Review

The fate of mercury in Arctic terrestrial and aquatic ecosystems, a review

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Environmental context.   Mercury, in its methylated form, is a neurotoxin that biomagnifies in marine and terrestrial foodwebs leading to elevated levels in fish and fish-eating mammals worldwide, including at numerous Arctic locations. Elevated mercury concentrations in Arctic country foods present a significant exposure risk to Arctic people. We present a detailed review of the fate of mercury in Arctic terrestrial and marine ecosystems, taking into account the extreme seasonality of Arctic ecosystems and the unique processes associated with sea ice and Arctic hydrology.

Abstract.   This review is the result of a series of multidisciplinary meetings organised by the Arctic Monitoring and Assessment Programme as part of their 2011 Assessment 'Mercury in the Arctic'. This paper presents the state-of-the-art knowledge on the environmental fate of mercury following its entry into the Arctic by oceanic, atmospheric and terrestrial pathways. Our focus is on the movement, transformation and bioaccumulation of Hg in aquatic (marine and fresh water) and terrestrial ecosystems. The processes most relevant to biological Hg uptake and the potential risk associated with Hg exposure in wildlife are emphasised. We present discussions of the chemical transformations of newly deposited or transported Hg in marine, fresh water and terrestrial environments and of the movement of Hg from air, soil and water environmental compartments into food webs. Methylation, a key process controlling the fate of Hg in most ecosystems, and the role of trophic processes in controlling Hg in higher order animals are also included. Case studies on Eastern Beaufort Sea beluga (*Delphinapterus leucas*) and landlocked Arctic char (*Salvelinus alpinus*) are presented as examples of the relationship between ecosystem trophic processes and biologic Hg levels. We examine whether atmospheric mercury depletion events (AMDEs) contribute to increased Hg levels in Arctic biota and provide information on the links between organic carbon and Hg speciation, dynamics and bioavailability. Long-term sequestration of Hg into non-biological archives is also addressed. The review concludes by identifying major knowledge gaps in our understanding, including: (1) the rates of Hg entry into marine and terrestrial ecosystems and the rates of inorganic and MeHg uptake by Arctic microbial and algal communities; (2) the bioavailable fraction of AMDE-related Hg and its rate of accumulation by biota and (3) the fresh water and marine MeHg cycle in the Arctic, especially the marine MeHg cycle.

Contents list

Terminology, abbreviations and location information

In the literature 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 measurements such as total Hg (THg) and reactive Hg (Hg_R).[1–3] Table 1 summarises the abbreviations we use in this paper and their descriptions. This paper discusses the results from research conducted throughout the Arctic. To simplify the identification of the various location names used we have provided a detailed map as Fig. 1.

Table 1.   A list of the abbreviations used in this paper and descriptions of what they represent

Abbreviation	Description
Hg^0	Elemental Hg
DGM	Hg^0 dissolved in water
GEM	Hg^0 as a gas-phase vapour in air or snowpack interstitial air
Hg^{II}	Inorganic divalent Hg
MeHg	Monomethyl Hg (CH_3Hg^+)
DMHg	Dimethyl Hg (($CH_3)_2Hg$)
THg	Total Hg
BioHg	Fraction of the Hg^{II} that is bioavailable to bacteria for methylation
HgR	Reactive Hg (approximately equivalent to the THg^{II} pool with colloids and ligands)

The Arctic as a unique location

Many of the unique aspects of the Arctic are the result of the interplay of physical, chemical and biological processes between the land (including rivers and lakes), the cryosphere, the sea and the atmosphere. With respect to the inputs and cycling of Hg, the Arctic, and particularly the Arctic Ocean, has several features that set it apart from all other regions. As a consequence, although many Hg processes (e.g. photochemical reactions, methylation) can be extrapolated from studies in temperate locations, the Hg cycle within the Arctic cannot be so inferred due to its unique physiographic and climatologic aspects. It has been argued that the cryospheric, atmospheric, terrestrial and marine 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.[4] These unique features of Arctic marine and terrestrial ecosystems are discussed in greater detail below.

First, the Arctic has an exceptional seasonality going from 24 h of darkness in winter to 24 h of sunlight in summer. This seasonality is synchronous around the Arctic so that spring melt (the 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 utilised by aquatic fresh water and terrestrial vegetation that receives almost continuous sunlight. Given that various species of Hg undergo photolytic reactions and that Hg is entrained into the Arctic carbon cycle, the Hg cycle will also exhibit exceptional seasonality.

Dr Thomas A. Douglas has worked as a geochemist at the U.S. Army's Cold Regions Research and Engineering Laboratory in Fairbanks, Alaska since 2001. He uses geochemical tracers to investigate environmental processes occurring in the snow pack, on sea ice, and in watersheds containing permafrost. Recent projects have focussed on the interactions between atmospheric chemical compounds, like mercury, and the snow surface and measurements of the chemical composition of permafrost ice features. He also has ongoing projects focussed on predicting the response of permafrost to climate warming and the potential release of carbon from permafrost soils.

Dr Lisa L. Loseto is an Arctic marine ecologist with Fisheries and Oceans Canada in Winnipeg. Her research focuses on characterising beluga health, habitat use, diet and contaminant exposure in context with surrounding ecosystem drivers. Her research programs are carried out in close partnership with northern communities and co-management boards to address ecosystem health and resource management questions. She uses biomarkers such as fatty acids to define ecosystem structure and connectivity from which to construct a baseline food web and consider responses to stressors or impacts such as climate change, contaminants and industrial activity.

Dr Robie Macdonald is a geochemical oceanographer with Fisheries and Oceans Canada specialising in ocean pathways. His interests include the organic carbon cycle, the hydrological cycle, climate change and contaminant pathways in the Arctic and Pacific Oceans. He directs interdisciplinary programs to study the environmental pathways of contaminants, including their delivery, transport and elimination from aquatic systems. He determines the behaviour of contaminants in the context of natural systems bringing to bear such tools as water-mass analysis, transient and steady state tracers, stable isotope analyses (oxygen, carbon and lead), the determination of particle fluxes and sedimentation rates, multivariate statistics and modelling.

Peter Outridge is a biogeochemist working on trace metals in the environment. His particular research interests are sedimentary metal chemistry, lead isotopes as tracers, mercury in polar regions, and the impacts of climate change on environmental metal dynamics and fate. He is co-chair of the Mercury Experts Group for the Arctic Monitoring and Assessment Programme, an inter-governmental agency concerned with contaminants in the Arctic.

Dr A. Dommergue has worked as a chemist at the Lab of Glaciology in Grenoble, France. He is also a teacher at the Université Joseph Fourier – Grenoble 1 since 2006. He studies the fate of mercury in polar snowpacks but he is also involved in retrieving the past atmospheric patterns of mercury using snow and firn air archives. He is also involved in the atmospheric monitoring program (GMOS Global Mercury Observation System) and he is in charge of two monitoring sites in Antarctica and a third one in the Indian Ocean (Amsterdam Island).

Dr Alexandre Poulain's research interests lie at the intersection of biogeochemistry, molecular biology and microbiology, using combined field and lab-based approaches. He is particularly interested in unravelling complex biogeochemical transformations at the interfaces of water, ice, snow, soil and air, and understanding the role of microbes in these processes. His laboratory develops and uses molecular biology and bacterial tools to track the mobility and toxicity of contaminants in the environment and to evaluate how environmental stressors affect microbial communities. The primary goal of his work is to provide data to improve models predicting the fate and toxicity of contaminants in the environment. He has been involved in remote, Northern and Arctic research for 9 years.

Dr Marc Amyot is full professor and chair of the department of biological sciences at Université de Montréal, Montreal, Canada. He has worked on mercury cycling in Arctic aquatic systems since 1995. His laboratory has studied the biological and photochemical redox transformations of Hg in water and snow. More recently, he has conducted studies on thaw ponds as sites of Hg methylation in the Eastern Canadian Arctic, and on the importance of photodemethylation of methylmercury in these ponds. He has also investigated the trophic transfer of mercury in Arctic food webs in the changing North.

Dr Tamar Barkay, a professor at Rutgers University, NJ, since 1999, has studied the microbiology of the mercury cycle for over 35 years. Her lab uses microbiological, environmental, and molecular tools to study the mechanisms by which microbes transform mercury and to define their role in the speciation and distribution of mercury in various environments. On-going projects examine the potential contribution of mercury reduction by Arctic bacteria to the formation of elemental mercury in Arctic environments, pathways of methylmercury formation in Northern wetland ecosystems and how these are affected by global warming and mercury biogeochemistry in Yellowstone National Park.

Prof Torunn Berg has been a professor at the Norwegian University of Science and Technology since 2006. She was a Ph.D. student, scientist and senior scientist at the Norwegian Institute for Air Research (NILU) from 1988 to 2009. She is responsible for the Norwegian mercury speciation measurements at the Zeppelin station as well as flux measurements at Ny-Ålesund, Svalbard. Her interest is also related to trace metals in precipitation-air and biomonitor mosses.

The fate of mercury deposited to the Arctic

Dr John Chételat is an aquatic ecologist that studies the fate of mercury in freshwater ecosystems. His research focuses on how environmental, biological and ecological processes affect the uptake and biomagnification of mercury in aquatic food webs. Currently, Dr Chételat is a Research Scientist with Environment Canada at the National Wildlife Research Centre in Ottawa, Canada.

Dr Philippe Constant did his Ph.D. (2004–08) under the supervision of Dr Richard Villemur (INRS-Institut Armand-Frappier; INRS-IAF) and Dr Laurier Poissant (Environment Canada) studying the biogeochemical processes of mercury and molecular hydrogen in temperate and subarctic ecosystems. After a postdoctoral fellow (2008–11) in the research group of Dr Ralf Conrad (Max Plank Institute for Terrestrial Microbiology), he joined the INRS-IAF as an assistant professor. He is currently investigating the interactions between soil microorganisms scavenging climate relevant atmospheric trace gases (e.g. H_2, CO) and those catalyzing other globally important biogeochemical processes in soil, such as carbon and nitrogen turnover.

Marlene Evans is a Research Scientist at Environment Canada's National Hydrology Research Centre in Saskatoon. In northern Canada, she is investigating contaminant trends in Great Slave Lake burbot and lake trout; sea-run char at two coastal communities; and contributing to landlocked char and ringed seal studies. In the Prairie Provinces, she is investigating mercury biomagnification rates in warm-water food webs (pike) and leading the temporal chapter assessing Canada-wide trends in mercury deposition in lakes and concentrations in biota. She is contributing to studies around Alberta's oil sands, focussing on mercury trends in fish and metals and PAHs in sediments.

Christophe Ferrari has been Professor at University of Grenoble (France) since 2004 and a researcher at the Laboratoire de Glaciologie et Géophysique de l'Environnement (CNRS/UJF) since 1996 as assistant Professor. He has been since 2003 junior member of the Institut Universitaire de France (IUF). He has been a chemist working on heavy metals in the environment and especially mercury in polar and alpine regions. His main focus has been to better understand methylation pathways in pristine regions and also to better understand mercury pathways from atmospheric deposition to contamination of polar ecosystems.

Dr Nikolaus Gantner is an Ecotoxicologist currently appointed as NSERC Banting Fellow and Adjunct Assistant Professor at the Department of Geography at the University of Victoria, Victoria, BC, Canada. Nikolaus' research focuses on the transfer of contaminants through aquatic food webs. Past research included the ecological characterisation of Arctic lake food webs using stable isotopes and parallel analysis of mercury and mercury isotopes, with the goal to better understand the transfer of mercury and potential for isotope fractionation in food webs. In his ongoing research, Nikolaus incorporates knowledge from multiple disciplines to address challenging environmental issues using a collaborative approach.

Matthew S. Johnson is a Senior Lecturer at the Department of Chemistry at the University of Copenhagen. He teaches courses on environmental chemistry, physical and quantum chemistry, and scientific writing. His main research interest is atmospheric chemistry, including kinetics and spectroscopy, and stable isotopes in atmospheric trace gases. He is a co-author of more than 70 articles in peer-reviewed journals. He has invented and patented a method for efficient emissions control and improving building energy efficiency. He has worked as a researcher for Honeywell and Medtronic and has research collaborations with groups around the world, including Ford Motor Company and the Tokyo Institute of Technology.

Jane Kirk is an Environment Canada Research Scientist at the Canada Centre for Inland Waters in Burlington, Ontario, Canada. She completed her Ph.D. in Environmental Biology and Ecology in 2009 from the University of Alberta. Jane's research examines the natural biogeochemical cycling of elements in the environment and human disruptions to these cycles. Jane is currently examining the transport and fate of mercury in Canadian temperate and Arctic ecosystems to try to understand why concentrations of methyl mercury, the toxic and bioaccumulative form of mercury, are so high in freshwater fishes and marine mammals.

Dr Niels Kroer is Head of the Department of Environmental Sciences at Aarhus University, Denmark. His research is focussed on the activity, functional diversity and evolution of natural microbial communities. Specifically, his expertise includes bacterial nutrient cycling, measurements of in situ microbial activity, environmental factors affecting the rate of horizontal exchange of genetic material between bacteria, and bacterial adaptation to environmental stressors such as mercury. Recent projects have focussed on microbial communities in snow and the role of bacteria in the Arctic Hg cycle.

Dr Catherine Larose is currently working at the Microbial Environmental Genomics Group at the University of Lyon in France. Her environmental genomics (mostly metagenomics) research involves exploring the functional and structural relationships between the environmental genetic resources within Arctic snow ecosystems. High throughput techniques, such as microarrays and pyrosequencing, are used to produce data that supports relevant hypotheses. Much of her current microbial ecology research is on the perturbations of microbial communities and the adaptation of microorganisms to xenobiotic compounds such as mercury.

Dr David Lean is a retired Professor of Ecotoxicology in the Department of Biology at the University of Ottawa. His research is focussed on the effects of toxic substances on living systems including processes that control the chemical transport, fate, persistence and biological accumulation of toxic substances.

After receiving his Ph.D. in 1990 in biological oceanography Torkel Gissel Nielsen was employed at the Danish Institute for Fisheries Research. From 1991 he was employed as a marine biologist at National Environmental Research Institute (NERI), department for Marine Ecology and Microbiology, since 1994 as Senior Research Scientist and since 1999 as Research Professor. During the employment at NERI he established extensive research in Arctic biological oceanography with the overall focus on the structure of the arctic pelagic food web and climate impacts on the pelagic food web. Since 2009 he has held a professorship in environmental biological oceanography at National Institute of Aquatic Resources, Technical University of Denmark, working primarily with Arctic biological oceanography leading a group of six M.Sc. and five Ph.D. students.

Dr Laurier Poissant is a retired Senior Scientific Researcher who worked at Environment Canada from 1991 to 2012. His specialty is in investigating the atmospheric processes of contaminants and their interaction with the environment. He has performed research on air-borne mercury and its interaction with northern, aquatic, land and plant environments, on pesticide use in agricultural environments, on the impact of greenhouse gases on St Lawrence and Arctic ecosystems and on contaminant fugacity (water, snow, air, soil, vegetation).

Sigurd Rognerud is a Senior Scientist at the Norwegian Institute for Water Research (NIVA). His interest is in limnology, especially with regard to contamination of mercury, other heavy metals, and persistent organic pollutants in freshwater ecosystems. Recent projects have focussed on contamination of mercury and other metals in aquatic ecosystems around a large copper–nickel smelter in Subartic Kola Peninsula, Russia. He has also been working with changes in mercury contamination in fish populations following clear cutting of catchments and temporal trends of mercury in lake sediments and fish in Norway.

Since 1993, Prof Henrik Skov has worked as Principal Scientist at the National Environmental Research Institute, now called Department of Environmental Science, Aarhus University, Denmark. He is an atmospheric chemist and for the last 15 years he has been working with the fate of long-range transported pollution to the Arctic. He is responsible for the monitoring station, Station Nord in north-east Greenland. During the last 3 years, he has also been involved in studies of short lived climate forcers. Furthermore, he is Adjunct Professor at the Institute of Chemical Engineering and Biotechnology and Environmental Technology, University of Southern Denmark.

Professor Søren Sørensen has been the team leader of the Molecular Microbial Ecology Group at the University of Copenhagen since 2008. The main objective of the group's studies is to evaluate the extent of genetic flow within the natural communities and the responses to environmental perturbations. Molecular techniques such as Q-PCR and pyrosequencing are used to investigate resilience and resistance of community structure in soil. The group has been pioneering in the environmental application of specific whole cell biosensors and other single cell technologies with a focus on flow cytometric analysis. He has co-authored more than 200 scientific papers in international peer reviewed journals, books and presentations at international meetings.

Dr Feiyue Wang is Professor of Environmental Chemistry and Biogeochemistry at the University of Manitoba, Winnipeg, Canada. An aquatic chemist by training, Dr Wang's research interests extend from molecular-level interactions of metal ions across environmental interfaces to global-scale interactions between chemical contamination and climate change. His recent research has centred on mercury as a global contaminant and as a tracer for other contaminants, and on sea ice geochemistry. Dr Wang leads the Sea–ice Environmental Research Facility (SERF), the first experimental sea ice facility in Canada.

Dr Simon J. Wilson is Deputy Executive Secretary of the Arctic Monitoring and Assessment Programme (AMAP) Secretariat, in Oslo, Norway. Based in the Netherlands, he has a background in environmental sciences and trace metal chemistry. His work areas include AMAP data management and communication and outreach, and in particular the development of AMAP science-based information products for policy-makers. His most recent activities involve work on assessments of mercury in the Arctic, and Arctic cryospheric change, and he is currently coordinating project work under and AMAP/UNEP international collaboration to produce an updated global inventory of anthropogenic emissions of mercury to air.

Dr Christian Zdanowicz is a glaciologist with the Geological Survey of Canada in Ottawa, where he has worked since 1999. He specialises in the study of climate and atmospheric changes in polar and alpine regions through the analysis of glacier cores. Over the past decade, he has conducted extensive work on the long-range transport and deposition of atmospheric contaminants in the Canadian Arctic and the Yukon Territory. His most recent work, conducted under the auspices of the 2007–08 International Polar Year, focussed on the cycling of atmospheric mercury in glaciated catchments of Baffin Island.

Fig. 1. A location map for the Arctic Ocean Basin identifying the places mentioned in the text. The Trulove Islands, Pechora Basin, and Amituk Lake are not included.

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 extends from viruses to polar bears. The formation of sea ice during winter contributes brine to the ocean, fostering mixing in the winter polar boundary layer and convection from the Arctic haloclines. Halogen aerosols can be emitted from sea ice where open water is exposed by leads or polynyas (locations where upwelling water or dynamic processes maintain openings in sea ice). When new sea ice (nilas) forms, brine and frost flowers fractionate halogens and other chemical compounds, depositing them onto the sea ice surface.[5–7] These sea ice processes, together with the seasonality of sunlight, are key factors underpinning Arctic Mercury Depletion Events (AMDEs), which are unique to polar regions. The most visible change in the Arctic over the past 30 years is the loss of multi-year sea ice from the Arctic Ocean and its replacement by seasonal sea ice.[8–11] This transition toward younger, more saline ice will have wide-ranging but poorly understood effects on the biogeochemical cycling of Hg.

Third, the Arctic Ocean is a semi-enclosed sea that 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 simplifies the construction of material budgets. In terms of atmospheric connections, the Arctic receives and mixes air masses and their associated contaminants from all of the major northern hemisphere continents (Europe, Asia, North America). Some of these air masses are returned back to temperate latitudes after cycling through the Arctic.

Fourth, the Arctic Ocean receives an exceptional input of freshwater runoff that physically links the land and sea.[12] Although the Arctic Ocean comprises ~4% of the world's oceans by area it receives 11% of global runoff. Much of this runoff is from locations underlain by permafrost that is degrading in response to climate warming.[13] A consequence of the high runoff is that the upper Arctic Ocean is strongly stratified and this 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 it from deeper water in the basins, which are supplied 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, faecal pellets and aggregates within the Arctic Ocean) and partly by imported regenerated products, especially those contained within Pacific water entering through the Bering Strait and passing over the Chukchi Shelf.

Fifth, the Arctic generally has a low sloping topography. There are some exceptions (Baffin Island, Labrador, Greenland) but for the most part, the land area consists of broad, low-lying plains. The Arctic Ocean contains the largest proportion of continental shelves (fully 50 % of the ocean's 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.[14] Flaw leads form when winds or currents open the ice pack and expose ocean water. 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 and this leads to a series of redox reactions that 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 (deep sea) area of the Arctic Ocean has an exceptionally low particulate export ('biological pump') because it is far from terrestrial sources and is oligotrophic. This 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. In addition, Hg can be recycled and revolatilised from the ocean to the atmosphere. All of these processes will be described in greater detail in this review.

The fate of net deposited atmospheric mercury in environmental media

Geochemical transformations of deposited mercury

The net deposition of atmospheric Hg to the Arctic is the product of multiple processes that can be associated either with deposition or loss of Hg. Inputs include 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 fresh water surfaces (i.e. wet or dry deposition not associated with AMDEs). Outputs are gaseous Hg^0 re-emitted from snow and ice surfaces due to microbial or photochemical reduction of Hg^{II} and the evasion of DGM (which includes all readily volatilised forms of Hg but is dominated by Hg^0) from freshwater or seawater.

In the Arctic, snow melt is a major aspect of the seasonal transition from winter to spring–summer. The inorganic Hg^{II} species present in snow melt are dominated by uncharged or negatively charged complexes with OH^-, Cl^- and Br^-, with an unquantified but possibly significant fraction of the Hg^{II} likely bound to organic matter.[15] A small increase in the MeHg concentration in the snowpack has been shown to occur just before snowmelt,[16,17] but it is not known how much of this MeHg is produced in the snowpack compared with what is delivered by falling snow. The effect of this net deposited Hg from snow melt on THg and MeHg concentrations in receiving waters (rivers, lakes, oceans) is the subject of ongoing research. Recent studies[18–20] focussed 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 freshwater, however, significant increases in THg fluxes to sediments during the 20th century indicate that deposited atmospheric Hg has had an effect on Hg levels in lake sediments and, by extension, on freshwater Hg budgets in the Arctic.[21–23] Results from a recent study of marine sediments from Hudson Bay indicate THg concentrations increased during the 20th century.[24]

Deposited Hg either enters aquatic environments (marine systems, melt ponds on sea ice, lakes or rivers) or remains in soils or the multi-year snow and ice found on glaciers and ice sheets (Fig. 2). 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[25–27] and melt ponds on sea ice.[28] DGM concentrations measured along an extensive transect crossing the North American boundary of the Arctic Ocean and the interior ocean (Fig. 3),[29] 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 the sea ice cover prevents evasion of the Hg^0 back into the atmosphere. Photo-demethylation likewise provides the means to convert MeHg into DGM with the sea ice cover modulating radiation and evasion.[30] Mercury photo-reduction and evasion from terrestrial and marine aquatic systems also occurs at lower latitudes where the air–sea exchange of Hg in aquatic systems has been explored in detail.[3,31]

The production of DGM in Arctic coastal streams and ponds, estuaries and marine waters is strongly affected by chloride, with lower DGM formation observed at higher salinities.[32] Halogens in general, and chloride ions in particular, have been shown to enhance Hg^0 photooxidation to Hg^{II} and hence hamper evasion.[31,33] Rivers provide a significant source of THg, including dissolved and particulate forms, to Arctic coasts.[34–37] 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 (Fig. 4).[29] It was proposed[29] that the high levels of DGM might either be supplied directly by the Mackenzie River or may be a sign of enhanced DGM production facilitated by riverine dissolved organic carbon (DOC).[38] Clearly, more seasonal measurements are required to determine the annual balance between supply of Hg to coastal regions, loss of Hg through evasion, burial or advection and entry of Hg into shelf and marine food webs (Fig. 5). Furthermore, such measurements need to be made in the context of the organic carbon cycle to provide a better understanding of the mechanisms involved in conversions between Hg forms. The suppression of Hg reduction due to chloride is also partly counterbalanced by the presence of particles (possibly particulate iron oxides), which favour the conversion of oxidised Hg into its elemental form, although the exact mechanisms have not been elucidated.[32]

There are three other important mechanisms by which net deposited Hg may be lost from 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 $\sim$2500 km^3 $year^{-1}$, which, if a 3-m layer of sea ice is assumed, implies the export of $\sim$0.8 $\times$ 10^6 km^2 $year^{-1}$ of snow-laden ice
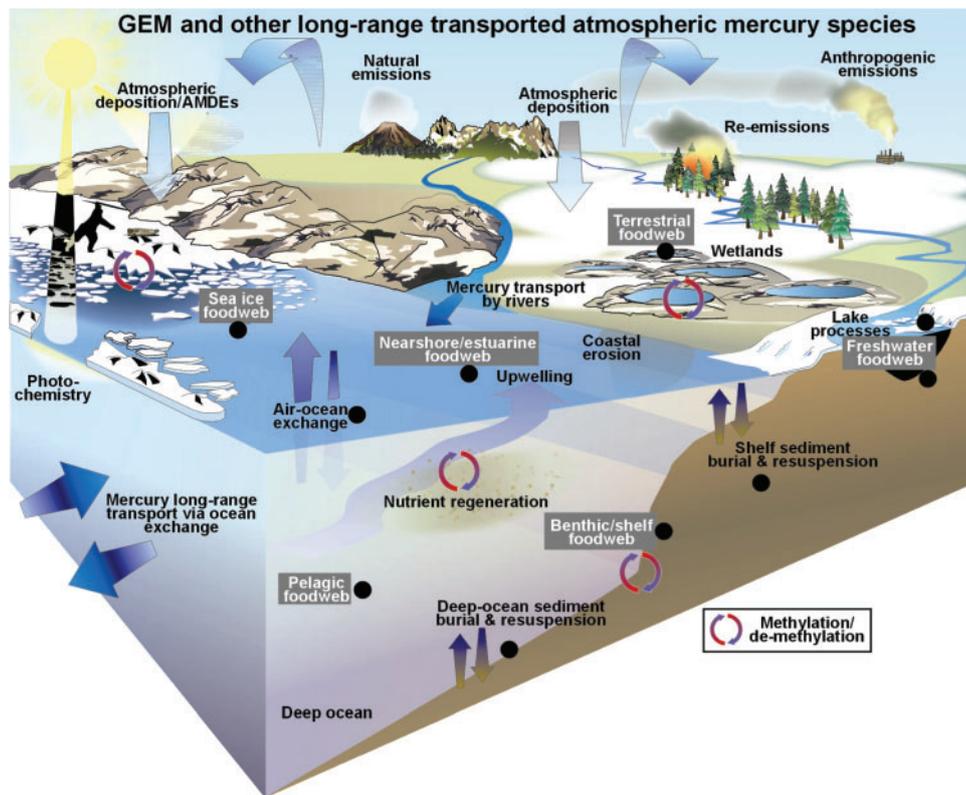
Fig. 2. A schematic diagram of the Hg sources and food web processes discussed in this paper. Black circles denote specific sources and food webs discussed in this paper. See text for definitions of acronyms and abbreviations. Adapted with permission.[6]
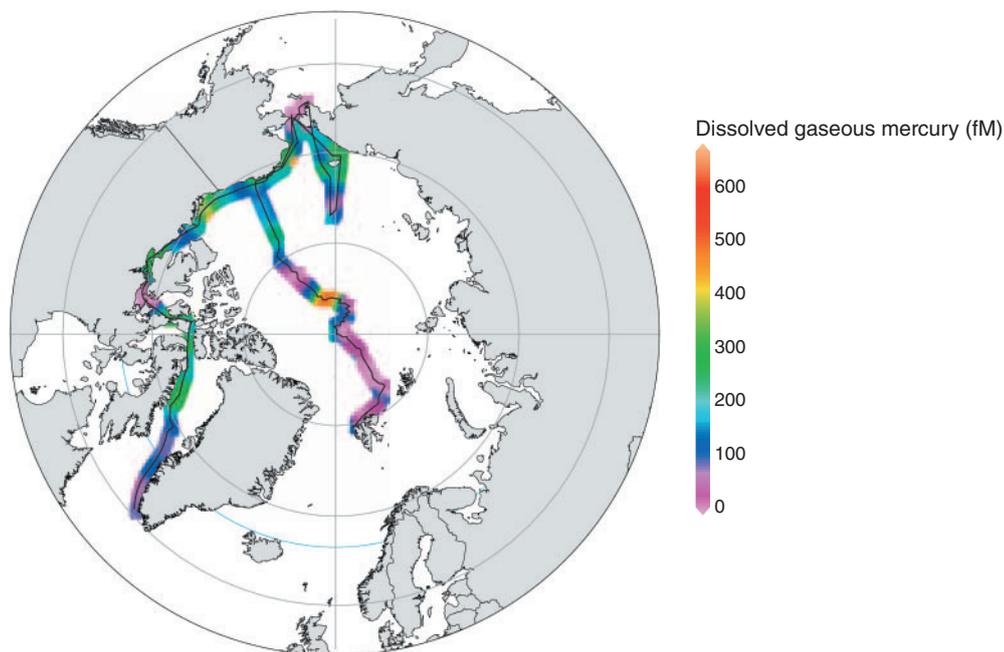
Fig. 3. Dissolved gaseous mercury (DGM) in surface water along the Beringia 2005 cruise track showing predominant supersaturation in the water, with generally higher DGM concentrations found under locations covered with sea ice. Modified from a paper reporting measurements collected along a transect of the Canadian Arctic Archipelago and Arctic Ocean.[29]

and its burden of deposited Hg. The time required for sea ice to leave the Arctic Ocean varies from 1 to 6 years depending on where it has been produced.[39] This sets an upper limit of 6 years for net Hg deposition to be held on or within sea ice and associated snow. Seasonal melting almost certainly reduces the ice residence time, placing Hg contained in snow or ice into the ocean. Mass balance calculations indicate that sea ice export was a minor loss process, amounting to only ~7 t year^{-1},

because of very low ice Hg concentrations.[36] Seawater in the upper Arctic Ocean has residence times varying from one to 3 years on the shelves, ~10 years in the polar mixed layer, and ~30 years in halocline waters beneath the mixed layer.[39,40] Deeper in the ocean, the residence times are up to several centuries based on ^{14}C and other tracers.[41,42] Again, these ocean circulation rates set the time scale over which deposited Hg can be held in the various ocean reservoirs within the Arctic.

Seawater export has been found to account for 68 t year^{-1} (range of estimates 22 to 113 t year^{-1}) of THg from the Arctic Ocean, or approximately one-third of total losses of Hg annually.[36] Finally, Hg may be scavenged by algae- and
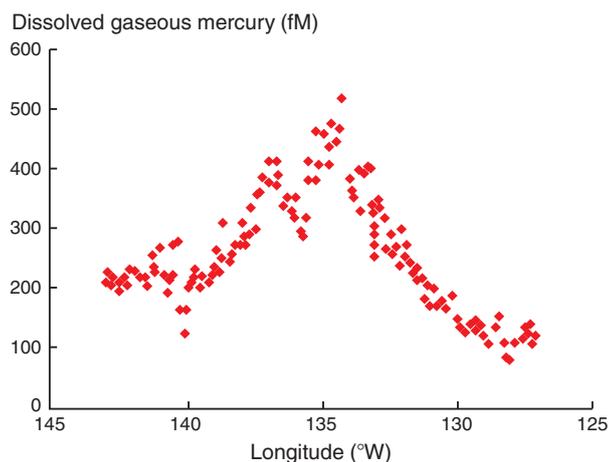

Fig. 4. Dissolved gaseous mercury (DGM) in surface water along the Beringia 2005 cruise track as it crossed the Mackenzie River plume. The high DGM concentrations in plume waters may indicate direct supply from the river or enhanced production of DGM facilitated by riverine dissolved organic carbon (DOC). Modified from a paper reporting measurements collected along a transect of the Canadian Arctic Archipelago and Arctic Ocean.[29]

microbe-derived particulate organic matter (POM) and exported to the deep ocean.[43,44] Globally, the vertical flux of Hg into the deep oceans appears to account for almost half of the contaminant Hg deposited into the ocean.[45] For the Arctic, first-order estimates suggest that over half (108 t year^{-1}, range 13 to 200 t year^{-1}) of the THg losses from the Arctic Ocean occur via this pathway.[36] This process may not be important in the interior ocean due to the low inherent particle fluxes,[46] and it may be that lateral transport of sediment from the margins to the deep interior is an important pathway.[47] 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. 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.[22] Thus the integration of this atmospheric Hg into ecosystem soils and vegetation may be limited. Erosion of thawed soils during summer, a process that seems to be accelerated by climate change, provides an important source of inorganic Hg to lakes in Alaska[21] and possibly elsewhere in the Arctic.[48,49] Soil loadings of Hg to Alaskan lakes were found to be associated primarily with silt[21] and were greater in lakes with higher watershed/lake area ratios.[50,51] Slumping, thermokarst activity and soil erosion also have the potential to alter lacustrine Hg cycles by reducing the penetration of solar radiation and consequent photochemistry, altering organic carbon cycling and providing the means to scavenge and bury Hg in lake sediments.

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. This can occur through photochemical or microbially mediated
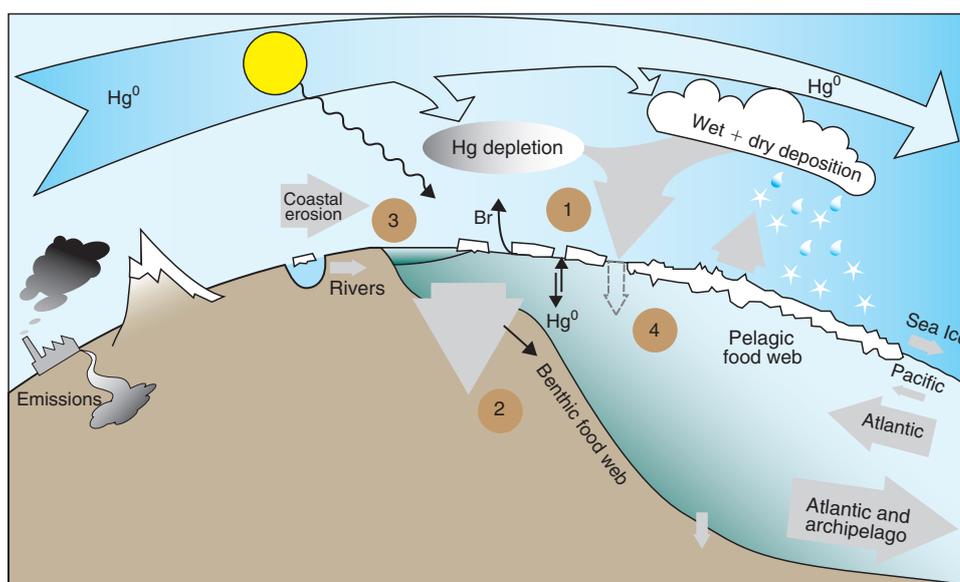
Fig. 5. Potential inorganic Hg input pathways underpinning Hg methylation and bio-uptake in distinct Arctic marine food webs. Circled numbers represent: (1) atmospheric deposition to the ocean surface; (2) sediment methylation processes; (3) riverine and terrestrial sources and (4) ocean water column processes. These sites may represent: (1) the route of entry for sea ice food webs; (2) benthic food webs; (3) shelf or estuarine food webs and (4) the pelagic food web. Reproduced from Macdonald and Loseto.[4]

reduction of Hg^{II}.[52–54] Arctic lakes generally contain supersaturated surface water concentrations of DGM.[55,56] The latter studies reported average DGM concentrations of the order of 200 fM (40 pg L^{-1}), representing ~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[56] but dry deposition of Hg species was not included in this budget. 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.[57–59] The relative importance of photochemical $v.$ biological processes in controlling the reduction rate of Hg^{II} in Arctic freshwaters remains to be elucidated. The rate is controlled by: the intensity of solar radiation, particularly the UV-B (280–320 nm) and UV-A (320–400 nm) wavebands, and the concentration of available photo-reducible Hg^{II} complexes.[55] A model for Hg^0 with depth in the water column incorporating photoreduction, photooxidation, bioreduction and biooxidation was recently developed.[60] The model results suggest that because of: (i) light energy attenuation with depth and (ii) the presence of chloride, biologically mediated processes are likely to dominate the production of Hg^0. This research focussed on the mercury resistance *mer*-operon, but there are likely other processes involved such as phytoplankton blooms as was initially postulated.[52] DOC also plays an important role in controlling 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.[61,62] Bioavailability and bioaccumulation processes are major controls on Hg retention and they are addressed in detail below. High Arctic lakes have extremely low biological production,[63,64] 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 characterisation of the sedimented organic matter.[62,65,66] 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,[67] occurs at low concentrations in nearshore and deep-water sediments of High Arctic lakes (typically less than 10 % dry weight (DW), total organic carbon).[23,67,68] Spatial variations in sediment concentrations of THg and MeHg are in general strongly correlated with organic carbon content.[62,68,69] 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 focussing of fine-grained inorganic soil particles.[51]

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

Half to three-quarters of the annual surface water runoff in polar regions is from spring snowmelt.[70,71] 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 marine and terrestrial ecosystems. The spring melt comprises the net Hg contribution from snowpacks after AMDE deposition and photochemical re-emission have occurred.

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[72–75] and dissolved and particulate Hg.[76] In Amituk Lake in the Canadian High Arctic, snowmelt delivered the most THg during spring in June and early July[22,77] but 59 % of the THg delivered to Amituk Lake during the snowmelt period was directly discharged through lake outflow because of the limited mixing between surface and underlying water.[22]

In Arctic regions, melt water concentrations of MeHg and THg were found to be elevated above full-column snowpack values at the onset of snow melt in some locations,[20,77–79] but not all.[28] 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^{-1} with an average of ~3 ng L^{-1}.[36] In a recent study at Ny-Ålesund, Svalbard, most of the Hg^{II} remaining in the snowpack before melt was rapidly expelled from snow matrixes, leading to a brief pulse of THg-enriched melt water.[20] Streams receiving snowpack melt runoff (averaging 3.5 ± 1.9 ng Hg L^{-1}; $n = 13$), and runoff waters originating from the Austre Lovénbreen glacier (2.2 ± 1.1 ng of Hg L^{-1}; $n = 7$), contributed 1.5 to 3.6 kg $year^{-1}$ 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 before as well as during the season's first AMDEs but subsequent concentrations during the melt period were at pre-AMDE levels.[80] The authors suggested that Hg pooled on surface snow during polar night was reduced and re-emitted from the snow pack in the spring. At Kuujjuarapik, Quebec, on Hudson Bay, a Hg^0 pulse in snowpack interstitial air was found to coincide with the initiation of snowmelt.[81] 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^{-1} of THg in snow, and from below detection to 5.1 ng L^{-1} in meltwater, and were comparable with surface snow measurements at other remote Arctic locations before polar spring.[28] 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.

Microbial carbon processing and mercury in the Arctic

The fate of Hg deposited to Arctic ecosystems depends not only on snow photochemistry[81,82] and fresh water or ocean water physical and chemical characteristics, but also on microbial processes.[60] There is good evidence that microbes are metabolically active at subzero temperatures in snow[54,83,84] and sea ice.[85] 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). A recent study found that up to 30 % of the culturable bacteria in snow were Hg resistant, and hence potential reducers of Hg^{II} to Hg^0, whereas the mercury resistance phenotype was observed in less than 2 % of the bacteria isolated from fresh water and brine.[54] The involvement of bacteria in the Hg cycle in the Arctic, however, has been understudied. It has recently been discovered that remineralisation of organic carbon can also generate MeHg within the water column, particularly at locations indicated by nutrient maxima,[44,86] including cold, ice-covered seas.[87]

In temperate environments some bacteria carry genes that make them resistant to Hg^{II} and MeHg toxicity because they convert these Hg compounds into the volatile and less toxic Hg^0.[88] Algae are also capable of catalysing Hg^0 production[43,58,59,89] and algae have been found in Arctic snow.[90] However, their contribution to the Hg redox cycle in snow is unknown. In a recent study it was suggested that up to 2 % of the total reduction of Hg^{II} in snow may be biological and that bacterial reduction is controlled by snow depth.[90] Sulfate-reducing bacteria are able to methylate Hg^{II} species under anaerobic conditions in Arctic sediments and wetlands.[77,91] Therefore, bacteria in Arctic snow, ice and aquatic (marine and fresh water) environments may play a critical role in the conversion of deposited Hg into MeHg or Hg^0 depending on several environmental factors including the level of oxygen present, the redox conditions and the presence (or absence) of sunlight. Although a correlation between heterotophic bacteria enumeration and MeHg concentrations in snow has been observed in subarctic ecosystems,[16] there is currently no report on the isolation of Hg-methylating bacteria from the cryosphere.

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 originates from autochthonous production (as bacterial and algal particulate detritus, exudates or DOC) and allochthonous sources (export from tundra soils, sedges and peat), helps regulate Hg in Arctic aquatic systems as it does at temperate latitudes. One of the dominant mechanisms by which carbon controls the ultimate fate of Hg is through absorption of light in the water column.[2,60,92–94] C-DOM (coloured dissolved organic matter), a powerful absorber of UV radiation, provides a particularly important limit 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.[56] Labile carbon also plays what is arguably its most crucial role of creating the circumstances to transform Hg^{II} to MeHg. The methylation process has long been known to occur in sub-oxic environments, like sediments or stagnant basins, where inorganic Hg is converted into MeHg by sulfate-reducing bacteria metabolising organic matter.[95,96] There are other interactions between the organic carbon and Hg cycles that are not as well understood. For example, DOM may provide stabilising ligands to maintain Hg in dissolved form,[97] and C-DOM absorbs UV radiation and thus provides an important control on photo-reduction and other photo-initiated processes in surface water.[15,56]

In saline waters, organic compounds produced by algae are able to promote oxidation of Hg^0 even under dark conditions.[15] Coastal environments are colonised by Hg-resistant bacteria potentially able to reduce Hg. Simple box modelling suggests that this bacterial reduction could be significant in ocean waters, although bacterial Hg reduction rates need to be directly quantified.[15]

In other oceans, it has recently been demonstrated that MeHg can be produced during the remineralisation of algal detritus in the water column.[44,86,98,99] The vertical transport of MeHg associated with particulate flux from surface waters was found to be relatively unimportant compared with the in situ production of MeHg that occurred in association with nutrient maxima at subsurface water depths.[86] Little is known about this process in the Arctic; however, the Arctic Ocean does possess pervasive strong nutrient maxima below the polar mixed layer.[100] MeHg, both in terms of concentration and as a percentage of THg, has been found to be highest in the middle and bottom depths of Hudson Bay and in waters of the Canadian Arctic Archipelago,[101] This suggests the in situ production of MeHg previously reported[44,86,99] may also occur in subsurface Arctic seawaters.

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.[102] However, even in the global environment, our understanding of marine Hg biogeochemistry is limited by under-sampling and under-study.[2] It may be assumed that the basic components of the marine Hg cycle as understood from temperate ocean studies[3,45,69,103] can be applied to the Arctic Ocean, with the caveat that the rates and relative importance of many processes will differ. Hg biogeochemistry in the Arctic Ocean appears to exhibit significant differences compared to temperate ocean basins.[2,45,104] 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 all contribute to a distinctly different Hg cycle in Arctic seas.[25,29,30]

The ability of Hg to transfer between environmental media and to transform from one chemical species to another (Fig. 6) makes the marine chemistry of this element a challenging subject. In the global ocean, THg is usually found in the range of 0.02 to 0.5 ng L^{-1} [1,3,44,104] with Arctic seas or out flowing water from the Arctic possibly at the low end of this range.[1,19,101] A recent paper reported an estimate that the top 200 m of the Arctic Ocean had a THg inventory of 620 to 945 t (best estimate 945 t), which is far larger than estimated annual fluxes into or out of the surface Arctic Ocean, and this implies Hg residence times of 5 to 10 years.[36] 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.[2,3,29,105] 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,[3,36] and through processes that produce Hg^{II} from Hg^0 or MeHg within the ocean.[99] 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 (Figs 3, 6).

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.[3,106,107] The reduction of Hg^{II} can be mediated by photons or microbes.[2] 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,[108] the microbial reduction of Hg^{II} to Hg^0 is likely to play a dominant role in the Arctic Ocean.[32] However, the exact nature of this process and the microbial organisms involved (bacteria, archaea or algae) remain to be determined. Recent ocean transect data show 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.[26,29] A surface-water DGM range was reported[29] of 0.002 to 0.14 ng L^{-1} and an average of ~0.044 ng L^{-1}, which is well above the value that would be in equilibrium with the Arctic's atmosphere (~0.008 ng L^{-1}). The high average concentration implies an
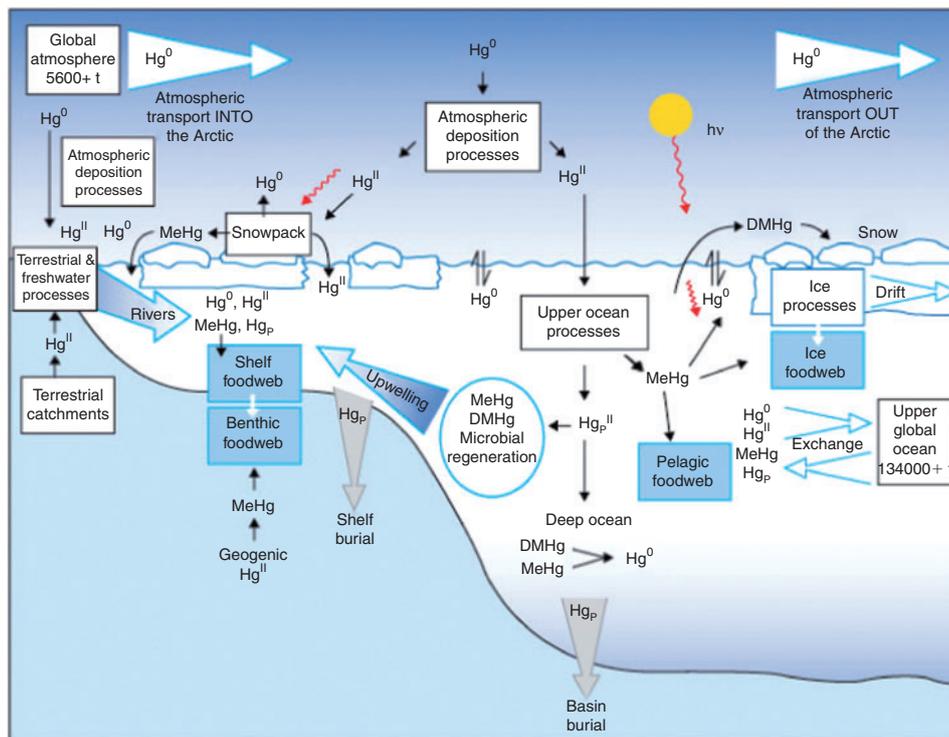
Fig. 6. The mercury cycle in the Arctic Ocean. Rectangular boxes show system processes, like food webs or atmospheric deposition chemistry, that have detailed schematic diagrams and discussion presented in the text. Large shaded arrows refer to atmospheric or oceanic transport processes that exchange 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. See text for definitions of acronyms and abbreviations used.

inventory of $\sim$6 t Hg^0 in the summer stratified surface layer ($\sim$top 10 m) of the Arctic Ocean and $\sim$30 t in the polar mixed layer ($\sim$top 50 m). Hg profiles with complete speciation are required, but these data suggest that DGM contributes a considerable fraction of the THg inventory in the Arctic Ocean, estimated at 945 t in the upper 200 m.[36]

For the global ocean, the evasion of Hg^0, estimated at 2800 t $year^{-1}$,[3] 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 $\sim$120 t of Hg would be transferred from the Arctic Ocean to the atmosphere annually. However, Arctic Hg^0 evasion should be comparatively lower than that of oceans from lower latitudes because the Henry's Law constant is lower at lower temperatures. In addition, 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 $\sim$50 % in summer, based on seasonal sea ice extent. Thus, the rate of evasion currently may be as little as 3 to 12 t $year^{-1}$.[36] Offsetting the negative effect of ice cover, however, is the supersaturation of Hg^0, from which an average summertime Hg^0 evasion of 60 ng m^{-2} day^{-1} (12.5 pmol m^{-2} h^{-1}) was estimated during a transect of the Canadian Arctic Archipelago and the Arctic Ocean.[29] The maximum evasion was calculated as high as 2300 ng m^{-2} day^{-1}. These observations suggest that Hg^0 is a dynamic component of the 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 (effective pressure) differential between air and water.

However, this fugacity difference may be less of a factor than Hg deposition, winds or redox conditions. 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 $\sim$1.6 ng m^{-3} after the onset of AMDEs in spring and summer.[26,82,109] 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} biogeochemistry shown in Fig. 6 is that divalent Hg interacts with DOC and chloride ions to form complexes[2] where rivers, coastal snow and sea ice meet. Complexes are likely to provide *the* important reservoir of Hg^{II} in the upper ocean, especially where DOC concentrations are high. A large component of Hg^{II} can be held in the colloidal fraction alone (10 to 50 %),[3] 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 Hg globally in the deep ocean.[3,45,110,111] In the coastal Arctic, where there is a plentiful supply of organic and inorganic particulates from rivers, coastal erosion and primary production,[112] the entrainment by particles and burial of Hg may be particularly important,[36] as has been reported from the temperate oceans.[45,107] Particle fluxes and burial processes are likely less important in the central (deep) Arctic Ocean than along the coastal zone or at shallow locations. Although all of these processes and reactions have the potential to play crucial roles in the marine 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.[29,34,35,37,113] Even though rivers collectively supply over $3500\,km^3\,year^{-1}$ of freshwater and $230 \times 10^6\,t$ of particulates to the Arctic Ocean,[36] Hg fluxes are poorly characterised for most of the inflow and thus represent a major uncertainty in the budget for the Arctic Ocean. Hg concentrations have not been measured in many of the major rivers and studies lack the appropriate temporal resolution to capture the extreme 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,[2] or simply produce a stratified surface layer effective at evading its Hg^0.[29] In contrast, the organic carbon associated with rivers may support the production of MeHg in estuarine and coastal sediments, which is then available for uptake into food webs. There are no Arctic data presently available to indicate which processes are most important.

As illustrated in Fig. 6, solar radiation, atmospheric chemical processes, and the organic carbon cycle are key controlling variables in the Arctic Ocean's Hg cycle. The Arctic has an annual light cycle with extremes of 24 h of darkness and 24 h of light, a snow and ice cover that control the penetration of radiation into water and riverine C-DOM, which strongly absorbs UV radiation. Variations in these parameters can alter the balance between the loss of Hg by burial, the reduction to Hg^0 and its 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.[46,114] Therefore, the rate of removal of particulate Hg from the surface, an apparently important component of the global ocean Hg cycle,[45] 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.[36]

Finally, and perhaps most importantly, Hg^{II} undergoes a complex set of reactions leading to DMHg and MeHg production. These processes (Fig. 6) are poorly quantified in the Arctic, but recent work has shown them to be potentially important in polar surface waters.[18,19,99,101] 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 melt water ponds in coastal regions.[18,19] By examining the predominant form of Hg as it enters the Arctic and then passes through aquatic systems (marine and fresh water) to eventually accumulate 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 oxidised to Hg^{II} and second, Hg^{II} must be methylated and accumulated in top predators (Fig. 7a).

It has long been hypothesised that Hg can be methylated in oxic environments, but only recently has this been demonstrated in the water column of temperate oceans[44,86] and the Arctic Ocean.[99] Methylation in oxic environments may occur in anoxic or sub-oxic microzones or in microzones with gradients in redox conditions. Methylation of Hg^{II} occurs during detrital regeneration and leads to elevated MeHg associated with oceanic nutrient maxima. This
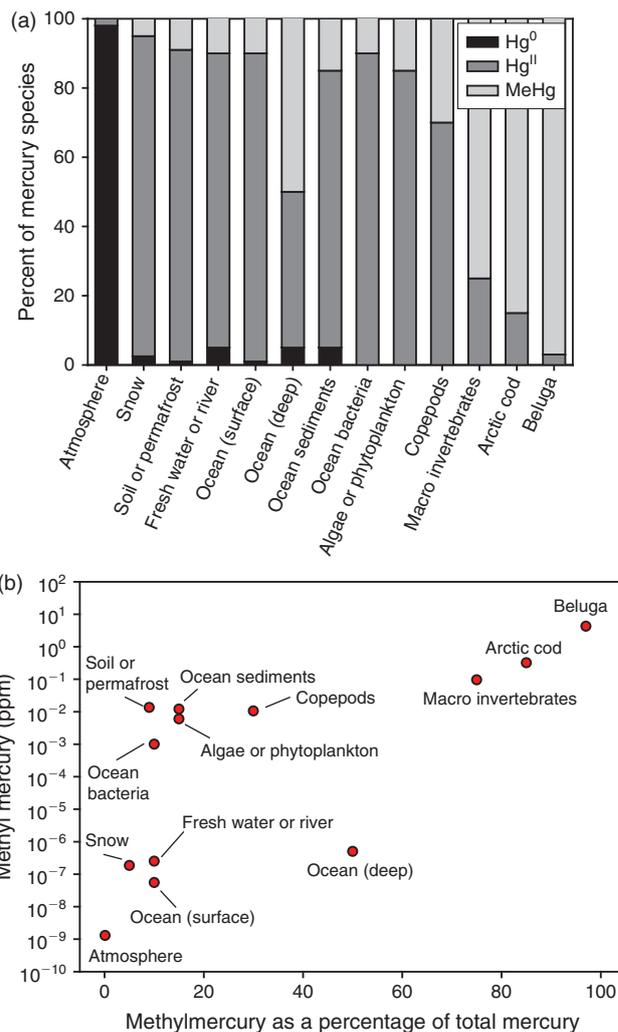
Fig. 7. (a) Changing proportions of different mercury species from the atmosphere to terrestrial and aquatic (marine and fresh water) media and food chains. To become bioavailable, the predominant form of Hg transported in the atmosphere, Hg^0, must undergo oxidation to Hg^{II} and then methylation to MeHg. (b) Methylmercury bioconcentrates and biomagnifies. In inorganic media, MeHg tends to represent a minor proportion of the total mercury ($\sim$20% or less), but progressively increases upward through aquatic food webs to become the predominant form of Hg at trophic levels 2 and above.

MeHg, which is produced from the abiotic Hg^{II} reservoir in the ocean rather than the particulate Hg carried by detritus,[86] could enter food webs either through upwelling[115] or through vertical migration of zooplankton.[116] Anoxic environments favourable to sulfate reduction also harbor microbes that can methylate Hg^{II}.[2] In particular, environments that favour 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 favoured are generally restricted to sediments in the Arctic. Within the Arctic Ocean's sediments, there is a wide range of 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.[117,118] Methylating processes are complicated by interactions between Hg and sulfide[2] 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.[2]

Transfer of mercury from the abiotic environment into food webs and 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 key to understanding the food web dynamics of the Hg cycle. It is generally acknowledged that MeHg is bioamplified more than inorganic Hg^{II}, which is most abundant in the abiotic environment.[2,119] Although both inorganic Hg 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.[69,120] Therefore, a critical question with respect to the biological uptake of Hg into Arctic food webs concerns the mechanisms and locations where inorganic Hg^{II} is predominantly transformed into MeHg and then assimilated into the lower levels of Arctic food webs.

Bioavailability of mercury

The concept of Hg 'bioavailability' includes the availability of inorganic Hg species to microbial populations responsible for Hg methylation and the transfer of MeHg in prey items to predators within food webs. 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). For our definition of 'bioavailability', we assume 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 by prey–predator interactions into higher trophic level organisms. Taken together, these processes lead to MeHg concentrations that span ∼10 orders of magnitude, for example, going from atmosphere to beluga (*Delphinapterus leucas*), and a shift from MeHg as a minor component of THg in air, snow or water to the predominant form in marine species at trophic levels 2 and above (Fig. 7b).

Bioavailability of Hg, in general, is likely to be controlled by many environmental and physiological factors. These include the chemical form and biochemical reactivity of environmental Hg, the activity of microbial communities, and the balance between dissolved *v.* particulate forms of Hg. The nature and quantities of ligands present define the extent and magnitude of microbial activities and surfaces in the environment and, as such, they control Hg speciation in solution, electron acceptors and redox conditions. Approximately four times as much MeHg is assimilated by phytoplankton compared with inorganic Hg.[119] Microbes do not represent a single type of biochemical binding entity for Hg, but are in effect variable ligands both taxonomically and physiologically because of their differing metabolisms and physical structures. The structure and function of microbial communities 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 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.[121–123] Uptake of MeHg and inorganic Hg by diatoms is influenced by Hg speciation, especially complexation with DOC and Cl$^-$.[124] 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.

In terms of its ability to sequester or transform Hg, not all organic carbon is equal. Carbon in aquatic systems comes from external and internal sources – terrigenous plants and soil carbon, and algal production within the water body.[112] These two sources of carbon exhibit a range of ages, chemical composition and lability,[62,125–129] which display different capacities to bind Hg.[130] In Antarctic lakes, algal and cyanobacterial planktonic and benthic mats, along with terrestrial mosses in watersheds, are the main sinks for Hg in summer meltwater.[131] The implication that fresh algal organic matter provides an important Hg complexation mechanism in Arctic freshwater 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.[62,65,66]

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).[132] The other is active transport of Hg species (e.g. by the amino acid transport system).[133] It was recently shown that the addition of low levels of cysteine significantly increased Hg^{II} methylation by a known Hg methylator.[134,135]

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.[136,137] MeHg may initially enter food webs either through consumption by heterotrophic feeders 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.[119]

Because of the unique adaptations of microbial populations to cold environments,[138] 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 differs substantially from those in other environments. Bacterial Hg uptake and methylation rates are poorly characterised 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 of up to 3 ng L^{-1} were found in water of shallow ponds on Ellesmere Island, probably due to relatively warm water temperatures compared to the Arctic Ocean or deeper lakes and abundant organic matter driving higher bacterial activity.[18] This demonstrates the Hg accumulation and methylation potential of Arctic microbial communities under favourable conditions.

Controls on arctic food chain mercury accumulation by methylation–demethylation processes

Methylmercury production pathways

A recent review identified the main biochemical Hg methylation pathways,[139] which are for the most part linked to microbiological activity. 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 marine and fresh water 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[140–142] and methanogens[143] in these anoxic environments. MeHg can also be produced during detrital remineralisation in oxic marine waters, associated with mid-depth nutrient maxima and oxygen utilisation.[44,86] Results from recent incubation experiments using Arctic seawater indicate that methylation of inorganic mercury in the water column accounts for almost half (47 %) of the monomethylmercury present in the Arctic Ocean.[99]

A pervasive nutrient maximum is associated with haloclines in the Arctic Ocean, especially in the Canada Basin. However, it is not known whether Arctic haloclines contain important reservoirs of MeHg or whether this Hg enters food webs. It is striking that high MeHg concentrations occur in lower levels of the food web in Canada Basin,[116] and in higher trophic level animals like the Beaufort beluga population, which ranges into the Canada Basin[144] relative to other Arctic marine food webs (e.g. the eastern Canadian Arctic).[145,146]

Another possible source of MeHg is the atmospheric photo-degradation of volatile DMHg evaded from seawater and lakes.[16,18,19,147,148] Production of DMHg by pure cultures of Antarctic marine bacteria,[149] and by macroalgae isolated from an Arctic fjord,[150] has been demonstrated. Results from recent work on Arctic seawater[101] and many studies in the Atlantic and Pacific Oceans[43,86,106] suggest that DMHg can also be produced in deep marine waters. Supersaturation of Arctic surface seawater over a wide area by DMHg[19,29] and the presence of elevated GEM in the marine boundary layer in areas rich in sea ice[26] 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} through abiotic processes,[151] by microbial activity, or by aqueous phase methylation in the atmosphere[152] may occur. These processes have been investigated in temperate locations[153] but their significance in the Arctic 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. A study of Arctic wetland soils showed that MeHg concentrations increased 100-fold after thawing and incubating at typical Arctic summer temperatures (4 to 8 °C).[91] Although 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.[91] This suggested either a methodological issue or that sulfate-reducers are in fact not the dominant microbial methylators in Arctic wetlands. Results from a study of the biogeochemical cycling of MeHg in lakes and tundra watersheds of Alaska (68°N) showed that the principal source of MeHg was in situ benthic production (80 to 91 % of total inputs), and that contributions from the tundra watershed snowpack and soils were modest.[51] A study of whether wet sedge meadow soils on the Trulove lowlands (75°N), typical of Arctic landscapes, act as sources or sinks for MeHg found significant methylation occurred after inorganic Hg^{II} was added to the soil.[154] This finding, together with the conclusion of the aforementioned study in Alaska[51] that benthic MeHg production in Alaskan lake sediments was inorganic Hg-limited, suggests that there is potential for a 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 the Alaskan lake and tundra watershed study,[51] results from investigations at Kuujjuarapik (55°N) on Hudson Bay suggest that tundra ecosystems there may represent a significant source of MeHg to aquatic systems.[16] Snow samples collected at three different stations on the Great Whale River and in the tundra were characterised 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^{-1}, significantly higher than what has been reported for typical Arctic snow.[155] A 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. A model was recently presented[17] for the aerobic methylation of BioHg (the fraction of the newly deposited Hg that is available to bacteria) in the snowpack involving the sulfur cycle based on correlations between MeHg, BioHg and methanesulfonate concentrations. However, further investigations are needed to estimate the relative contributions by in situ production and by atmospheric deposition to MeHg levels in snow.

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.[156] Similarly, biological decomposition of MeHg by mercury resistant bacteria may potentially occur[157] although no data are available on its significance. In a study of four Alaskan lakes the annual loss of MeHg to photo-decomposition, although limited to a 100-day ice-free season, accounted for 66 to 88 % of total MeHg inputs annually.[50] Linked as it is to ice cover and radiation penetration into the ocean, photo-demethylation appears to be an important, large-scale process likely to be affected by ice cover. Sea ice cover impedes the photo-decomposition of MeHg in Arctic marine waters for much of the year, and recent evidence from Hg stable isotopes in Alaskan seabird eggs suggests that climate-driven ice reduction during the 21st century will increase the breakdown of MeHg in surface seawater.[30] In particular the authors inferred from Hg isotope analyses that recent declines in sea ice cover in the Bering Sea may have led to lower exposure of the ecosystem to MeHg simply due to increased photolysis in the upper ocean. 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.[16] Night-time demethylation reactions involving nitrate radicals were proposed as the mechanism but this needs to be confirmed.

How trophic processes influence mercury levels in higher order animals

Introduction

Mercury concentrations in higher trophic level organisms are controlled by 'bottom-up' or 'top-down' processes
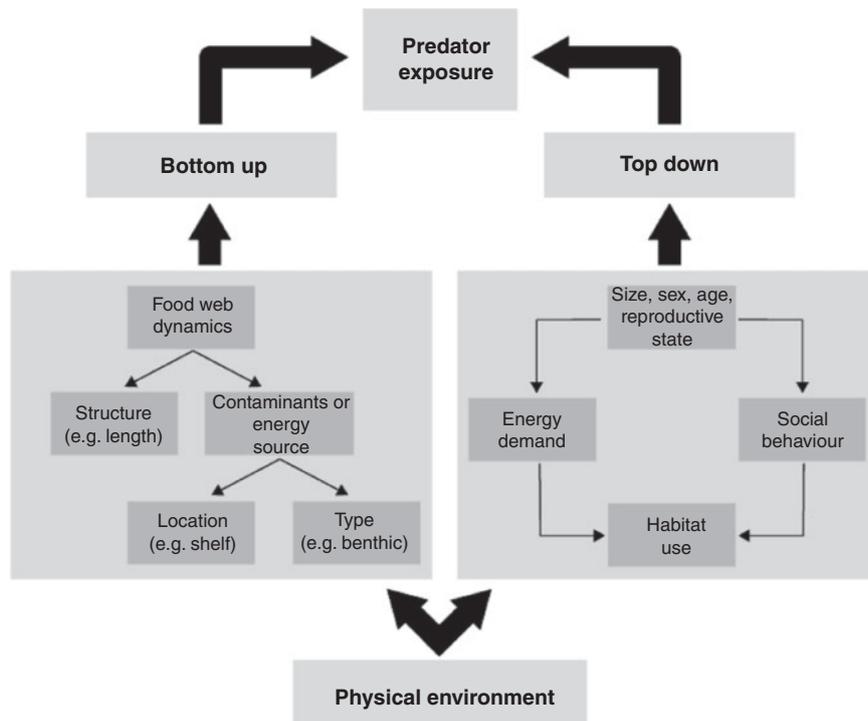
Fig. 8. The processes affecting Hg concentrations in a higher level species. Food web interactions determine the sources, bioaccumulation and biomagnification of Hg (in the form of MeHg). Dietary preferences are shaped by many factors including the sex, size, age and reproductive status of an animal. These in turn dictate energy requirements as well as social behaviour that together describe the habitat use. Figure modified from Loseto.[158]

(Fig. 8).[158] 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 affect bioaccumulation or biodilution (bottom-up); (iii) the food web structure or guild that defines the transfer of energy and Hg among trophic levels or between food webs, such as benthic-pelagic coupling (bottom-up) and (iv) predator behaviour defining diet and feeding ecology (top-down).

Diet is the main source of MeHg for higher-order consumers (e.g. invertebrates, fish, mammals).[159,160] 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 rate of MeHg into higher trophic level species.[136,161] MeHg strongly bioaccumulates in organisms because it is efficiently assimilated into tissues and is slowly eliminated from the body.[121,162] 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. Individuals with faster growth rates will have lower MeHg concentrations – the so-called 'biodilution effect'.[163–166]

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 ∼4 to 10 (see Fig. 7b).[144–146] A study using $\delta^{15}N$ to infer the trophic positions of species[145] reported log concentration-$\delta^{15}N$ relationship slopes of 0.197 and 0.223 for THg and MeHg 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[146] as well as in food webs along the west coast of Greenland that had log concentration-$\delta^{15}N$ relationship slopes of 0.18 and 0.34 for THg and MeHg.[167] Regression slopes of these Arctic marine examples were noted to be remarkably similar to others in different systems regardless of productivity, latitude or salinity.[145]

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 (Fig. 7a).[69,145] In Arctic marine food webs the MeHg fraction is variable in zooplankton, ranging from 30 % in the Beaufort Sea[116,144] to 70 % in Baffin Bay.[145] This may be attributed to significant spatial and seasonal heterogeneity[116] or variability among zooplankton species as observed in halogenated organic contaminants.[168] Fish such as Arctic cod have 80 to 97 % Hg as MeHg in the Beaufort Sea and its shelf, and 100 % in Baffin Bay.[116,144] Despite these variations, the predictable increase in the MeHg fraction of THg with increasing trophic level 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 organise prey species spatially (e.g. along fronts, convergent zones, persistent polynyas, persistent upwelling zones) in ways that affect both Hg uptake into the prey and the likelihood that the prey will be consumed.[116]

Bottom-up trophic processes in Arctic aquatic food webs

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 system or be created within the environment by 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 (Fig. 6).[4] 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 organisms at the bottom of a food web, which define carbon and Hg or MeHg acquisition. With these potential sources in mind, the four major types of Arctic marine food webs are reviewed 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 and shelf ecosystem (with riverine inputs dominating Hg deposition). 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. We have focussed on food webs that include the potential prey items for higher trophic level species of the marine environment.

Sea ice food webs. Sea ice and snow receive Hg deposited from the atmosphere. Sea ice may broadly be categorised 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[169] and more than 50 % in multi-year floe ice.[170] 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^{-1} DW ($n = 1$).[145]

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.[171] Calanoid copepods (e.g. *Calanus glacialis* and *C. hyperboreus*) are the dominant Arctic marine zooplankton.[172–174] Mercury concentrations in copepods were observed to decrease through the winter (~0.1 to 0.04 µg g^{-1} DW) in the Chukchi and Beaufort Seas and then to increase in the summer and autumn.[116] MeHg levels were typically 30 % of the THg.[144]

Gammaridean amphipods are the dominant macrofauna feeding under sea ice on detritus (e.g. ice algae, bacteria and crustacean remains).[175] 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.[176–181] Gammarids in Lancaster Sound had Hg concentrations of 0.1 µg g^{-1} DW.[146]

Arctic cod are thought to be a keystone species linking under ice food webs to many marine mammals and birds.[176,180–182] Total Hg concentrations in Arctic cod collected under the ice in the Amundsen Gulf–Franklin Bay averaged 0.38 µg g^{-1} DW, with 80 % of the THg as MeHg.[144] Similar levels were measured in winter in the Chukchi and Beaufort Seas.[116]

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 when AMDEs are active. Flaw leads or polynyas provide an opportunity for primary productivity to sustain local food webs.[145,183] The overall primary productivity in flaw leads (<15 % of the annual total) is considered to be relatively low,[184,185] 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.[186,187] 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.[188] In the central Arctic Basin, production under the pack ice is an order of magnitude lower than on the shelves.[170,188] Understanding these seasonal and regional carbon sources is key as they will affect where and when Hg uptake will occur as well as enable the quantification of this pathway to higher trophic species. As the euphotic zone exhausts its nutrients the blooms collapse, giving a deep chlorophyll maximum where food production continues,[108,189] and carbon and associated Hg sources may become more accessible to other food webs such as the epibenthos or demersal food webs.

The main grazers of plankton and microzooplankton in the open water column are the marine calanoid copepods *C. glacialis* and *C. hyperboreus*.[190] Mercury measured in copepods during the open water season from the Chukchi and Beaufort Sea ranged from 0.04 to 0.11 µg g^{-1} DW,[116] to as low as 0.025 µg g^{-1} DW in the Northwater Polynya.[145] The hyperiid amphipod *Themisto libellula*, which is the dominant predator of calanoid copepods,[176,180] had Hg levels ranging from 0.06 µg g^{-1} DW in Lancaster Sound to 0.13 µg g^{-1} DW in Amundsen Gulf where MeHg (0.095 µg g^{-1} DW) was 75 % of the total.[144–146] The east-to-west increase in THg and in the proportion of MeHg in 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^{-1} DW in Lancaster Sound[145,146] to 0.4 µg g^{-1} DW in the Chukchi and Beaufort Seas.[116,144] These concentrations are considerably higher than levels measured near Svalbard (0.05 µg g^{-1} DW).[191]

Estuarine, nearshore and shelf-associated food webs. Slightly over 50 % of the Arctic Ocean is continental shelf.[192] Shelves receive large inputs of freshwater along with particulates, organic carbon and Hg.[35,112,193] These inputs strongly affect the physical and biological oceanography of coastal regions,[14] but they also provide important controls on Hg pathways including 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*.[194] 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 or overwinter (e.g. the Mackenzie Delta of Canada[195] and Prudhoe Bay in Alaska).[196] Nearshore fishes such as rainbow smelt (*Osmerus mordax*), Pacific herring (*Clupea pallasii*), Arctic cisco and least cisco occurring along the Mackenzie Shelf had Hg levels below $0.2\,\mu g\,g^{-1}$ DW (with the exception of saffron cod, *Eleginus gracilis*), of which MeHg accounted for 78 to 94 % of THg in adult fish.[144] Arctic cod had Hg levels similar to other continental shelf fish, which were significantly lower than Hg levels in Arctic cod offshore.[144]

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 receive Hg not only from atmospheric deposition, but also from shelf–basin water exchange and riverine input.[34,35] In the case of the Beaufort Shelf an annual delivery of $2.2\,t\,year^{-1}$ of THg and $15\,kg\,year^{-1}$ of MeHg was estimated for the Mackenzie River alone.[35] Rivers clearly provide a conduit for terrestrial Hg and MeHg from wetlands and snowmelt[91] 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. Finally, estuarine sediments usually have high labile organic carbon fluxes that produce anoxic environments in sediments where Hg may be methylated. 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 *v.* offshore differences.[144]

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.[114] The quality and quantity of settling particulates along with bottom substrate (e.g. sand, silt, clay) determine the faunal community.[197] 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).[125,198,199] Due to ice scouring, which occurs most prevalently at 10- to 50-m water depth in association with flaw leads,[14] faunal composition is patchy and continually undergoing community succession.[200] Of special interest regarding Hg is the potential for producing localised anoxic conditions in scour marks that contain dense, salty water produced by ice formation.[201] 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 experience increased MeHg exposure by burrowing and dwelling in anoxic sediments.[202] 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 $0.07\,\mu g\,g^{-1}$ DW.[146]

Demersal fish are important prey items for higher trophic level animals. For example, the Greenland halibut (*Reinhardtius*
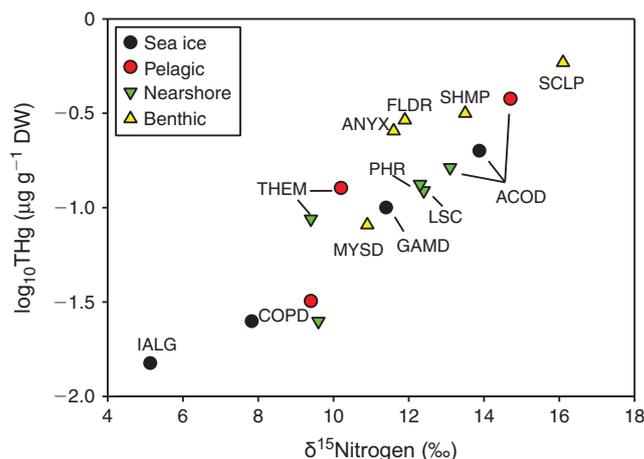
Fig. 9. Arctic marine food webs represented by a few key studies (sea ice[145,146]; pelagic, benthic, nearshore[144]). The benthic food web shows some of the highest Hg concentrations while the sea ice and nearshore food webs are some of the lowest. IALG, ice algae; COPD, copepods; THEM, *Themisto* spp.; MYSD, mysid; GAMD, gammarid; PHR, pacific herring; LSC, least cisco; ACOD, arctic cod; ANYX, anonyx spp.; FLDR, flounder; SHMP, shrimp; SCLP, sculpin.

hippoglossoides) 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 $0.24\,\mu g\,g^{-1}$ DW in Lancaster Sound[146] to $0.59\,\mu g\,g^{-1}$ DW in the Beaufort Sea.[144] 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.

Summary of Arctic marine food webs. Comparing and contrasting among the four marine Arctic food webs provides the opportunity to evaluate differences among them and to consider the underlying drivers for those differences. Despite some of the valuable insight comparisons will bring it is important to recognise the challenges of such a comparison. A particular limitation is the low sample size of food webs to adequately represent them. The low sample size reduces the ability to consider seasonal–temporal or spatial variability that may be defining food web patterns. Thus for the purposes of comparing among food webs, variability is minimised by focusing on a few studies in a few regions (Fig. 9). To represent the pelagic, nearshore and shallow benthic food webs, data from one area and study are used,[144] and for the sea ice food web data from the Northwater Polynya and Lancaster Sound are used.[145,146] Additionally, here as with the discussion above we do not discuss the top predators given the variability among one species (see case studies below) whereas few food webs have data at the start of the food web (i.e. primary producers). Having recognised these caveats there are features among the food webs that we discuss here. The first level consumers, copepods, remain similar among the food webs with pelagic copepods being slightly higher in Hg but this does not result in the highest Hg levels in predators. The predatory invertebrates exhibit an increase in Hg concentrations but show mimimal increase in $\delta^{15}N$ in the pelagic and nearshore foodwebs. The benthic food web has some of the highest Hg concentrations that range in

$\delta^{15}N$ (trophic position) whereas the nearshore food web exhibits the lowest Hg concentrations. Of interest is the variability in both Hg and $\delta^{15}N$ in Arctic cod, which demonstrates the importance of habitat and prey sources. The within-species variability has shown to have effects on their predators (e.g. beluga).[144] Based on our Arctic marine food web comparison a shift in predator feeding away from sea ice food webs towards benthic or pelagic food webs may result in higher exposure to Hg.

Freshwater food webs

Bottom-up trophic processes (see Fig. 8) 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.[203] 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.[204] On a broad geographic scale, a study of wild fish populations in the United States found that approximately two-thirds of the geographic variation in Hg levels of largemouth bass (*Micropterus salmoides*) was related to the rate of wet atmospheric Hg deposition.[51] Similarly, MeHg bioaccumulation in a fresh water aquatic invertebrate (mosquitoes) was positively correlated with wet atmospheric Hg deposition across a latitudinal gradient in North America that included Alaska.[205] In Alaskan lakes, sediment production of MeHg is limited by the availability of porewater inorganic Hg.[51]

Currently available data from the High Arctic indicate a significant but weak link between watershed Hg loading and freshwater food web accumulation of Hg. Mercury levels in Arctic char from 19 lakes were positively correlated with watershed-to-lake area ratios, which explained approximately one-quarter of the variation in length-adjusted Hg concentrations in fish.[206,207] MeHg concentrations in fresh water aquatic invertebrates (Diptera, Chironomidae) from 22 lakes and ponds were found to be only weakly correlated with measures of Hg supply (i.e. watershed-to-lake area ratios, MeHg concentrations in water and sediment).[208] 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 the supply of inorganic Hg^{II}.

Results from three studies in different Arctic regions of North America indicate that freshwater invertebrates can vary considerably in their MeHg concentrations, from 3 to $414\,ng\,g^{-1}$ in Alaska,[209] the Canadian North-west Territories[210,211] and the Canadian Arctic Archipelago.[208] This variation may be due to the trophic level of the invertebrates,[212] variable MeHg supply to their food webs[120] or taxonomic differences.[208] 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.[208]

Freshwater fish in Arctic lakes of Alaska, Canada and Greenland often have elevated Hg concentrations relative to government-established guidelines for human consumption.[213–215] The higher Hg concentrations (>0.5 to $1\,\mu g$ THg g^{-1} wet weight (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 (*Salvelinus alpines*; Lockhart et al.[214]). 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.[210]

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,[144,216,217] which relate to the animals' size, age, sex and reproductive status. These in turn influence energetic demands, social behaviour and habitat use (see Fig. 8). Although 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 behaviour. Several studies have tested for the effects of sex and age in marine mammals[218] and fish[219] on contaminant loads. The effect of animal size 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 behaviour and energy requirements, inferred from stable C and N isotopic composition of tissues,[220] can influence a population's Hg accumulation.[144,146] 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 concentrations in polar bears.[221] It was similarly found that feeding habitat explained Hg concentrations in polar bears. Beaufort Sea polar bears,[217] who fed in longer pelagic food webs, had higher Hg concentrations compared with polar bears in Hudson Bay, who fed in shorter, more benthic food webs. The following sections explore these top-down effects in two well studied high trophic level Arctic species: beluga and Arctic char.

Eastern Beaufort Sea beluga

Reports of high Hg levels in Beaufort Sea beluga compared with other Arctic populations[214] instigated several studies focussed on the habitat use and diet preferences of this beluga population, along with its associated food webs (guild and trophic transfer of Hg). Results from satellite telemetry analyses of beluga, matched with physical environmental features (e.g. sea ice, bathymetry), indicate the Beaufort Sea beluga population sexually segregated during the summer.[222] 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 energetic requirements, has consequences for feeding ecology and Hg exposure in the beluga.[144] With this in mind, Beaufort Sea food webs were coupled with beluga habitat use groups to characterise Hg exposure among different sex and size classes.[144]

The feeding groups were hypothetical, yet they provided a framework to begin merging predator behaviour 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 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.[35] Beluga thought to feed on the epibenthic and Amundsen Gulf pelagic food webs had the highest liver and muscle Hg levels.[144]

To investigate feeding behaviour 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.[160] Fatty acids indicated that overall the beluga diet was dominated by Arctic cod and was poor in benthic prey.[223] However, size-related dietary differences were evident, with larger beluga preferring offshore Arctic cod, and smaller beluga feeding on near-shore prey including Arctic cod; prey species in near-shore areas have lower Hg concentrations than in offshore pelagic areas.[144] Unlike fish, beluga reach a mature length at a certain age, and subsequently feed in relation to their size and energetic demands of reproductive needs rather than age.[160] If these size-related trends can be explained by energetics then the large males may need to maintain body mass by adjusting foraging behaviour to feed either on energy-rich prey or to feed more often.[224] If so, the beluga pattern suggests a greater abundance or availability of Arctic cod in pelagic offshore regions of the Arctic Ocean.

To summarise, factors such as predation, resource selection and reproductive status 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 hypothesised that Mackenzie River inorganic Hg and 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.[144] Alternatively, the inorganic and organic loads delivered by the river may have the capacity to scavenge Hg from ocean water in excess of what the river delivers, or the chemical composition of the river (e.g. DOC) and stratification produce an environment favouring photo-reduction to Hg^0, which then evades to the atmosphere.[29]

Landlocked Arctic char

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, or as cannibals on other char[206,225] while some adults exhibit cannibalistic feeding behaviour on juveniles.[166,226] Between 2005 and 2007, Hg biomagnification was investigated in the food webs supporting landlocked Arctic char populations in 18 lakes on: Ellesmere Island ($n = 4$), Cornwallis Island ($n = 9$), Victoria Island ($n = 1$), Kent Peninsula ($n = 3$) and Ungava Peninsula ($n = 1$).[206] 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 analysed 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.[208] 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.[227] Of 212 char investigated in this survey, the majority consumed larvae (82 %) whereas pupae and adult chironomids were consumed in lesser amounts (52 and 11 %). However, on Cornwallis Island, adult chironomids were generally not present in char stomachs in the past[227] or recently,[206] although they were consumed in Char Lake.[226] Recent $\delta^{15}N$ data on insectivorous char show low variability in THg and $\delta^{15}N$ among Cornwallis Island lakes.[206,207] On Ellesmere Island, larger char fed selectively on pupae at the lake surface during the period of emergence, whereas smaller char (<20 cm) inhabited very shallow areas and fed mostly on chironomid larvae.[228]

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,[208] 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,[229] which is also evident from lower MeHg concentrations and more depleted $\delta^{15}N$ signatures in juvenile char from Cornwallis Island lakes.[206] The proposed effect of differential feeding behaviour of adult char[208] on their Hg levels cannot 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.[225,226,230] Moreover, 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 s.d. = 0.3 to 0.8 ‰), and higher in other lakes with observed opportunistic cannibalism (2 s.d. up to ~2.4 ‰).

Cannibalism played an important role in Arctic char Hg levels in a lake on Svalbard.[231] The highest concentrations were observed in piscivorous Arctic char (0.04 to 0.44 µg g^{-1} 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.

It has been 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.[208] 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 ~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.[207]

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 emphasises 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 landlocked char THg concentrations. It is important to note that THg concentrations in land locked char, resident char, and sea-run char are driven by life history differences in particular as they relate to diet, growth, and habitat use.[166]

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.[160] Understanding the organisms' physiology is also critical when using other biomarkers such as stable isotopes.[232]

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.[233,234] Therefore, the linear increase in the liver total Hg concentration (i.e. the non-methylated form) with age suggests that the bioaccumulated Hg will complicate attempts to interpret recent dietary Hg sources.[160] In contrast, Hg concentrations in beluga muscle (known to be almost entirely MeHg) are most strongly correlated with animal length.[160] This relationship suggests that muscle Hg concentrations reflect

dietary Hg uptake and to a lesser extent bioaccumulation over time.[223] Larger beluga were either feeding at higher trophic levels or in different food webs with higher Hg sources. Conversely, age was not significantly correlated with muscle Hg levels,[160] as also occurs with Hg in ringed seal muscle.[146] Overall, muscle tissue is a better indicator of dietary Hg sources and the processes of Hg biomagnification driven by food web structure whereas liver Hg best reflects age-related accumulation. Mercury concentrations in other tissues, such as *muktuk* (skin) in beluga, are closely correlated with muscle Hg,[234] and this is also thought to apply to fur or hair in mammals.[235] This finding supports the use of skin biopsy or fur samples to estimate dietary Hg loads and body burdens in high order mammals.

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 mercury (as RGM oxidised from GEM) from the atmosphere to frozen surfaces during polar sunrise,[236–244] and have been hypothesised to contribute significantly to the high Hg levels in some Arctic biota.[245] In contrast, it is now well established that the Hg deposited during AMDEs can be readily re-emitted from the snowpack during winter conditions following AMDEs[7,16,25,80,101,187,241,246–248] and during snow metamorphism and melt.[20,79] 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 marine and fresh water ecosystems that 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 a whole-cell biosensor detecting cytoplasmic inorganic mercury (in the pM range), 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.[237,249] More recent investigations in Svalbard also found that surface snow during AMDEs contained less than 20 % bioavailable Hg, measured with a bacterial mer-lux reporter.[250] Snow samples were collected over a two-month Arctic field campaign in 2008. In surface snow, concentrations of BioHg were related to atmospheric Hg deposition, and snow fall events were shown to contribute to higher proportions of BioHg than AMDEs. Based on these data, AMDEs represent a potential source of 20 t year^{-1} of BioHg, whereas wet and dry deposition pathways may provide 135–225 t year^{-1} of BioHg to Arctic surfaces. Interestingly, those authors found higher proportions of bioavailable Hg (60–100 %) in snow associated with wet and dry deposition pathways. In a similar study, melted snow samples collected at Kuujjuarapik, Quebec, were analysed using a suite of bioassays involving living organisms or cells representative of three trophic levels.[251] Comparison of bioassay test responses of snow samples collected before and after AMDEs demonstrated that,

Snowpack THg, % loss from $T = 0$
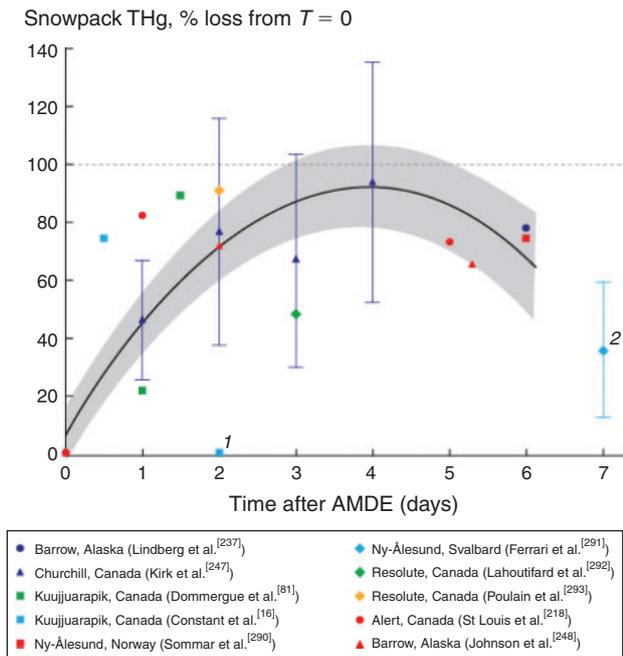
Fig. 10. The rate of total mercury loss from Arctic surface snow (0- to 10-cm depth) following atmospheric mercury depletion events (AMDEs).[6,247] Data points represent mean ± 1 standard deviation. For other studies median values are used. The polynomial quadratic regression is THg (ng L^{-1}) = $5.77 + 44.7x - 5.75x^2$ ($R^2 = 0.78$, $P < 0.0001$, total d.f. = 26). The shaded area indicates 95 % confidence intervals around regression. Data points 1 and 2 were excluded from regression analysis.

following AMDEs, *Hydra attenuata* acute sublethality and rainbow trout (*Oncorhynchus mykiss*) hepatocyte acute cytotoxicity responses increased 1.6- and 4.4-fold. Furthermore, an algal bioassay revealed that the growth of *Pseudokirchneriella subcapitata* was stimulated by snow collected before the occurrence of AMDEs, but was 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.[252]

Results from many Arctic locations suggest that 60–80 % of total deposited Hg is photo-reduced to volatile Hg^0 and re-emitted back to the atmosphere within days of AMDEs.[7,80,101,187,241,247,248] Fig. 10 includes a summary of the results from 10 different studies[247] that monitored the THg concentration in snow with time since an AMDE was active.[6] The results suggest that at least half of the AMDE Hg is lost within 1 week since deposition but that ~10 to 25 % remains. A recent study based on snow collected on land and on the sea ice near Barrow, Alaska,[5] provides some insight into why the results in Fig. 10 suggest that the variance in Hg concentrations increases with time. The authors argue that a variety of factors, including the snow crystal type and its formation history, can greatly affect the retention or loss of AMDE Hg. The major snow grain processes that control the fate of Hg deposited to snow during AMDEs include deposition, condensation, reemission, sublimation and turbulent diffusive uptake. The compounding affects of these processes likely increases with time since deposition. Regardless of the processes that control Hg retention in snow and ice it is obvious that the fraction of AMDE-deposited atmospheric Hg that is highly photoreactive

may not be bioavailable to the microbes thriving in snow in polar spring.[84]

From the perspective of mass inputs, based on currently available data, AMDE Hg entering the upper Arctic Ocean and Hudson Bay (predominantly during spring melt events) is believed to contribute a relatively small amount to what are already large reservoirs of dissolved THg.[36,253] According to a modified Global–Regional Atmospheric Heavy Metals Model (GRAHM), a net amount of 45 t year^{-1} THg (46 % of total annual atmospheric inputs) enters the Arctic Ocean during spring when AMDEs occur, compared with total inputs of 206 t year^{-1}.[36] The springtime input includes other wet and dry Hg deposition not associated with AMDEs, thus 45 t year^{-1} is likely to be an overestimate of the AMDE input. The existing Arctic Ocean reservoir of dissolved THg is ~7900 t (~950 t in the upper 200 m). The intense seasonality of the Arctic environment appears to have a corollary in the seasonal net balance of AMDE Hg deposition and re-volatilisation. On the basis of modelling of GEM measurements at the Zeppelin station on Svalbard it was reported[254] 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. During the summer, the Arctic was a GEM source, probably as a result of evasion from the ocean during the open water season and (less likely) re-emission of previously deposited Hg as the snow and ice melts. The overall net balance between these periods was not reported.

Biogeochemical processes in water and sediment transform some Hg^{II} to MeHg, which then becomes available to biota. Recent stable-isotopic measurements[99] have found that methylation and de-methylation processes are surprisingly rapid. This implies ecosystem exposure to MeHg at a given location depends mostly on local inputs and geochemistry rather than on transportation of MeHg produced elsewhere.

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?).[4,204] In considering the MeHg burden in high trophic level species, it is difficult to estimate which component derives from AMDEs and which derives from the now globally contaminated pool of Hg^{II} cycling in the atmosphere–ocean system. It seems clear that ecosystems in the Arctic Ocean are contaminated with industrial Hg,[255] but it is unclear whether AMDEs contribute significantly to making Arctic ecosystems especially vulnerable to the global Hg cycle. Post-depositional methylation processes must play an important and perhaps dominant role.[4] Because a majority of the AMDE Hg deposited to snow and ice is affected by dynamic spring melt processes there may be a disconnect between total deposition of AMDE Hg and the actual incorporation (or methylation) of AMDE Hg into ecosystem compartments and ultimately, into food webs. There is substantial knowledge concerning Hg methylation processes at lower latitudes.[256,257] However, the applicability of these processes may be limited with respect to Arctic ecosystems and further work measuring methylation and de-methylation rates along the lines pioneered recently for marine waters[99] is required for a variety of Arctic settings.

From a spatial perspective (the third line of evidence regarding AMDEs), the results from several transect studies provide contradictory evidence of a possible link between AMDEs and biotic Hg levels. Total Hg in moss has shown higher levels along the north-western coast of Norway compared with areas further inland since measurements started in 1985, a trend that appears

to be particularly strong in the northernmost area.[258,259] This pattern 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.[260] 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,[186] and in coastal Hudson Bay,[187] suggest a potentially 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 effect on Hg bioaccumulation in these aquatic invertebrates.[209] High re-emission rates from snow to the atmosphere before snowmelt were suggested as a possible explanation. This finding is consistent with a synoptic scale study that 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 with those further inland.[23]

The rate of long-term sequestration of mercury through burial in arctic sediment, soil, peat and ice archives

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 and inter-glacial cycles and tectonic activity may remobilise long-term sequestered Hg. Table 2 summarises the best available estimates of average areal rates and total masses of Hg sequestered by the various archives.

Recent estimates of long-term sequestration rates for Hg in Arctic marine sediments are available for the Arctic Ocean[36] and Hudson Bay,[253] 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 year^{-1} occurs in the continental shelf seas and 13 t year^{-1} in the Central Basin for a total sequestration of 108 t year^{-1}. Sedimentation was the largest single loss pathway for Arctic marine Hg, representing 59 % of the total ~182 t year^{-1} 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 year^{-1}, suggesting the possibility of a scavenging of deposited atmospheric Hg from the shelf water column into sediments.[36] 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 Hudson Bay was 147 ± 69 t year^{-1}, with a modern Hg sedimentation rate of 4.5 ± 3.2 t year^{-1}, which includes a contribution of 1.7 t year^{-1} of Hg from the resuspended material.[253] The modern sedimentary Hg flux (2.4 t year^{-1}) was estimated to be almost 2-fold higher than in pre-industrial times and, comparable to the Arctic Ocean, was approximately 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 Hudson Bay was ultimately captured and buried in sediments.[253]

For freshwater sediments, estimates of focus-corrected modern Hg fluxes, averaged over recent decades, are available for 76 lakes from Northern Canada,[23,261] Alaska,[21,262] West Greenland,[263,264] Northern Sweden (above 60°N), Finland (above 60°N) and Russia.[262] These lakes gave an overall median modern Hg flux of 11.5 µg m^{-2} year^{-1} (mean ± s.d., 20.3 ± 22.3 µg m^{-2} year^{-1}; geometric mean = 12.7 µg m^{-2} year^{-1}). Recent decadal rates in the Canadian Arctic have increased ~2-fold on average over pre-1900 rates, believed to be due to the combined effects of pollution inputs[23] and increased transfer efficiency from the water column because of climate-driven increases in aquatic primary productivity and associated Hg scavenging.[62,65] 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. A GIS-based estimate was

Table 2. Areal rates and total masses of mercury sequestered annually in non-biological archives in the Arctic

Archive	Annual flux (µg m^{-2} year^{-1})	Total area (10^6 km^2)	Annual Hg mass (t year^{-1})	Data source
Marine sediments				
Arctic Ocean	11.3[A]	9.54	108	[36]
Hudson Bay	5.4[A]	0.84	4.5	[253]
Freshwater sediments	11.5[B]	0.6	6.9	Areal Hg flux[B]; total Arctic lake surface area[265]
Terrestrial soils				
Soils	~5	–	–	[259,267,272,274]
Peatlands	2–20[C]	3.5	7–70[C]	
Ice caps and glaciers				
Greenland Ice Sheet	0.1–0.6	1.69	0.2–1[282]	[17,18,20,277,278,280–282]
Other	0.1–0.3	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.[21,23,261,263,264]
[C]Estimated range only, based on few data.[259,273,274]

calculated[265] of 589 500 km^2 for 202 756 lakes of 0.1 km^2 or more in the land area lying north of 45.5°N (which is the southernmost extent of permafrost near James Bay, Canada). Although this figure is possibly an overestimate, we note that 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. As a consequence, lakes present a relatively important Hg sink in the north.[265] The tendency to over-estimation is also balanced by GIS techniques consistently under-estimating the number and surface areas of lakes in a given area,[266] 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 ~6.8 t year^{-1}. 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 smaller total area that freshwater sediments represent (Table 2).

Estimation of Hg sequestration in Arctic soils (including peatlands, as these are recognised as a soil type) is complicated by the fact that Hg in soils and peatlands may be subjected to significant remobilisation 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.[267] 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.[268,269] Plants act as interceptors of Hg-bearing dusts and RGM.[270] Consequently, Hg deposition rates to soils under forests and grasslands are estimated to be respectively ~4- and 2-fold higher on average than to adjacent lake surfaces.[267] Photo-reduction and re-volatilisation rates of deposited Hg are also several-times lower under trees than from adjacent sun-exposed areas.[270] 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 to organic matter.[269] Data on THg concentrations in Arctic soils are sparse. Mean soil Hg values reported from the Kola and Taymir Peninsulas and the Pechora Basin, Russia, ranged from 0.06 to 0.12 µg g^{-1} DW.[271] However, without a better understanding of soil development and accumulation processes in the Arctic, sequestration rates cannot be derived from these concentration data. An estimate of the average soil THg accumulation rate for northern hemisphere temperate and boreal forest soils was ~5 µg m^{-2} year^{-1}.[267] However, this estimate should be treated cautiously in relation to most of the High Arctic's terrestrial areas that 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 (~3.5 × 10^6 km^2),[272] and their well known capacity to accumulate Hg from the atmosphere and groundwater inflows,[273,274] 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. Average fluxes of 2.1 to 11.1 µg m^{-2} year^{-1} (median 4.3 µg m^{-2} year^{-1}) were reported over the past century for four peat bogs in Norway north of 60°N.[259] A rate of ~14 µg m^{-2} year^{-1} was calculated for southern Greenland in the 1990s after a rapid decline from a peak of 164 µg m^{-2} year^{-1} in

the 1950s,[273] whereas a flux of 16 µg m^{-2} year^{-1} was reported in the late 1990s in a Faroe Islands peat deposit.[274] Given the paucity of data, a range of areal rates of 2 to 20 µg m^{-2} year^{-1} was used to constrain minimum and maximum values of 7 to 70 t year^{-1} for the THg mass sequestered. Thawing of peatlands contained within permafrost may also have released significant amounts of this sequestered Hg into local watercourses, especially during recent decades, 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 (compacted snow from previous winters that has been recrystallised),[275] and by the entrapment of particulate Hg (from dry and wet deposition) in the ice matrix itself.[276] 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 and different investigators have used different analytical methods, making comparisons difficult. For THg measured by cold vapour (CV) generation, published figures appear to vary within a narrow range of <0.2 to ~5 ng L^{-1} in recent (<10-year old) firn layers.[17,18,20,252,277–282] Data from older studies[283] that reported much higher levels in Greenland, for example, are probably suspect due to contamination issues.[284] Because the mean Hg levels in circumarctic glaciers are somewhat similar, geographic differences in sequestration rates are largely determined by net ice accumulation rates at these sites.

The net sequestration rate of THg in any glacier is largely determined by the mean concentration of THg in snow and firn below the photolytic zone and by the net ice accumulation rate. For Greenland, reported THg figures suggest sequestration rates varying between 0.1 and 0.6 µg m^{-2} year^{-1}.[277,278,282] A recent study[275] reported much higher THg concentrations (3–20 ng L^{-1}), in snow and firn at Summit, Greenland, suggesting a considerably greater sequestration rate, but this study remains an exception. For Canadian Arctic ice caps the sequestration rate for THg appears to be in the order of 0.1 µg m^{-2} year^{-1}.[18,280,281]

Sequestration rates of THg could be higher on the small Svalbard or Alaskan glaciers owing to higher snowfall rates in these regions, but data are presently too scarce or lacking for a proper estimation. More than 80 % (0.2–1 t year^{-1}) of the Hg stored in Arctic glaciers and ice caps may be stored in the Greenland Ice Sheet. It was recently estimated[282] that 13 t year^{-1} of THg are sequestered annually on the Greenland Ice Sheet; however, this estimate erroneously applied a Hg flux to the entire area of the ice sheet (14 × 10^6 km^{-2}) whereas the actual net snow accumulation area is 1.69 × 10^6 km^{-2} (see Table 2). The net sequestration in Canadian Arctic ice caps is probably much smaller than on Greenland, in the order of 0.03 t year^{-1} based on published fluxes,[18,280,281] and the sum accumulation area of glaciers and ice caps.[285–287] Despite the uncertainties in these estimates it is likely that glacial ice storage is a relatively small sink of THg, compared with sediment, soil and peat, and particularly compared to marine sediments (Table 2). Furthermore, at least some of the Hg presently stored in glacial ice is being prematurely released as Arctic glaciers diminish under a warmer climate.[287–289]

Conclusions, knowledge gaps and recommendations for further research

The fate of net deposited atmospheric mercury in environmental media

1. Most of the Hg entering aquatic (marine and fresh water) and terrestrial ecosystems following atmospheric deposition is inorganic (Hg^{II}). Present knowledge suggests that the small amount of MeHg found in snowpacks before spring snowmelt does not add significantly to the extant MeHg levels in aquatic systems.
2. Photo-reduction and re-volatilisation (evasion) of part of the deposited Hg in snow, ice, Arctic lakes and marine waters may constrain its overall rate of incorporation into aquatic food webs.
3. The production, speciation (dissolved *v.* particulate, labile *v.* 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 bioavailability of Hg in aquatic systems is closely tied to the sources, composition and dynamics of organic carbon.

The rates of Hg entry into the alternative pathways in aquatic (marine and fresh water) 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.

Transfer of mercury from the abiotic environment into food webs and the factors influencing this movement

4. MeHg is significantly more readily bioaccumulated than inorganic Hg forms, 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 *v.* particulate Hg^{II}, the reactivity of deposited Hg and the metabolic activity of microbes.
7. 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 recent evidence indicates that MeHg is also formed in the mid-water column, similar to temperate oceans.
8. 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.

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.

The role of methylation and demethylation in controlling mercury accumulation rates in Arctic food chains

9. MeHg can be produced by methylation of inorganic Hg and by photolysis of gaseous DMHg produced by marine bacteria and macro-algae.
10. In Arctic Alaskan fresh water lakes, production of MeHg was almost balanced by summertime photo-demethylation, which effectively competed for MeHg with lake food webs. Variations in the productivity of 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.
11. 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.

The aquatic MeHg cycle in the Arctic is 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 by traditional animal foods. Although it is unknown whether MeHg formation occurs in Arctic seawater, the Arctic Ocean exhibits nutrient maxima, which may be suggestive of this effect. Confirmation and measurement of this process in the Arctic Ocean would significantly advance our understanding of the Arctic Hg cycle.

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

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

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

14. 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.
15. A small fraction (<20 %) of the Hg deposited by AMDEs onto snow surfaces has been reported to be bioavailable to bacteria. However, the rapid re-volatilisation of up to 80 % of AMDE Hg from snowpacks may limit the exposure of food webs to Hg from this source.

The net flux of mercury in wet and dry deposition over the Arctic area needs to be established in terms of geographical and temporal variations. 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. The potential effects of climate warming on AMDEs and their role in the Arctic Hg cycle are not well known.

The rate of long-term sequestration of mercury through burial in Arctic non-biological archive sediments, soils and ice

16. Marine sediments sequester the largest mass of Hg in the Arctic annually (more than $110\,t\,year^{-1}$ combined in the Arctic Ocean and Hudson Bay alone) with northern peat-lands also likely to be an important sink ($\leq 70\,t\,year^{-1}$). Lake sediments and glaciers are negligible sinks; soils are possibly also important but data are lacking.

17. 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.

The remote nature of the Arctic and the small amount of long-term archival measurements available limit our ability to synthesise results from sediment measurements at a pan-Arctic scale. A collaborative, spatially ranging effort is needed to facilitate better communication of archival results across borders, regions and ecosystem locations.

Acknowledgements

References

[1] R. P. Mason, K. R. Rolfhus, W. F. Fitzgerald, Mercury in the North Atlantic. *Mar. Chem.* **1998**, *61*, 37. doi:10.1016/S0304-4203(98)00006-1

[2] W. F. Fitzgerald, C. H. Lamborg, C. R. Hammerschmidt, Marine biogeochemical cycling of mercury. *Chem. Rev.* **2007**, *107*, 641. doi:10.1021/CR050353M

[3] S. A. Strode, L. Jaeglé, N. E. Selin, D. J. Jacob, R. J. Park, R. M. Yantosca, R. P. Mason, F. Slemr, Air-sea exchange in the global mercury cycle. *Global Biogeochem. Cycles* **2007**, *21*, GB1017. doi:10.1029/2006GB002766

[4] R. W. Macdonald, L. L. Loseto, Are Arctic Ocean ecosystems exceptionally vulnerable to global emissions of mercury? A call for emphasised research on methylation and the consequences of climate change. *Environ. Chem.* **2010**, *7*, 133. doi:10.1071/EN09127

[5] T. A. Douglas, M. Sturm, W. Simpson, J. Blum, L. Alvarez-Aviles, G. Keeler, D. Perovich, A. Biswas, K. Johnson, The influence of snow and ice crystal formation and accumulation on mercury deposition to the Arctic. *Environ. Sci. Technol.* **2008**, *42*, 1542. doi:10.1021/ES070502D

[6] T. A. Douglas, M. Amyot, T. Barkay, T. Berg, J. Chetelat, P. Constant, A. Dommergue, M. Evans, C. Ferrari, N. Gantner, M. Johnson, J. Kirk, N. Kroer, C. Larose, D. Lean, L. Loseto, R. Macdonald, D. Muir, T. G. Nielsen, P. Outridge, A. Poulain, L. Poissant, S. Rognerud, H. Skov, S. Sorensen, F. Wang, C. Zdanowicz, Chapter 3. What is the Fate of Mercury Entering the Arctic Environment?, in *AMAP Assessment 2011. Mercury in the Arctic* **2011**, pp. 45–65 (Arctic Monitoring and Assessment Programme: Oslo, Norway).

[7] L. S. Sherman, J. D. Blum, K. P. Johnson, G. P. Keeler, J. A. Barres, T. A. Douglas, Mass-independent fractionation of mercury isotopes during atmospheric mercury depletion events. *Nat. Geosci.* **2010**, *3*, 173. doi:10.1038/NGEO758

[8] I. G. Rigor, J. M. Wallace, Variations in the age of Arctic sea ice and summer sea ice extent. *Geophys. Res. Lett.* **2004**, *31*, L09401. doi:10.1029/2004GL019492

[9] S. V. Nghiem, Y. Chao, G. Neumann, P. Li, D. K. Perovich, T. Street, P. Clemente-Colon, Depletion of perennial sea ice in the eastern Arctic Ocean. *Geophys. Res. Lett.* **2006**, *33*, L17501. doi:10.1029/2006GL027198

[10] J. A. Maslanik, C. Fowler, J. Stroeve, S. Drobot, J. Zwally, D. Yi, W. Emery, A younger, thinner Arctic ice cover: increased potenial for rapid, extensive sea-ice loss. *Geophys. Res. Lett.* **2007**, *34*, L24501. doi:10.1029/2007GL032043

[11] P. B. Shepson, P. B. Ariya, C. Deal, D. J. Donaldson, T. A. Douglas, T. Maksym, P. A. Matrai, L. M. Russell, B. Saenz, J. Stefels, N. Steiner, OASIS: bringing scientists together from multiple disciplines to study changes and feedbacks in the polar environments. *Eos Trans. AGU* **2012**, *93*, 117. doi:10.1029/2012EO110001

[12] R. M. Holmes, J. W. McClelland, B. J. Peterson, S. E. Tank, E. Bulygina, T. I. Eglinton, V. V. Gordeev, T. Y. Gurtovaya, P. A. Raymond, D. J. Repeta, R. Staples, R. G. Striegl, A. V. Zhulidov, S. A. Zimov, Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. *Estuaries Coasts* **2012**, *35*, 369. doi:10.1007/S12237-011-9386-6

[13] M. T. Jorgenson, Y. L. Shur, E. R. Pullman, Abrupt increase in permafrost degradation in Arctic Alaska. *Geophys. Res. Lett.* **2006**, *33*, L02503. doi:10.1029/2005GL024960

[14] E. C. Carmack, R. W. Macdonald, Oceanography of the Canadian Shelf of the Beaufort Sea: a setting for marine life. *Arctic* **2002**, *55*, 29.

[15] A. J. Poulain, E. Garcia, M. Amyot, P. G. C. Campbell, P. A. Ariya, Mercury distribution, partitioning and speciation in coastal vs. inland High Arctic snow. *Geochim. Cosmochim. Acta* **2007**, *71*, 3419. doi:10.1016/J.GCA.2007.05.006

[16] P. Constant, L. Poissant, R. Villemur, E. Yumvihoze, D. Lean, Fate of inorganic mercury and methyl mercury within the snow cover in the low arctic tundra on the shore of Hudson Bay (Québec, Canada). *J. Geophys. Res.* **2007**, *112*, D08309. doi:10.1029/2006JD007961

[17] C. Larose, A. Dommergue, M. DeAngelis, D. Cossa, B. Averty, N. Marusczak, N. Soumis, N. Schneider, D. Schneider, C. Ferrari, Springtime changes in snow chemistry lead to new insights into mercury methylation in the Arctic. *Geochim. Cosmochim. Acta* **2010**, *74*, 6263. doi:10.1016/J.GCA.2010.08.043

[18] V. L. St Louis, M. J. Sharp, A. Steffen, A. May, J. Barker, J. L. Kirk, D. J. A. Kelly, S. E. Arnott, B. Keatley, J. P. Smol, Some sources and sinks of monomethyl and inorganic mercury on Ellesmere Island in the Canadian High Arctic. *Environ. Sci. Technol.* **2005**, *39*, 2686. doi:10.1021/ES049326O

[19] V. L. St Louis, H. Hintelmann, J. A. Graydon, J. L. Kirk, J. Barker, B. Dimock, M. J. Sharp, I. Lehnherr, Methylated mercury species in Canadian high arctic marine surface waters and snowpacks. *Environ. Sci. Technol.* **2007**, *41*, 6433. doi:10.1021/ES070692S

[20] A. Dommergue, C. Larose, X. Fain, O. Clarisse, D. Foucher, H. Hintelmann, D. Schneider, C. P. Ferrari, Deposition of mercury species in the Ny-Ålesund area (79°N) and their transfer during snowmelt. *Environ. Sci. Technol.* **2010**, *44*, 901. doi:10.1021/ES902579M

[21] W. F. Fitzgerald, D. R. Engstrom, C. H. Lamborg, C.-M. Tseng, P. H. Balcom, C. R. Hammerschmidt, Modern and historic atmospheric mercury fluxes in northern Alaska: global sources and arctic depletion. *Environ. Sci. Technol.* **2005**, *39*, 557. doi:10.1021/ES049128X

[22] R. G. Semkin, G. Mierle, R. J. Neureuther, Hydrochemistry and mercury cycling in a High Arctic watershed. *Sci. Total Environ.* **2005**, *342*, 199. doi:10.1016/J.SCITOTENV.2004.12.047

[23] D. C. G. Muir, X. Wang, F. Yang, N. Nguyen, T. A. Jackson, M. S. Evans, M. Douglas, G. Köck, S. Lamoureux, R. Pienitz, J. P. Smol, W. F. Vincent, A. Dastoor, Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. *Environ. Sci. Technol.* **2009**, *43*, 4802. doi:10.1021/ES8035412

[24] A. A. Hare, G. A. Stern, Z. Z. Kuzyk, R. W. Macdonald, S. C. Johannessen, F. Wang, Natural and anthropogenic mercury distribution in marine sediments from Hudson Bay, Canada. *Environ. Sci. Technol.* **2010**, *44*, 5805. doi:10.1021/ES100724Y

[25] J. Sommar, I. Wangberg, T. Berg, K. Gardfelt, J. Munthe, A. Richter, A. Urba, F. Wittrock, W. H. Schroeder, Circumpolar transport and air–surface exchange of atmospheric mercury at Ny-Alesund (79°N), Svalbard, spring 2002. *Atmos. Chem. Phys.* **2007**, *7*, 151. doi:10.5194/ACP-7-151-2007

[26] J. Sommar, M. E. Andersson, H.-W. Jacobi, Circumpolar measurements of speciated mercury, ozone and carbon monoxide in the boundary layer of the Arctic Ocean. *Atmos. Chem. Phys.* **2010**, *10*, 5031. doi:10.5194/ACP-10-5031-2010

[27] A. L. Soerensen, H. Skov, D. J. Jacob, B. T. Soerensen, M. S. Johnson, Global concentrations of gaseous elemental mercury and reactive gaseous mercury in the marine boundary layer. *Environ. Sci. Technol.* **2010**, *44*, 7425. doi:10.1021/ES903839N

[28] K. Aspmo, C. Temme, T. Berg, C. Ferrari, P.-A. Gauchard, X. Fain, G. Wibetoe, Mercury in the atmosphere, snow and melt water ponds in the North Atlantic Ocean during Arctic summer. *Environ. Sci. Technol.* **2006**, *40*, 4083. doi:10.1021/ES052117Z

[29] M. E. Andersson, J. Sommar, K. Gårdfeldt, O. Lindqvist, Enhanced concentrations of dissolved gaseous mercury in the surface waters of the Arctic Ocean. *Mar. Chem.* **2008**, *110*, 190. doi:10.1016/J.MARCHEM.2008.04.002

[30] D. Point, J. E. Sonke, R. D. Day, D. G. Roseneau, K. A. Hobson, S. S. Vander Pol, A. J. Moors, R. S. Pugh, O. F. X. Donard, P. R. Becker, Methylmercury photodegradation influenced by sea-ice cover in Arctic marine ecosystems. *Nat. Geosci.* **2011**, *4*, 188. doi:10.1038/NGEO1049

[31] L. Whalin, E.-H. Kim, R. P. Mason, Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. *Mar. Chem.* **2007**, *107*, 278. doi:10.1016/J.MARCHEM.2007.04.002

[32] A. J. Poulain, E. Garcia, M. Amyot, P. G. C. Campbell, F. Raofie, P. A. Ariya, Biological and chemical transformations of mercury in fresh and saltwaters of the High Arctic during spring and summer. *Environ. Sci. Technol.* **2007**, *41*, 1883. doi:10.1021/ES061980B

[33] J. Lalonde, M. Amyot, A. M. L. Kraepiel, F. M. M. Morel, Photooxidation of Hg^0 in artificial and natural waters. *Environ. Sci. Technol.* **2001**, *35*, 1367. doi:10.1021/ES001408Z

[34] M. Coquery, D. Cossa, J. M. Martin, The distribution of dissolved and particulate mercury in three Siberian estuaries and adjacent arctic coastal waters. *Water Air Soil Pollut.* **1995**, *80*, 653. doi:10.1007/BF01189718

[35] D. R. Leitch, J. Carrie, D. R. S. Lean, R. W. Macdonald, G. A. Stern, F. Wang, The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. *Sci. Total Environ.* **2007**, *373*, 178. doi:10.1016/J.SCITOTENV.2006.10.041

[36] P. M. Outridge, R. W. Macdonald, F. Wang, G. A. Stern, A. P. Dastoor, A mass balance inventory of mercury in the Arctic Ocean. *Environ. Chem.* **2008**, *5*, 89. doi:10.1071/EN08002

[37] J. L. Kirk, V. L. St Louis, Multiyear total and methyl mercury exports from two major sub-Arctic rivers draining into Hudson Bay. *Environ. Sci. Technol.* **2009**, *43*, 2254. doi:10.1021/ES803138Z

[38] Y. Gu, B. Bian, C. L. Miller, W. Dong, X. Jiang, L. Liang, Mercury reduction and complexation by natural organic matter in anoxic environments. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 1479. doi:10.1073/PNAS.1008747108

[39] R. W. Macdonald, T. Harner, J. Fyfe, Recent climate change in the Canadian Arctic and its impact on contaminant pathways and interpretation of temporal trend data. *Sci. Total Environ.* **2005**, *342*, 5. doi:10.1016/J.SCITOTENV.2004.12.059

[40] R. W. Macdonald, J. M. Bewers, Contaminants in the arctic marine environment: priorities for protection. *ICES J. Mar. Sci.* **1996**, *53*, 537. doi:10.1006/JMSC.1996.0077

[41] P. Schlosser, B. Kromer, G. Östlund, B. Ekwurzel, G. Bönisch, H. H. Loosli, R. Furtschert, On the ^{14}C and ^{39}Ar distribution in the central Arctic Ocean: implications for deep water formation. *Radiocarbon* **1983**, *36*, 327.

[42] R. W. Macdonald, E. C. Carmack, D. W. R. Wallace, Tritium and radiocarbon dating of Canada Basin deep waters. *Science* **1993**, *259*, 103. doi:10.1126/SCIENCE.259.5091.103

[43] R. P. Mason, W. F. Fitzgerald, The distribution and biogeochemical cycling of mercury in the equatorial Pacific. *Deep-Sea Res.* **1993**, *40*, 1897. doi:10.1016/0967-0637(93)90037-4

[44] E. M. Sunderland, D. P. Krabbenhoft, J. W. Moreau, S. A. Strode, W. M. Landing, Mercury sources, distribution and bioavailability in the North Pacific Ocean: insights from data and models. *Global Biogeochem. Cycles* **2009**, *23*, GB2010. doi:10.1029/2008GB003425

[45] E. M. Sunderland, R. P. Mason, Human impacts on open ocean mercury concentrations. *Global Biogeochem. Cycles* **2007**, *21*, GB4022. doi:10.1029/2006GB002876

[46] S. Honjo, R. A. Krishfield, T. I. Eglinton, S. J. Manganini, J. N. Kemp, K. Doherty, J. Hwang, T. K. McKee, T. Takizawa, Biological pump processes in the cryopelagic and hemipelagic Arctic Ocean: Canada Basin and Chukchi Rise. *Prog. Oceanogr.* **2010**, *85*, 137. doi:10.1016/J.POCEAN.2010.02.009

[47] M. C. O'Brien, H. Melling, T. F. Pederson, R. W. Macdonald, The role of eddies and energetic ocean phenomena in the transport of sediment from shelf to basin in the Arctic. *J. Geophys. Res.* **2011**, *116*, C08001. doi:10.1029/2010JC006890

[48] J. Klaminder, K. Yoo, J. Rydberg, R. Giesler, An explorative study of mercury export from a thawing palsa mire. *J. Geophys. Res.* **2008**, *113*, G04034. doi:10.1029/2008JG000776

[49] J. Rydberg, J. Klaminder, P. Rosen, R. Bindler, Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes. *Sci. Total Environ.* **2010**, *408*, 4778. doi:10.1016/J.SCITOTENV.2010.06.056

[50] C. R. Hammerschmidt, W. F. Fitzgerald, Photodecomposition of methylmercury in arctic Alaskan Lakes. *Environ. Sci. Technol.* **2006**, *40*, 1212. doi:10.1021/ES0513234

[51] C. R. Hammerschmidt, W. F. Fitzgerald, C. H. Lamborg, P. H. Balcom, C. M. Tseng, Biogeochemical cycling of methylmercury in lakes and tundra watersheds of Arctic Alaska. *Environ. Sci. Technol.* **2006**, *40*, 1204. doi:10.1021/ES051322B

[52] M. F. Costa, P. S. Liss, Photoreduction of mercury in seawater and its possible implications for Hg^0 air–sea fluxes. *Mar. Chem.* **1999**, *68*, 87. doi:10.1016/S0304-4203(99)00067-5

[53] N. J. O'Driscoll, S. D. Siciliano, D. R. S. Lean, M. Amyot, Gross photo-reduction kinetics of mercury in temperate freshwater lakes and rivers: application to a general model for DGM dynamics. *Environ. Sci. Technol.* **2006**, *40*, 873.

[54] A. K. Møller, T. Barkay, W. A. Al-Soud, S. J. Sørensen, H. Skov, N. Kroer, Diversity and characterization of mercury-resistant bacteria in snow, freshwater and sea-ice brine from the High Arctic. *FEMS Microbiol. Ecol.* **2011**, *75*, 390. doi:10.1111/J.1574-6941.2010.01016.X

[55] M. Amyot, D. Lean, G. Mierle, Photochemical formation of volatile mercury in High Arctic Lakes. *Environ. Toxicol. Chem.* **1997**, *16*, 2054. doi:10.1002/ETC.5620161010

[56] C. M. Tseng, C. Lamborg, W. F. Fitzgerald, D. R. Engstrom, Cycling of dissolved elemental mercury in Arctic Alaskan lakes. *Geochim. Cosmochim. Acta* **2004**, *68*, 1173. doi:10.1016/J.GCA.2003.07.023

[57] G. M. Vandal, R. P. Mason, W. F. Fitzgerald, Cycling of volatile mercury in temperate lakes. *Water Air Soil Pollut.* **1991**, *56*, 791. doi:10.1007/BF00342317

[58] R. P. Mason, F. M. M. Morel, H. F. Hemond, The role of microorganisms in elemental mercury formation in natural waters. *Water Air Soil Pollut.* **1995**, *80*, 775. doi:10.1007/BF01189729

[59] A. J. Poulain, M. Amyot, D. Findlay, S. Telor, T. Barkay, H. Hintelman, Biological and photochemical production of dissolved gaseous mercury in a boreal lake. *Limnol. Oceanogr.* **2004**, *49*, 2265. doi:10.4319/LO.2004.49.6.2265

[60] A. J. Poulain, S. M. Ni Chadhain, P. A. Ariya, M. Amyot, E. Garcia, P. G. C. Campbell, G. Zylstra, T. Barkay, Potential for mercury reduction by microbes in the high Arctic. *Appl. Environ. Microbiol.* **2007**, *73*, 2230. doi:10.1128/AEM.02701-06

[61] P. M. Outridge, G. A. Stern, P. B. Hamilton, J. B. Percival, R. McNeely, W. L. Lockhart, Trace metal profiles in the varved sediment of an Arctic lake. *Geochim. Cosmochim. Acta* **2005**, *69*, 4881. doi:10.1016/J.GCA.2005.06.009

[62] P. M. Outridge, H. Sanei, G. A. Stern, P. B. Hamilton, F. Goodarzi, Evidence for control of mercury accumulation rates in Canadian High Arctic sediments by variations of aquatic primary productivity. *Environ. Sci. Technol.* **2007**, *41*, 5259. doi:10.1021/ES070408X

[63] H. E. Welch, J. Kalff, Benthic photosynthesis and respiration in Char Lake. *J. Fish. Res. Board Can.* **1974**, *31*, 609. doi:10.1139/F74-093

[64] S. Markager, W. F. Vincent, E. P. Y. Tang, Carbon fixation by phytoplankton in high Arctic lakes: implications of low temperature for photosynthesis. *Limnol. Oceanogr.* **1999**, *44*, 597. doi:10.4319/LO.1999.44.3.0597

[65] G. A. Stern, H. Sanei, P. Roach, J. Delaronde, P. M. Outridge, Historical interrelated variations of mercury and aquatic organic matter in lake sediment cores from a subarctic lake in Yukon, Canada: further evidence toward the algal-mercury scavenging hypothesis. *Environ. Sci. Technol.* **2009**, *43*, 7684. doi:10.1021/ES902186S

[66] J. Carrie, G. A. Stern, H. Sanei, R. W. Macdonald, P. M. Outridge, F. Wang, Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate. *Environ. Sci. Technol.* **2010**, *44*, 316. doi:10.1021/ES902582Y

[67] W. F. Fitzgerald, C. H. Lamborg, Geochemistry of mercury in the environment, in *Treatise on Geochemistry Volume 9: Environmental Chemistry* (Eds B. S. Lollar, H. D. Holland, K. K. Turekian) **2004**, pp. 107–148 (Elsevier–Pergamon: Oxford, UK).

[68] J. Chételat, M. Amyot, L. Cloutier, A. Poulain, Metamorphosis in chironomids, more than mercury supply, controls methylmercury transfer to fish in High Arctic lakes. *Environ. Sci. Technol.* **2008**, *42*, 9110. doi:10.1021/ES801619H

[69] F. M. M. Morel, A. M. L. Kraepiel, M. Amyot, The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* **1998**, *29*, 543. doi:10.1146/ANNUREV.ECOLSYS.29.1.543

[70] M. K. Woo, Hydrology of a drainage basin in the Canadian High Arctic. *Ann. Assoc. Am. Geogr.* **1983**, *73*, 577. doi:10.1111/J.1467-8306.1983.TB01860.X

[71] J. P. McNamara, D. L. Kane, L. D. Hinzman, An analysis of streamflow hydrology in the Kuparuk River Basin, Arctic Alaska: a nested watershed approach. *J. Hydrol.* **1998**, *206*, 39. doi:10.1016/S0022-1694(98)00083-3

[72] M. Tranter, P. Brimblecombe, T. D. Davies, C. E. Vincent, P. W. Abrahams, I. Blackwood, The composition of snowfall, snowpack and meltwater in the Scottish Highlands – evidence for preferential elution. *Atmos. Environ.* **1986**, *20*, 517. doi:10.1016/0004-6981(86)90092-2

[73] R. C. Bales, R. E. Davis, D. A. Stanley, Ion elution through shallow homogeneous snow. *Water Resour. Res.* **1989**, *25*, 1869. doi:10.1029/WR025I008P01869

[74] M. W. Williams, J. M. Melack, Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada. *Water Resour. Res.* **1991**, *27*, 1575. doi:10.1029/90WR02774

[75] R. Harrington, R. C. Bales, Interannual, seasonal, and spatial patterns of meltwater and solute fluxes in a seasonal snowpack. *Water Resour. Res.* **1998**, *34*, 823. doi:10.1029/97WR03469

[76] P. F. Schuster, J. B. Shanley, M. Marvin-Dipasquale, M. M. Reddy, G. R. Aiken, D. A. Roth, H. E. Taylor, D. P. Krabbenhoft, J. F. DeWild, Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. *Water Air Soil Pollut.* **2008**, *187*, 89. [Published online early 12 October 2007]. doi:10.1007/S11270-007-9500-3

[77] L. L. Loseto, D. S. Lean, S. D. Siciliano, Snowmelt sources of methylmercury to High Arctic ecosystems. *Environ. Sci. Technol.* **2004**, *38*, 3004. doi:10.1021/ES035146N

[78] T. Berg, S. Sekkesæter, E. Steinnes, A. Valdal, G. Wibetoe, Springtime depletion of mercury in the European Arctic as observed at Svalbard. *Sci. Total Environ.* **2003**, *304*, 43. doi:10.1016/S0048-9697(02)00555-7

[79] A. Dommergue, C. P. Ferrari, P.-A. Gauchard, C. F. Boutron, L. Poissant, M. Pilote, P. Jitaru, F. C. Adams, The fate of mercury species in a sub-arctic snowpack during snowmelt. *Geophys. Res. Lett.* **2003**, *30*, 1621. doi:10.1029/2003GL017308

[80] A. O. Steen, K. Aspmo, T. Berg, A. P. Dastoor, D. A. Durnford, L. R. Hole, Dynamic exchange of gaseous elemental mercury during polar night and day in Ny-Ålesund. *Atmos. Environ.* **2009**, *43*, 5604. doi:10.1016/J.ATMOSENV.2009.07.069

[81] A. Dommergue, C. P. Ferrari, L. Poissant, P. A. Gauchard, C. F. Boutron, Diurnal cycles of gaseous mercury within the snowpack at Kuujjuarapik/Whapmagoostui, Quebec, Canada. *Environ. Sci. Technol.* **2003**, *37*, 3289. doi:10.1021/ES026242B

[82] A. Steffen, T. A. Douglas, M. Amyot, P. Ariya, K. Aspmo, T. Berg, J. Bottenheim, S. Brooks, F. Cobbett, A. Dastoor, A. Dommergue, R. Ebinghaus, C. Ferrari, K. Gårdfeldt, M. E. Goodsite, D. Lean, A. Poulain, C. Scherz, H. Skov, J. Sommar, C. Temme, A synthesis of atmospheric mercury depletion event chemistry linking atmosphere, snow and water. *Atmos. Chem. Phys. Discuss.* **2007**, *7*, 10 837. doi:10.5194/ACPD-7-10837-2007

[83] E. J. Carpenter, S. Lin, D. G. Capone, Bacterial activity in South Pole snow. *Appl. Environ. Microbiol.* **2000**, *66*, 4514. doi:10.1128/AEM.66.10.4514-4517.2000

[84] P. Amato, R. Hennebelle, O. Magnand, M. Sancelme, A.-M. Delort, C. Barbante, C. Boutron, C. Ferrari, Bacterial characterization of the snow cover at Spitzberg, Svalbard. *FEMS Microbiol. Ecol.* **2007**, *59*, 255. doi:10.1111/J.1574-6941.2006.00198.X

[85] K. Junge, H. Eicken, B. D. Swanson, J. W. Deming, Bacterial incorporation of leucine into protein down to $-20\,°C$ with evidence for potential activity in sub-eutectic saline ice formations. *Cryobiology* **2006**, *52*, 417. doi:10.1016/J.CRYOBIOL.2006.03.002

[86] D. Cossa, B. Averty, N. Pirrone, The origin of methylmercury in open Mediterranean waters. *Limnol. Oceanogr.* **2009**, *54*, 837. doi:10.4319/LO.2009.54.3.0837

[87] D. Cossa, L.-E. Heimburger, D. Lannuzel, S. R. Rintoul, C. V. Butler, A. R. Bowie, B. Averty, R. J. Watson, T. Remenyi, Mercury in the Southern Ocean. *Geochim. Cosmochim. Acta* **2011**, *75*, 4037. doi:10.1016/J.GCA.2011.05.001

[88] T. Barkay, S. M. Miller, A. O. Summers, Bacterial mercury resistance from atoms to ecosystems. *FEMS Microbiol. Rev.* **2003**, *27*, 355. doi:10.1016/S0168-6445(03)00046-9

[89] D. Ben-Bassat, A. M. Mayer, Light-induced Hg volatilization and O_2 evolution in *Chlorella* and the effect of DCMU and methylamine. *Physiol. Plant.* **1978**, *42*, 33. doi:10.1111/J.1399-3054.1978.TB01534.X

[90] M. Stibal, J. Elster, Growth and morphology variation as a response to changing environmental factors in two Arctic species of *Raphidonema* (Trebouxiophyceae) from snow and soil. *Polar Biol.* **2005**, *28*, 558. doi:10.1007/S00300-004-0709-Y

[91] L. L. Loseto, S. D. Siciliano, D. R. S. Lean, Methyl mercury production in High Arctic wetlands. *Environ. Toxicol. Chem.* **2004**, *23*, 17. doi:10.1897/02-644

[92] J. D. Lalonde, A. J. Poulain, M. Amyot, The role of mercury redox reactions in snow on snow–to–air mercury transfer. *Environ. Sci. Technol.* **2002**, *36*, 174. doi:10.1021/ES010786G

[93] J. D. Lalonde, M. Amyot, M.-R. Doyon, J.-C. Auclair, Photoinduced Hg^{II} reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada). *J. Geophys. Res.* **2003**, *108(D6)*, 4200. doi:10.1029/2001JD001534

[94] E. Garcia, M. Amyot, P. Ariya, Relationship between DOC photochemistry and mercury redox transformations in temperate lakes and wetlands. *Geochim. Cosmochim. Acta* **2005**, *69*, 1917. doi:10.1016/J.GCA.2004.10.026

[95] E. B. Ekstrom, F. M. M. Morel, J. M. Benoit, Mercury methylation independent of the acetyl-coenzyme: a pathway in sulfate-reducing-bacteria. *Appl. Environ. Microbiol.* **2003**, *69*, 5414. doi:10.1128/AEM.69.9.5414-5422.2003

[96] L. Lambertsson, M. Nilsson, Organic material: the primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. *Environ. Sci. Technol.* **2006**, *40*, 1822. doi:10.1021/ES051785H

[97] W. Dong, L. Liang, S. Brooks, G. Southworth, B. Gu, Roles of dissolved organic matter in the speciation of mercury and methyl-mercury in a contaminated ecosystem in Oak Ridge, Tennessee. *Environ. Chem.* **2010**, *7*, 94. doi:10.1071/EN09091

[98] L.-E. Heimbürger, D. Cossa, J.-C. Marty, C. Migon, B. Averty, A. Dufour, J. Ras, Methyl mercury distributions in relation to the presence of nano and picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). *Geochim. Cosmochim. Acta* **2010**, *74*, 5549. doi:10.1016/J.GCA.2010.06.036

[99] I. Lehnherr, V. L. St Louis, H. Hintelmann, J. L. Kirk, Methylation of inorganic mercury in polar marine waters. *Nat. Geosci.* **2011**, *4*, 298. doi:10.1038/NGEO1134

[100] D. Wang, S. M. Henrichs, L. Guo, Distributions of nutrients, dissolved organic carbon and carbohydrates in the western Arctic Ocean. *Cont. Shelf Res.* **2006**, *26*, 1654. doi:10.1016/J.CSR.2006.05.001

[101] J. L. Kirk, V. L. St Louis, H. Hintelmann, I. Lehnherr, B. Else, L. Poissant, Methylated mercury species in marine waters of the Canadian High and sub-Arctic. *Environ. Sci. Technol.* **2008**, *42*, 8367. doi:10.1021/ES801635M

[102] AMAP, *Arctic Monitoring and Assessment Programme Assessment 2009: Human Health in the Arctic* **2009** (Arctic Monitoring and Assessment Programme: Oslo, Norway).

[103] C. H. Lamborg, W. F. Fitzgerald, J. O'Donnell, J. T. Torgerson, A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric gradients. *Geochim. Cosmochim. Acta* **2002**, *66*, 1105. doi:10.1016/S0016-7037(01)00841-9

[104] F. J. G. Laurier, R. P. Mason, G. A. Gill, L. Whalin, Mercury distributions in the North Pacific Ocean – 20 years of observations. *Mar. Chem.* **2004**, *90*, 3. doi:10.1016/J.MARCHEM.2004.02.025

[105] R. P. Mason, N. M. Lawson, G.-R. Sheu, Mercury in the Atlantic Ocean: factors controlling air–sea exchange of mercury and its distribution in the upper waters. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2001**, *48*, 2829. doi:10.1016/S0967-0645(01)00020-0

[106] R. P. Mason, K. R. Rolfus, W. F. Fitzgerald, Methylated and elemental mercury cycling in surface and deep ocean waters of the North Atlantic. *Water Air Soil Pollut.* **1995**, *80*, 665. doi:10.1007/BF01189719

[107] A. L. Soerensen, E. M. Sunderland, C. D. Holmes, D. J. Jacob, R. Yantosca, H. Skov, J. Christensen, S. A. Strode, R. P. Mason, A global simulation of mercury air–sea exchange for evaluating impacts on marine boundary layer concentrations. *Environ. Sci. Technol.* **2010**, *44*, 8574. doi:10.1021/ES102032G

[108] M. A. Granskog, R. W. Macdonald, C. J. Mundy, D. G. Barber, Distribution, characteristics and potential impacts of chromophoric dissolved organic matter (CDOM) in the Hudson Strait and the Hudson Bay. *Cont. Shelf Res.* **2007**, *27*, 2032. doi:10.1016/J.CSR.2007.05.001

[109] H. T. Nguyen, K.-H. Kim, Z.-H. Shon, S. Hong, A review of atmospheric mercury in the polar environment. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39*, 552. doi:10.1080/10643380701764308

[110] J. L. Guentzel, R. T. Powell, W. M. Landing, R. P. Mason, Mercury associated with colloidal material in an estuarine and an open-ocean environment. *Mar. Chem.* **1996**, *55*, 177. doi:10.1016/S0304-4203(96)00055-2

[111] R. P. Mason, K. A. Sullivan, The distribution and speciation of mercury in the South and equatorial Atlantic. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **1999**, *46*, 937. doi:10.1016/S0967-0645(99)00010-7

[112] A. D. McGuire, L. G. Anderson, T. R. Christensen, S. Dallimore, L. Guo, D. J. Hayes, M. Heimann, T. D. Lorenson, R. W. Macdonald, N. Roulet, Sensitivity of the carbon cycle in the Arctic to climate change. *Ecol. Monogr.* **2009**, *79*, 523. doi:10.1890/08-2025.1

[113] J. A. Graydon, C. A. Emmerton, L. F. W. Lesack, E. N. Kelly, Mercury in the Mackenzie River delta and estuary: concentrations and fluxes during open-water conditions. *Sci. Total Environ.* **2009**, *407*, 2980. doi:10.1016/J.SCITOTENV.2008.12.060

[114] M. C. O'Brien, R. W. Macdonald, H. Melling, K. Iseki, K., Geochemistry and physical forcing of sediment transport and deposition in the Canadian Beaufort Sea. *Cont. Shelf Res.* **2006**, *26*, 41.

[115] C. H. Conaway, F. J. Black, M. Gault-Ringold, J. T. Pennington, F. P. Chavez, A. R. Flegal, Dimethylmercury in coastal upwelling waters, Monterey Bay, California. *Environ. Sci. Technol.* **2009**, *43*, 1305. doi:10.1021/ES802705T

[116] G. A. Stern, R. W. Macdonald, Biogeographic provinces of total and methyl mercury in zooplankton and fish from the Beaufort and Chukchi Seas: results from the SHEBA drift. *Environ. Sci. Technol.* **2005**, *39*, 4707. doi:10.1021/ES0482278

[117] C. Gobeil, R. W. Macdonald, B. Sundby, Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. *Geochim. Cosmochim. Acta* **1997**, *61*, 4647. doi:10.1016/S0016-7037(97)00255-X

[118] C. Gobeil, B. Sundby, R. W. Macdonald, J. N. Smith, Recent change in organic carbon flux to Arctic Ocean deep basins: evidence from acid volatile sulfide, manganese and rhenium discord in sediments. *Geophys. Res. Lett.* **2001**, *28*, 1743. doi:10.1029/2000GL012491

[119] R. P. Mason, J. R. Reinfelder, F. M. M. Morel, Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environ. Sci. Technol.* **1996**, *30*, 1835. doi:10.1021/ES950373D

[120] C. J. Watras, R. C. Back, S. Halvorsen, R. J. M. Hudson, K. A. Morrison, S. P. Wente, Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* **1998**, *219*, 183. doi:10.1016/S0048-9697(98)00228-9

[121] N. M. Lawson, R. P. Mason, Accumulation of mercury in estuarine food chains. *Biogeochem.* **1998**, *40*, 235. doi:10.1023/A:1005959211768

[122] P. C. Pickhardt, N. S. Fisher, Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. *Environ. Sci. Technol.* **2007**, *41*, 125. doi:10.1021/ES060966W

[123] P. R. Gorski, D. E. Armstrong, J. P. Hurley, D. P. Krabbenhoft, Influence of natural dissolved organic carbon on the bioavailability of mercury to a freshwater alga. *Environ. Pollut.* **2008**, *154*, 116. doi:10.1016/J.ENVPOL.2007.12.004

[124] H. Zhong, W.-X. Wang, Controls of dissolved organic matter and chloride on mercury uptake by a marine diatom. *Environ. Sci. Technol.* **2009**, *43*, 8998. doi:10.1021/ES901646K

[125] M. A. Goñi, M. B. Yunker, R. W. Macdonald, T. I. Eglinton, The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean. *Mar. Chem.* **2005**, *93*, 53. doi:10.1016/J.MARCHEM.2004.08.001

[126] L. Guo, R. W. Macdonald, Source and transport of terrigenous organic matter in the upper Yukon River: evidence from isotope ($\delta^{13}C$, $\Delta^{14}C$, and $\delta^{15}N$) composition of dissolved, colloidal, and particulate phases. *Global Biogeochem. Cycles* **2006**, *20*, GB2011. doi:10.1029/2005GB002593

[127] L. Guo, C.-L. Ping, R. W. Macdonald, Mobilization pathways of organic carbon from permafrost to Arctic rivers in a changing climate. *Geophys. Res. Lett.* **2007**, *34*, L13603. doi:10.1029/2007GL030689

[128] Z. Z. A. Kuzyk, M. A. Goni, G. A. Stern, R. W. Macdonald, Sources, pathways and sinks of particulate organic matter in Hudson Bay: evidence from lignin distributions. *Mar. Chem.* **2008**, *112*, 215. doi:10.1016/J.MARCHEM.2008.08.001

[129] K. Fu, P. Kawamura, J. Chen, L. A. Barrie, Isoprene, monoterpene, and sesquiterpene oxidation products in the High Arctic aerosols during late winter to early summer. *Environ. Sci. Technol.* **2009**, *43*, 4022. doi:10.1021/ES803669A

[130] H. Sanei, F. Goodarzi, Relationship between organic matter and mercury in recent lake sediment: the physical–geochemical aspects. *Appl. Geochem.* **2006**, *21*, 1900. doi:10.1016/J.APGEOCHEM.2006.08.015

[131] R. Bargagli, F. Monaci, C. Bucci, Environmental biogeochemistry of mercury in Antarctic ecosystems. *Soil Biol. Biochem.* **2007**, *39*, 352. doi:10.1016/J.SOILBIO.2006.08.005

[132] J. M. Benoit, C. C. Gilmour, R. P. Mason, A. Heyes, Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Technol.* **1999**, *33*, 951. doi:10.1021/ES9808200

[133] G. R. Golding, C. A. Kelly, R. Sparling, P. C. Loewen, J. W. M. Rudd, T. Barkay, Evidence for facilitated uptake of Hg^{II} by *Vibrio anguillarum* and *Escherichia coli* under anaerobic and aerobic conditions. *Limnol. Oceanogr.* **2002**, *47*, 967. doi:10.4319/LO.2002.47.4.0967

[134] J. K. Schaefer, F. M. M. Morel, High methylation rates of mercury bound to cysteine by *Geobacter sulfurreducens*. *Nat. Geosci.* **2009**, *2*, 123. doi:10.1038/NGEO412

[135] J. K. Schaefer, S. S. Rocks, W. Zheng, L. Liang, B. Gu, F. M. M. Morel, Active transport, substrate specificity, and methylation of Hg^{II} in anaerobic bacteria. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 8714. doi:10.1073/PNAS.1105781108

[136] C. J. Watras, N. S. Bloom, Mercury and methylmercury individual zooplankton-implications for bioaccumulation. *Limnol. Oceanogr.* **1992**, *37*, 1313. doi:10.4319/LO.1992.37.6.1313

[137] W. Baeyens, M. Leermakers, T. Papina, A. Saprykin, N. Brion, J. Noyen, M. De Gieter, L. Goeyens, Bioconcentration and biomagnification of mercury and methylmercury in North Sea and Scheldt Estuary fish. *Arch. Environ. Contam. Toxicol.* **2003**, *45*, 498. doi:10.1007/S00244-003-2136-4

[138] B. A. Methe, K. E. Nelson, J. W. Deming, B. Momen, E. Melamud, X. J. Zhang, J. Moult, R. Madupu, W. C. Nelson, R. J. Dodson, L. M. Brinkac, S. C. Daugherty, A. S. Durkin, R. T. DeBoy, J. F. Kolonay, S. A. Sullivan, L. W. Zhou, T. M. Davidsen, M. Wu, A. L. Huston, M. Lewis, B. Weaver, J. F. Weidman, H. Khouri, T. R. Utterback, T. V. Feldblyum, C. M. Fraser, The psychrophilic lifestyle as revealed by the genome sequence of *Colwellia psychrerythraea* 34H through genomic and proteomic analyses. *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10 913. doi:10.1073/PNAS.0504766102

[139] T. Barkay, A. J. Poulain, Mercury (micro)biogeochemistry in polar environments. *FEMS Microbiol. Ecol.* **2007**, *59*, 232. doi:10.1111/J.1574-6941.2006.00246.X

[140] C. C. Gilmour, E. A. Henry, R. Mitchell, Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* **1992**, *26*, 2281. doi:10.1021/ES00035A029

[141] E. J. Fleming, E. E. Mack, P. G. Green, D. C. Nelson, Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. *Appl. Environ. Microbiol.* **2006**, *72*, 457. doi:10.1128/AEM.72.1.457-464.2006

[142] E. J. Kerin, C. C. Gilmour, E. Roden, M. T. Suzuki, J. D. Coates, R. P. Mason, Mercury methylation by dissimilatory iron-reducing bacteria. *Appl. Environ. Microbiol.* **2006**, *72*, 7919. doi:10.1128/AEM.01602-06

[143] S. Hamelin, M. Amyot, T. Barkay, Y. Wang, D. Planas, Methanogens: principal methylators of mercury in Lake Periphyton. *Environ. Sci. Technol.* **2011**, *45*, 7693. doi:10.1021/ES2010072

[144] L. L. Loseto, G. A. Stern, D. Deibel, T. L. Connelly, A. Prokopowicz, D. R. S. Lean, L. Fortier, S. H. Ferguson, Linking mercury exposure to habitat and feeding behaviour in Beaufort Sea beluga whales. *J. Mar. Syst.* **2008**, *74*, 1012. doi:10.1016/J.JMARSYS.2007.10.004

[145] L. M. Campbell, R. J. Norstrom, K. A. Hobson, D. C. G. Muir, S. Backus, A. Fisk, Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Sci. Total Environ.* **2005**, *351–352*, 247. doi:10.1016/J.SCITOTENV.2005.02.043

[146] L. Atwell, K. A. Hobson, H. E. Welch, Biomagnification and bioaccumulation of mercury in an Arctic marine food web: insights from stable nitrogen isotope analysis. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 1114. doi:10.1139/F98-001

[147] H. Niki, P. D. Maker, C. M. Savage, L. P. Breitenbach, A long-path Fourier-transform infrared study of the kinetics and mechanism for the HO-radical initiated oxidation of dimethylmercury. *J. Phys. Chem.* **1983**, *87*, 4978. doi:10.1021/J150642A041

[148] H. Niki, P. S. Maker, C. M. Savage, L. P. Breitenbach, A Fourier-transform infrared study of the kinetics and mechanism of the reaction of atomic chlorine with dimethylmercury. *J. Phys. Chem.* **1983**, *87*, 3722. doi:10.1021/J100242A029

[149] R. Pongratz, K. G. Heumann, Production of methylated mercury, lead, and cadmium by marine bacteria as a significant natural source for atmospheric heavy metals in polar regions. *Chemosphere* **1999**, *39*, 89. doi:10.1016/S0045-6535(98)00591-8

[150] R. Pongratz, K. G. Heumann, Production of methylated mercury and lead by polar macroalgae – a significant natural source for atmospheric heavy metals in clean room compartments. *Chemosphere* **1998**, *36*, 1935. doi:10.1016/S0045-6535(97)10078-9

[151] K. Gårdfeldt, J. Munthe, D. Strömberg, O. Lindqvist, A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase. *Sci. Total Environ.* **2003**, *304*, 127. doi:10.1016/S0048-9697(02)00562-4

[152] C. R. Hammerschmidt, C. H. Lamborg, W. F. Fitzgerald, Aqueous phase methylation as a potential source of methylmercury in wet deposition. *Atmos. Environ.* **2007**, *41*, 1663. doi:10.1016/J.ATMOSENV.2006.10.032

[153] S. D. Siciliano, N. J. O'Driscoll, R. Tordon, J. Hill, S. Beauchamp, D. R. Lean, Abiotic production of methylmercury by solar radiation. *Environ. Sci. Technol.* **2005**, *39*, 1071. doi:10.1021/ES048707Z

[154] L. Oiffer, S. D. Siciliano, Methyl mercury production and loss in Arctic soil. *Sci. Total Environ.* **2009**, *407*, 1691. doi:10.1016/J.SCITOTENV.2008.10.025

[155] L. Poissant, H. Zhang, J. Canario, P. Constant, Critical review of mercury fates and contamination in the Arctic tundra ecosystem. *Sci. Total Environ.* **2008**, *400*, 173. doi:10.1016/J.SCITOTENV.2008.06.050

[156] I. Lehnherr, V. L. St Louis, Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. *Environ. Sci. Technol.* **2009**, *43*, 5692. doi:10.1021/ES9002923

[157] T. Barkay, S. M. Miller, A. O. Summers, Bacterial mercury resistance from atoms to ecosystems. *FEMS Microbiol. Rev.* **2003**, *27*, 355. doi:10.1016/S0168-6445(03)00046-9

[158] L. L. Loseto, *Beaufort Sea beluga whales: an ecological approach to examining diet and dietary sources of mercury* **2007**, Ph.D. thesis,, University of Manitoba, Winnipeg.

[159] B. D. Hall, D. M. Rosenberg, A. P. Wiens, Methyl mercury in aquatic insects from an experimental reservoir. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 2036. doi:10.1139/F98-079

[160] L. L. Loseto, G. A. Stern, S. H. Ferguson, Size and biomagnification: how habitat selection explains Beluga Mercury levels. *Environ. Sci. Technol.* **2008**, *42*, 3982. doi:10.1021/ES7024388

[161] G. Cabana, J. B. Rasmussen, Modelling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. *Nature* **1994**, *372*, 255. doi:10.1038/372255A0

[162] C. M. Headon, R. J. Hall, G. Mierle, Dynamics of radiolabelled methylmercury in crayfish (*Orconectes virilis*). *Can. J. Fish. Aquat. Sci.* **1996**, *53*, 2862. doi:10.1139/F96-222

[163] K. A. Kidd, M. J. Paterson, R. H. Hesslein, D. C. G. Muir, R. E. Hecky, Effects of northern pike (*Esox lucius*) additions on pollutant bioaccumulation and food web structure, as determined by δ^{13}C and δ^{15}N, in a eutrophic and an oligotrophic lake. *Can. J. Fish. Aquat. Sci.* **1999**, *56*, 2193. doi:10.1139/F99-148

[164] R. Karimi, C. Y. Chen, P. C. Pickhardt, N. S. Fisher, C. L. Folt, Stoichiometric controls of mercury dilution by growth. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 7477. doi:10.1073/PNAS.0611261104

[165] H. K. Swanson, K. A. Kidd, Mercury concentrations in arctic food fishes reflect the presence of anadromous arctic charr (*Salvelinus alpinus*), species, and life history. *Environ. Sci. Technol.* **2010**, *44*, 3286. doi:10.1021/ES100439T

[166] H. Swanson, N. Gantner, K. A. Kidd, D. Muir, J. D. Reist, Comparison of mercury concentrations in landlocked, resident, and sea-run fish (*Salvelinus* spp.) from Nunavut, Canada. *Environ. Toxicol. Chem.* **2011**, *30*, 1459. doi:10.1002/ETC.517

[167] F. F. Rigét, P. Møller, R. Dietz, T. G. Nielsen, G. Asmund, J. Strand, M. M. Larsen, K. A. Hobson, Transfer of mercury in the marine food web at West Greenland. *J. Environ. Monit.* **2007**, *9*, 877. doi:10.1039/B704796G

[168] I. G. Hallanger, A. Ruus, D. Herzke, N. A. Warner, A. Evenset, E. S. Heimstad, G. W. Gabrielsen, K. Borgå, Influence of season, location, and feeding strategy on bioaccumulation of halogenated organic contaminants in Arctic marine zooplankton. *Environ. Toxicol. Chem.* **2011**, *30*, 77. doi:10.1002/ETC.362

[169] L. Legendre, S. F. Ackley, G. S. Dieckmann, B. Gulliksen, R. Horner, T. Hoshiai, I. A. Melnikov, W. S. Reeburgh, M. Spindler, C. W. Sullivan, Ecology of sea ice biota. *Polar Biol.* **1992**, *12*, 429. doi:10.1007/BF00243114

[170] M. Gosselin, M. Levasseur, P. A. Wheeler, R. A. Horner, B. C. Booth, New measurements of phytoplankton and ice algal production in the Arctic Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **1997**, *44*, 1623. doi:10.1016/S0967-0645(97)00054-4

[171] R. A. Horner, *Sea Ice Biota* **1985**, pp. 173–190 (CRC Press: Boca Raton, FL).

[172] A. K. Geynrikh, Mass species of oceanic phytophagous copepods and their ecology. *Oceanology (Mosc.)* **1986**, *26*, 213.

[173] A. M. Springer, C. P. McRoy, M. V. Flint, The Bering Sea green belt: shelf-edge process and ecosystem production. *Fish. Oceanogr.* **1996**, *5*, 205. doi:10.1111/J.1365-2419.1996.TB00118.X

[174] H. Auel, W. Hagen, Mesozooplankton community structure, abundance and biomass in the central Arctic Ocean. *Mar. Biol.* **2002**, *140*, 1013. doi:10.1007/S00227-001-0775-4

[175] M. Poltermann, Arctic sea ice as feeding ground for amphipods – food sources and strategies. *Polar Biol.* **2001**, *24*, 89. doi:10.1007/S003000000177

[176] M. S. W. Bradstreet, W. E. Cross, Trophic relationships at high Arctic ice edges. *Arctic* **1982**, *35*, 1.

[177] P. C. Craig, W. Griffiths, L. Haldorson, L. McElderry, Ecological studies of Arctic cod (Boreogadus saida) in Beaufort Sea coastal waters, Alaska. *Can. J. Fish. Aquat. Sci.* **1982**, *39*, 395. doi:10.1139/F82-057

[178] M. S. W. Bradstreet, K. J. Finley, A. D. Sekerak, W. B. Griffiths, C. R. Evans, M. Fabijan, H. E. Stallard, *Aspects of the biology of Arctic cod (*Boreogadus saida*) and its importance in Arctic marine food chains, Canada Department of Fisheries and Oceans, Central and Arctic Region, Technical Report 1491* **1986** (Fisheries and Oceans Canada: Winnipeg).

[179] T. G. Smith, The ringed seal, *Phoca hispida*, of the Canadian western Arctic. *Can. Bull. Fish. Aquat. Sci.* **1987**, *216*, 43.

[180] O. J. Lønne, B. Gulliksen, Size, age and diet of polar cod, *Boreogadus saida* (Lepechin 1773) in ice covered waters. *Polar Biol.* **1989**, *9*, 187. doi:10.1007/BF00297174

[181] O. J. Lønne, G. W. Gabrielsen, Summer diet of seabirds feeding in sea-ice-covered waters near Svalbard. *Polar Biol.* **1992**, *12*, 685. doi:10.1007/BF00238868

[182] K. J. Frost, L. F. Lowry, Trophic importance of some marine gadids in Northern Alaska and their body-otolith size relationships. *Fish Bull.* **1981**, *79*, 187.

[183] K. A. Hobson, A. Fisk, N. Karnovsky, M. Holst, J.-M. Gagnon, M. Fortier, A stable isotope (δ^{13}C, δ^{15}N) model for the North Water food web: implications for evaluating trophodynamics and the flow of energy and contaminants. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2002**, *49*, 5131. doi:10.1016/S0967-0645(02)00182-0

[184] R. A. Horner, G. C. Schrader, Relative contributions of ice algae, phytoplankton and benthic microalgae to primary production in nearshore regions of the Beaufort Sea. *Arctic* **1982**, *35*, 485.

[185] D. Hamel, A. de Vernal, M. Gosselin, C. Hillaire-Marcel, Organic-walled microfossils and geochemical tracers: sedimentary indicators of productivity changes in the North Water and northern Baffin Bay during the last centuries. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2002**, *49*, 5277. doi:10.1016/S0967-0645(02)00190-X

[186] R. Bargagli, C. Agnorelli, F. Borghini, F. Monaci, Enhanced deposition and bioaccumulation of mercury in Antarctic terrestrial ecosystems facing a coastal polynya. *Environ. Sci. Technol.* **2005**, *39*, 8150. doi:10.1021/ES0507315

[187] J. Carignan, J. Sonke, The effect of atmospheric mercury depletion events on the net deposition flux around Hudson Bay, Canada. *Atmos. Environ.* **2010**, *44*, 4372. doi:10.1016/J.ATMOSENV.2010.07.052

[188] E. Sakshaug, Primary and secondary production in the Arctic Seas, in *The Organic Carbon Cycle in the Arctic Ocean* (Eds R. Stein, R. W. Macdonald) **2004**, pp. 57–81 (Springer: Berlin).

[189] D. Lavoie, R. W. Macdonald, K. L. Denman, Primary productivity and export fluxes on the Canadian shelf of the Beaufort Sea: a modelling study. *J. Mar. Syst.* **2009**, *75*, 17. doi:10.1016/J.JMARSYS.2008.07.007

[190] N. Mumm, H. Auel, H. Hanssen, W. Hagen, C. Richter, H.-J. Hirche, Breaking the ice: large-scale distribution of mesozooplankton after a decade of Arctic and transpolar cruises. *Polar Biol.* **1998**, *20*, 189. doi:10.1007/S003000050295

[191] I. Jæger, H. Hop, G. W. Gabrielsen, Biomagnification of mercury in selected species from an Arctic marine food web in Svalbard. *Sci. Total Environ.* **2009**, *407*, 4744. doi:10.1016/J.SCITOTENV.2009.04.004

[192] R. Stein, R. W. Macdonald (Eds), *The Organic Carbon Cycle in the Arctic Ocean* **2004** (Springer: Berlin).

[193] M. C. Serreze, A. P. Barrett, A. G. Slater, R. A. Woodgate, K. Aagaard, R. B. Lammers, M. Steel, R. Moritz, M. Meredith, C. M. Lee, The large-scale freshwater cycle of the Arctic. *J. Geophys. Res.* **2006**, *111*, C11010. doi:10.1029/2005JC003424

[194] G. Darnis, D. G. Barber, L. Fortier, Sea ice and the onshore–offshore gradient in pre-winter zooplankton assemblages in southeastern Beaufort Sea. *J. Mar. Syst.* **2008**, *74*, 994. doi:10.1016/J.JMARSYS.2007.09.003

[195] B. J. Gallaway, W. B. Griffiths, P. C. Craig, W. T. Gazey, J. W. Helmericks, An assessment of the Colville River delta stock of Arctic cisco: migrants from Canada. *Biol. Pap. Univ. Alaska* **1983**, *21*, 4.

[196] R. G. Fechhelm, L. R. Martin, B. J. Gallaway, W. J. Wilson, W. B. Griffiths, Prudhoe Bay causeways and the summer coastal movements of Arctic cisco and least cisco. *Arctic* **1991**, *52*, 139.

[197] A. Forest, M. Sampei, H. Hattori, R. Makabe, H. Sasaki, M. Fukuchi, P. Wassmann, L. Fortier, Particulate organic carbon fluxes on the slope of the Mackenzie Shelf (Beaufort Sea): physical and biological forcing of shelf-basin exchanges. *J. Mar. Syst.* **2007**, *68*, 39. doi:10.1016/J.JMARSYS.2006.10.008

[198] D. M. Schell, Carbon-13 and carbon-14 abundances in Alaskan aquatic organisms: delayed production from peat in Arctic food webs. *Science* **1983**, *219*, 1068. doi:10.1126/SCIENCE.219.4588.1068

[199] M.-È. Garneau, W. F. Vincent, L. Alonso-Sàez, Y. Gratton, C. Lovejoy, Prokaryotic community structure and heterotrophic production in a river-influenced coastal arctic ecosystem. *Aquat. Microb. Ecol.* **2006**, *42*, 27. doi:10.3354/AME042027

[200] K. E. Conlan, H. S. Lenihan, R. G. Kvitek, J. S. Oliver, Ice scour disturbance to benthic communities in the Canadian High Arctic. *Mar. Ecol. Prog. Ser.* **1998**, *166*, 1. doi:10.3354/MEPS166001

[201] R. G. Kvitek, K. E. Conlan, O. J. Iampietro, Black pools of death: hypoxic, brine-filled ice gouge depressions become lethal traps for benthic organisms in a shallow Arctic embayment. *Mar. Ecol. Prog. Ser.* **1998**, *162*, 1. doi:10.3354/MEPS162001

[202] J. P. Coelho, M. Nunes, M. Dolbeth, M. E. Pereira, A. C. Duarte, M. A. Pardal, The role of two sediment-dwelling invertebrates on the mercury transfer from sediments to the estuarine trophic web. *Estuar. Coast. Shelf Sci.* **2008**, *78*, 505. doi:10.1016/J.ECSS.2008. 01.017

[203] J. M. Benoit, C. C. Gilmour, A. Heyes, R. P. Mason, C. L. Miller, Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems, in *Biogeochemistry of Environmentally Important Trace Elements, ACS Symposium Series Number 835* **2002**, pp. 262–297 (American Chemical Society: Washington, DC).

[204] R. C. Harris, J. W. M. Rudd, M. Amyot, C. L. Babiarz, K. G. Beaty, P. J. Blanchfield, R. A. Bodaly, B. A. Branfireun, C. C. Gilmour, J. A. Graydon, A. Heyes, H. Hintelmann, J. P. Hurley, C. A. Kelly, D. P. Krabbenhoft, S. E. Lindberg, R. P. Mason, M. J. Paterson, C. L. Podemski, A. Robinson, K. A. Sandilands, G. R. Southworth, V. L. St Louis, M. T. Tate, Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 16 586. doi:10.1073/PNAS.0704186104

[205] C. R. Hammerschmidt, W. F. Fitzgerald, Methylmercury in mosquitoes related to atmospheric mercury deposition and contamination. *Environ. Sci. Technol.* **2005**, *39*, 3034. doi:10.1021/ES0485107

[206] N. Gantner, M. Power, D. Iqaluk, M. Meili, H. Borg, M. Sundbom, K. Solomon, G. Lawson, D. C. Muir, Mercury concentrations in landlocked Arctic char (*Salvelinus alpinus*) from the Canadian High Arctic. Part I – Insights from trophic relationships in 18 lakes. *Environ. Toxicol. Chem.* **2010**, *29*, 621. doi:10.1002/ETC.95

[207] N. Gantner, D. C. Muir, M. Power, D. Iqaluk, J. D. Reist, J. A. Babaluk, M. Meili, H. Borg, J. Hammar, W. Michaud, J. B. Dempson, K. R. Solomon, Mercury Concentrations in Landlocked Arctic char (*Salvelinus alpinus*) from the Canadian High Arctic. Part II – Influence of lake biotic and abiotic characteristics on geographical trends in 27 populations. *Environ. Toxicol. Chem.* **2010**, *29*, 633. doi:10.1002/ETC.96

[208] J. Chételat, M. Amyot, Elevated methylmercury in High Arctic Daphnia and the role of productivity in controlling their distribution. *Glob. Change Biol.* **2009**, *15*, 706. doi:10.1111/J.1365-2486.2008. 01729.X

[209] C. R. Hammerschmidt, W. F. Fitzgerald, Methylmercury in arctic Alaskan mosquitoes: implications for impact of atmospheric mercury depletion events. *Environ. Chem.* **2008**, *5*, 127. doi:10.1071/ EN08003

[210] M. S. Evans, W. L. Lockhart, L. Doetzel, G. Low, D. Muir, K. Kidd, G. Stephens, J. Delaronde, Elevated mercury concentrations in fish in lakes in the Mackenzie River Basin: the role of physical, chemical, and biological factors. *Sci. Total Environ.* **2005**, *351–352*, 479. doi:10.1016/J.SCITOTENV.2004.12.086

[211] M. S. Evans, D. Muir, W. L. Lockhart, G. Stern, M. Ryan, P. Roach, Persistent organic pollutants and metals in the freshwater biota of the Canadian Subarctic and Arctic: an overview. *Sci. Total Environ.* **2005**, *351–352*, 479. doi:10.1016/J.SCITOTENV.2004.12.086

[212] F. Cremona, D. Planas, M. Lucotte, Assessing the importance of macroinvertebrate trophic dead ends in the lower transfer of methylmercury in littoral food webs. *Can. J. Fish. Aquat. Sci.* **2008**, *65*, 2043. doi:10.1139/F08-116

[213] F. F. Rigét, G. Asmund, P. Aastrup, Mercury in Arctic char (*Salvelinus alpinus*) populations from Greenland. *Sci. Total Environ.* **2000**, *245*, 161. doi:10.1016/S0048-9697(99)00441-6

[214] L. W. Lockhart, G. A. Stern, G. Low, M. Hendzel, G. Boila, P. Roach, M. S. Evans, B. N. Billeck, J. DeLaronde, S. Friesen, K. Kidd, S. Atkins, D. S. G. Muir, M. Stoddart, G. Stephens, S. Stephenson, S. Harbicht, N. Snowshoe, B. Grey, S. Thompson, N. DeGraff, A history of total mercury in edible muscle of fish from lakes in northern Canada. *Sci. Total Environ.* **2005**, *351–352*, 427. doi:10.1016/J.SCITOTENV.2004.11.027

[215] S. C. Jewett, L. K. Duffy, Mercury in fishes of Alaska, with emphasis on subsistence species. *Sci. Total Environ.* **2007**, *387*, 3. doi:10.1016/ J.SCITOTENV.2007.07.034

[216] B. Young, L. Loseto, S. Ferguson, Diet differences among age classes of Arctic seals: evidence from stable isotope and mercury biomarkers. *Polar Biol.* **2010**, *33*, 153. doi:10.1007/S00300-009-0693-3

[217] V. L. St Louis, A. E. Derocher, I. Stirling, J. A. Graydon, C. Lee, E. Jocksch, E. Richardson, S. Ghorpade, A. K. Kwan, J. L. Kirk, I. Lehnherr, H. K. Swanson, Differences in mercury bioaccumulation between polar bears (*Ursus maritimus*) from the Canadian high- and sub-Arctic. *Environ. Sci. Technol.* **2011**, *45*, 5922. doi:10.1021/ES2000672

[218] L. A. Dehn, G. G. Sheffield, E. H. Follmann, L. K. Duffy, D. L. Thomas, G. R. Bratton, R. J. Taylor, T. M. O'Hara, Trace elements in tissues of phocid seals harvested in the Alaskan and Canadian Arctic: influence of age and feeding ecology. *Can. J. Zool.* **2005**, *83*, 726. doi:10.1139/Z05-053

[219] P. B. McIntyre, D. A. Beauchamp, Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. *Sci. Total Environ.* **2007**, *372*, 571. doi:10.1016/J.SCITOTENV.2006.10.035

[220] S. Tucker, W. D. Bowen, S. J. Iverson, Dimensions of diet segregation in grey seals *Halichoerus grypus* revealed through stable isotopes of carbon (δ^{13}C) and nitrogen (δ^{15}N). *Mar. Ecol. Prog. Ser.* **2007**, *339*, 271. doi:10.3354/MEPS339271

[221] T. W. Horton, J. D. Blum, Z. Xie, M. Hren, C. P. Chamberlain, Stable isotope food-web analysis and mercury biomagnification in polar bears (*Ursus maritimus*). *Polar Res.* **2009**, *28*, 443. doi:10.1111/ J.1751-8369.2009.00114.X

[222] L. L. Loseto, P. Richard, G. A. Stern, J. Orr, S. H. Ferguson, Segregation of Beaufort Sea beluga whales during the open-water season. *Can. J. Zool.* **2006**, *84*, 1743. doi:10.1139/Z06-160

[223] L. L. Loseto, G. A. Stern, T. L. Connelly, D. Deibel, B. Gemmill, A. Prokopowicz, L. Fortier, S. H. Ferguson, Summer diet of beluga whales inferred by fatty acid analysis of the eastern Beaufort Sea food web. *J. Exp. Mar. Biol. Ecol.* **2009**, *374*, 12. doi:10.1016/ J.JEMBE.2009.03.015

[224] B. J. Le Boeuf, D. E. Crocker, D. P. Costa, S. B. Blackwell, P. M. Webb, D. S. Houser, Foraging ecology of northern elephant seals. *Ecol. Monogr.* **2000**, *70*, 353. doi:10.1890/0012-9615(2000)070 [0353:FEONES]2.0.CO;2

[225] K. R. R. A. Guiguer, J. D. Reist, M. Power, J. A. Babaluk, Using stable isotopes to confirm the trophic ecology of Arctic charr morphotypes from Lake Hazen, Nunavut, Canada. *J. Fish Biol.* **2002**, *60*, 348. doi:10.1111/J.1095-8649.2002.TB00285.X

[226] K. A. Hobson, H. E. Welch, Cannibalism and trophic structure in a high Arctic lake: insights from stable-isotope analysis. *Can. J. Fish. Aquat. Sci.* **1995**, *52*, 1195. doi:10.1139/F95-116

[227] D. B. Stewart, M. J. Bernier, *An aquatic resource survey of Melville Peninsula, Southampton Island, and the Northeastern District of Keewatin, Northwest Territories, Background Report 2.*, **1982**, p. 108 (Environment Canada, Lands Directorate, Indian and Northern Affairs Canada, Northern Environment Branch: Quebec, QC).

[228] H. H. Parker, L. Johnson, Population structure, ecological segregation and reproduction in non-anadromous arctic charr, *Salvelinus alpinus* (L.), in four unexploited lakes in the Canadian high Arctic. *J. Fish Biol.* **1991**, *38*, 123. doi:10.1111/J.1095-8649.1991. TB03098.X

[229] F. F. Rigét, K. H. Nygaard, B. Christensen, Population structure, ecological segregation, and reproduction in a population of Arctic

charr (*Salvelinus alpinus*) from Lake Tasersuaq, Greenland. *Can. J. Fish. Aquat. Sci.* **1986**, *43*, 985. doi:10.1139/F86-121

[230] N. Gantner, M. Power, J. A. Babaluk, J. D. Reist, G. Kock, L. W. Lockhart, K. R. Solomon, D. C. G. Muir, Temporal trends of mercury, cesium, potassium, selenium, and thallium in arctic char (*Salvelinus alpinus*) from Lake Hazen, Nunavut, Canada: effects of trophic position, size, and age. *Environ. Toxicol. Chem.* **2009**, *28*, 254. doi:10.1897/08-054.1

[231] S. Rognerud, J. O. Grimalt, B. O. Rosseland, P. Fernandez, R. Hofer, R. Lackner, B. Lauritzen, L. Lien, J. C. Massabuau, A. Ribes, Mercury and organochlorine contamination in brown trout (*Salmo trutta*) and Arctic charr (*Salvelinus alpinus*) from high mountain lakes in Europe and the Svalbard archipelago. *Water Air Soil Pollut. Focus* **2002**, *2*, 209. doi:10.1023/A:1020110810195

[232] K. A. Hobson, R. T. Alisauskas, R. G. Clark, Stable-nitrogen isotope enrichment in avian tissues due to fasting and nutritional stress: implications for isotopic analysis of diet. *Condor* **1993**, *95*, 388. doi:10.2307/1369361

[233] F. F. Farris, R. L. Dedrick, P. V. Allen, J. C. Smith, Physiological model for the pharmacokinetics of methyl mercury in the growing rat. *Toxicol. Appl. Pharmacol.* **1993**, *119*, 74. doi:10.1006/TAAP. 1993.1046

[234] R. Wagemann, E. Trebacz, G. Boila, L. Lockhart, Methylmercury and total mercury in tissues of arctic marine mammals. *Sci. Total Environ.* **1998**, *218*, 19. doi:10.1016/S0048-9697(98) 00192-2

[235] J. F. Young, W. D. Wosilait, R. H. Luecke, Analysis of methylmercury deposition in umans utilizing a PBPK model and animal pharmacokinetic data. *J. Toxicol. Environ. Health A* **2001**, *63*, 19. doi:10.1080/152873901750128344

[236] W. H. Schroeder, K. G. Anlauf, L. A. Barrie, J. Y. Lu, A. Steffen, D. R. Schneeberger, T. Berg, T. Arctic springtime depletion of mercury. *Nature* **1998**, *394*, 331. doi:10.1038/28530

[237] S. E. Lindberg, S. Brooks, C.-J. Lin, K. J. Scott, M. S. Landis, R. K. Stevens, M. Goodsite, A. Richter, Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* **2002**, *36*, 1245. doi:10.1021/ES0111941

[238] C. Banic, S. T. Beauchamp, R. J. Tordon, W. H. Schroeder, A. Steffen, K. A. Anlauf, Vertical distribution of gaseous elemental mercury in Canada. *J. Geophys. Res.* **2003**, *108(D9)*, 4264. doi:10.1029/2002JD002116

[239] T. A. Douglas, M. Sturm, W. Simpson, S. Brooks, S. Lindberg, D. Perovich, Elevated mercury measured in snow and frost flowers near arctic sea ice leads. *Geophys. Res. Lett.* **2005**, *32*, L04502. doi:10.1029/2004GL022132

[240] T. A. Douglas, F. Domine, M. Barret, C. Anastasio, H. J. Beine, J. Bottenheim, A. Grannas, S. Houdier, S. Netcheva, G. Rowland, R. Staebler, A. Steffen, Frost flowers growing in the arctic ocean–atmosphere–sea ice–snow interface: 1. Chemical composition. *J. Geophys. Res. – Atmos.* **2012**, *117*, D00R09. doi:10.1029/ 2011JD016460

[241] S. B. Brooks, A. Saiz-Lopez, H. Skov, S. E. Lindberg, J. M. C. Plane, M. E. Goodsite, The mass balance of mercury in the springtime arctic environment. *Geophys. Res. Lett.* **2006**, *33*, L13812. doi:10.1029/ 2005GL025525

[242] H. Skov, S. Brooks, M. E. Goodsite, S. E. Lindberg, T. P. Meyers, M. S. Landis, M. R. B. Larsen, B. Jensen, G. McConville, J. Christensen, Measuring reactive gaseous mercury flux by relaxed eddy accumulation. *Atmos. Environ.* **2006**, *40*, 5452. doi:10.1016/ J.ATMOSENV.2006.04.061

[243] A. P. Dastoor, D. Davignon, N. Theys, M. Van Roozendael, A. Steffen, P. A. Ariya, Modeling dynamic exchange of gaseous elemental mercury at polar sunrise. *Environ. Sci. Technol.* **2008**, *42*, 5183. doi:10.1021/ES800291W

[244] A. O. Steen, T. Berg, A. P. Dastoor, D. A. Durnford, L. R. Hole, K. A. Pfaffhuber, Natural and anthropogenic atmospheric mercury in the European Arctic: a speciation study. *Atmos. Chem. Phys.* **2011**, *11*, 6273. doi:10.5194/ACP-11-6273-2011

[245] AMAP, *Arctic Monitoring and Assessment Programme Assessment 2002: Heavy Metals in the Arctic* **2005** (Arctic Monitoring and Assessment Programme: Oslo, Norway).

[246] C. P. Ferrari, P.-A. Gauchard, K. Aspmo, A. Dommergue, O. Magand, E. Bahlmann, S. Nagorski, C. Temme, R. Ebinghaus, A. Steffen, C. Banic, T. Berg, F. Planchon, C. Barbante, P. Cescon, C. F. Boutron, Snow-to-air exchanges of mercury in an Arctic seasonal snow pack in Ny-Ålesund, Svalbard. *Atmos. Environ.* **2005**, *39*, 7633. doi:10.1016/J.ATMOSENV.2005.06.058

[247] J. L. Kirk, V. L. St Louis, M. J. Sharp, Rapid reduction and reemission of mercury deposited to snowpacks during atmospheric mercury depletion events at Churchill, Manitoba, Canada. *Environ. Sci. Technol.* **2006**, *40*, 7590. doi:10.1021/ES061299+

[248] K. P. Johnson, J. D. Blum, G. J. Keeler, T. A. Douglas, Investigation of the deposition and emission of mercury in arctic snow during an atmospheric mercury depletion event. *J. Geophys. Res. – Atmos.* **2008**, *113*, D17304. doi:10.1029/2008JD009893

[249] K. J. Scott, Bioavailable mercury in arctic snow determined by a light-emitting mer-lux bioreporter. *Arctic* **2001**, *54*, 92.

[250] C. Larose, A. Dommergue, N. Murusczak, J. Coves, C. P. Ferrari, D. Schneider, Bioavailable mercury cycling in polar snowpacks. *Environ. Sci. Technol.* **2011**, *45*, 2150. doi:10.1021/ES103016X

[251] F. Gagné, L. Poissant, C. Blaise, Ecotoxicity of snowpack collected from selected sites in Québec, Canada. *Water Air Soil Pollut.* **2009**, *201*, 121. doi:10.1007/S11270-008-9932-4

[252] D. Durnford, A. Dastoor, The behavior of mercury in the cryosphere: a review of what we know from observations. *J. Geophys. Res.* **2011**, *116*, D06305. doi:10.1029/2010JD014809

[253] A. Hare, G. A. Stern, R. W. Macdonald, Z. Z. Kuzyk, F. Wang, Contemporary and preindustrial mass budgets of mercury in the Hudson Bay Marine System: the role of sediment recycling. *Sci. Total Environ.* **2008**, *406*, 190. doi:10.1016/J.SCITOTENV.2008. 07.033

[254] D. Hirdman, K. Aspmo, J. F. Burkhart, S. Eckhardt, H. Sodemann, A. Stohl, Transport of mercury in the Arctic atmosphere: evidence for a springtime net sink and summer-time source. *Geophys. Res. Lett.* **2009**, *36*, L12814. doi:10.1029/2009GL038345

[255] R. Dietz, P. M. Outridge, K. A. Hobson, Anthropogenic contributions to mercury levels in present-day Arctic animals – a review. *Sci. Total Environ.* **2009**, *407*, 6120. doi:10.1016/J.SCITOTENV.2009. 08.036

[256] C. T. Driscoll, J. Holsapple, C. L. Schofield, R. Munson, The chemistry and transport of mercury in a small wetland in the Adirondack region of New York, USA. *Biogeochem.* **1998**, *40*, 137. doi:10.1023/A:1005989229089

[257] M. E. Galloway, B. A. Branfireun, Mercury dynamics of a temperate forested wetland. *Sci. Total Environ.* **2004**, *325*, 239. doi:10.1016/ J.SCITOTENV.2003.11.010

[258] E. Steinnes, T. Berg, T. E. Sjøbakk, Temporal and spatial trends in Hg deposition monitored by moss analysis. *Sci. Total Environ.* **2003**, *304*, 215. doi:10.1016/S0048-9697(02)00570-3

[259] E. Steinnes, T. E. Sjobakk, Order-of-magnitude increase of Hg in Norwegian peat profiles since the outset of industrial activity in Europe. *Environ. Pollut.* **2005**, *137*, 365. doi:10.1016/J.ENVPOL. 2004.10.008

[260] T. Berg, K. Aspmo, E. Steinnes, Transport of Hg from atmospheric mercury depletion events to the mainland of Norway and its possible influence on Hg deposition. *Geophys. Res. Lett.* **2008**, *35*, L09802. doi:10.1029/2008GL033586

[261] W. L. Lockhart, P. Wilkinson, B. N. Billeck, R. A. Danell, R. V. Hunt, G. J. Brunskill, J. Delaronde, V. St Louis, Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochem* **1998**, *40*, 163. doi:10.1023/A:1005923123637

[262] D. H. Landers, C. Gubala, M. Verta, M. Lucotte, K. Johansson, T. Vlasova, W. L. Lockhart, Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. *Atmos. Environ.* **1998**, *32*, 919. doi:10.1016/S1352-2310(97)00116-7

[263] R. Bindler, I. Renberg, P. G. Appleby, N. J. Anderson, N. L. Rose, Mercury accumulation rates and spatial patterns in lake sediments from West Greenland: a coast to ice margin transect. *Environ. Sci. Technol.* **2001**, *35*, 1736. doi:10.1021/ES0002868

[264] R. Bindler, C. Olofsson, I. Renberg, W. Frech, Temporal trends in mercury accumulation in lake sediments in Sweden. *Water Air Soil Pollut. Focus* **2001**, *1*, 343. doi:10.1023/A:1017561701141

[265] L. C. Smith, Y. Sheng, G. M. MacDonald, A first-pan-Arctic assessment of the influence of glaciation, permafrost, topography and peatlands on Northern Hemisphere lake distribution. *Permafrost Periglac. Proc* **2007**, *18*, 201. doi:10.1002/PPP.581

[266] K. E. Frey, L. C. Smith, How well do we know northern land cover? Comparison of four global vegetation and wetland products with a new ground-truth database for West Siberia. *Global Biogeochem. Cycles* **2007**, *21*, GB1016. doi:10.1029/2006GB002706

[267] D. F. Grigal, Inputs and outputs of mercury from terrestrial watersheds: a review. *Environ. Rev.* **2002**, *10*, 1. doi:10.1139/A01-013

[268] R. P. Mason, W. F. Fitzgerald, F. M. M. Morel, The biogeo-chemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191. doi:10.1016/0016-7037(94)90046-9

[269] D. F. Grigal, Mercury sequestration in forests and peatlands: a review. *J. Environ. Qual.* **2003**, *32*, 393. doi:10.2134/JEQ2003.0393

[270] A. J. Poulain, V. Roy, M. D. Amyot, Influence of temperate mixed and deciduous tree covers on Hg concentrations and photoredox transformations in snow. *Geochim. Cosmochim. Acta* **2007**, *71*, 2448. doi:10.1016/J.GCA.2007.03.003

[271] S. A. Melnikov, S. V. Vlasov, A. N. Gorshkov, Activity 4. Study of biomagnification in Arctic food-chains, in *Arctic Monitoring and Assessment Programme Assessment 2002. Heavy Metals in the Arctic* **2005** (Arctic Monitoring and Assessment Programme: Oslo, Norway).

[272] E. Gorham, Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecol. Appl.* **1991**, *1*, 182. doi:10.2307/1941811

[273] W. Shotyk, M. E. Goodsite, F. Roos-Barraclough, R. Frei, J. Heinemeier, G. Asmund, C. Lohse, T. S. Hansen, Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the ^{14}C 'bomb pulse curve'. *Geochim. Cosmochim. Acta* **2003**, *67*, 3991. doi:10.1016/S0016-7037(03)00409-5

[274] W. Shotyk, M. E. Goodsite, F. Roos-Barraclough, N. Givelet, G. Le Roux, D. Weiss, A. K. Cheburkin, K. Knudsen, J. Heinemeier, W. O. Van Der Knaap, S. A. Norton, C. Lohse, Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands. *Geochim. Cosmochim. Acta* **2005**, *69*, 1. doi:10.1016/J.GCA.2004.06.011

[275] X. Faïn, C. P. Ferrari, A. Dommergue, M. Albert, M. Battle, L. Arnaud, J.-M. Barnola, W. Cairns, C. Barbante, C. Boutron, Mercury in the snow and firn at Summit Station, Central Greenland, and implications for the study of past atmospheric mercury levels. *Atmos. Chem. Phys.* **2008**, *8*, 3441. doi:10.5194/ACP-8-3441-2008

[276] F. Dominé, P. B. Shepson, Air–snow interactions and atmospheric chemistry. *Science* **2002**, *297*, 1506. doi:10.1126/SCIENCE.1074610

[277] C. F. Boutron, G. M. Vandal, W. F. Fitzgerald, C. P. Ferrari, A forty year record of mercury in central Greenland snow. *Geophys. Res. Lett.* **1998**, *25*, 3315. doi:10.1029/98GL02422

[278] J. L. Mann, S. E. Long, C. A. Shuman, W. R. Kelly, Determination of mercury content in a shallow firn core from greenland by isotope dilution inductively coupled plasma mass spectrometry. *Water Air Soil Pollut.* **2005**, *163*, 19. doi:10.1007/S11270-005-7607-Y

[279] P. Jitaru, H. G. Infante, C. P. Ferrari, A. Dommergue, C. F. Boutron, F. C. Adams, Present century record of mercury species pollution in high altitude alpine snow and ice. *J. Phys. IV* **2003**, *107*, 683. doi:10.1051/JP4:20030395

[280] C. Zdanowicz, D. Lean, I. Clark, Atmospheric deposition and release of methylmercury in glacially fed catchments of Auyuittuq National Park, Baffin Island, in *Synopsis of Research Conducted under the 2008–2009 Northern Contaminants Program* (Eds S. Smith, J. Stow, J. Edwards) **2009**, pp. 193–199 (Indian and Northern Affairs Canada: Ottawa, ON).

[281] J. Zheng, D. Fisher, R. Koerner, C. Zdanowicz, C. Bourgeois, G. Hall, P. Pelchat, W. Shotyk, M. Krachler, F. Ke, Temporal studies of atmospheric Hg deposition with ice cores and snow in the Canadian High Arctic, in *Synopsis of Research Conducted under the 2008–2009 Northern Contaminants Program* (Eds S. Smith, J. Stow, J. Edwards) **2009**, pp. 221–225 (Indian and Northern Affairs Canada: Ottawa, ON).

[282] S. B. Brooks, C. Moore, D. Lew, B. Lefer, G. Huey, D. Tanner, Temperature and sunlight controls of mercury oxidation and deposition atop the Greenland Ice Sheet. *Atmos. Chem. Phys.* **2011**, *11*, 8295. doi:10.5194/ACP-11-8295-2011

[283] H. V. Weiss, M. Koide, E. D. Goldberg, Mercury in a Greenland Ice Sheet: evidence of recent input by man. *Science* **1971**, *174*, 692. doi:10.1126/SCIENCE.174.4010.692

[284] T. A. Jackson, Long-range atmospheric transport of mercury to ecosystems, and the importance of anthropogenic emissions – a critical review and evaluation of the published evidence. *Environ. Rev.* **1997**, *5*, 99. doi:10.1139/A97-005

[285] M. B. Dyurgerov, M. F. Meier, *Glaciers and the changing Earth system: a 2004 snapshot. Occasional paper 58* **2005** (Institute of Arctic and Alpine Research, University of Colorado: Boulder, CO).

[286] D. B. Bahr, M. Dyurgerov, M. F. Meier, Sea-level rise from glaciers and ice caps: a lower bound. *Geophys. Res. Lett.* **2009**, *36*, L03501. doi:10.1029/2008GL036309

[287] A. S. Gardner, G. Mohold, B. Wouter, G. J. Wolken, D. O. Burgess, M. J. Sharp, G. Cogley, C. Braun, C. Labine, Sharply increased mass loss from glaciers and ice caps in the Canadian Arctic Archipelago. *Nature* **2011**, *473*, 357. doi:10.1038/NATURE10089

[288] M. Sharp, D. Burgess, J. G. Cogley, M. Ecclestone, C. Labine, G. J. Wolken, Extreme melt on Canada's Arctic ice caps in the 21st century. *Geophys. Res. Lett.* **2011**, *38*, L11501. doi:10.1029/2011GL047381

[289] D. S. Arndt, J. Blunden, M. O. Baringer, State of the climate in 2010. *B. Am. Meteorol. Soc.* **2011**, *92*, S17.

[290] J. Sommar, I. Wangberg, T. Berg, K. Gardfeldt, J. Munthe, A. Richeter, A. Urba, F. Wittrock, W. H. Schroeder, Circumpolar transport and air-surface exchange of atmospheric mercury at Ny-Alesund (79°N), Svalbard, spring 2002. *Atmos. Chem. Phys. Discus.* **2004**, *4*, 1727. doi:10.5194/ACPD-4-1727-2004

[291] C. P. Ferrari, C. Padova, X. Faïn, P. A. Gauchard, A. Dommergue, K. Aspmo, T. Berg, W. Cairns, C. Barbante, P. Cescon, L. Kaleschke, A. Richter, F. Wittrock, C. Boutron, Atmospheric mercury depletion event stuy in Ny-Alesund (Svalbard) in spring 2005. Deposition and transformation of Hg in surface snow during springtime. *Sci. Total Environ.* **2008**, *397*, 167. doi:10.1016/J.SCITOTENV.2008.01.064

[292] N. Lahoutifard, M. Sparling, D. Lean, Total and methyl mercury patterns in Arctic snow during springtime at Resolute, Nunavut, Canada. *Atmos. Environ.* **2005**, *39*, 7597. doi:10.1016/J.ATMOSENV.2005.07.071

[293] A. J. Poulain, J. D. Lalonde, M. Amyot, J. A. Shead, F. Raofie, P. A. Ariya, Redox transformations of mercury in an Arctic snow-pack at springtime. *Atmos. Environ.* **2004**, *38*, 6763. doi:10.1016/J.ATMOSENV.2004.09.013