controlled by: the intensity of solar radiation, particularly UV-B (280-320 nm) and UV-A (320-400 nm) wavebands; and the concentration of available photo-reducible Hg(II) complexes. DOC is also important as it controls the penetration of ultraviolet (UV) radiation into water.

Aquatic productivity can strongly mediate the retention of Hg in Arctic lakes, particularly in high latitude polar desert regions, by increasing the rate of scavenging of Hg from the water column and its accumulation in lake sediments (Outridge et al., 2005b, 2007). These High Arctic lakes have extremely low biological production (Welch and Kalff, 1974; Markager et al., 1999), resulting in a low capacity to retain aqueous Hg through scavenging by algae and suspended detrital organic matter. In studies of four lakes in the Canadian Arctic Archipelago and the Yukon, sediment fluxes of THg increased during the 20th century and were correlated with an increase in aquatic productivity inferred by diatom abundances and chemical characterization of the sedimented organic matter (Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2010). Similarly, the amount of organic matter is an important factor explaining the spatial distribution of Hg in sediments within and among Arctic lakes. Organic matter, which strongly binds Hg (Fitzgerald and Lamborg, 2004), occurs at low concentrations in nearshore and deep-water sediments of High Arctic lakes (typically less than 10% dry weight, total organic carbon; Outridge et al., 2007; Chételat et al., 2008; Muir et al., 2009). Spatial variations in sediment concentrations of THg and MeHg are in general strongly correlated with organic carbon content (Morel et al., 1998; Outridge et al., 2007; Chételat et al., 2008). In Alaskan lakes, sediment MeHg concentrations were found to be strongly correlated with organic carbon content whereas inorganic Hg concentrations were related primarily to the focusing of fine-grained inorganic soil particles (Hammerschmidt et al., 2006).

3.2.1. Spring snowmelt as a major seasonal transition in the Arctic mercury cycle

Roughly half to three-quarters of the annual surface water runoff in polar regions is from spring snowmelt (McNamara et al., 1998). As a consequence, the spring melt runoff event is the most important time for Hg that accumulated in snowpacks over winter to be transferred into aquatic and terrestrial ecosystems. The spring melt comprises the net Hg contribution from snowpacks after re-emission has had its effect (see Section 2.6). It is well known from work in temperate latitudes that the early pulse of water from initial snow melt typically includes an 'ionic' pulse of major elements (Tranter et al., 1986; Bales et al., 1989; Williams and Melack, 1991; Harrington and Bales, 1998), and which includes dissolved and particulate Hg (Schuster et al., 2008).

In Arctic regions, both MeHg and THg in melt water occur at concentrations elevated above full-column snowpack values at the onset of snow melt in many locations (Berg et al., 2003; Dommergue et al., 2003b, 2010; Loseto et al., 2004a), but not in all (Aspmo et al., 2006). A summary of meltwater THg concentrations reported by six studies at nine sites across the Canadian and Greenland Arctic revealed a range from 0.3 to 10 ng/L with an average of about 3 ng/L (Outridge et al., 2008). In a recent study at Ny-Ålesund, Svalbard, most of the Hg(II) remaining in the snowpack prior to melt was rapidly expelled from snow matrices, leading to a brief pulse of THg-enriched melt water (Diommergue et al., 2010). Streams receiving snowpack melt runoff (averaging 3.5 ± 1.9 ng Hg/L; n=13), and runoff waters originating from the Austre Lovénbreen glacier (2.2 ± 1.1 ng Hg/L; n=7), contributed 1.5 to 3.6 kg/y of THg to the fjord at Ny-Ålesund (i.e., 8% to 21% of the fjord's THg content). In another study at Ny-Ålesund, snow samples showed increased THg concentrations during the season's first AMDEs, but subsequent concentrations during the melt period were at pre-AMDE levels (Steen et al., 2009). At Kuujjuarapik, on Hudson Bay, a Hg(0) pulse in snowpack interstitial air was found to coincide with the initiation of snowmelt (Dommergue et al., 2003a). However, gas phase exchange did not remove Hg from the snowpack, and more than 90% of the Hg present in the surface snow was believed to have been released with meltwater. On sea ice off northern Greenland, snow and meltwater pond samples contained between 1.3 and 8.1 ng/L of THg in snow, and from below detection to 5.1 ng/L in meltwater, and were comparable with surface snow measurements at other remote Arctic locations prior to polar spring (Aspmo et al., 2006). As a result, the authors concluded that there was no long-term accumulation of Hg in these compartments following the springtime AMDE season, suggesting that the net deposited Hg was released each year in meltwater.

3.2.2. Microbial carbon processing and mercury in the Arctic

The fate of Hg deposited onto Arctic ecosystems depends not only on snow photochemistry (Dommergue et al., 2003a; Steffen et al., 2008b) and ocean water physical and chemical characteristics, but probably also on microbial processes (Poulain et al., 2007c). There is good evidence that microbes actively metabolize at subzero temperatures in snow (Amato et al., 2007) and sea ice (Junge et al., 2006). This raises the question of whether deposited Hg(II) can be actively transformed into other species (GEM or MeHg) by microbes in the Arctic cryosphere (snow, sea ice, freshwater ice). The involvement of bacteria in the Hg cycle in the Arctic, however, has been almost completely overlooked. In temperate environments it is known that some bacteria carry genes that make them resistant to Hg(II) and MeHg because they convert these Hg compounds into the volatile and less toxic Hg(0) (Barkay et al., 2003). Sulfate-reducing bacteria are able to methylate Hg(II) species under anaerobic conditions in Arctic sediments and wetlands (Loseto et al., 2004a,b). Therefore, bacteria in Arctic ice/snow and in the aquatic environment may well play a critical role in the conversion of deposited Hg to MeHg and/or Hg(0) depending on a number of environmental factors including the level of oxygen present.

Microbes can also influence Hg speciation and fate in other ways through processes involving the carbon cycle. The presence of carbon, which in the treeless Arctic mostly originates from autochthonous production (as bacterial and algal particulate detritus, exudates or DOC) helps to regulate the fate of Hg in Arctic aquatic systems, as it does at temperate latitudes; one of the mechanisms by which it does this is absorption of light in the water column (Lalonde et al., 2002, 2003; Fitzgerald and Lamborg, 2004; Poulain et al., 2007c). C-DOM (colored dissolved organic matter), a powerful absorber of UV radiation, provides a particularly important control on photo-demethylation and photo-reduction rates. As a consequence, an inverse relationship has been observed between DOC levels and DGM formation in Arctic lakes (Tseng et al., 2004). In saline waters, organic compounds produced by algae are able to promote oxidation of Hg(0) even under dark conditions (Poulain et al., 2007c). Coastal environments are colonized by Hg-resistant bacteria potentially able to reduce Hg. Simple box modeling suggests that this bacterial reduction could be significant in ocean waters, although bacterial Hg reduction rates need to be directly quantified (Poulain et al., 2007c).

In other oceans, it has recently been demonstrated that MeHg can be produced during the remineralization of algal detritus in the water column (Sunderland et al., 2009; Cossa et al., 2009). Cossa et al. (2009) showed that the vertical transport of MeHg associated with particulate flux from surface waters was relatively unimportant compared to the *in situ* production of MeHg which occurred in association with nutrient maxima at subsurface water depths. Little is known about this process in the Arctic; however, the Arctic Ocean does possess pervasive strong nutrient maxima below the polar mixed layer (Wang et al., 2006). Kirk et al. (2008) reported that MeHg, both in terms of concentration and as a percentage of THg, was highest in the middle and bottom depths of Hudson Bay and waters of the Canadian Arctic Archipelago, suggesting that the *in situ* production of MeHg reported by Sunderland et al. (2009) and Cossa et al. (2009) may also occur in subsurface Arctic seawaters.

3.2.3. The fate of mercury in the Arctic Ocean

Most of the human exposure to Hg in the Arctic is attributable to the consumption of traditional marine foods (AMAP, 2009b). However, even in the global environment, understanding of marine Hg biogeochemistry is limited by under-sampling and under-study (Fitzgerald et al., 2007). Nevertheless, it may be assumed that the basic components of the marine Hg cycle as understood from temperate ocean studies (e.g., Morel et al., 1998; Lamborg et al., 2002a; Fitzgerald et al., 2007; Strode et al., 2007; Sunderland and Mason, 2007) can be applied to the Arctic Ocean, with the caveat that the rates and relative importance of many processes will differ. Indeed, Hg biogeochemistry appears to exhibit significant differences even between temperate ocean basins (c.f., Laurier et al., 2004; Fitzgerald et al., 2007; Sunderland and Mason, 2007). Therefore, it is likely that features characteristic of the Arctic Ocean such as seasonal ice cover, strong seasonality in light and primary production, AMDEs, large river inputs and exceptionally large shelves will all contribute to a distinctly different Hg cycle in Arctic seas (e.g., see Andersson et al., 2008; Sommar et al., 2010).

The ability of Hg to transfer between environmental media and transform from one chemical species to another (Figure 3.3) makes the environmental chemistry of this element a challenging subject. In the global ocean, THg is usually found in the range 0.02 to 0.5 ng/L (Mason et al., 1998; Laurier et al., 2004; Strode et al., 2007; Sunderland et al., 2009) with Arctic seas or outflowing water from the Arctic possibly at the low end of this range (Mason et al., 1998; St. Louis et al., 2007; Kirk et al., 2008). Outridge et al. (2008) estimated that the top 200 m of the Arctic Ocean had a THg inventory of 620 to 945 tonnes (best estimate 945 tonnes), which is far larger than estimated

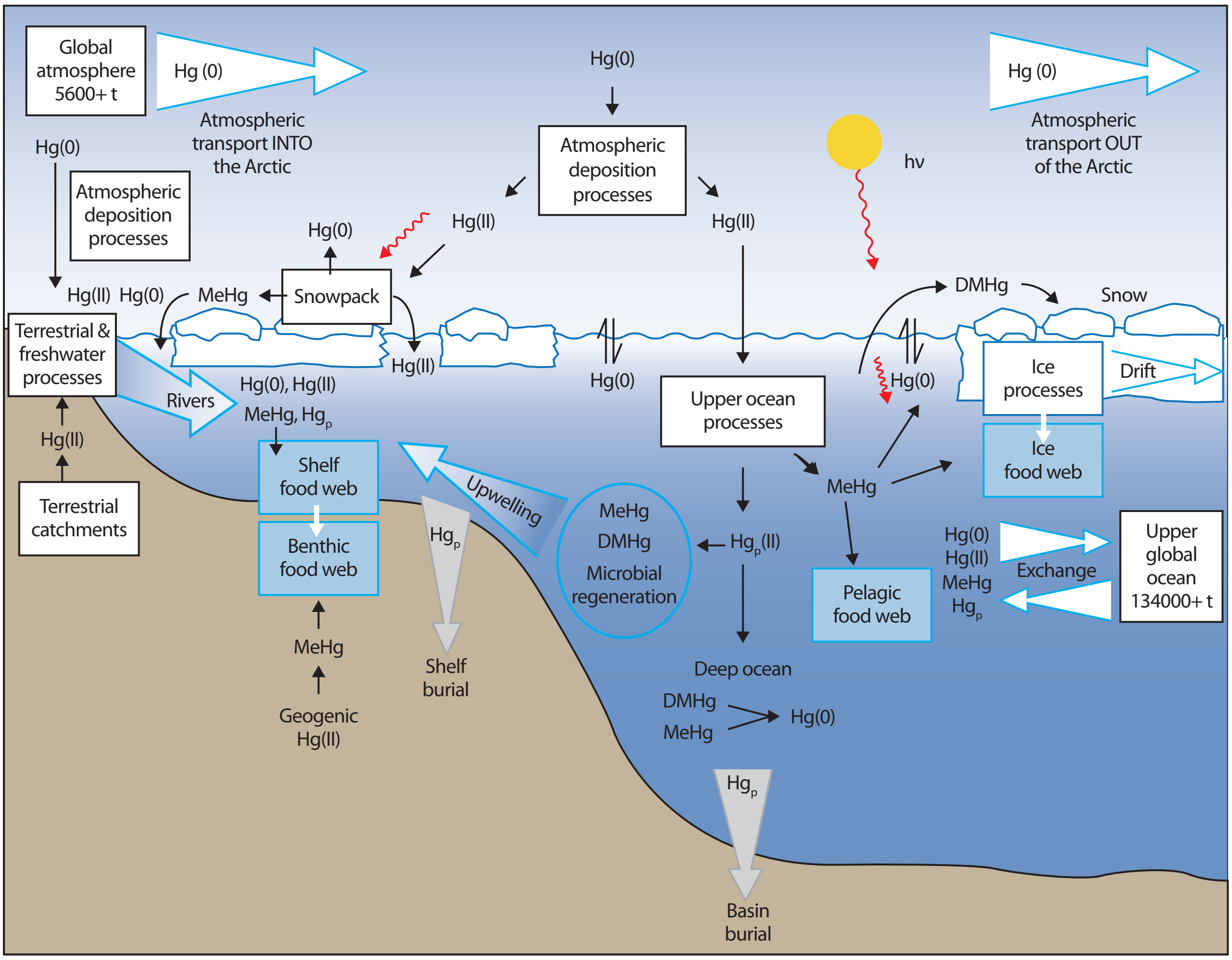

Figure 3.3. The mercury cycle in the Arctic Ocean. Rectangular boxes show system processes, like food webs or atmospheric deposition chemistry, that have detailed schematics and discussion presented elsewhere. Large shaded arrows refer to atmospheric or oceanic transport processes that exchange Hg with the global environment and move Hg between reservoirs within the Arctic Ocean. Small black arrows refer to chemical processes that produce changes between Hg species.

annual fluxes into or out of the surface Arctic Ocean, implying Hg residence times of five to ten years. Of the large inventory of Hg held in the surface Arctic Ocean, Hg(II) plays a central role due to its reactivity. The two predominant Hg species in the upper ocean are Hg(II) and Hg(0), each of which may dominate under different circumstances or at different locations (e.g., Mason et al., 1998, 2001; Strode et al., 2007; Fitzgerald et al., 2007; Andersson et al., 2008). Divalent Hg is supplied to the Arctic Ocean through atmospheric deposition, coastal erosion, river input, and exchange of water from the Pacific and Atlantic Oceans (Strode et al., 2007; Outridge et al., 2008; see Section 2.4), and through processes that produce Hg(II) from Hg(0) and/or MeHg within the ocean. These processes are at least partly balanced by reduction to Hg(0), which then leads to super-saturation of DGM and net evasion of Hg(0) back to the atmosphere (Figures 3.1 and 3.3).

This sequence of Hg(II) supply to the ocean, reduction to Hg(0), and evasion back to the atmosphere is common to all oceans, and is an important component of the global Hg budget (Mason et al., 1995; Strode et al., 2007). The reduction of Hg(II) can be mediated by photons or microbes (Fitzgerald and Lamborg 2004). Partly because the Arctic Ocean's photochemistry is inhibited by ice cover during winter and partly because snow, ice, C-DOM and suspended particulates limit light penetration at many locations during other times of the year (e.g., Granskog et al., 2007), the microbial reduction of Hg(II) to Hg(0) is likely to play a dominant role in the Arctic Ocean (Poulain et al., 2007b). Recent ocean transect data show very clearly that surface waters in the Arctic have enhanced concentrations of DGM possibly due to ice cover reducing the rate of gas evasion to the atmosphere (Andersson et al., 2008; Sommar et al., 2010). Andersson et al. (2008) reported a surface-water DGM range of 0.002 to 0.14 ng/L and an average of about 0.044 ng/L, which is well above the value that would be in equilibrium with the Arctic's atmosphere (~ 0.008 ng/L). The high average concentration implies an inventory of Hg(0) in the top 200 m of the Arctic Ocean of about 120 tonnes, which is a considerable fraction of the THg inventory (945 tonnes, Outridge et al., 2008). For the global ocean, the evasion of Hg(0), estimated at 2800 t/y (Strode et al., 2007), rivals global anthropogenic emissions and, therefore, this process is a major feature of the marine Hg cycle. If the global Hg(0) evasion is allocated on a pro rata basis to the Arctic Ocean based on surface area, then about 120 tonnes of Hg would be transferred from ocean to atmosphere annually. However, as previously mentioned, ice cover may reduce the capacity of the Arctic Ocean to evade its Hg(0) to perhaps less than 10% in winter, and about 50% in summer, based on seasonal sea-ice extent. Thus, the rate of evasion currently may be as little as 3 to 12 t/y (Outridge et al., 2008). Offsetting the negative effect of ice cover, however, is the relatively high supersaturation of Hg(0), from which Andersson et al. (2008) estimated an average summertime Hg(0) evasion of 60 ng/m^2/d (12 pmol/m^2/h), with a hypothetical maximum as high as 2300 ng/m^2/d, during their transect of the Canadian Arctic Archipelago and Arctic Ocean. These observations suggest that Hg(0) is a dynamic component of exchange between seawater and air in the Arctic, and one that is highly susceptible to the extent of sea-ice cover. Furthermore, AMDEs, while depositing Hg(II) onto the ice, could actually force greater net evasion of Hg(0) out of the ocean due to the consequent increased fugacity differential between air and water. The evasion of Hg(0) from seawater is likely to contribute to the observed *positive* excursions of atmospheric GEM concentrations that rise well above the Arctic background of about 1.6 ng/m^3 after the onset of AMDEs in spring and later during summer (Steffen et al., 2008b; Sommar et al., 2010). These estimates clearly underscore the potential for the Arctic Ocean to evade annually a substantial amount of Hg(0), possibly as much as any other ocean.

A second important feature of marine Hg(II) geochemistry is that divalent Hg interacts with DOC and chloride ions to form complexes (Fitzgerald et al., 2007). Complexes are likely to provide *the* important reservoir of Hg(II) in the upper ocean, especially where DOC is in high concentration. A large component of Hg(II) can be held in the colloidal fraction alone (10% to 50%, Strode et al., 2007), but some of the reactive Hg enters the vertical particle flux to the deep ocean through packaging and flocculation, making POC (particulate organic carbon) also important to the Hg cycle. The vertical flux out of the polar mixed layer is likely to provide the other major process internal to the Arctic Ocean that helps to balance Hg(II) deposited at the surface, and this process also appears to be crucial to the storage of contaminant Hg globally in the deep ocean (Guentzel et al., 1996; Mason and Sullivan, 1999; Strode et al., 2007; Sunderland and Mason, 2007). In the coastal Arctic, where there is a plentiful supply of organic and inorganic particulates from rivers, coastal erosion and primary production (McGuire et al., 2009), the entrainment by particles and burial of Hg may be particularly important (Outridge et al., 2008), as also seems to be the case for temperate oceans (Sunderland and Mason, 2007). While all of these processes and reactions have the potential to play crucial roles in the aquatic biogeochemical cycle of Hg, little is known quantitatively about their relative importance in polar seas or what sort of balance between processes is achieved in coastal, shelf or interior ocean waters.

Rivers supply Hg(0), Hg(II), MeHg and particulate Hg to Arctic coastal waters (Coquery et al., 1995; Leitch et al., 2007; Andersson et al., 2008; Graydon et al., 2009). Even though rivers collectively supply over 3500 km^3/y of freshwater and 230 million t/y of particulates to the Arctic Ocean (see Outridge et al., 2008), Hg fluxes are poorly characterized for most of the inflow and thus represent a major uncertainty in the budget for the Arctic Ocean. Concentrations have not been measured in many of the major rivers and studies lack the appropriate temporal resolution to capture some of the seasonality in discharge. Whether or not the riverine Hg load is an important source of MeHg to marine biota, either directly or indirectly, remains unclear. Not only do rivers supply Hg, but they also supply organic and inorganic components (DOC, POC) that can sequester and bury Hg, or incorporate Hg(II) as organic ligands (Fitzgerald et al., 2007), or simply produce a stratified surface layer effective at evading its Hg(0) (Andersson et al., 2008). On the other hand, the organic carbon associated with rivers may support the production of MeHg in estuarine and coastal sediments, which is then available for uptake in food webs. There are no Arctic data presently available to indicate which processes are most important.

Figure 3.3 strongly implicates solar radiation and the organic carbon cycle as key controlling variables in the Arctic Ocean's Hg cycle. The Arctic has an annual light cycle that goes from 24-hour darkness to 24-hour light, snow and ice cover that control the penetration of radiation into water, and riverine C-DOM which strongly absorbs UV radiation. Variation in these parameters can alter the balance between the loss of Hg by burial, or the reduction to Hg(0) and evasion, or the production of MeHg and its subsequent entry into food webs. The interior part of the Arctic Ocean is oligotrophic, supporting a low particle flux (O'Brien et al., 2006). Therefore, the rate of removal of particulate Hg from the surface, an apparently important component of the global ocean Hg cycle (Sunderland and Mason, 2007), may operate weakly in the central basin of the Arctic Ocean compared with other oceans. However, burial rates may be more important in Arctic continental shelf areas. Of the 108 t/y of the total Hg lost from the upper Arctic Ocean by sedimentation, 95 t/y was estimated to occur over shelves, a rate which approximates the net atmospheric input of Hg (Outridge et al., 2008).

Finally, and perhaps most importantly, Hg(II) undergoes a complex set of reactions leading to DMHg and MeHg production. These processes (Figure 3.3) are poorly quantified in the Arctic, but recent work has shown them to be potentially important in polar surface waters (St. Louis et al., 2005, 2007; Kirk et al., 2008). Clearly, the processes controlling the production of MeHg and its entry into the bottom of the food web are fundamental to understanding Hg trends at all trophic levels of the marine food web. Like Hg(0), DMHg evades readily into the atmosphere where rapid photolytic decomposition to MeHg followed by deposition has been proposed as the source of MeHg in snow and meltwater ponds in coastal regions (St. Louis et al., 2005, 2007). By examining the predominant form of Hg as it enters the Arctic and then passes through aquatic systems to eventually accumulate at concentrations of concern in top predators, it is clear that two transformations play crucial roles. First, the relatively benign Hg(0) circulating globally in air or water must be oxidized to Hg(II) and second, Hg(II) must be methylated and accumulated in top predators (Figure 3.4).

It has long been hypothesized that Hg can be methylated in oxic environments, but only recently has this been demonstrated in the water column of temperate oceans (Cossa et al., 2009; Sunderland et al., 2009). Methylation of Hg(II) occurs during detrital regeneration and leads to elevated MeHg associated with oceanic nutrient maxima. This MeHg, which is produced from the abiotic Hg(II) reservoir in the ocean rather than the particulate Hg carried by detritus (Cossa et al., 2009), could enter food webs either through upwelling (Conaway et al., 2009) or through vertical migration of zooplankton (Stern and Macdonald, 2005). Anoxic environments favorable to sulfate

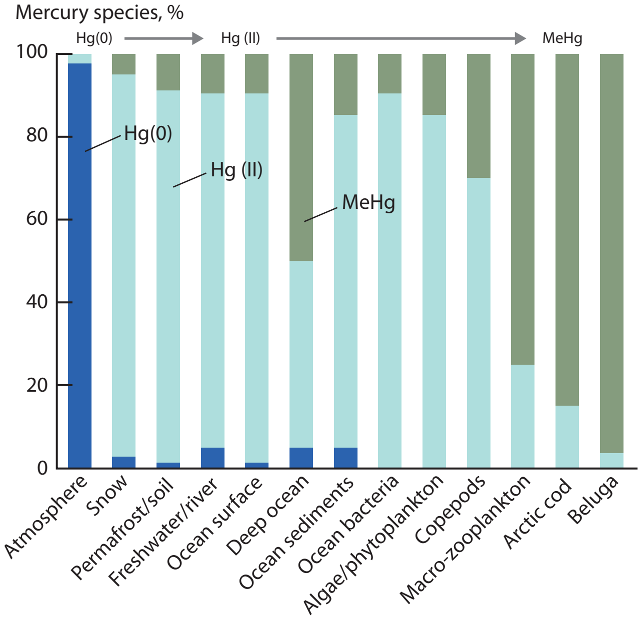

Figure 3.4. To present a risk, the predominant form of Hg transported in the atmosphere, Hg(0), must undergo oxidation to Hg(II) and then methylation to MeHg. Risk to top aquatic predators, therefore, is a consequence not only of the amount of Hg(0) cycling in the atmosphere, but also of the balance between processes leading to Hg(0) conversion.

reduction also harbor microbes that can methylate Hg(II) (Fitzgerald and Lamborg, 2004; Fitzgerald et al., 2007). In particular, environments that favor sulfate reducers and have a gradient in redox conditions are more ideal for methylation than truly 'anoxic' environments. The clearest circumstances where anoxic methylation processes would be favored are generally restricted to sediments in the Arctic. Within the Arctic Ocean's sediments there is a wide range in redox conditions, with shelf and estuarine sediments generally exhibiting sulfidic conditions near the sediment surface; basin sediments exhibiting oxic or suboxic conditions may be found from the surface down to tens of centimetres deep into the sediment (e.g., Gobeil et al., 1997, 2001b). Methylating processes are complicated by interactions between Hg and sulfide (Fitzgerald et al., 2007) such that sulfide sequestration of inorganic Hg(II) may compete with MeHg production if conditions lead to sufficiently high sulfide accumulation. Sediments, especially in estuaries, shelves and slopes, therefore provide another potential source of MeHg to shelf benthos and bottom waters (e.g., Fitzgerald et al., 2007).

3.3. How does mercury move from the abiotic environment into food webs, and what are the factors influencing this movement?

In the abiotic environment, Hg that is taken up by biological organisms is by definition in a chemical form and a physical location where it is available to biota. Thus, 'bioavailability' is a key issue. It is generally acknowledged that MeHg is significantly more bioavailable than the inorganic Hg(II) which is most abundant in the environment (Mason et al., 1996; Fitzgerald et al., 2007). Although both inorganic and MeHg species may be assimilated by biota at the lowest levels of food chains (bacteria, archaea, phytoplankton and other algae), only MeHg is biomagnified within food chains and thus presents the key exposure risk to Arctic wildlife and humans. Therefore, a critical question with respect to the bio-uptake of Hg into Arctic food webs concerns the mechanisms and locations where inorganic Hg(II) in the abiotic environment is predominantly transformed into MeHg and then assimilated into the lower levels of Arctic food webs.

3.3.1. Bioavailability of mercury

The concept of 'bioavailability' of Hg includes the availability of inorganic Hg forms to microbial populations responsible for Hg methylation and the availability of MeHg in prey items to predators within food webs. This definition requires that after production at a certain location, MeHg is transported to and then bioaccumulated by the lowest trophic levels of terrestrial, freshwater and marine communities before being transferred via prey-predator interactions into higher trophic level organisms. Taken together, these processes lead to MeHg concentrations that span about ten orders of magnitude going from atmosphere to beluga, and a shift from MeHg as a minor component of THg in air, snow or water to the predominant form in aquatic species at trophic levels 2 and above (Figure 3.5).

Bioavailability is likely to be controlled by many environmental and physiological factors that include: the chemical form and biochemical reactivity of environmental Hg; the activity of microbial communities; the nature and quantities of ligands, electron acceptors, and surfaces in the environment; and the balance between dissolved versus particulate forms of Hg. Around four times as much MeHg is assimilated by phytoplankton compared to inorganic Hg (Mason et al., 1996). Microbes do not represent a single type of biochemical binding entity for Hg, but are in effect variable ligands both taxonomically and physiologically due to their differing metabolisms and physical structures. Microbes also constantly change in response to physical and chemical alterations in their environment, thereby potentially affecting inorganic Hg uptake and methylation rates. Whether in snow, water, ice, soil

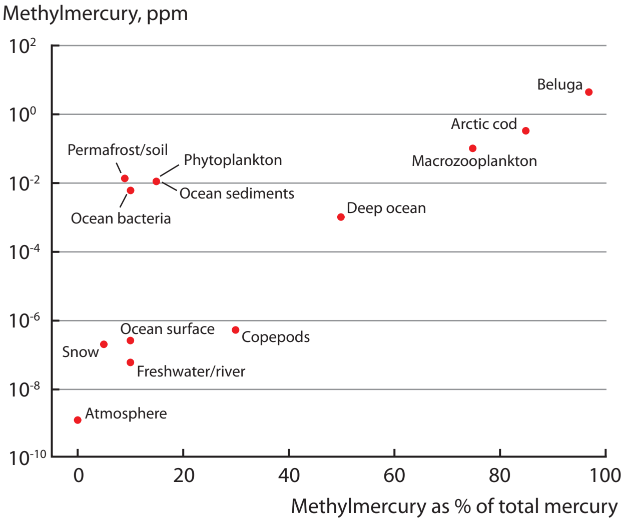

Figure 3.5. Methylmercury bioconcentrates and biomagnifies. In inorganic media, MeHg tends to represent a minor proportion of the total mercury (about 20% or less), but progressively increases upward through aquatic food webs to become the predominant form of Hg at trophic levels 2 and above.

or sediments, the metabolism of microbes will be influenced to some extent by the availability (or absence) of electron acceptors such as oxygen, nitrate, sulfate, or Fe(III), which are also likely to affect Hg methylation rates. Complexation with organic ligands can reduce or enhance microbial cell Hg accumulation (Lawson and Mason, 1998; Pickhardt and Fisher, 2007; Gorski et al., 2008). Uptake of MeHg and inorganic Hg by diatoms is influenced by Hg speciation, especially complexation with DOC and Cl^- (Zhong and Wang, 2009). Thus, the factors controlling MeHg bioavailability and uptake from water by algae or phytoplankton are critical, yet have been poorly investigated in Arctic aquatic systems.

3.3.2. Transfer pathways for mercury into Arctic food webs

In temperate environments, inorganic Hg is methylated predominantly by microbes. From a combination of laboratory and field studies, it is believed that there are two main inorganic Hg uptake pathways by microbes that lead to Hg methylation. One is passive diffusion of dissolved uncharged Hg species through the lipidic bilayer of microbial cell walls (e.g., Hg(II) associated with sulfide or polysulfides Hg(II)-S; Benoit et al., 1999). The other is active transport of Hg species (e.g., by the amino acid transport system; Golding et al., 2002). It was recently shown that the addition of low levels of cysteine significantly increased Hg(II) methylation by a known Hg methylator (Schaefer and Morel, 2009).

Unicellular organisms (e.g., bacteria, microalgae, protozoans) are also thought to be the main entry point of MeHg into aquatic food webs. The MeHg bioaccumulation step from water to phytoplankton and other seston represents the largest single increase for MeHg concentrations in aquatic ecosystems, and can be 10^4 or greater (Watras and Bloom, 1992; Baeyens et al., 2003). MeHg may initially enter food webs either through consumption by heterotrophic consumers of the MeHg-containing microbial populations responsible for its formation, or the release of dissolved MeHg into water followed by its assimilation by phytoplankton and algae. MeHg uptake in diatoms mainly occurs passively in the form of uncharged, lipophilic MeHg-containing complexes (Mason et al., 1996).

Because of the unique adaptations of microbial populations to cold environments (Methe et al., 2005), including their ability to adapt their membrane lipid assemblage to withstand low temperatures, it is possible that the availability and uptake rates of Hg species to microbes in the Arctic will differ substantially from those in other environments. Bacterial Hg uptake and methylation rates are poorly characterized for High Arctic lakes and marine systems. This information is critical to determine the capacity of microbial communities to transform inorganic Hg into MeHg in these extreme environments, which typically have low sedimentary organic matter contents that may be expected to limit methylation rates. Highly elevated MeHg concentrations – up to 3 ng/L – were found in water of shallow ponds on Ellesmere Island, probably due to relatively warm water temperatures and abundant organic matter driving higher bacterial activity (St. Louis et al., 2005). This example demonstrates the Hg accumulation and methylation potential of Arctic microbial communities under favorable conditions.

3.4. What role does methylation/demethylation play in controlling mercury accumulation rates in Arctic food chains?

3.4.1. Methylmercury production pathways

A recent review identified the main biochemical Hg methylation pathways (Barkay and Poulain, 2007), which are for the most part linked to microbiological activities. There are several possible environmental sources of MeHg but few studies have measured production rates from these various sources in Arctic environments especially in marine settings. In temperate aquatic environments, wetlands and benthic sediments are major MeHg sources and this is thought to be due to the activity of sulfate- and iron-reducing bacteria in these anoxic environments (Gilmour et al., 1992; Fleming et al., 2006; Kerin et al., 2006). MeHg can also apparently be produced during detrital remineralization in oxic marine waters, associated with mid-depth nutrient maxima and oxygen utilization (Sunderland et al., 2009; Cossa et al., 2009). A nutrient maximum is pervasively associated with haloclines in the Arctic Ocean, especially in Canada Basin, but it remains unknown whether Arctic haloclines contain important reservoirs of MeHg or whether this Hg enters food webs. However, it is striking that high MeHg concentrations occur in lower levels of the food web in Canada Basin (Stern and Macdonald, 2005), and in higher trophic level animals like the Beaufort beluga population which ranges into Canada Basin (Loseto et al., 2008b).

Another possible source of MeHg is the atmospheric photo-reduction of volatile DMHg evaded from seawater and lakes (Niki et al., 1983a,b; St. Louis et al., 2005, 2007; Constant et al., 2007). Production of DMHg by pure cultures of Antarctic marine bacteria (Pongratz and Heumann, 1999), and by macroalgae isolated from an Arctic fjord (Pongratz and Heumann, 1998), has been demonstrated. Recent work on Arctic seawater (Kirk et al., 2008) as well as many studies in the Atlantic and Pacific Oceans (Mason and Fitzgerald., 1993, 1995; Cossa et al., 1997) suggests that DMHg can also be produced in deep marine waters. Supersaturation of Arctic surface seawater over a wide area by DMHg (St. Louis et al., 2007; Andersson et al., 2008) and the presence of elevated GEM in the marine boundary layer in areas rich in sea ice (Sommar et al., 2010) point to the potential importance of this process in the Arctic MeHg cycle. Other possible mechanisms of MeHg production, such as methylation of Hg(II) in snowpacks through abiotic processes (Gårdfeldt et al., 2003) or by aqueous phase methylation in the atmosphere (Hammerschmidt et al., 2007) may occur but their significance is unknown.

Although all of these processes also occur in temperate and tropical oceans, the unique physiographic features of the Arctic described earlier suggest that the relative rates and specific characteristics of these processes could be different in this region. Loseto et al. (2004b) showed that MeHg concentrations increased 100-fold in Arctic wetland soils, after thawing and incubating at typical Arctic summer temperatures (4 to 8 °C). While sulfate-reducing bacteria are thought to be the predominant MeHg producers in temperate anoxic environments, the genes responsible for dissimilatory sulfate-reduction could not be detected from all the wetland sites studied by Loseto et al. (2004b). This suggested either a methodological issue, or that sulfate-reducers are in fact not the dominant microbial methylators in Arctic wetlands. Hammerschmidt et al. (2006) investigated the biogeochemical cycling of MeHg in lakes and tundra watersheds of Arctic Alaska (68° N). They concluded that the principal source of MeHg was *in situ* benthic production (80% to 91% of total inputs), and that the contributions from the tundra watershed snowpack and soils were modest. Oiffer and Siciliano (2009) evaluated the potential for wet sedge meadow soils on Trulove lowlands (75° N), typical of Arctic landscapes, to act as sources or sinks for MeHg. Significant methylation occurred after inorganic Hg(II) was added to the soil. This finding, together with Hammerschmidt et al.'s (2006) conclusion that benthic MeHg production in Alaskan lake sediments was inorganic Hg-limited, suggests that there is a potential for relatively high production of MeHg in Arctic wetland soils and sediments during spring melt when a flush of inorganic Hg enters these systems.

In contrast to Hammerschmidt et al.'s (2006) Alaskan study, investigations at Kuujjuarapik (55° N) on Hudson Bay suggest that tundra ecosystems there may represent a significant source of MeHg to aquatic systems (Constant et al., 2007). Snow samples collected at three different stations on the Great Whale River and in the tundra were characterized by different MeHg levels, with the highest concentrations at the tundra site. During the snow melt period, MeHg concentrations observed at this sampling site reached 700 pg/L, significantly higher than has generally been reported in Arctic snow (Poissant et al., 2008 and references therein). Correlation between MeHg snow concentrations and heterotrophic bacteria abundances, and the increasing proportion of MeHg during the snow melt period, suggested the presence of an active microbial methylation process within the snow cover. However, further investigations are needed to estimate the relative contributions by *in situ* production and atmospheric deposition to MeHg levels in snow.

3.4.2. Methylmercury destruction pathways

Photo-decomposition of MeHg may be an important process in the Arctic summer when nearly continuous sunlight prevails, although there are few data available with which to evaluate its overall role. In four Alaskan lakes, Hammerschmidt and Fitzgerald (2006a) calculated that the annual loss of MeHg to photo-decomposition, although limited to about a 100-day ice-free season, accounted for 66% to 88% of total MeHg inputs annually. At Kuujjuarapik, MeHg originating from marine sources appeared to be unstable in the snow cover, as 15% to 56% of the MeHg was lost overnight (Constant et al., 2007). Night-time demethylation reactions involving nitrate radicals were proposed as the mechanism but need to be confirmed.

3.5. How do trophic processes influence mercury levels in higher order animals?

3.5.1. Introduction

Mercury concentrations in higher trophic level organisms (Figure 3.6) can be affected by 'bottom-up' or 'top-down' trophic processes. Those known to influence Hg in higher order animals include: (i) initial MeHg concentrations entering the biota at the bottom of the food web (bottom-up); (ii) species-specific characteristics such as growth rates, age, size, and Hg elimination rates that impact bioaccumulation or biodilution (bottom-up); (iii) the food web structure and/or guild that defines the transfer of energy and Hg among trophic levels and/or between food webs, such as benthic-pelagic coupling (bottom-up); and (iv) predator behavior defining diet and feeding ecology (top-down).

Methylmercury concentrations increase over time (bioaccumulate) in an animal, and increase by up to an order of magnitude or more at each successive trophic level (biomagnify). Diet is the main source of MeHg for higher-order consumers (e.g., invertebrates, fish, mammals; Hall et al., 1997; Tsui and Wang, 2004; Loseto et al., 2008a). In general, trophic interactions (predator-prey relationships) and the initial Hg concentration at the base of food chains may be most influential in determining the pathway and transfer

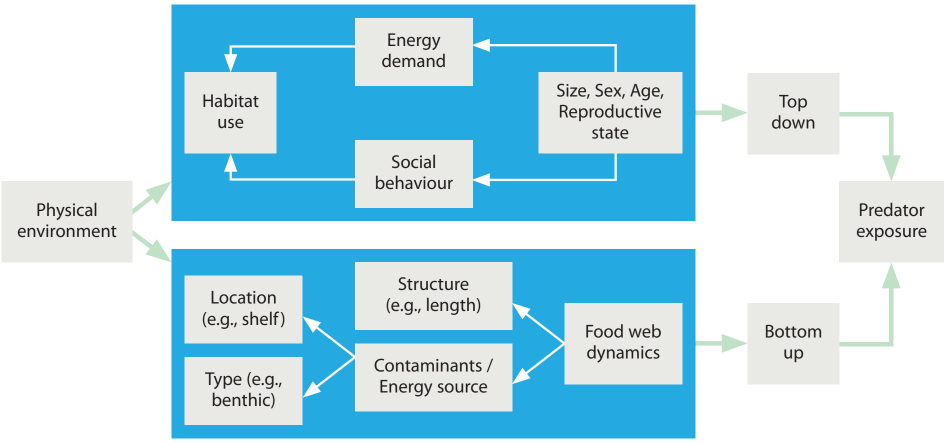

Figure 3.6. The processes affecting Hg concentrations in a high trophic level species. Food web interactions determine the sources, bioaccumulation and biomagnification of Hg (in the form of MeHg). Dietary preferences are shaped by many factors including the sex, size, age, and reproductive status of an animal. These in turn dictate energy requirements as well as social behavior that together describe the habitat use. Figure modified from Loseto (2007).

rate of MeHg into higher trophic level species (Watras and Bloom, 1992; Cabana and Rasmussen, 1994). MeHg strongly bioaccumulates in organisms because it is efficiently assimilated into tissues and only slowly eliminated from the body (Headon et al., 1996; Lawson and Mason, 1998). The growth rates of consumer animals also affect their accumulation of MeHg. Individuals with slower growth rates tend to have higher MeHg concentrations because less biomass is produced per unit of Hg consumed – the so-called 'biodilution effect' (Kidd et al., 1999; Karimi et al., 2007).

Once MeHg has been incorporated into microbial communities at the base of the food chain, subsequent biomagnification factors for MeHg concentrations at successively higher trophic levels range from about 4 to 10 (Atwell et al., 1998; Campbell et al., 2005; Loseto et al., 2008b; see Figure 3.5). Using $\delta^{15}N$ to infer the trophic positions of species, Campbell et al. (2005) reported log concentration – $\delta^{15}N$ relationship slopes of 0.197 and 0.223 for THg and MeHg, respectively, in the marine food web of the Northwater Polynya, Baffin Bay. A similar slope for the log THg – $\delta^{15}N$ relationship (0.20) was reported for the adjacent Lancaster Sound food web (Atwell et al., 1998). Campbell et al. (2005) noted that the regression slopes of these Arctic marine examples were remarkably similar to others in different systems, and concluded that *…MeHg is biomagnified through these diverse food webs, as measured by $\delta^{15}N$, regardless of productivity (eutrophic vs. oligotrophic), latitude (Arctic vs. tropical) or salinity (marine vs. freshwater) of the ecosystem.*

Because only MeHg is biomagnified, the fraction of MeHg increases progressively with trophic level, typically reaching over 90% of THg in the muscle tissues of predatory fish and other high trophic level species (Campbell et al., 2005; reviewed for freshwater ecosystems by Morel et al., 1998). In Arctic marine food webs the MeHg fraction is variable in zooplankton, ranging from 30% in the Beaufort Sea (Stern and Macdonald, 2005; Loseto et al., 2008b) to 70% in Baffin Bay (Campbell et al., 2005), and demonstrates significant spatial and seasonal heterogeneity (Stern and Macdonald, 2005). Fish such as Arctic cod have 80% to 97% Hg as MeHg in the Beaufort Sea and its shelf, and 100% in Baffin Bay (Campbell et al., 2005; Loseto et al., 2008b). Despite these variations, the predicable increase in the MeHg fraction of THg up food chains demonstrates that a small increase in bioavailable MeHg at the bottom of the food web can result in relatively large increases in higher trophic level organisms. The previous examples are representative of pelagic systems. However, predators can feed in both pelagic and benthic ecosystems, or in near shore and offshore food webs, that differ in carbon sources, biogeochemical cycling and food web structure, all factors that can influence the trophic transfer of MeHg. Furthermore, oceanic processes can organize prey species spatially (e.g., along fronts, convergent zones, persistent polynyas, persistent upwelling) in ways that affect both Hg uptake into the prey and the likelihood that the prey will be consumed (e.g., Stern and Macdonald, 2005).

3.5.2. Bottom-up trophic processes in Arctic aquatic food webs

3.5.2.1. Marine food webs

Physical features influence biogeochemical cycling, ecosystem productivity and energy flow to top predators, and provide a basis for Hg trophic level transfer processes. The Arctic marine environment has several physical features that are considered here to evaluate Hg sources and food web dynamics. The coupling of food webs and carbon and Hg sources provides a framework for this approach. Mercury in the form of MeHg may enter the Arctic marine environment or be created within the environment via several possible sources that include: (i) atmospheric transport (AMDEs and other wet and dry processes) and deposition to snow, ice and open water; (ii) riverine input draining terrestrial sources; (iii) *in situ* sediment production; and (iv) *in situ* water column production (Macdonald and Loseto, 2010; Figure 3.7). How Hg and MeHg from these various sources enter food webs is determined by factors such as the relative bioavailability for uptake/absorption and the seasonality and location of the organisms at the bottom of a food web. These dynamics define carbon and Hg or MeHg acquisition. With these potential sources in mind, the four major types of Arctic marine food webs are reviewed

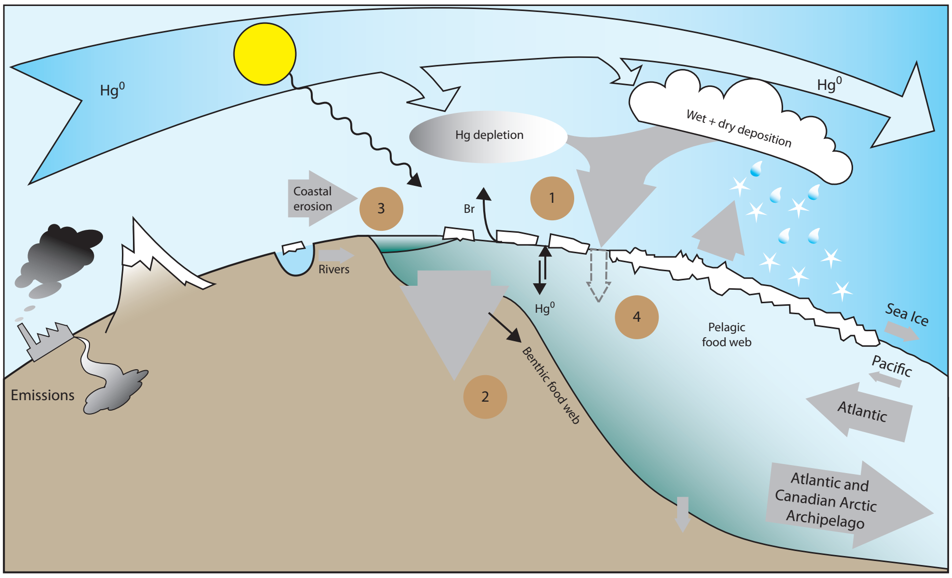

Figure 3.7. Potential inorganic Hg input pathways underpinning Hg methylation and bio-uptake in distinct Arctic marine food webs. Circled numbers represent atmospheric deposition to the ocean surface (1), sediment methylation processes (2), riverine and terrestrial sources (3), and ocean water column processes (4). These sites may represent the route of entry for sea-ice food webs (1), benthic food webs (2), shelf / estuarine food webs (3), and the pelagic food web (4). Figure from Macdonald and Loseto (2010).

to examine the pathways of Hg to higher trophic species. The food webs include: the sea ice-associated ecosystem (which has a predominantly atmospheric Hg source); the pelagic ecosystem (oceanic Hg source); the benthic ecosystem (with sediments the predominant Hg source); and the estuarine/shelf ecosystem (with riverine inputs dominating Hg deposition)(Figure 3.8). Although these four food webs are presented separately, there is a sea-ice–pelagic–estuarine–benthic coupling that complicates the interpretation of Hg food web sources and transfer to high trophic level species. The food webs presented include the potential prey items for higher trophic level species of the marine environment.

3.5.2.1.1. ***Sea-ice food webs***

Sea ice and snow are receptacles for Hg deposited from the atmosphere. Sea ice may broadly be categorized as either fast ice, which is formed and melted annually and remains attached to the coast, or pack ice, which comprises floes of varied age and size. Ice algae grow in sea ice and provide the carbon source to fuel a sympagic ('ice-associated') food web. Ice algae contribute 4% to 26% of total primary productivity in fast ice or annual sea ice (Legendre et al., 1992) and more than 50% in multi-year floe ice (Gosselin et al., 1997). Due to the challenges of collecting organisms associated with sea ice, data on Hg concentrations in species within this food web are extremely limited. To date there has only been one published measurement of Hg levels in sea ice algae; 0.015 µg/g dw (n=1) (Campbell et al., 2005).

Organisms that feed on ice algae represent the next step in trophic transfer, and include calanoid copepods, nematodes, and the larvae of benthic polychaetes and gastropods (Horner, 1985). Calanoid copepods (e.g., *Calanus glacialis* and *C. hyperboreus*) are the dominant Arctic marine zooplankton (Geynrikh, 1986; Springer et al., 1996; Auel and Hagen, 2002). Mercury concentrations in copepods were observed to decrease through the winter (~ 0.1 to 0.04 µg/g dw) in the Chukchi and Beaufort Seas and then to increase in the summer and autumn (Stern and Macdonald, 2005). MeHg levels were typically 30% of the THg (Loseto et al., 2008b).

Gammaridean amphipods are the dominant macrofauna feeding under sea ice on detritus (e.g., ice algae, bacteria and crustacean remains; Poltermann, 2001). They represent an important energy and Hg link between the base of sea-ice food webs and higher trophic level predators that include Arctic cod (*Boreogadus saida*), ringed seals (*Phoca hispida*) and birds (Bradstreet and Cross, 1982; Craig et al., 1982; Bradstreet et al., 1986; Smith, 1987; Lonne and Gulliksen, 1989; Lonne and Gabrielsen, 1992). Gammarids in Lancaster Sound had Hg concentrations of 0.1 µg/g dw (Atwell et al., 1998).

Arctic cod is thought to be a keystone species linking under ice food webs to many marine mammals and birds (Frost and Lowry, 1981; Bradstreet and Cross, 1982; Lonne and Gulliksen, 1989; Lonne and Gabrielsen, 1992). Total Hg concentrations in Arctic cod collected under the ice in Amundsen Gulf / Franklin Bay averaged 0.38 µg/g dw, with 80% of the THg as MeHg (Loseto et al., 2008b). Similar levels were measured in winter in the Chukchi and Beaufort Seas (Stern and Macdonald, 2005).

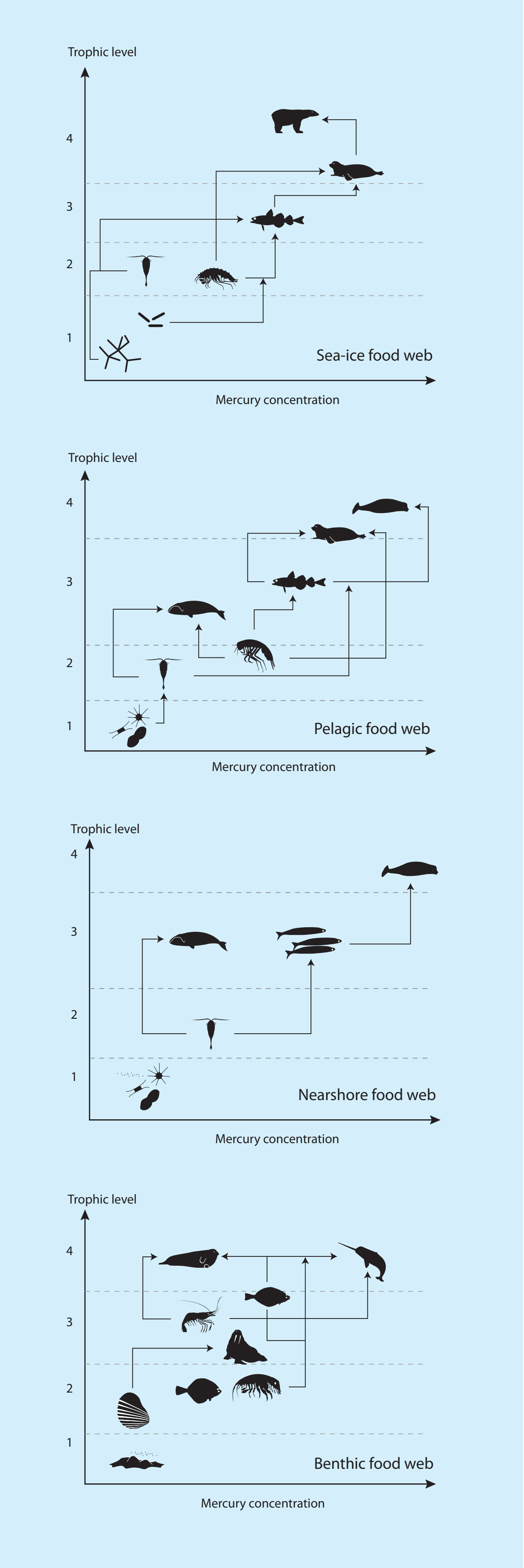

Figure 3.8. Mercury flow through marine food webs in the Beaufort Sea, northern Canada (seabirds and humans not included).

3.5.2.1.2. ***Pelagic food webs***

Although atmospheric Hg deposition can occur directly onto open water, the seasonal sea-ice cover limits this pathway, especially in winter and early spring. Flaw leads or polynyas provide an opportunity for primary productivity to sustain local food webs (Hobson et al., 2002; Campbell et al., 2005). The overall primary productivity in flaw leads (<15% of the annual total) is considered to be relatively low (Horner and Schrader, 1982; Hamel, et al., 2002), but these special open-water zones may provide early season nourishment coincident with peak Hg deposition (from AMDEs), thus facilitating the entry of Hg into food webs beyond what the area of open water alone might imply. For example, elevated Hg concentrations were found in moss and lichens on the coast downwind from an Antarctic polynya, which was presumed to be an AMDE effect (Bargagli et al., 2005).

As the Arctic warms in the spring and sea ice retreats, light and nutrients in the euphotic zone initiate phytoplankton blooms. Blooms tend to start earliest in the marginal ice zones and then progress toward the interior ocean, accounting for up to 50% of the total primary productivity in Arctic waters (Sakshaug, 2004). In the central Arctic Basin, production under the pack ice is an order of magnitude lower than on the shelves (Gosselin et al., 1997; Sakshaug, 2004). Understanding this seasonal carbon source as it affects Hg bio-uptake is critical to quantifying this pathway of Hg to top predators. As the euphotic zone exhausts its nutrients, the blooms collapse to a deep chlorophyll maximum where food production continues (Lavoie et al., 2009; Granskog et al., 2007) with as yet unknown importance for Hg uptake.

The main grazers of plankton and microzooplankton in the open water column are the marine calanoid copepods *C. glacialis* and *C. hyperboreus* (Mumm et al., 1998). Mercury measured in copepods ranged from 0.04 to 0.11 µg/g dw in the Chukchi and Beaufort Seas (Stern and Macdonald, 2005), to as low as 0.025 µg/g dw in the Northwater Polynya (Campbell et al., 2005). The hyperiid amphipod *Themisto libellula*, which is the dominant predator of calanoid copepods (Bradstreet and Cross, 1982; Lonne and Gulliksen, 1989), had Hg levels ranging from 0.06 µg/g dw in Lancaster Sound to 0.13 µg/g dw in Amundsen Gulf where MeHg (0.095 µg/g dw) was 75% of the total (Atwell et al., 1998; Campbell et al., 2005; Loseto et al., 2008b). The east-to-west increase in THg and in the proportion of MeHg of THg may explain similar longitudinal differences at the next trophic level, in Arctic cod. Mercury concentrations in Arctic cod collected in ice-free summer waters ranged from 0.2 µg/g dw in Lancaster Sound (Atwell et al., 1998; Campbell et al., 2005) to 0.4 µg/g dw in the Chukchi and Beaufort Seas (Loseto et al., 2008b; Stern and Macdonald, 2005). These concentrations are considerably higher than levels measured near Svalbard (0.05 µg/g dw; Jaeger et al., 2009).

3.5.2.1.3. ***Estuarine, nearshore and shelf-associated food webs***

Slightly over 50% of the Arctic Ocean is continental shelf (Stein and Macdonald, 2004). Shelves receive large inputs of freshwater along with particulates, organic carbon and Hg (Serreze et al., 2006; McGuire et al., 2009; Leitch et al., 2007). These inputs strongly affect the physical and biological oceanography of coastal regions (Carmack and Macdonald, 2002), but they also provide important controls on Hg pathways including its partitioning, speciation, vertical flux, burial and conditions for methylation. Because shelves are shallow (< 200 m), coupling with benthic food webs is important (see next section).

No published values for Hg in Arctic nearshore phytoplankton were found in the literature. Zooplankton communities in shelf regions are numerically dominated by *Psuedocalanus* spp. yet biomass is dominated by *Calanus hyperboreus* (Darnis et al., 2008). Anadromous fish such as Arctic cisco (*Coregonus autumnalis*) and least cisco (*C. sardinella*) feed in the estuaries in the warm ice-free season and may migrate between freshwater systems to spawn and/or overwinter (e.g., the Mackenzie Delta of Canada and Prudhoe Bay in Alaska; Gallaway et al., 1983; Fechhelm et al., 1991). Nearshore fish such as rainbow smelt (*Osmerus mordax*), Pacific herring (*Clupea pallasii*), Arctic cisco and least cisco occurring along the Mackenzie Shelf had Hg levels below 0.2 µg/g dw (with the exception of saffron cod, *Eleginus gracilis*), of which MeHg accounted for 78% to 94% of THg in adult fish (Loseto et al., 2008b). Arctic cod had similar Hg levels to other continental shelf fish, which were significantly lower than Hg levels in Arctic cod offshore (Loseto et al., 2008b).

An open question remains as to whether effects or processes associated with rivers and estuaries amplify or attenuate Hg entry into resident biota. Estuarine shelf food webs may obtain Hg not only from atmospheric deposition, but also from shelf-basin water exchange and riverine input (Leitch et al., 2007; Coquery et al., 1995). In the case of the Beaufort Shelf, Leitch et al. (2007) estimated an annual delivery of 2.2 t/y of THg and 15 kg/y of MeHg by the Mackenzie River alone. Rivers clearly provide a conduit for terrestrial Hg and MeHg from wetlands and snowmelt (Loseto et al., 2004b) to enter estuaries. Arctic rivers also provide DOC, POC and suspended sediment, which may sequester Hg and MeHg thus preventing their entry into estuarine food webs. Lower Hg levels in copepods, zooplankton and Arctic cod in the shallow Mackenzie Shelf area than in the offshore pelagic environment suggest that factors other than the Hg supply by the Mackenzie River explain the nearshore/offshore differences (Loseto et al., 2008b).

3.5.2.1.4. ***Benthic deep-ocean and shallow-shelf food webs***

The main source of energy to benthic and epibenthic food webs is particulate organic material that settles from the strongly seasonal primary pelagic production (O'Brien et al., 2006). The quality and quantity of settling particulates along with bottom substrate (e.g., sand, silt, clay) determine the faunal community (Forest et al., 2007). To some degree, nearshore and shelf benthos take advantage of POC from riverine discharge in addition to the ice-associated primary productivity and grazer production (Schell, 1983; Goñi et al., 2005; Garneau et al., 2006). Due to ice scouring, which occurs most prevalently in 10 to 50 m water depth in association with flaw leads (e.g., Carmack and Macdonald, 2002), faunal composition is patchy and continually undergoing community succession (Conlan et al., 1998). Of special interest regarding Hg is the potential for producing localized anoxic conditions in scour marks that contain dense, salty water produced by ice formation (Kvitek et al., 1998). These areas could provide an as yet unevaluated source of Hg methylation.

Invertebrates occupy the benthos and epibenthos, including echinoderms (brittle stars), decapods, amphipods, isopods, crabs, molluscs, and polychaetes, most of which are poorly studied from a Hg perspective. Invertebrates can increase MeHg exposure by burrowing and dwelling in anoxic sediments (Coelho et al., 2008). Most benthic invertebrates are not thought to be key species for high trophic marine mammals, with the exception of the bivalves *Macoma* spp. and *Mya truncata* that are important prey items for walrus (*Odobenus rosmarus)* and bearded seal (*Erignathus barbatus*). *M. truncata* in Lancaster Sound had Hg levels comparable to other primary consumers at 0.07 µg/g dw (Atwell et al., 1998).

Demersal fish are important prey items for higher trophic level animals. For example, the Greenland halibut/turbot (*Reinhardtíus híppoglossoides*) as well as Arctic cod and Pacific cod (*Gadus macrocephalus*) that spend time in deep water regions are important prey items for narwhal (*Monodon monoceros*). Other demersal fish include sculpins whose Hg concentrations range from 0.24 µg/g dw in Lancaster Sound (Atwell et al., 1998) to 0.59 µg/g dw in the Beaufort Sea (Loseto et al., 2008b). Some of the higher concentrations in benthic species such as sculpins and shrimp may be a function of factors including trophic level, and their dependence on a food web whose base source of Hg may be high due to dwelling in anoxic sediments. These organisms may also ingest re-suspended matter, which can be highly heterogeneous in both carbon and Hg content.

3.5.2.2. Freshwater food webs

Bottom-up trophic processes appear to play a particularly important role in controlling MeHg levels in Arctic freshwater food webs. In general, inorganic Hg loading and its subsequent methylation by bacteria in sediment are key processes that affect Hg levels in freshwater ecosystems (Benoit et al., 2003). In a temperate whole-ecosystem experiment that used additions of stable Hg isotopes to trace the movement of Hg, fish MeHg concentrations responded rapidly to inorganic Hg deposited directly onto the lake surface (Harris et al., 2007). On a broad geographic scale, a study of wild fish populations in the United States found that about two-thirds of the geographic variation in Hg levels of largemouth bass (*Micropterus salmoides*) was related to the rate of wet atmospheric Hg deposition (Hammerschmidt and Fitzgerald, 2006b). Similarly, MeHg bioaccumulation in an aquatic invertebrate (mosquitoes) was positively correlated with wet atmospheric Hg deposition across a latitudinal gradient in North America that included Alaska (Hammerschmidt and Fitzgerald, 2005). In Alaskan lakes, sediment production of MeHg is limited by the availability of porewater inorganic Hg (Hammerschmidt et al., 2006).

Currently available data from the High Arctic indicate a significant but weak link between watershed Hg loading and freshwater food web accumulation of Hg. In the High Arctic, snowmelt from the watershed is the largest source of THg to lakes (Semkin et al., 2005). Mercury levels in Arctic char from 19 lakes were positively correlated with watershed to lake area ratios, which explained about one-quarter of the variation in length-adjusted Hg concentrations in fish (Gantner et al., 2010b; see Section 3.5.3.2). Chételat et al. (2008) found that MeHg concentrations in aquatic invertebrates (Diptera, Chironomidae) from 22 lakes and ponds were only weakly correlated to measures of Hg supply (i.e., watershed to lake area ratios, MeHg concentrations in water and sediment). Sites in that study had consistently low levels of MeHg in sediment and water along a gradient in THg loading from the watershed, suggesting that MeHg production in the High Arctic may be limited by environmental factors other than inorganic Hg(II) supply.

Three studies in different Arctic regions of North America indicate that freshwater invertebrates can vary considerably in their MeHg concentrations, from 3 to 414 ng/g in Alaska (Hammerschmidt and Fitzgerald, 2005), the Canadian Northwest Territories (Evans et al., 2005b), and the Canadian Arctic Archipelago (Chételat et al., 2008). This variation may be due to the trophic level of the invertebrates (Cremona et al., 2008), variable MeHg supply to their food webs (Watras et al., 1998), and/or taxonomic differences (Chételat and Amyot, 2009). Taxonomic composition can be an important determinant of MeHg bioaccumulation in zooplankton communities in the Canadian High Arctic; different species vary several-fold in their MeHg concentrations despite low levels of Hg in the water (Chételat and Amyot, 2009).

Freshwater fish in Arctic lakes of Alaska, Canada and Greenland often have elevated Hg concentrations relative to government-established guidelines for human consumption (Rigét et al., 2000; Lockhart et al., 2005a; Jewett and Duffy, 2007). The higher Hg concentrations (> 0.5 to 1 mg THg/g ww) are typically found in predatory species that feed at higher trophic levels, such as lake trout (*Salvelinus namaycush*), northern pike (*Exos lucius*), walleye (*Stizostedion vitreum*), and Arctic char (Lockhart et al., 2005a). Fish populations in the Arctic are often older (due to low fishing pressure) and have slower growth rates compared with populations at lower latitudes, and these factors contribute to enhanced Hg bioaccumulation (Evans et al., 2005b).

3.5.3. Case studies of top-down trophic influences on biotic mercury levels

Predators can exert a top-down influence on biotic Hg concentrations depending on their feeding ecology and diet preferences (Loseto et al., 2008b; Young et al., 2010), which relate to the animals' size, age, sex and reproductive status. These in turn influence energetic demands, social behavior and habitat use (see Figure 3.6). While dietary breadth and trophic level help describe contaminant exposure there is often a large spatial component to foraging in high trophic level species. For example, many marine mammals have large home ranges, can undergo extensive migrations, and may seasonally feed in different ecosystems. This complicates the interpretation of Hg exposure and the associated risks.

Variability in energy requirements within and among species that feed at similar trophic levels may be manifested by differences in feeding behavior. Several studies have tested for the effects of sex and age in marine mammals (Dehn et al., 2005) and fish (McIntyre and Beauchamp, 2007) on contaminant loads. Evaluating size effects on contaminant loads is difficult to assess accurately in mature birds and mammals because after they reach maturity they do not continue to grow (as fish typically do). Changes in feeding behavior and energy requirements, inferred from stable C and/or N isotopic composition of tissues (e.g., Tucker et al., 2007), can influence a population's Hg accumulation (Atwell et al., 1998; Loseto et al., 2008a). For example, $\delta^{13}C$ and $\delta^{15}N$ values revealed a switch of polar bear (*Ursus maritimus*) diet from sympagic to pelagic food webs, which resulted in an increase in Hg levels in the bears (Horton et al., 2010). The following sections explore these top-down effects in two well studied high trophic level Arctic species: beluga and Arctic char.

3.5.3.1. Eastern Beaufort Sea beluga

High Hg levels have been reported in Beaufort Sea beluga compared to other Arctic populations (Lockhart et al., 2005a). This led to several studies focused on the habitat use and diet preferences of this beluga population, along with its associated food webs (guild and trophic transfer of Hg). Using satellite telemetry data on beluga matched with physical environmental features (e.g., sea ice, bathymetry), the Beaufort Sea population was found to sexually segregate during summer (Loseto et al., 2006). Three summer habitat use groups were defined on the basis of length, sex and reproductive status. Intra-species segregation over time and space, relating to different requirements (Stevick et al., 2002), has consequences for feeding ecology and Hg exposure in the beluga (Loseto et al., 2008a). With this in mind, prior knowledge about Beaufort Sea food webs was coupled with beluga habitat use groups to characterize Hg exposure among different sex and size classes (Loseto et al., 2008b).

The feeding groups were hypothetical, yet they provided a framework to begin merging predator behavior and food web dynamics with the aim of explaining beluga Hg levels. Results from this analysis demonstrated the importance of Hg concentrations at the bottom of the food web, and of food web length, in explaining beluga Hg levels. They also showed that benthic food webs were complicated by heterogeneous food sources and potentially different mechanisms driving bioaccumulation and biomagnification. In contrast to previous suggestions, the riverine source of Hg and MeHg to the Mackenzie Delta (see Leitch et al., 2007) did not result in high concentrations in the estuarine-shelf food web, and beluga believed to feed there had the lowest Hg levels of the overall population. Beluga thought to feed on the epibenthic and Amundsen Gulf pelagic food webs had the highest liver and muscle Hg levels (Loseto et al., 2008b).

To investigate feeding behavior further, dietary fatty acid biomarkers were measured together with carbon and nitrogen stable isotopes, and Hg in liver and muscle tissues. The results revealed a strong relationship between beluga size and diet, and suggested the existence of dietary differences among size classes and habitat use groups (Loseto et al., 2008a). Fatty acids indicated that overall the beluga diet was dominated by Arctic cod and poor in benthic prey (Loseto et al., 2009). However, size-related dietary differences were evident, with larger beluga preferring offshore Arctic cod, and smaller beluga feeding on prey including Arctic cod in nearshore habitats. Unlike fish, beluga reach an asymptotic length at a certain age, and subsequently feed in relation to their size rather than age (Loseto et al., 2008a). If these size-related trends can be explained by energetics, then the large males may need to maintain body mass by adjusting foraging behavior to feed either on energy-rich prey, or feed more often (Le Bouef et al., 2000). If so, the beluga pattern suggests a greater abundance or availability of Arctic cod in pelagic offshore regions of the Arctic Ocean.

To summarize, factors such as predation, resource selection, and nursing that influence the habitat use of higher trophic level species like beluga also relate to differential feeding strategies and to dietary Hg exposure. Questions that remain unresolved include the reason for the unexpected variation in Hg concentrations in Arctic cod and its associated food web, which were highest in offshore fish and lowest in the nearshore environment. Given the high Hg and MeHg inputs from the Mackenzie River, the opposite trend would be expected. Thus, it is hypothesized that Mackenzie River inorganic Hg and/or MeHg may not be bioavailable upon entering the Delta, but rather may be deposited and re-distributed, perhaps to the biologically active shelf break where Hg may become bioavailable for methylation and/or MeHg may be available for uptake in the offshore food web.

3.5.3.2. Landlocked Arctic char

Arctic char is used internationally as a sentinel species to detect spatial distributions and temporal trends of Hg in Arctic fresh waters (AMAP, 2005). Lakes in the Canadian Arctic Archipelago have simple food webs in which Arctic char are often the only species of fish present, feeding primarily on the dominant benthic invertebrate – chironomids (Guiguer et al., 2002; Gantner et al., 2010a). Between 2005 and 2007, Hg biomagnification was investigated in the food webs supporting landlocked Arctic char populations in the following locations: on Ellesmere Island (n=4), Cornwallis Island (n=9), Victoria Island (n=1), Kent Peninsula (n=3) and Ungava Peninsula (n=1) (Gantner et al., 2010a). The sites covered a latitudinal gradient from 61° to 82° N. The study included full food web sampling of Arctic char, periphyton, zooplankton, benthic invertebrates, and ninespine stickleback (*Pungitius pungitius*) at each lake, as well as sediment and surface water samples. All biota, sediment, and water samples were analyzed for MeHg and THg, as well as stable isotopes ($\delta^{15}N$ and $\delta^{13}C$). Trophic relationships were inferred from the isotopic data, and food chain length and trophic magnification factors for Hg were determined.

The main finding of the study was that benthic invertebrates (mainly chironomid larvae and pupae) were the main source of nutrients, and thus also of MeHg and THg, in the char. Chironomids undergo metamorphosis and their MeHg concentrations increase during growth from larvae to pupae to adults (Chételat et al., 2008). As a result, chironomid larvae, pupae and adults are quantitatively different sources of MeHg, and differential consumption of these stages may affect Hg uptake by char. Pelagic zooplankton contributed very little to the diet, or to MeHg or THg levels of the fish. Surprisingly, trophic magnification factors, which assume linear Hg uptake based on the trophic level of all food web organisms, were not predictive of MeHg and THg concentrations in adult fish.

There was evidence of differential consumption of chironomid stages by char based on stomach content analyses in the Arctic Archipelago by Stewart and Bernier (1982). Of 212 char investigated in this survey, the majority consumed larvae (82%) while pupae and adult chironomids were consumed in lesser amounts (52% and 11%, respectively). However, on Cornwallis Island, adult chironomids were generally not present in char stomachs in the past (Stewart and Bernier, 1982) or recently (Gantner et al., 2010a), although they were consumed in Char Lake (Hobson and Welch, 1995). Recent $\delta^{15}N$ data on insectivorous char show low variability in THg and $\delta^{15}N$ among Cornwallis Island lakes (Gantner et al., 2010a,b). On Ellesmere Island, larger char fed selectively on pupae at the lake surface during the period of emergence, while smaller char (< 20 cm) inhabited very shallow areas, feeding mostly on chironomid larvae (Parker and Johnson, 1991).

Life stage-related differences in habitat use and diet of the fish, which exposed them to different stable N isotope ratios and MeHg concentrations among larval, pupal, and adult chironomids (Chételat et al., 2008), could explain some of the variability in $\delta^{15}N$ and Hg concentrations of char, particularly the differences between juvenile and adult fish. Younger char that often inhabit the littoral zone may feed more on larvae (Rigét et al., 1986), which is also evident from lower MeHg concentrations and more depleted $\delta^{15}N$ signatures in juvenile char from Cornwallis Island lakes (Gantner et al., 2010a). The proposed effect of differential feeding behavior of adult char (Chételat et al., 2008) on their Hg levels can not currently be distinguished from the effect of opportunistic cannibalism, a factor that is known to contribute greatly to variability of $\delta^{15}N$ (and thus Hg) in char (Hobson and Welch, 1995; Guiguer et al., 2002; Gantner et al., 2009). In Cornwallis Island lakes the variability of $\delta^{15}N$ (and Hg) in insectivorous char in which no cannibalism was observed is small ($\delta^{15}N$ 2 SD = 0.3‰ to 0.8‰), and higher in other lakes with observed opportunistic cannibalism (2 SD up to ~2.4‰).

Cannibalism played an important role in Arctic char Hg levels in a lake on Svalbard (Rognerud et al., 2002). The highest concentrations were observed in piscivorous Arctic char (0.04 to 0.44 µg/g ww), whereas the invertebrate-feeding Arctic char had significantly lower concentrations. Cannibalism was the major force structuring age and length class distribution of the population. Stable isotope analysis indicated that the oldest fish were tertiary consumers, living on smaller piscivorous individuals. It was concluded that biomagnification in the food chain, fish longevity and growth rates were the most important variables explaining char THg concentrations and variability.

Chételat and Amyot (2009) proposed that an increase in the abundance of Hg-rich *Daphnia* in High Arctic lakes could lead to an increase in Hg accumulation in char. The potential colonization by *Daphnia* of a High Arctic lake could lead to a shift in energy and Hg transfer from the benthic to pelagic pathway, and to an increase in Hg transfer to char. Meretta Lake (Cornwallis Island) provided an opportunity to examine this hypothesis because anthropogenic eutrophication resulted in the proliferation of *Daphnia* in the lake's water column. Meretta char were significantly younger, larger, and heavier than char from other Cornwallis Island lakes, but they were comparable in their $\delta^{15}N$ values (implying similar trophic position). Based on the $\delta^{13}C$ values of zooplankton, chironomids and char, the diet of adult char was about 50% zooplankton and 50% benthic chironomids. The appearance of *Daphnia* caused the pelagic transfer of Hg to become important in Meretta Lake, unlike the benthic-dominated food webs of other lakes. However, *Daphnia* consumption did not have a dramatic effect on Hg uptake by char, because Hg concentrations in Meretta fish were similar to those in other lakes within the same watershed that lacked *Daphnia* (Char and Resolute lakes). A growth dilution effect may have occurred, as Meretta char grew more rapidly than in other Cornwallis Island lakes probably because of the zooplankton prey available. In four southern and more productive lakes with diverse food webs on Kent Peninsula (69° N), char THg concentrations were lower than in the low productivity northern lakes (~75° N), which again could suggest a biodilution effect (Gantner et al., 2010b).

The dominance of benthic prey in the char diet may mean that newly deposited atmospheric Hg is less likely to be directly reflected in Arctic char Hg concentrations. Responses of fish Hg levels to inputs from the surrounding environment may be delayed until Hg is taken up by chironomids from lake sediments. Overall, THg concentrations in landlocked Arctic char in the study lakes were significantly related to catchment-to-lake area ratio, which emphasizes the importance of input/loading of the surrounding landscape on Hg in lake food webs. THg in Arctic char were not related to THg in surface water or sediment, or to latitude or longitude. Thus, food web processes, specifically biomagnification, cannibalism and the chironomid diet, are key determinants of char THg concentrations.

3.5.4. Physiological factors determining dietary mercury exposure in predators

When evaluating Hg levels in high trophic level species such as marine mammals, many tissues can be selected for analysis. These range from skin, liver, fur, and muscle to brain and blood. To best evaluate the exposure or body burden in a high trophic level species, it is important to select the most appropriate matrix due to the different forms of Hg that occur in various tissues, and because of the different turnover rates associated with tissues (Loseto et al., 2008a). Understanding the organisms' physiology is also critical when using other biomarkers such as stable isotopes (Hobson et al., 1993).

To use beluga as an example, Hg concentrations in liver tissue typically correlate strongly with age due to the continuous internal demethylation of MeHg to inorganic Hg and the accumulation of mercuric selenide, a biologically unavailable complex (Farris et al., 1993; Wagemann et al., 1998). Therefore, the linear increase in liver Hg with age suggests that the additive processes of Hg bioaccumulation over time will complicate any attempt at interpretation of recent dietary Hg sources (Loseto et al., 2008a). In contrast, Hg concentrations in beluga muscle (known to be almost entirely MeHg) are most strongly correlated to animal length (Loseto et al., 2008a). This relationship suggests that muscle Hg concentrations reflect dietary Hg uptake and to a lesser extent bioaccumulation over time (Loseto et al., 2009). Larger beluga were either feeding at higher trophic levels or in different food webs with higher Hg sources. Conversely, age was not significantly correlated to muscle Hg levels (Loseto et al., 2008a), as also occurs with Hg in ringed seal muscle (Atwell et al., 1998). Overall, muscle tissue is a better indicator of dietary Hg sources and the processes of Hg biomagnification driven by food web structure, while liver Hg best reflects age-related accumulation. Mercury concentrations in other tissues, such as *muktuk* (skin) in beluga, have strong linear relationships with muscle Hg (Wagemann et al., 1998), and this is also thought to apply to fur or hair in mammals (Young et al., 2001). This finding supports the use of skin biopsy or fur samples to estimate dietary Hg loads and body burdens in high order mammals.

3.6. Do atmospheric mercury depletion events contribute to the increased mercury levels found in biota in different parts of the Arctic?

Atmospheric mercury depletion events provide a mechanism for rapid deposition of substantial amounts of GEM from the atmosphere to the frozen surface environment during polar sunrise (see Chapter 2), and have been hypothesized to contribute significantly to the high Hg levels in some Arctic biota (AMAP, 2005). However, it is now well established that the Hg deposited during AMDEs can be readily re-emitted from the snowpack (see Section 2.6.2). Establishing a link between AMDEs and enhanced Hg levels in Arctic biota is complicated partly by a poor understanding of the net outcome of the AMDE deposition pathway, and partly by the complex Hg biogeochemistry of aquatic ecosystems which contain inorganic Hg(II) from a variety of sources (of which AMDEs are but one) and methylate the inorganic Hg(II) into MeHg. Three lines of evidence pertaining to this question are reviewed here: the bioavailability of AMDE-deposited Hg; the amounts and fate of inorganic Hg inputs from AMDEs compared with those from other entry pathways; and comparison of the spatial patterns of AMDE occurrence and biotic Hg concentrations.

A fraction of the Hg deposited by AMDEs in the Arctic has been reported to be bioavailable to microbes under controlled conditions. Using *Vibrio anguillarum* pRB28, a *mer-lux* reporter organism, as a Hg bioavailability indicator, it was found that exposure to melted Alaskan snow samples resulted in a positive signal in snow collected after AMDEs; 13% to 15% of the Hg in snow was bioavailable to this bacterium (Scott, 2001; Lindberg et al., 2002). In a similar study, melted snow samples collected at Kuujjuarapik, Quebec, were analyzed using a suite of bioassays involving living organisms or cells representative of three trophic levels (Gagné et al., 2009). Comparison of bioassay test responses of snow samples collected before and after AMDEs demonstrated that, following AMDEs, *Hydra attenuata* acute sublethality and rainbow trout (*Oncorhynchus mykiss*) hepatocyte acute cytotoxicity responses increased 1.6- and 4.4-fold, respectively. Furthermore, an algal bioassay revealed that the growth of *Pseudokirchneriella subcapitata* was stimulated by snow collected before the occurrence of AMDEs, but inhibited in post-AMDE snow samples. These investigations provided interesting insights about the potential availability of deposited Hg to lower trophic level Arctic biota, but the actual significance of AMDEs remains to be demonstrated. Results from many Arctic locations suggest that in most locations about 80% of the total deposited Hg is photo-reduced to volatile Hg(0) and re-emitted back to the atmosphere within a day or more following an AMDE (see Section 2.6.2). Hence, the fraction of newly deposited atmospheric Hg that is highly photoreactive may not be bioavailable to the microbes thriving in snow in polar spring (Amato et al., 2007).

From the perspective of mass inputs, based on currently available data, AMDE Hg entering the upper Arctic Ocean and Hudson Bay is believed to contribute a relatively small amount to what are already large reservoirs of dissolved Hg (Outridge et al., 2008; Hare et al., 2008). According to a modified GRAHM model, a net amount of 45 t/y THg (46% of total annual atmospheric inputs) entered the Arctic Ocean during spring when AMDEs occur, compared to total inputs of 206 t/y (Outridge et al., 2008). The springtime input includes other wet and dry Hg deposition not associated with AMDEs, thus 45 t/y is likely to be an overestimate of the AMDE input. The existing Arctic Ocean reservoir of dissolved THg of about 7900 t (~950 t in the upper 200 m) is maintained as part of the global Hg cycle (through atmospheric and oceanic transport), and includes a natural background of Hg augmented during the past two centuries by human activities (Sunderland and Mason, 2007). Photo-reduction and evasion, export of water from the Arctic Ocean, and particle flux operate on the resident Hg(II), regardless of source, to remove it from the ocean's surface waters. The intense seasonality of the Arctic environment appears to have a corollary in the seasonal net balance of AMDE Hg deposition and re-volatilization. On the basis of modeling of GEM measurements at the Zeppelin station, Svalbard, Hirdman et al. (2009) reported that the Arctic was a strong net sink region for GEM in spring (April and May), suggesting that Hg accumulates in the Arctic snowpack as a result of AMDEs. But for summer, the Arctic was a GEM source, probably as a result of evasion from the ocean during its open water season and (less likely) re-emission of previously deposited Hg as the snow and/or ice melts. The overall net balance between these periods was not reported.

Processes in the water transform a proportion of the Hg(II) to MeHg which then becomes the component of exposure to biota. The methylation rate in Arctic marine systems is a poorly understood variable that is probably controlled by the ocean's organic carbon cycle, itself highly variable in time and space. An important question that needs to be answered is whether or not AMDE Hg is in some way more prone to methylation than the resident Hg(II) (i.e., does AMDE Hg take a 'fast track' to biota?; see Harris et al., 2007; Macdonald and Loseto, 2010). In considering the MeHg burden in high trophic level species, it is therefore difficult to estimate which proportion derives from AMDEs, and which proportion derives from the now globally-contaminated pool of Hg(II) cycling in the atmosphere-ocean system. It seems clear from comparative studies using biological samples pre-dating and post-dating the Industrial Revolution that global aquatic systems including the Arctic Ocean are contaminated with industrial Hg (see Section 5.2). It remains unclear whether AMDEs contribute significantly to making Arctic ecosystems especially vulnerable to the global Hg cycle, but post-depositional methylation processes must play an important and perhaps dominant role (Macdonald and Loseto, 2010). There is a substantial knowledge base concerning Hg and Hg methylation processes at lower latitudes (Driscoll et al., 1998; Galloway and Branfireun, 2004, and references therein). However, the applicability of these processes may be limited with respect to Arctic ecosystems (see Section 3.4).

From a spatial perspective (the third line of evidence regarding AMDEs), the results from several studies provide contradictory evidence of a possible link between AMDEs and biotic Hg levels. Total Hg in moss has shown a pronounced tendency toward higher concentrations along the northwestern coast of Norway compared to areas further inland, since measurements started in 1985, a trend which appears to be particularly strong in the northernmost area (Steinnes et al., 2003; Steinnes and Sjøbakk, 2005). This trend is not due to higher wet deposition along the coast. Measurements of GEM in the same region have indicated that this pattern could be due to transport of inorganic Hg from AMDEs to the mainland of Norway (Berg et al., 2008b). Coincident measurements of RGM are required before the extent of AMDE Hg contributions to moss can be firmly established. However, this study, and comparable findings of elevated Hg levels in moss and lichens adjacent to an Antarctic polynya where AMDEs could be expected to occur (Bargagli et al., 2005), suggest a significant role for AMDEs in contributing inorganic Hg to coastal terrestrial ecosystems.

In contrast, a recent study in Alaska on mosquito MeHg concentrations revealed little variation and no gradient along a 200- km transect from the coast to inland areas, suggesting that springtime AMDEs along the coast had little impact on Hg bioaccumulation in these aquatic invertebrates (Hammerschmidt and Fitzgerald, 2008). High re-emission rates from snow to the atmosphere prior to snowmelt were suggested as a possible explanation. This finding is consistent with a large-scale spatial study which reconstructed atmospheric Hg deposition rates from the sediments of many lakes across Arctic Canada, and found no evidence for significant AMDE Hg loading in coastal lakes compared to those further inland (Muir et al., 2009).

3.7. What are the effects of organic carbon on mercury speciation, dynamics, and bioavailability?

Increasing evidence suggests that the speciation, dynamics, and bioavailability of Hg in aquatic systems are closely tied to the sources, composition, and dynamics of organic carbon, especially from aquatic sources. In terms of its ability to sequester or transform Hg, not all organic carbon is equal. Carbon in aquatic systems comes predominantly from external and internal sources – terrigenous plants and soil carbon, and algal production within the waterbody (McGuire et al., 2009). These two sources of carbon exhibit a range of ages, chemical composition and lability (e.g., Goñi et al., 2005; Guo and Macdonald, 2006; Guo et al., 2007; Outridge et al., 2007; Kuzyk et al., 2008; Fu et al., 2009), which display different capacities to bind Hg (Sanei and Goodarzi, 2006). In Antarctic lakes, algal and cyanobacterial planktonic and benthic mats, along with terrestrial mosses in the watershed, are the main sinks for Hg in summer meltwater (Bargagli et al., 2007). The suggestion of fresh algal organic matter providing an important Hg complexation mechanism in Arctic freshwaters is further supported by the strong association between historical fluxes and concentrations of Hg and algal organic carbon in sediment cores from several Arctic lakes (Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2010).

Labile carbon also plays what is arguably its most crucial role of creating the circumstances to transform Hg(II) to MeHg, the form that presents almost all of the toxicological risk. The methylation process has long been known to occur in sub-oxic environments, like sediments or stagnant basins, where inorganic Hg is converted to MeHg by sulfate-reducing bacteria metabolizing organic matter (Ekstrom et al., 2003; Lambertsson and Nilsson, 2006). In the Arctic marine environment, the sub-oxic environments are associated with estuarine, shelf and slope sediments where the labile organic carbon flux is sufficient to support a vigorous metabolism that overwhelms oxygen diffusion (e.g., Gobeil et al., 1997, 2001b). It has recently been discovered that remineralization of organic carbon can also generate MeHg within the water column, particularly at locations indicated by nutrient maxima (Sunderland et al., 2009; Cossa et al., 2009). In summary, the organic carbon cycle provides the means to sequester Hg onto particles, transport them and assist burial through vertical flux, while the metabolism of organic carbon supports the transformation of Hg(II) to MeHg. There are other interactions between the organic carbon and Hg cycles that are not as well understood. For example, DOM may provide stabilizing ligands to maintain Hg in the dissolved form (e.g., Dong et al., 2010), and C-DOM absorbs UV radiation thus providing an important control on photo-reduction and other photo-initiated processes in surface water (Tseng et al., 2004; Poulain et al., 2007c).

3.8. What is the rate of long-term sequestration of mercury through burial in Arctic non-biological archives (sediments, soils and ice)?

For the purposes of this assessment, 'long-term' sequestration is defined as the removal of Hg from the biogeochemically active environment for periods likely to exceed several centuries. Over longer periods, from millennia to geological time scales, reworking of terrestrial archives, shallow coastal sediments and even deep ocean sediments by geomorphological processes associated with glacial / inter-glacial cycles and tectonic activity may remobilize long-term sequestered Hg. Table 3.1 summarizes the best available estimates of average areal rates and total masses of Hg sequestered by the various non-biological archives.

Recent estimates of long-term sequestration rates for Hg in Arctic marine sediments are available for the Arctic Ocean (Outridge et al., 2008) and Hudson Bay (Hare et al., 2008), but comprehensive estimates are not available for terrestrial areas (soils and peatlands) or for marine sediments of the Canadian Arctic Archipelago, the Labrador Sea and Davis Strait, and the Greenland Sea. In the Arctic Ocean, an estimated sediment Hg flux of 95 t/y occurs in the continental shelf seas and 13 t/y in the Central Basin for a total sequestration of 108 t/y. Sedimentation was the largest single loss pathway for Arctic marine Hg, representing 59% of the total ~182 t/y removed from the Arctic Ocean by all processes. It is also noteworthy that the shelf sequestration rate almost balanced the net atmospheric Hg input of 98 t/y, suggesting the possibility of a scavenging of deposited atmospheric Hg from the shelf water column into sediments (Outridge et al., 2008). In Hudson Bay, the situation is more complicated, because of an extraordinarily large resuspension and lateral transport of ancient glacier-derived till material from shallow coastal waters into deeper waters. Ultimately, this process is related to ongoing post-glacial isostatic rebound of the regional landscape, together with wind and wave action as well as ice scour of inshore sediments. The estimated total sediment flux for the Bay was 147 ± 69 Mt/y, with a modern Hg sedimentation rate of 4.5 ± 3.2 t/y which includes a contribution of 1.7 t/y of Hg from the resuspended material (Hare et al., 2008). The modern sedimentary Hg flux (2.4 t/y) was estimated to be almost two-fold higher than in

Table 3.1. Areal rates and total masses of mercury sequestered annually in non-biological archives in the Arctic.

Archive	Annual Hg flux, μg/m^2/y	Total area, million km^2	Annual Hg mass, t/y	Data source
Marine sediments				
Arctic Ocean	11.3[a]	9.54	108	Outridge et al., 2008
Hudson Bay	5.4[a]	0.84	4.5	Hare et al., 2008
Freshwater sediments	11.5[b]	0.6	6.9	See note [b] for areal Hg flux; total Arctic lake surface area – Smith et al., 2007
Terrestrial soils				Grigal, 2002; Gorham, 1991; Steinnes and Sjøbakk, 2005; Shotyk et al., 2005b
soils	~5	??	??	
peatlands	2 – 20[c]	3.5	7 – 70[c]	
Ice caps and glaciers				Mann et al., 2005; Boutron et al., 1998; Faïn et al., 2009b; St. Louis et al., 2005; Zdanowicz et al., 2009; Zheng et al., 2009
Greenland Ice Sheet	0.1	1.69	0.17	
Other	0.1	0.31	0.03	

[a] Calculated by dividing THg mass removed by surface area; see corresponding articles for details; [b] median modern flux calculated from 76 Arctic and sub-Arctic lakes reported by Lockhart et al. (1998), Bindler et al. (2001a), Fitzgerald et al. (2005) and Muir et al. (2009); [c] estimated range only, based on few data (see Steinnes and Sjøbakk, 2005; Shotyk et al., 2003, 2005b).

pre-industrial times and, comparable to the Arctic Ocean, was about equal to increased inputs from atmospheric deposition and riverine flows. The balance between increased Hg inputs and increased sequestration implies that most of the modern increase in Hg inputs to the Bay was ultimately captured and buried in sediments (Hare et al., 2008).

For freshwater sediments, estimates of focus-corrected modern Hg fluxes, averaged over recent decades, are available for 76 lakes from northern Canada (Lockhart et al., 1998; Muir et al., 2009), Alaska (Landers et al., 1998; Fitzgerald et al., 2005), West Greenland (Bindler et al., 2001a), northern Sweden (above 60° N), Finland (above 60° N), and Russia (Landers et al., 1998). These lakes gave an overall median modern Hg flux of 11.5 μg/m^2/y (mean ± SD, 20.3 ± 22.3 μg/m^2/y; geometric mean = 12.7 μg/m^2/y). Recent decadal rates in the Canadian Arctic have increased about two-fold on average over pre-1900 rates, believed to be due to the combined effects of pollution inputs (Muir et al., 2009), and increased transfer efficiency from the water column because of climate-driven increases in aquatic primary productivity and associated Hg scavenging (Outridge et al., 2007; Stern et al., 2009). A first-order estimate of THg mass sequestered in sediments was obtained by multiplying the median flux above by the total surface area of lakes in the circumpolar Arctic region. No precise figure is available for the AMAP area of interest. Smith et al. (2007) arrived at a GIS-based estimate of 589 500 km^2 for 202 756 lakes of 0.1 km^2 or more in area lying north of 45.5° N (which is the southernmost extent of permafrost near James Bay, Canada). Although this figure is possibly an over-estimate for these purposes, in fact most of the lakes in this region occur within the AMAP area of interest because lake area as a fraction of unit land area is several-times higher in permafrost and glaciated terrains than in non-permafrost and non-glaciated landscapes, and are thus are concentrated in the north (Smith et al., 2007). The tendency towards over-estimation is also balanced by GIS techniques consistently under-estimating the number and surface areas of lakes in a given area (Frey and Smith, 2007), and by the exclusion of waterbodies of less than 0.1 km^2 in area from this compilation. Using these area data, the THg mass sequestered by Arctic freshwater sediments amounts to about 6.8 t/y. It is difficult to provide error estimates around this figure. However, even a 100% error would not alter the conclusion that freshwater sediments sequester a small amount of Hg relative to marine sediments, mainly because of the small total area that freshwater sediments represent (Table 3.1).

Estimation of Hg sequestration in Arctic soils (including peatlands, as these are recognized as a soil type) is complicated by the fact that Hg in soils and peatlands may be subjected to significant remobilization by wildfires, freeze/thaw processes, wind action, erosion and runoff, and biological activity. Much of the Hg contained in the upper sections of a soil profile therefore may not be sequestered over the long-term. Furthermore, soil accumulation rates have not been estimated in Arctic regions but are known to be highly variable in temperate areas (Grigal, 2002). Vegetative cover is an important variable in soil Hg sequestration, with a proportion of the Hg contained in forest plants and their leaf litter derived from GEM in the atmosphere (Mason et al., 1994; Grigal, 2003). Plants act as interceptors of Hg-bearing dusts and RGM (Poulain et al., 2007d). Consequently, Hg deposition rates to soils under forests and grasslands are estimated to be about 4-fold and 2-fold higher on average, respectively, than to adjacent lake surfaces (Grigal, 2002). Photo-reduction and re-volatilization rates of deposited Hg are also several-times lower under trees than from adjacent sun-exposed areas (Poulain et al., 2007d). Soil organic matter content, which is closely allied to the degree and type of vegetation cover, is a strong controller of the Hg content of soils in the Northern Hemisphere, because of the strong binding of various Hg chemical forms with organic matter (Grigal, 2003). Data on THg concentrations in Arctic soils are sparse; Melnikov et al. (2002) reported mean soil Hg values from the Kola and Taymir Peninsulas and the Pechora Basin, Russia, ranging from 0.06 to 0.12 μg/g dw. However, without a better understanding of soil development and accumulation processes in the Arctic, sequestration rates cannot be derived from these concentration data. Grigal (2002) estimated the average soil THg accumulation rate for northern hemisphere temperate and boreal forest soils to be ~ 5 μg/m^2/y. However, this estimate should be treated cautiously in relation to most of the High Arctic's terrestrial areas which are sparsely vegetated; the actual value is likely to be significantly lower. Given these uncertainties, a total mass sequestration figure cannot be derived for Arctic soils.

The large areal extent of circumpolar Arctic peatlands (about 3.5×10^6 km^2; Gorham, 1991), and their well-known capacity to accumulate Hg from the atmosphere and groundwater inflows (Shotyk et al., 2003, 2005b), suggests that both ombrotrophic and minerotrophic peat bogs could be significant regional Hg sinks. Unfortunately, few studies of modern Hg accumulation rates in Arctic or sub-Arctic peat bogs have been published. Steinnes and Sjøbakk (2005) reported average fluxes of 2.1 to 11.1 μg/m^2/y (median 4.3 μg/m^2/y) over the past century for four peat bogs in Norway north of 60° N, whereas Shotyk et al. (2003) calculated a rate of about 14 μg/m^2/y in southern Greenland in the 1990s after a rapid decline from a peak of 164 μg/m^2/y in the 1950s, and Shotyk et al. (2005b) reported a flux of 16 μg/m^2/y in the late 1990s in a Faroe Islands peat deposit. Given the paucity of data, a range of areal rates of 2 to 20 μg/m^2/y was used to constrain minimum and maximum values of 7 to 70 t/y for the THg mass sequestered. Thawing of peatlands contained within permafrost may also release significant amounts of this sequestered Hg into local watercourses, especially during recent decades (see Section 4.9.3), suggesting that much of the accumulated Hg is not stored over the long term.

A small fraction of the Hg present in the Arctic atmosphere is removed and preserved in the accumulation area of glaciers and ice caps. This occurs partly through occlusion of GEM in interstitial spaces of the snow and firn (Faïn et al., 2008), and by the entrapment of particulate Hg (from dry and wet deposition) in the ice matrix itself (Dominé and Shepson, 2002). Because mean GEM concentrations in Arctic air are low (< 1 to 2 ng/m^3) and the volumetric fraction of air in glacial firn at the pore-close off depth is less than 10%, the second process is by far the most important for sequestering Hg in ice. The Hg trapped in ice can remain stored for decades to millennia depending on the size, regime, turnover rate, and mass balance trend of glaciers. Data on Hg levels in circumpolar Arctic glaciers are scarce, but published figures only vary within the narrow range of about 0.5 to 2 ng/L in recent (< 10-yr old) firn layers (Boutron et al., 1998; Mann et al., 2005; St. Louis et al., 2005; Faïn et al., 2008; Zdanowicz et al., 2009; Zheng et al., 2009). Since the mean Hg levels are similar, geographic differences in sequestration rates are largely determined by net ice accumulation rates at these sites. The present sequestration rate of Hg in central Greenland firn can be estimated at about 0.1 μg/m^2/y for reactive Hg, or about 1.0 μg/m^2/y for THg (Mann et al., 2005; Faïn et al., 2008). For Canadian Arctic ice caps the sequestration rate for Hg_R is 0.1 to 0.2 μg/m^2/y (St. Louis et al., 2005; Zdanowicz et al., 2009; Zheng et al., 2009).

Using an average net Hg accumulation value of 0.1 μg/m^2/y, and the sum accumulation area of Arctic glaciers and ice caps (Dyurgerov and Meier, 2005; Bahr et al., 2009), it is estimated that a net mass of about 0.2 t/y Hg may be sequestered annually in Arctic glaciers and ice caps, of which more than 80% may be stored in the Greenland Ice Sheet. Alaskan glaciers were excluded from this computation because their accumulation rates and areas are poorly constrained. The ice archive is thus a very small sink of THg, both in areal rate and total mass sequestered, compared to other non-biological archives and particularly marine sediments (Table 3.1). Furthermore, at least some of the Hg presently stored in glacial ice may be prematurely released as Arctic glaciers diminish under a warmer climate (see Section 4.9.1).

3.9. Conclusions and recommendations

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

What is the fate of net deposited atmospheric mercury in the various environmental media?

1. Most of the Hg entering aquatic and terrestrial ecosystems following atmospheric deposition is in inorganic (Hg(II)) forms. Present knowledge suggests that the small amount of monomethyl-Hg (MeHg) found in snowpacks prior to spring snowmelt does not add significantly to the extant MeHg levels in aquatic systems.

2. Photo-reduction and re-volatilization (evasion) of part of the deposited Hg in Arctic lakes and marine waters may constrain its overall rate of incorporation into aquatic food webs.

3. The production, speciation (dissolved *vs.* particulate, labile *vs.* non-labile) and concentrations of organic carbon are among the most important factors determining the various fate pathways of inorganic Hg in aquatic and terrestrial ecosystems, that is, evasion from waters, methylation and incorporation into food chains, and scavenging into sediments and soils.

The rates of Hg entry into the alternative pathways in aquatic and terrestrial ecosystems are poorly constrained, and require further elucidation. As the marine environment is the penultimate source of most of the risk of Hg exposure to wildlife and people in northern communities, a particular focus on the fate of Hg entering marine systems would be appropriate. The role of microbial communities in Hg fate in the Arctic has been largely overlooked but could be crucial to our understanding.

How does mercury move from the abiotic environment into food webs, and what are the factors influencing this movement?

4. MeHg is significantly more bioavailable than inorganic Hg forms, and so the net MeHg production rate is expected to be key in controlling the uptake rate of Hg at the base of food webs.

5. The methylation of inorganic Hg requires a labile organic carbon source to drive bacterial activity.

6. The bioavailability of inorganic Hg to bacteria is likely to be linked to the nature and quantities of competing ligands and surfaces in the environment, the relative amounts of dissolved versus particulate Hg(II), the reactivity of deposited Hg and the metabolic activity of microbes.

7. Environmental factors such as low organic matter content in sediment, low temperatures, well-oxygenated waters, water clarity, and alkaline pH may limit the capacity of bacterial communities to generate MeHg in Arctic lakes and marine systems.

8. The primary sites of MeHg formation in Arctic lakes are

anoxic sediments and wetlands. In the Arctic Ocean, estuarine, shelf and slope sediments are likely to be important but it is possible that MeHg is also formed in the mid-water column as has recently been found in temperate oceans.

It is unknown whether MeHg enters Arctic food webs mainly through the microbial populations responsible for its formation, or primarily as dissolved MeHg assimilated by phytoplankton and algae. Rates of inorganic and MeHg uptake by Arctic microbial and algal communities have not been adequately determined.

What role does methylation/demethylation play in controlling mercury accumulation rates in Arctic food chains?

9. As MeHg is the most bioavailable Hg form, its rate of production and destruction in the abiotic environment, and transfer within food webs, govern Hg accumulation in biota.

10. Monomethyl-Hg (MeHg) can be produced by methylation of inorganic Hg, and by photolysis of gaseous dimethyl-Hg (DMHg) produced by marine bacteria and macro-algae.

11. In Arctic Alaskan lakes, production of MeHg was almost balanced by summertime photo-demethylation which essentially competed for MeHg with lake food webs.

The aquatic MeHg cycle in the Arctic is very poorly understood, and requires further research as a matter of priority. In particular, little is known about the Arctic marine MeHg cycle, which is key to understanding the human risk developed from Hg exposure via traditional animal foods.

How do trophic processes influence mercury levels in higher order animals?

12. Dietary exposure represents the primary means by which higher trophic level organisms are exposed to Hg, especially the most toxic form, MeHg. This is the Hg form which biomagnifies by several orders of magnitude in concentration as it passes upward through food webs.

13. Biomagnification results in MeHg increasing as a percentage of THg in Arctic animal tissues from about 30% in zooplankton to more than 90% in upper trophic level predators.

14. Mercury exposure at the higher levels of food webs is influenced by both ‘top-down’ and ‘bottom-up’ trophic processes (e.g., predator dietary strategy, and bioaccumulation rate of MeHg influenced by ecosystem productivity and organism growth rates, respectively).

Do atmospheric mercury depletion events contribute to the increased mercury levels found in biota in different parts of the Arctic?

15. Contradictory results about the importance of AMDEs to biotic Hg levels have been reported in spatial studies of Hg concentrations in Arctic mosses, zooplankton and mosquitoes, and no general conclusions can yet be reached.

16. A small fraction (13% to 15%) of the Hg deposited by AMDEs onto snow surfaces has been reported to be bioavailable to bacteria, yet the rapid re-volatilization of about 80% of AMDE Hg from snowpacks may limit the exposure of food webs to Hg from this source.

The bioavailable fraction of AMDE-related Hg, and its rate of accumulation by biota, is a priority for further investigation as it is a potentially important process contributing to Hg exposure in aquatic food webs.

What are the effects of organic carbon on mercury speciation, dynamics, and bioavailability?

17. Increasing evidence suggests the speciation, dynamics, and bioavailability of Hg in aquatic systems is closely tied to the sources, composition, and dynamics of organic carbon.

18. Variations in the productivity of Arctic freshwater lakes over recent centuries and decades may play an important role in influencing the sedimentary Hg flux rate through scavenging of inorganic Hg from the water column by particulate organic matter.

19. Labile organic carbon mainly (but not exclusively) from algae plays a crucial role in aquatic systems by providing a substrate and physical focus for bacterial methylation of Hg(II) to MeHg, the form that presents almost all of the toxicological risk to wildlife and humans.

20. In addition to the importance of sediments as methylation sites, it has recently been discovered in temperate oceans that re-mineralization of organic carbon in the water column can generate MeHg, particularly at locations indicated by nutrient maxima.

Although it is unknown whether MeHg formation also takes place in Arctic seawaters, the Arctic Ocean does exhibit nutrient maxima which may be suggestive of this effect. Confirmation and measurement of this process in the Arctic Ocean would be a significant advance in understanding of the Arctic Hg cycle.

What is the rate of long-term sequestration of mercury through burial in Arctic non-biological archives (sediments, soils and ice)?

21. Marine sediments sequester the largest mass of Hg in the Arctic annually (more than 110 t/y combined in the Arctic Ocean and Hudson Bay alone), with northern peatlands also likely to be an important sink (≤ 70 t/y). Lake sediments and glaciers are negligible sinks; soils are possibly also important but data are lacking.

22. In the Arctic Ocean and Hudson Bay, the near balance between rates of Hg inputs and sequestration in sediments implies that most of the annual Hg inputs to seawater are ultimately captured and buried in sediments.