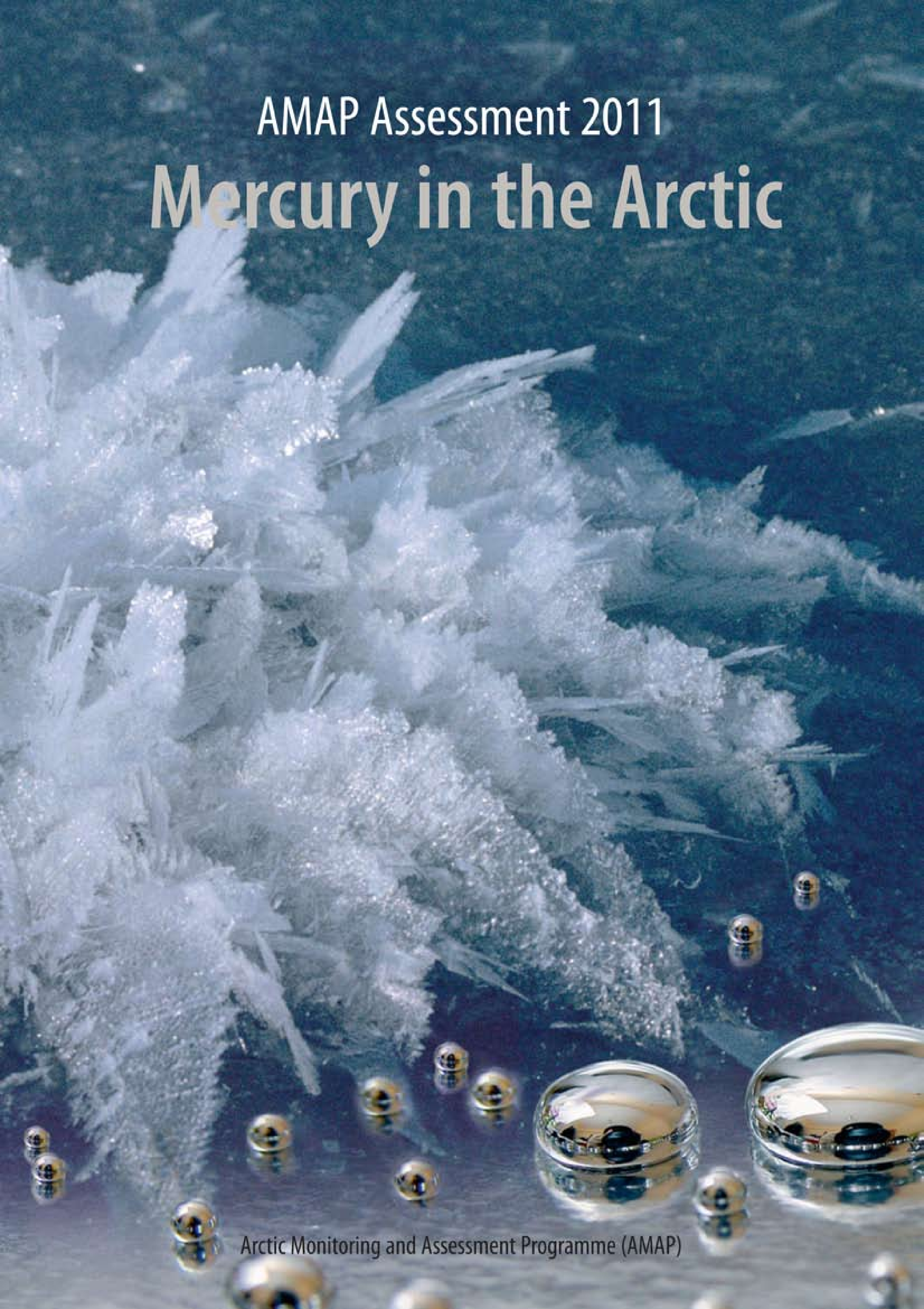
AMAP Assessment 2011

# Mercury in the Arctic



Arctic Monitoring and Assessment Programme (AMAP)

## AMAP Assessment 2011:

# Mercury in the Arctic

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Frost flowers, frozen extrusions of salt formed on new sea ice as salt water freezes – are enriched in bromine, and are a possible source of the bromine that is believed to be an important component in reactions that cause atmospheric mercury depletion events. Photo: © Bryan & Cherry Alexander (arcticphoto.co.uk).

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# Preface

*This assessment report details the results of the 2011 AMAP Assessment of Mercury in the Arctic. It builds upon the previous AMAP heavy metals assessments that were presented in 1998* and 2005*.*

*The Arctic Monitoring and Assessment Programme (AMAP) is a group working under the Arctic Council. The Arctic Council Ministers have requested AMAP to:*

- *produce integrated assessment reports on the status and trends of the conditions of the Arctic ecosystems;*
- *identify possible causes for the changing conditions;*
- *detect emerging problems, their possible causes, and the potential risk to Arctic ecosystems including indigenous peoples and other Arctic residents; and to*
- *recommend actions required to reduce risks to Arctic ecosystems.*

*This report provides the accessible scientific basis and validation for the statements and recommendations made in the AMAP State of the Arctic Environment report, 'Arctic Pollution 2011' that was delivered to Arctic Council Ministers at their meeting in Nuuk, Greenland in May 2011. It includes extensive background data and references to the scientific literature, and details the sources for figures reproduced in the 'Arctic Pollution 2011'*** report. Whereas the 'Arctic Pollution 2011' report contains recommendations that specifically focus on actions aimed at improving the Arctic environment, the conclusions and recommendations presented in this report also cover issues of a more scientific nature, such as proposals for filling gaps in knowledge, and recommendations relevant to future monitoring and research work, etc.*

*To allow readers of this report to see how AMAP interprets and develops its scientifically-based assessment product in terms of more action-orientated conclusions and recommendations, the 'Executive Summary of the Arctic Pollution 2011 Ministerial Report' is reproduced in this report on pages xi to xiv.*

*The AMAP assessment is not a formal environmental risk assessment. Rather, it constitutes a compilation of current knowledge about the Arctic region, an evaluation of this information in relation to agreed criteria of environmental quality, and a statement of the prevailing conditions in the area. The assessment presented in this report was prepared in a systematic and uniform manner to provide a comparable knowledge base that builds on earlier work and can be extended through continuing work in the future.*

*The AMAP scientific assessments are prepared under the direction of the AMAP Assessment Steering Group and are subject to a formal and comprehensive peer review process. The product is the responsibility of the scientific experts involved in the preparation of the assessment. Lead countries for this AMAP Mercury Assessment were Canada and Denmark. The assessment is based on work conducted by a large number of scientists and experts from the Arctic countries (Canada, Denmark/Greenland/Faroe Islands, Finland, Iceland, Norway, Russia, Sweden, and the United States), together with contributions from indigenous peoples organizations, from other organizations, and from experts in other countries.*

*AMAP would like to express its appreciation to all of these experts, who have contributed their time, effort, and data; and especially to the lead experts who coordinated the production of this report, and to referees who provided valuable comments and helped ensure the quality of the report. A list of the main contributors is included in the acknowledgements on page vii of this report. The list is not comprehensive. Specifically, it does not include the many national institutes, laboratories and organizations, and their staff, which have been involved in the various countries. Apologies, and no lesser thanks, are given to any individuals unintentionally omitted from the list. Special thanks are due to the lead authors responsible for the preparation of the various chapters of this report.*

*The support of the Arctic countries is vital to the success of AMAP. AMAP work is essentially based on ongoing activities within the Arctic countries, and the countries also provide the necessary support for most of the experts involved in the preparation of the assessments. In particular, AMAP would like to express its appreciation to Canada and Denmark for undertaking a lead role in supporting the Mercury assessment. Special thanks are also offered to the Nordic Council of Ministers for their financial support to the work of AMAP, and to sponsors of projects that have delivered data for use in this assessment.*

*The AMAP Working Group that was established to oversee this work, and the AMAP mercury expert group are pleased to present its assessment.*

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*Oslo, August 2011*

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* AMAP, 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xii+859 pp.

** AMAP, 2005. AMAP Assessment 2002: Heavy Metals in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xvi+265 pp.

*** AMAP, 2011. Arctic Pollution 2011. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. vi+38 pp.

# Executive Summary and Key Recommendations from the *Arctic Pollution 2011* Ministerial Report

Previous AMAP assessments of mercury in the Arctic published in 1997 and 2002, reported that a substantial amount of the mercury in the Arctic arrives via long-range transport from human sources at lower latitudes and that, owing to their traditional diet some Arctic populations receive high dietary exposure to mercury, raising concern for human health. This situation prompted calls by the Arctic Council for global action to reduce mercury emissions.

The previous AMAP assessments also identified fundamental questions regarding what controls mercury levels in the Arctic, and how (and when) these levels are likely to fall in response to controls on emissions. The cycling of methylmercury (one of the most toxic forms of mercury) is paramount in this respect. The likely impact of future climate change in altering mercury delivery and fate in the Arctic is also extremely important. The effects of mercury on biota may be particularly relevant for species at the limits of their tolerance to other stressors. The overarching goal of this assessment was therefore to update information relevant to answering the question: *WHAT CONTROLS MERCURY LEVELS IN THE ARCTIC AND WHAT ARE THE EFFECTS ON ARCTIC BIOTA?*

Mercury continues to present risks to Arctic wildlife and human populations. Despite many remaining gaps in knowledge, this assessment confirms the need for concerted international action if mercury levels in the Arctic (and in the rest of the world) are to be reduced. It is of particular concern that mercury levels are continuing to rise in some Arctic species in large areas of the Arctic, despite reductions in emissions from human activities over the past 30 years in some parts of the world.

The human health components of this assessment reflect information on mercury and human health that was presented in the 2009 AMAP Assessment of human health in the Arctic. Risk communication and dietary advice have been used to reduce human mercury exposure in some regions of the Arctic; however, solutions that are more effective over the longer term still need to be found. Reducing human and environmental exposure to mercury in the Arctic will ultimately depend on global action to reduce the quantities of mercury entering the 'environmental reservoirs', in which mercury has already been accumulating as a result of human activities for several hundred years. It is therefore important that the momentum for global action is maintained.

## Policy-relevant science recommendations

***On supporting international processes***

- *A legally-binding global agreement to control mercury emissions must be established to complement national and regional efforts to reduce environmental mercury concentrations and to lower human exposures to mercury in the Arctic. The Arctic Council should continue to support the ongoing intergovernmental negotiations under UNEP to develop a comprehensive, legally-binding global instrument that will significantly reduce global mercury use and releases.*
- *Existing international agreements such as those under the UN ECE LRTAP Convention, should continue to receive the support of the Arctic Council to ensure that the best-available scientific information from Arctic studies is made available to these processes.*

***On reducing human exposure in the Arctic***

- *Health authorities should collaborate with communities to develop effective, culturally appropriate communication strategies concerning contaminants and human health. Any advice to Arctic residents should include both the benefits of traditional/local food consumption and the results of risk assessments concerning contaminants, including mercury.*
- *Health authorities should work with relevant food agencies to promote the availability and consumption of imported food items with high nutritional value and to promote consumption of traditional/local foods such as fish and terrestrial mammals that have lower levels of mercury and high nutrient value.*

***On reducing emissions from human activities***

- *Support efforts by those countries where mercury emissions are increasing or have been identified as major global sources, to adopt measures and technologies that can reduce their mercury emissions. The support could include the transfer and sharing of knowledge on pre-treatment of raw materials and mercury capture technology, which have already been successfully implemented in a number of countries.*
- *Reduce human-induced re-emissions (e.g., by avoiding intentional burning and forest clearance) to slow re-emission of mercury to the global environment.*
- *Take advantage of co-benefits of reducing mercury emissions and other contaminants, including greenhouse gas and soot emissions to reduce global warming and related impacts.*

## Where does mercury in the Arctic environment come from, and how does it get there?

Mercury enters the global environment from natural sources (such as volcanoes and weathering of rock that is naturally enriched in mercury) and from human activities (that either extract mercury for intentional uses or release mercury that is present as a natural impurity in fuels and other raw materials used for industrial processes). Coal burning is the main source of human emissions. Once released, naturally emitted mercury is indistinguishable from mercury from human sources. Humans have been mining and using mercury for thousands of years, however emissions from human activities have increased dramatically during the past 150 years due to industrialization. The total amount released to the air each year from present-day human sources is estimated at about 2000 tonnes. A further 3000 to 4000 tonnes are released to the air either from natural sources, or as a result of re-emission of mercury that has previously been deposited to surfaces, back into the air. It is important to recognize that much of the re-emitted mercury was originally released by human activities. Climate warming is likely to promote re-emission.

Mercury is transported to the Arctic by air currents (within a matter of days) and ocean currents (that may take decades) and by rivers. The form in which mercury is released and processes that transform mercury between its various chemical forms are key in determining how mercury is transported to the Arctic and what happens to it when it gets there.

It has been estimated that about 100 tonnes of mercury are delivered to the Arctic Ocean from the air each year, with about the same amount in inflow from the Atlantic and Pacific Oceans, rivers and coastal erosion. Recent budget calculations suggest that Arctic Ocean seawater accumulates about 25 tonnes of mercury each year.

***In order to** improve validation of atmospheric modeling estimates, to constrain Arctic Ocean models and to improve Arctic mercury budgets, **it is recommended** to implement monitoring of mercury in air and mercury deposition at additional Arctic sites and to extend mercury measurements in the central basins of the Arctic Ocean.*

## What is the fate of mercury entering the Arctic environment?

Mercury is mostly deposited from the air in inorganic forms. The pathways and chemical transformations of inorganic mercury in aquatic and terrestrial ecosystems are to a large extent influenced by organic carbon. Methylmercury is an organic form of mercury that bioaccumulates more readily than inorganic forms; it is also one of the most toxic forms of mercury. Sediments and wetlands in which oxygen levels are very low are the main sites of methylmercury formation in Arctic lakes and terrestrial environments. In the marine environment, methylmercury is formed in seabed sediments, and possibly by bacteria in the mid-water column of the Arctic Ocean.

The rate of methylmercury production (and destruction) in the physical environment, and its transfer within food webs, governs mercury accumulation in Arctic biota. Methylmercury biomagnifies through food chains and dietary intake is the main source of mercury exposure in top predators. Atmospheric mercury depletion events enhance deposition of mercury from the air to snow and ice surfaces, however it is now understood that a large fraction of this deposited mercury is re-emitted from the snowpack within a few days. The role of these events as a source of mercury to Arctic food webs remains unclear.

Less is known about mercury dynamics and pathways in the ocean than the atmosphere. There are virtually no time-series datasets with which to evaluate what is happening in ocean pathways, but budget calculations suggest that at present about 75 to 90 tonnes of mercury are exported from the Arctic Ocean in ocean outflow each year and that about 110 tonnes are deposited in Arctic Ocean shelf and deep ocean sediments.

## How does climate change influence Arctic mercury?

Climate change (and its associated impacts on the environment) is already having discernable effects on some aspects of the transport pathways and behavior of mercury within the Arctic, and may further increase Arctic ecosystem and human exposure to mercury. The potential for future profound effects is large. For example, warmer and longer ice-free seasons could promote the production of methylmercury, one of the most toxic forms of mercury to biota. At the same time a loss of sea ice may reduce the mercury burden of the Arctic Ocean, by providing more water surface area for gaseous mercury to escape or by reducing release of bromine that is believed to promote atmospheric mercury deposition in the Arctic. Large quantities of mercury, accumulated during previous millennia and including recent emissions from human activities, are currently stored in permafrost, soils, sediments and glaciers. A portion of this mercury could be remobilized if these stores are disrupted by climate change.

## Are mercury levels in Arctic biota increasing or decreasing, and why?

Studies suggest that there has been a ten-fold increase in mercury levels in upper trophic level marine animals (beluga, ringed seal, polar bear, birds of prey) over the past roughly 150 years. Over 90% of the present-day mercury in these animals, and possibly some Arctic human populations, is therefore believed to have originated from human sources. The average rate of increase in wildlife species over the past 150 years is 1% to 4% per year.

Most of the time-series datasets showing increasing trends in recent decades are for marine species, followed by predatory freshwater fish species. No significant recent increases were found for terrestrial animals. The fact that trends are increasing in some marine species in Canada and West Greenland despite reductions in North American emissions is a particular cause for concern, as these include species used for food. Increasing trends are less apparent in northern Europe, and trends are mostly downward in this area, possibly reflecting their closer proximity to areas where emissions are declining.

Several factors, including factors influenced by climate change, can affect mercury accumulation in biota, particularly in species at the tops of food chains. The extent to which mercury concentrations in Arctic animals are being affected by regional shifts in emissions of mercury, from source regions in Europe and North America to those in Asia, is currently not clear.

***In order to*** *monitor the impacts of climate change, human emissions and the effectiveness of mitigation strategies for mercury,* ***it is recommended*** *to continue monitoring of temporal trends of mercury in air, humans and wildlife, and extend coverage of such monitoring in particular in Alaska and the Russian Arctic.*

## What are the toxicological effects of mercury in Arctic biota?

Arctic biota, especially higher trophic level predators are mainly exposed to mercury (mostly as methylmercury) through their diet. The presence or absence of other contaminants and nutrients (such as selenium) is believed to affect the toxicity of mercury and its impact in some Arctic species, including humans. For example, there is some evidence that selenium, if present in large enough quantities, can act as an antioxidant, providing wildlife and humans with some protection from methylmercury.

Some Arctic species, in particular marine top predators, exhibit levels of mercury in their tissues and organs that are believed to exceed thresholds for biological effects. In the past, these thresholds have been largely derived from laboratory studies on non-Arctic species, but in recent years knowledge arising from studies of Arctic species has increased.

Those species where thresholds are exceeded include a number of species of toothed whale, polar bears and some bird species. Polar bears and marine birds can excrete mercury through replacement of hair and feathers. Toothed whales appear to be one of the most vulnerable groups, with high concentrations of mercury recorded in brain tissue and associated signs of neurochemical effects. Evidence of increasing trends in mercury in some biota in Arctic Canada and Greenland is therefore a concern with respect to human and ecosystem health.

## What are the likely changes in mercury concentration in the Arctic atmosphere and ocean under future emissions scenarios?

Global mercury emissions to air have been fairly constant since around 1990, but with emissions decreasing in Europe and North America and increasing in Asia. East Asia currently contributes about 50% of global mercury emissions to air from human sources. There are indications that, after decreasing from a peak in the 1970s, global emissions from human sources may be starting to increase again. If measures are not taken to reduce emissions, models suggest that global emissions could increase by 25% by 2020.

Models suggest that East Asia may now be responsible for much of the present-day mercury deposition in the Arctic. However, emissions scenarios project that if currently available emission reduction measures are implemented globally, then mercury deposition in the Arctic might be expected to decrease by as much as 20% by 2020 (relative to 2005 levels). There are no reliable global estimates of mercury released to the marine and freshwater environments.

Control technologies installed at industrial facilities remove mercury that would otherwise be emitted to air. There is little information about the ultimate fate of the mercury removed in this way and about how the mercury-containing wastes are subsequently disposed of. However, it can be assumed that these technologies will reduce the amount of mercury that is transported to the Arctic, by concentrating it, at least temporarily, in material that is disposed of in the source regions.

The atmosphere responds relatively quickly to changes in mercury emissions, but the large reservoirs of mercury in soils and ocean waters mean that there may be a long lag time (of the order of tens of decades) before changes in mercury inputs are reflected in the concentrations in these media, and thus in wildlife taking up mercury from them.

## What is the impact of mercury contamination on human health in the Arctic?

Some Arctic human populations, especially some indigenous communities that consume large quantities of certain species of freshwater fish or marine mammal tissues for their traditional/local food, receive high dietary exposure to mercury. This raises concerns about human health effects, such as effects on brain development, and effects on the reproductive, immune and cardiovascular systems.

Exposure at current levels in the Arctic can have adverse impacts on human health, particularly for the developing fetus and children. Pregnant women, mothers and children are critical groups for monitoring and measures to reduce dietary exposure. There has been an overall decline in the proportion of Arctic people that exceed (U.S. and Canadian) blood mercury guidelines, but a significant proportion of people including women of child-bearing age from communities in the eastern Canadian Arctic and Greenland still exceed these guidelines. Dietary advice has been effective in reducing mercury exposure in some critical groups, but such advice needs to be carefully formulated to balance risks and benefits of traditional/local food consumption. The general dietary transition from traditional/local to more 'western' diets is also reducing mercury exposure, but at the same time is raising risks of other conditions or diseases associated with a western diet and lifestyle (such as obesity, diabetes, and heart disease). Since traditional/local foods low in mercury are not always available to Arctic indigenous people, the achievement of declining mercury levels in the environment is imperative to allow for the safe promotion of traditional/local food consumption.

## Gaps in knowledge remain

The scientific background document to this assessment details recommendations to address this issue. Some of the main areas identified include:

- Further improving understanding of atmospheric mercury depletion events, with a particular focus on understanding how much of the deposited mercury is readily available to biota.
- Investigating further the fate of mercury entering marine systems.
- Ascertaining how methylmercury enters Arctic food webs and better understanding the Arctic marine methylmercury cycle.
- Developing a more detailed understanding of the impact of climate change on mercury.
- Undertaking further wildlife studies to measure mercury levels in different tissues and organs to assess mercury-induced health effects.
- Exploring the effects of multiple stressors (both chemical and environmental) and nutritional factors on the toxicity of mercury in biota.
- Addressing key knowledge gaps to reduce uncertainty in mercury models.
- Gathering more accurate information on worldwide economic and social variables, to improve future emissions scenarios.
- Studying the health impacts of mercury in human populations and determinants of food choice and availability.

# Chapter 1

# Why Are We Doing this Assessment?

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This introductory chapter provides relevant background information on the issue of Arctic mercury contamination, impacts on Arctic indigenous peoples, and the way in which the Arctic Council, AMAP, and indigenous peoples' organizations have responded to the issue through the publication of scientific assessments and engagement in international initiatives related to mercury in the environment. The chapter concludes with an outline of the report and provides a brief explanation as to the question-based chapter format. The outline makes use of a schematic illustration to provide the reader with a road-map to scientific information provided in the report.

## 1.1. Why is mercury a concern in the Arctic?

Mercury is a naturally occurring element that is ubiquitous in the global environment and can be measured in virtually all environmental media in proportions that, in the absence of anthropogenic influence, are defined by natural geochemical cycles. Until recently the natural release of mercury was generally in balance with the natural processes leading to its removal. Certain anthropogenic activities, however, extract mercury-containing materials from the Earth and process them to produce commercial goods, or in the case of fossil fuels, burn them to produce energy. Over time, and particularly since the Industrial Revolution, these types of industrial activity have mobilized vast quantities of mercury from a relatively inert state in the Earth's crust and redistributed it throughout the more biologically active and mobile compartments of the environment (surface soils, atmosphere, lakes, rivers, oceans). The increased amount of mercury now circulating in the global environment presents an increased risk to biological systems in which the highly toxic species, methylmercury, is biomagnified (AMAP, 2005). Increased mercury in the Arctic environment is of particular ecological concern because of its well-known ability to bioaccumulate and biomagnify in food webs. Despite a lack of major industrial sources within the Arctic, mercury concentrations can reach levels of toxicological significance in high trophic level species (AMAP, 2005). The ecological risks of mercury contamination in the Arctic are compounded by the presence of other contaminants, such as persistent organic pollutants (POPs), which add to the overall toxic burden on Arctic wildlife and human populations (AMAP, 2003, 2005, 2009b; Letcher et al., 2010). The potential threats from toxic contaminants must also be considered in the context of ecosystems and species that are already being subjected to the environmental stresses imposed by climate change (ACIA, 2005).

A substantial proportion of the mercury found in high trophic level Arctic species today is derived from anthropogenic sources (Dietz et al., 2009a; see Section 5.2). Elevated mercury concentrations in the Arctic environment, and especially in Arctic biota, can greatly affect Arctic indigenous peoples who rely on subsistence hunting and fishing for their nutritional, social and cultural well-being. Arctic indigenous peoples such as Inuit, Yupik, and Iñupiat consume marine mammals including seals, whales and polar bears that are high in the food web and which are known from previous assessments to be a major source of dietary mercury exposure. Mercury concentrations in most Arctic marine mammal species and some seabirds and predatory freshwater fish regularly exceed guidelines for consumption. This presents a significant exposure pathway to many indigenous communities for which marine mammals and fish such as lake trout and pike are important traditional/local foods. As a result, high levels of mercury have been measured in Arctic indigenous peoples (AMAP, 2009b; and summarized in Chapter 8). Results of blood monitoring surveys in Arctic communities have shown that a significant percentage of indigenous women from certain communities in Alaska, northern Canada, Greenland, and northern Russia still exceed the US Environmental Protection Agency and Health Canada guideline values. Although human blood levels in several communities have declined somewhat since the first AMAP assessment (AMAP, 1998, 2009b; see also Chapter 8), there are few indications of declining trends in mercury in wildlife in the corresponding areas (see Chapter 5). The reasons for the declining levels in humans are therefore complicated and involve additional factors, such as changes in dietary preferences (discussed in Chapter 8). Epidemiological studies have shown that infants born to mothers with elevated mercury exposure are at risk of neuro-developmental and behavioral effects. It has also been shown that elevated mercury exposure is associated with a higher incidence of cardiovascular disease, further demonstrating the unacceptable level of mercury-associated health risks to which some Arctic indigenous people are exposed (AMAP, 2009b).

The potential health effects of mercury have recently been discussed from an economic perspective (e.g., Hylander and Goodsite, 2006; Sundseth et al., 2010). Sundseth et al. (2010) estimated the annual global economic loss resulting from the impact of methylmercury exposure on IQ. The estimate, based on a forecasted 25% increase in global anthropogenic mercury emissions to air between 2005 and 2020, predicted an annual economic loss, associated only with diminished IQ due to ingestion of methylmercury, of USD 3.7 billion (2005 USD) in 2020. Conversely, scenarios under which global anthropogenic emissions to air were reduced by 50-60% were predicted to have a net economic benefit of between USD 1.2 and USD 1.8 billion (2005 USD). The study illustrates how the human health effects of methylmercury exposure could have global economic consequences and quantifies the potential economic advantages of reducing mercury emissions.

The presence of mercury and other contaminants in traditional/local foods contributes to increasing concern about food security for Arctic indigenous peoples. At the same time these foods are known to be important sources of energy and nutrients. This situation has led to what has been termed the 'Arctic Dilemma' (AMAP, 1997). Concern about contaminants in traditional/local foods can aggravate the ongoing nutritional transition in which indigenous peoples gradually and increasingly substitute their traditional diet with store-bought foods. High prices, low quality and limited availability of healthy store-bought food items have led to consumption of cheaper and less nutritious 'junk foods' that are high in sugar and saturated fats. Along with a more sedentary lifestyle, this diet increases the risks of developing obesity and related diseases, such as diabetes and coronary heart disease (see Chapter 8). Apart from its nutritional importance, traditional/local food is also an important part of cultural and social life for indigenous peoples in the Arctic as it reflects the connection with the land and traditional values such as sharing. It may be argued that the ability of indigenous communities to participate in traditional harvesting and sharing of local foods is one of the most important determinants of community health and cultural identity. Therefore, the importance of 'clean' local food for Arctic indigenous peoples cannot be overstated. Although reductions in mercury exposure in the short-term may be achieved through the development and implementation of appropriate dietary advice, a better long-term solution to mitigating the negative effects of mercury exposure among Arctic residents lies in reducing mercury concentrations in traditional/local foods.

The purpose of this assessment is to help better understand the sources, pathways, processes and effects of mercury in the Arctic. It is hoped that this improved understanding of the science will lead to improved policies on mercury emissions that will eventually lead to a decrease in Arctic mercury levels.

## 1.2. How has AMAP addressed mercury pollution?

The primary task assigned to AMAP by Ministers of the eight Arctic countries at the time of its establishment in 1991 was to prepare assessments of the 'state of the Arctic environment' with respect to defined pollution issues (AEPS, 1991). One of these priority pollution issues was heavy metals, including mercury. Through implementation of a circumpolar monitoring program based on national monitoring programs in the eight Arctic countries, and review of available information from monitoring and research activities, AMAP prepared its first assessment reports in 1997 (AMAP, 1997, 1998). These reports included international input from hundreds of Arctic scientists as well as from Arctic indigenous representatives and provided the first comprehensive picture of the contamination status of the Arctic region as a whole, and established an important baseline for further work. Mercury was found to be ubiquitous in Arctic abiotic media (air, snow/ice, sediments, water) and biota, due partly to long-range transport from source regions to the south, and partly to natural sources of mercury present in the Arctic and elsewhere. An important task of research since that time has been to determine the relative importance of each of these sources in various media and at various locations. Higher concentrations have been found in top predators due to bioaccumulation and biomagnification; in certain Arctic animals, levels were high enough to exceed thresholds associated with effects in laboratory animals, raising concerns about population and ecosystem health effects. Also, from previous AMAP assessments of mercury in the Arctic (AMAP, 1998, 2005) it became apparent that almost no mercury effects studies on relevant high trophic-level Arctic species had been conducted.

One of the findings highlighted when AMAP presented its first assessment results to Ministers in 1997, was that some Arctic human populations, in particular indigenous groups that utilized marine mammals as an important part of their traditional diet, received some of the highest exposures to mercury of any groups on Earth, raising concerns about possible human health effects (AMAP, 1997).

Between 1998 and 2002, AMAP prepared follow-up assessments, including an assessment of heavy metals, that built on the initial assessments, filling gaps in geographical coverage, and expanding the work to consider temporal trends in contaminant levels (relative to the ca. 1990-1995 baseline data compiled in the 1997 assessment report). As part of the assessment, AMAP also sponsored and contributed to the production of an updated global anthropogenic mercury emissions inventory, for use in modeling activities. A particular focus of attention in the 2002 AMAP assessment of heavy metals in the Arctic (AMAP, 2002, 2005) concerned new information on the potential of 'atmospheric mercury depletion events' to enhance deposition of mercury in the Arctic region. In both the 1997 and 2002 AMAP assessment rounds, human health effects of mercury were addressed in separate reports dealing specifically with the health effects of contaminants (AMAP, 1998, 2003).

This third AMAP assessment concerning metals in the Arctic differs from the assessments performed in 1997 and 2002, most importantly in that it focuses only on mercury, and does not include other heavy metals. This decision recognizes the fact that, although cadmium and lead in particular continue to be found in high levels in some Arctic wildlife and human populations, the associated issues are very different. In the case of cadmium, routes of exposure such as consumption of caribou/reindeer tissues and organs are relatively well-defined and have been covered adequately in previous AMAP assessments. Cigarette smoking remains the dominant route of cadmium exposure in most individuals that exhibit high blood cadmium levels (AMAP, 2003). In the case of lead, the introduction of lead-free gasoline has led to decreased deposition across the Arctic, although the continuing use of leaded petrol in Russia remains a potential area for action. Human exposure to lead has also been linked in the Arctic to the use of lead shot in hunting; this exposure pathway has been reduced by encouraging the use of lead-free ammunition (already mandatory in most countries) and communicating the risks associated with lead shot (Fontaine et al., 2008). Mercury, on the other hand, continues to present uncontrolled risks to Arctic wildlife and human populations with levels in at least some areas still increasing. Despite the continued concern, however, no global policy has been instituted to reduce emissions of mercury and, thereby, reduce human and environmental exposure. Previous assessments also identified a number important gaps associated with environmental trends, pathways, processes and toxic effects (AMAP, 2005). Given the known complexity of the biogeochemical cycle of mercury, it has recently been recognized that climate change has the potential to significantly alter mercury pathways and processes of transformation (e.g., methylation). Presently, however, the role of climate change in the mercury cycle remains an inadequately explored area of study. Given the prevailing interest in mercury from a global policy context and the need for improved scientific understanding, mercury was identified as a continuing priority for assessment by AMAP.

**The recommendations for mercury-related monitoring and research made in the 2002 AMAP assessment (AMAP, 2002)[1] are as follows:**

- The Arctic Council should encourage expanded and accelerated research on critical aspects of the mercury cycle and budget in the Arctic. Such research should include long-range transport, mercury deposition mechanisms, processes leading to biological exposure and effects, and the influence of climate variability and change on these processes.
- The Arctic Council should promote efforts at global, regional, and national levels to quantify all sources of mercury and report results in a consistent and regular manner to improve emission inventories. Particular efforts should focus on measuring contributions made by the burning of coal for residential heating and small-scale power plants as well as by waste incineration.
- AMAP should be asked to continue temporal trend monitoring and the assessment of effects of mercury in key indicator media and biota. This will enable assessment of whether the measures taken in the LRTAP Protocol are being effective in driving down mercury levels in the Arctic.
- In view of the fact that reducing exposure to mercury can only be addressed by regional and global action to reduce worldwide emissions, and acknowledging the assessment for global action undertaken by UNEP and its resulting proposals, the Arctic Council should take appropriate steps to ensure that Arctic concerns are adequately addressed and to promote the development of regional and global actions.
- AMAP should be asked to further investigate how climate change and variability may influence the ways in which POPs, heavy metals, and radionuclides move with respect to the Arctic environment and accumulate in and affect biota. This will enable Arctic States to better undertake strategic planning when considering the potential effectiveness of present and possible future national, regional, and global actions concerning contaminants.

## 1.3. How can the AMAP assessment contribute to the development of global policies to reduce mercury impacts in the Arctic?

The linkage between the present assessment, the Arctic Council, and relevant international processes is shown in Figure 1.1.

The information on metals in the Arctic presented by AMAP in 1997 (AMAP, 1997) supported the negotiations that eventually led to the establishment of the Heavy Metals Protocol to the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) that was adopted on 24 June 1998 in Aarhus (Denmark). This regional agreement aims to cut emissions from industrial sources, combustion processes and waste incineration, by suggesting best available techniques to limit emissions from stationary sources. The agreement also introduced measures to lower emissions from products, such as mercury in batteries, and proposed the introduction of management measures for other mercury-containing products, such as electrical components (thermostats, switches), measuring devices (thermometers, manometers, barometers), fluorescent lamps, dental amalgam, pesticides and paint. Under the 1998 Aarhus Protocol on Heavy Metals, parties are required to reduce their emissions below levels in 1990 (or an alternative year between 1985 and 1995) (*www.unece.org/env/lrtap/hm_h1.htm*). The Protocol entered into force on 29 December 2003, and (as of 1 March 2011) has been signed and ratified by all Arctic countries apart from Iceland (which has signed but not ratified), the Russian Federation (which has neither signed nor ratified), and the United States (which has 'accepted' but not ratified). The information on mercury in the Arctic which AMAP compiled in its 1997 and 2002 assessments, especially information concerning temporal trends in mercury levels, was summarized by AMAP in a special contribution to the first effectiveness and sufficiency review of the Heavy Metals Protocol in 2006.

In September 2000, as a contribution to the Second Ministerial Meeting of the Arctic Council, AMAP prepared an 'Update Report on Issues of Concern', including mercury in the Arctic (AMAP, 2000). On the basis of this report (and the 1997 assessment report; AMAP, 1997), and in addition to calling upon those Arctic countries that had not already done so to ratify the UNECE Heavy Metals Protocol, the Arctic Council Ministers: "*…called upon the United Nations Environment Programme to initiate a global assessment of mercury that could form the basis for appropriate international action in which the Arctic States would participate actively*" (Arctic Council, 2000).

This message was communicated to UNEP's Governing Council (GC), with the result that, at its 21st session in February 2001, the UNEP GC, specifically referring to the Barrow Declaration, agreed to initiate the UNEP Global Mercury Assessment (UNEP, 2002). This process effectively established the UNEP Mercury Programme (*www.chem.unep.ch/mercury/*).

Welcoming the UNEP initiative, the Arctic Council requested AMAP to continue to support the UNEP mercury process and the implementation of agreements such as the UNECE LRTAP Convention. In this context, AMAP was requested by the UNEP Chemicals Division in 2007 to coordinate the work to prepare a report on global atmospheric mercury emissions, in response to the UNEP GC's (2007)

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[1] The recommendations listed in this box include the mercury-related recommendations from AMAP (2002) under the *Heavy Metals* subheading and the *Changing Pathways* subheading. They do not include the mercury-related recommendations under the *Human Health* subheading, since the present assessment does not follow up on the human health recommendations.

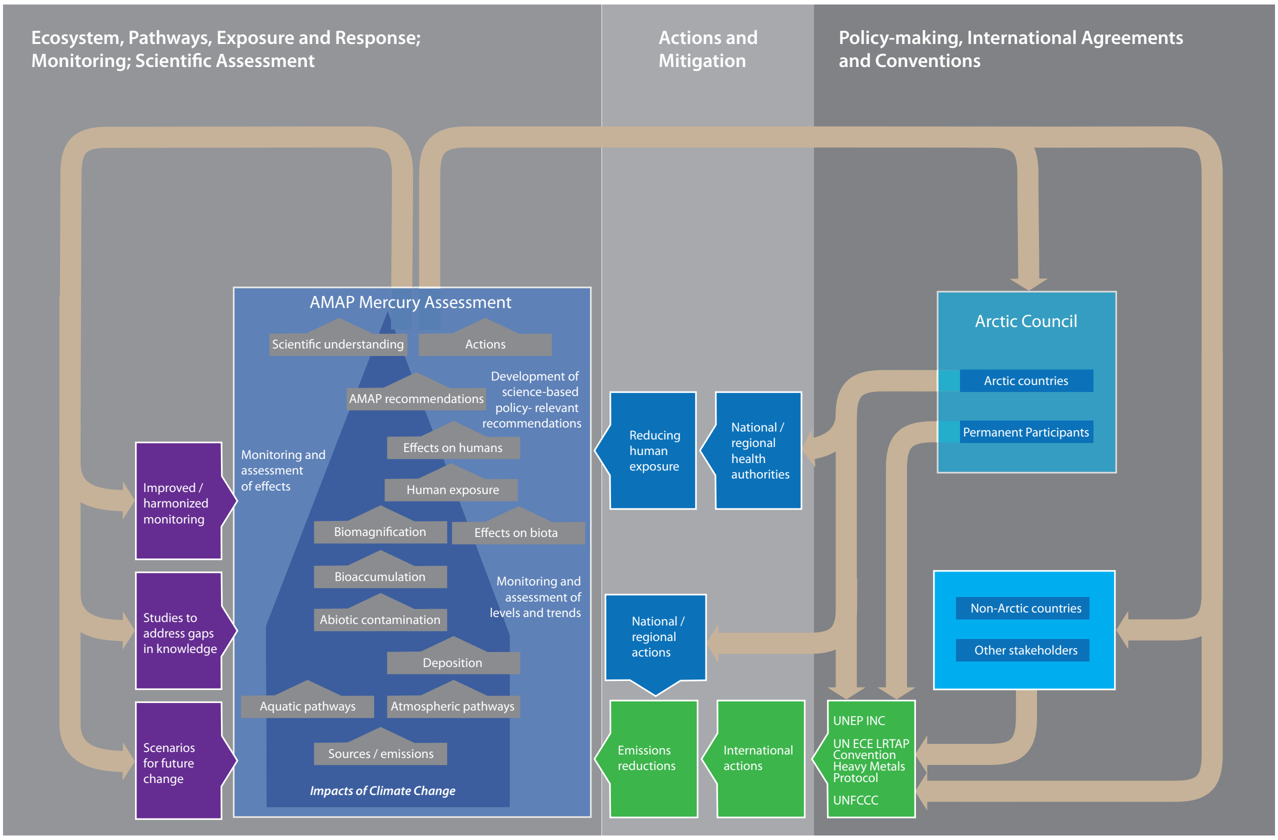

Figure 1.1. Linkage between the present AMAP assessment on mercury in the Arctic, the Arctic Council and relevant international processes.

decision 24/3 IV requesting preparation of a report addressing: *(a) Best available data on mercury atmospheric emissions* and *(b) Current results from modelling on a global scale and from other information sources.*

The resulting report (UNEP, 2008) is a summary for policymakers based on a technical report prepared by AMAP experts in association with UNEP Chemicals Branch (AMAP/UNEP, 2008). The information presented in this technical report also provided part of the basis for the AMAP 2011 assessment of mercury in the Arctic (this report). The UNEP Chemicals Branch *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* report (UNEP, 2008) was presented to the UNEP GC at its 25th meeting in 2009.

At its 22nd meeting in 2003, the UNEP GC had agreed that there was …*sufficient evidence of significant global adverse impacts from mercury and its compounds to warrant further international action to reduce the risks to human health and the environment from the release of mercury and its compounds to the environment*. Following their consideration of, among other things, the 2008 *Global Atmospheric Mercury Assessment* report, the UNEP GC further decided to initiate a process aimed at negotiating, by 2013, a legally-binding international agreement to limit emissions of mercury (*www.chem.unep.ch/MERCURY/mandates.htm*).

Such an agreement has the potential to significantly reduce Arctic mercury contamination, and it is anticipated that AMAP information, including the 2011 AMAP assessment of mercury in the Arctic (this report), will provide input to and be used in the international negotiating process that is currently underway.

Finally, at the regional level, AMAP information has spurred coordinated actions within the Arctic countries to address mercury contamination. From 2003 to 2008, the Arctic Council endorsed the Arctic Contaminants Action Program (ACAP) 'Mercury Project' called *Reduction of Atmospheric Mercury releases from Arctic States*. The project called for the identification of main source categories for mercury emissions within the Arctic region. Based on this information, the project then identified and prioritized source categories for possible reduction measures, and promoted development of action plans or strategies for reducing mercury emissions for those

**Timeline of negotiations for a legally binding instrument on mercury**

The meeting of the Ad Hoc Open-Ended Working Group on mercury was held in Bangkok, Thailand, 19-23 October 2009. Its purpose was to prepare for the upcoming meetings of the Intergovernmental Negotiating Committee (INC), where negotiations for a legally binding agreement on mercury will begin. Tentative timelines of INCs:

INC 1: 7 to 11 June 2010, Stockholm, Sweden
INC 2: 24 to 28 January 2011, Chiba, Japan
INC 3: 31 October to 4 November 2011, Nairobi, Kenya
INC 4: June 2012, Montevideo, Uruguay (to be confirmed)
INC 5: Early 2013, Brazil or Geneva, Switzerland (to be confirmed)
Diplomatic Conference: 2013, Japan.

countries or regions that did not have such plans. This involved the identification and proposal of cost effective measures at one or a few specific sources or plants where progress of reduction activities had been slow. Reduction measures were supported through fund raising, technology transfer and technical assistance.

AMAP human health assessment results concerning mercury have been utilized in various initiatives that aim to reduce mercury exposure, in particular among highly exposed critical groups. Development of health advisories has been effective in at least some areas in reducing such exposure, for example in reducing exposure to mercury of pregnant women in the Faroe Islands through limiting the consumption of pilot whale.

Future AMAP monitoring results on, for example, temporal trends of mercury in the environment are expected to constitute information necessary to evaluate the effectiveness of agreements such as the UNECE LRTAP Convention and an eventual UNEP agreement. The AMAP monitoring program was used, in connection with the Stockholm Convention on Persistent Organic Pollutants, as a model for the development of a global POPs monitoring program. The experience gained in implementing a monitoring program for mercury in the Arctic has potential lessons for such programs in other regions.

Following the successful cooperation between UNEP and AMAP on the recent preparation of the *Global Atmospheric Mercury Assessment*, it is anticipated that AMAP will play an important role in supporting the Intergovernmental Negotiating Committee (INC) process with up-to-date scientific information on mercury in the Arctic region. This assessment, also including information on biotic pathways, biomagnification, temporal trends and effects evaluation, etc., is intended to make a major contribution to that process, and could serve as a model for future development of components of a global mercury agreement implementation strategy.

## 1.4. How are Arctic indigenous peoples involved in national/international research, policy and decision-making processes?

Since Arctic indigenous peoples are greatly affected by high mercury/contaminant levels in the Arctic, the need for their involvement in policy and decision-making processes, as well as in research efforts, is well recognized by Arctic countries, as can be seen by statements in Arctic Council declarations. In particular, in the Salekhard Declaration (Arctic Council, 2006) the Arctic Council stressed …*the importance of enhancing well-being and eradicating poverty among the indigenous peoples and other Arctic residents, and the need for their inclusion in decision-making in relation to policy planning and implementation*, and in this context, the importance of facilitating closer cooperation at the regional and local level. In the Salekhard Declaration, the Arctic Council also stated that it wants to …*support the continued cooperation with indigenous peoples of the Arctic, welcome the contribution of their traditional knowledge of flora and fauna to the scientific research, and encourage further cooperation in the development of community-based monitoring of the Arctic's living resources*.

In the recent Tromsø Declaration (Arctic Council, 2009) the Arctic Council reiterated …*the engagement of indigenous peoples as being fundamental to addressing circumpolar challenges and opportunities*. The Arctic Council also acknowledged at the Tromsø Ministerial Meeting that more work needs to be done to engage indigenous peoples. It further requested that Arctic Council member states …*explore ways and means to enhance the participation of Permanent Participants in the activities of the Arctic Council*, and …*recognize the importance of providing adequate funding to Permanent Participants to support their preparations for, and participation in, the Arctic Council and its Working Groups*.

Within the Arctic Council, the category of the Permanent Participants allows for an active participation of, and full consultation with, Arctic indigenous peoples in all activities and meetings, including meetings of the Senior Arctic Officials, Ministerial meetings, and Regional meetings. Permanent Participants are also invited to participate in Arctic Council Working Group meetings and can be involved in any of the projects organized by the Working Groups. Within AMAP, Permanent Participants are active in Working Group and Expert Group meetings and in the development of assessment reports. This involvement is particularly important to indigenous groups, since AMAP assessment reports are utilized to inform and therefore influence international policy. Even though indigenous organizations may be present as observers at United Nation (UN) meetings, there is currently no formal process that ensures indigenous peoples' participation and consultation in international policy development at the UN level. The participation of Arctic indigenous peoples' organizations within Arctic Council Working Groups and with AMAP assessment reports is therefore crucial to allow for their input in the development of international policies which affect them. Permanent Participants to the Arctic Council include: the Inuit Circumpolar Council, the Saami Council, the Russian Association of Indigenous Peoples of the North, Siberia and the Far East, the Aleut International Association, the Arctic Athabaskan Council, and the Gwich'in Council International.

## 1.5. What are the structure and aims of this assessment?

In contrast to previous AMAP assessment reports, this report is structured around a series of key questions, which are aimed at discussing the most important current scientific issues concerning environmental mercury in the Arctic, and in a format that is likely to be most useful to policy-makers. The multi-disciplinary nature of many of the questions required considerable 'crossing of boundaries' between scientific disciplines, thereby encouraging more debate and synthesis of knowledge from disparate areas of science. Focusing this assessment on mercury alone, unlike previous heavy metals assessments, allows for a greater level of detail, including a higher degree of inter-disciplinary linkage, while also facilitating greater clarity in communicating messages to policy-makers and other relevant stakeholders.

The overall objective for the assessment is to provide the best possible scientific information in response to the questions: *What controls mercury levels in the Arctic and what*

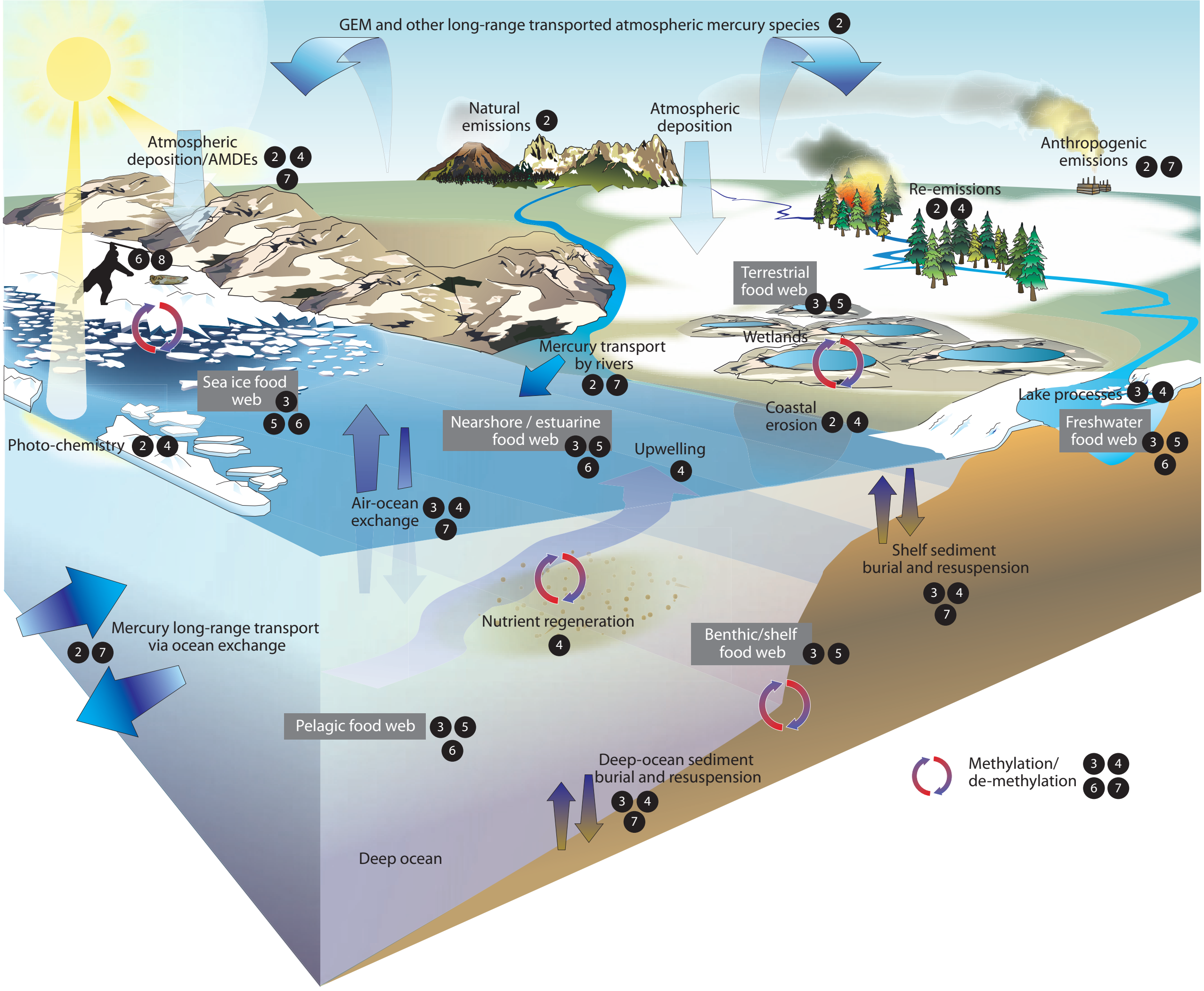

Figure 1.2. A simplified scheme showing the main components of the Arctic mercury cycle. The numbers indicate the chapters of this report in which the issue is addressed. For simplicity, the diagram does not show mercury speciation, however, this important property is discussed in detail throughout the rest of the assessment.

*are the effects on Arctic biota?* Each individual chapter of this assessment report centers around a key question; this in turn is answered through a more focused layer of additional questions. The questions were formulated and refined during and between two meetings of the AMAP Mercury Experts Group in November 2007 and December 2008. The report is written with the goal of providing as concise a response as possible, using the best available scientific data and information, while also describing the existing uncertainty and knowledge gaps.

The report presents information that contributes to an improved understanding of global mercury sources, pathways to the Arctic, and biogeochemical cycling and fate within the Arctic, including the uptake and accumulation of mercury in food webs and the associated ecological and human health risks. The mercury cycle within the Arctic is shown schematically in Figure 1.2, which also represents a 'road-map' for how information on various stages of the mercury cycle is distributed through different chapters of the report. Each sub-component in the diagram points the reader to the relevant chapter in this assessment report.

By way of an introduction, **Chapter 1** answers the question: *Why are we doing this assessment?* and in doing so provides important background information on Arctic mercury contamination, impacts on Arctic indigenous peoples, and the way in which the Arctic Council, AMAP, and indigenous peoples' organizations have responded to the issue through the publication of scientific assessments and engagement in international initiatives related to mercury in the environment.

**Chapter 2** discusses global sources of mercury and describes how they are transported to the Arctic by addressing the question: *Where does mercury in the Arctic environment come from, and how does it get there?* The chapter covers natural and anthropogenic sources of mercury, different modes of long-range transportation and their relative importance to the delivery of mercury to the Arctic, the processes that influence transport, and models that have been used to describe mercury transport, deposition and distribution. Particular attention is paid to the importance of atmospheric mercury depletion events (AMDEs) as a means of delivering mercury to Arctic ecosystems.

**Chapter 3** provides a detailed examination of the biogeochemical cycle of mercury in Arctic terrestrial, freshwater and marine ecosystems in response to the question: *WHAT IS THE FATE OF MERCURY ENTERING THE ARCTIC ENVIRONMENT?* The chapter begins by examining what happens to mercury once it has been transported into the Arctic, how it moves from abiotic media into and then up the food chain, and ends with a discussion of mercury sequestration in natural archives. The environmental chemistry surrounding mercury speciation and the formation of methylmercury, and the importance of these processes for ecosystem uptake, are discussed.

**Chapter 4** examines the question: *HOW DOES CLIMATE CHANGE INFLUENCE ARCTIC MERCURY?* Climate change is already having significant impacts on nearly all facets of the Arctic environment, from reductions in sea-ice cover and duration, coastal erosion, permafrost degradation, warming of air, water and soil, to changing biological communities. The chapter examines how these changes influence the various aspects of the mercury cycle described in Chapters 2 and 3, and discusses the impacts that these changes may have on mercury uptake and accumulation in Arctic ecosystems in the future.

**Chapter 5** summarizes the latest data and information on temporal trends of mercury in Arctic biota in an answer to the question: *ARE MERCURY LEVELS IN ARCTIC BIOTA INCREASING OR DECREASING, AND WHY?* First, the long-term temporal trends of mercury in hard tissues of biota are assessed from pre-industrial times to the present day to establish the proportions of natural and anthropogenic mercury in modern Arctic biota. Recent decadal trends are then examined, based on monitoring programs of biological soft tissues and organs carried out over the past 10 to 30 years in various Arctic countries. Finally, the chapter discusses what may be driving the recent trends, and especially the relative role that anthropogenic sources and changing environmental processes might have played.

**Chapter 6** provides an assessment of ecological risks associated with mercury in the Arctic by addressing the question: *WHAT ARE THE TOXICOLOGICAL EFFECTS OF MERCURY IN ARCTIC BIOTA?* The question is addressed through a combined assessment of recent toxicological studies on Arctic wildlife and a detailed comparison of mercury concentrations in wildlife with established thresholds for effects determined for other species. Different modes of mercury toxicity are examined and a discussion of thresholds and their relevance to Arctic wildlife is provided. The chapter concludes with a look to the future and the anticipated risks of mercury toxicity based on projections of temporal trends in biota.

**Chapter 7** is entitled *TO WHAT EXTENT WILL PROJECTED CHANGES IN GLOBAL EMISSIONS AFFECT MERCURY LEVELS IN THE ARCTIC ATMOSPHERE AND OCEAN?* The chapter predicts how mercury concentrations in the Arctic atmosphere and ocean will respond under various possible scenarios of global emission reductions. The answer to this question is intended to provide policy makers with realistic expectations of how quickly environmental benefits may be achieved through actions taken to reduce global emissions.

**Chapter 8**, the final chapter of the report, presents a link between the rest of the assessment and the people of the Arctic by responding to the question: *WHAT IS THE IMPACT OF MERCURY CONTAMINATION ON HUMAN HEALTH IN THE ARCTIC?* The chapter provides a summary of mercury-related health effects information derived from AMAP human health assessment reports, and draws clear links between human health risks and mercury in the Arctic environment.

# Chapter 2

# Where Does Mercury in the Arctic Environment Come From, and How Does it Get There?

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**Data contributors:** Alex Poulain, Jesper Christensen

## 2.1. Introduction

Very little of the Hg present in the Arctic is derived from pollution sources within this region; most is transported in from anthropogenic and natural sources outside the Arctic (AMAP, 2005). Previous AMAP assessments (AMAP, 1998, 2005) have discussed in detail the atmospheric, oceanic, riverine and terrestrial pathways by which mercury is transported into the Arctic. As a result, these pathways are only considered in relation to specific issues in this report. However, it remains the case that the Arctic is intimately and inextricably linked by these pathways to the global Hg cycle.

This chapter begins by summarizing recent information about Hg in the global environment and, specifically, about the global Hg reservoirs that interact with the regional Arctic environment, essentially through the atmosphere and oceans. This is followed by an introduction to the physical linkages between the global and regional environmental 'reservoirs', and the chemical species of Hg involved. To provide a conceptual linkage to Chapter 3, an ordered perspective is also placed on the important processes that deliver transported Hg to the Arctic ecosystems. For each process, the reader is directed to corresponding discussion in subsequent sections of this chapter and in Chapter 3.

### 2.1.1. The Arctic in a global setting

A recent model of the Hg cycle in the contemporary global environment is summarized in Figure 2.1. It is clear that surface soils contain by far the largest Hg reservoir. However, with the exception of soils present in the Arctic itself, global soil Hg only interacts with the Arctic on meaningful time scales indirectly through the atmosphere and ocean. Sunderland and Mason (2007) estimated that about 134 000 t of Hg presently reside in the upper oceans and about 5600 t in the atmosphere. These reservoirs include pollution-related increases of about 25% in the upper oceans and 300% to 500% in the atmosphere, relative to the pre-industrial period. The most recently available (2005) estimates of global anthropogenic Hg emissions to air are discussed in Section 2.2.

The global model shows that there are large air-sea Hg exchanges that make it difficult to determine the net direction of flux. The upper global oceans (top 1500 m) contain about one third of the total ocean inventory but clearly there is the suggestion of vigorous processes (particle flux, deep-water formation) that remove Hg from the surface to deep oceans. Another important point is that almost all of the Hg transported from land to oceans via rivers becomes stored in estuaries and on continental shelves. From an Arctic perspective, the most important pathways for Hg transport to the Arctic involve the upper oceans and the atmosphere, because these reservoirs directly and relatively rapidly interact with the corresponding

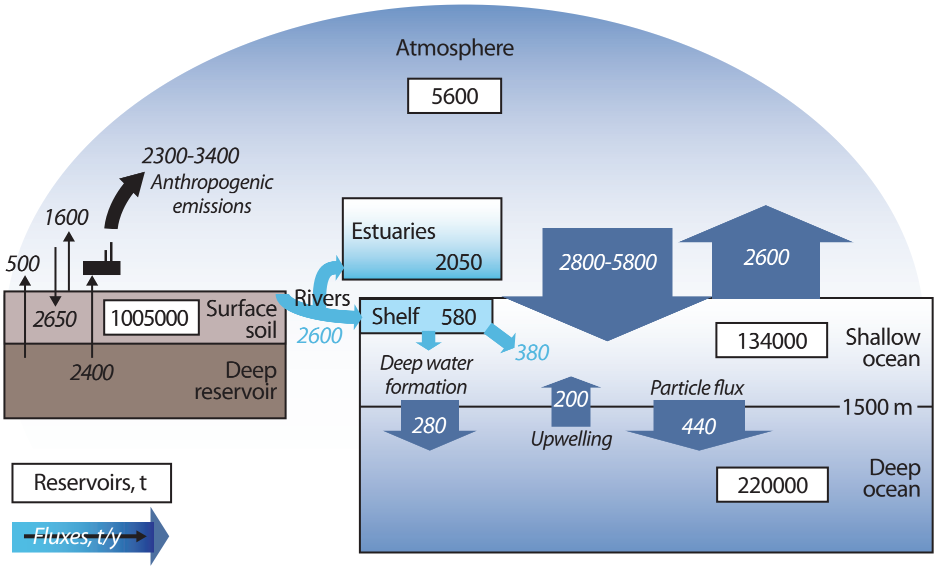


Figure 2.1. A global model of mercury inventories in present-day air, ocean and soil reservoirs, and the fluxes which indirectly or directly contribute to mercury levels in the Arctic. Adapted from Sunderland and Mason (2007).

reservoirs in the Arctic over biologically relevant time frames (Outridge et al., 2008).

One important conclusion from the air-ocean modeling work is that, on average, the global oceans have not yet reached equilibrium with the present-day atmospheric Hg levels. This means that average seawater Hg concentrations are likely to increase slowly for periods of decades to several centuries, even if there is no further increase in atmospheric Hg levels (Sunderland and Mason, 2007). Regional differences in seawater Hg trends are expected, with the time taken to reach equilibrium predicted to differ as a result of varying circulation patterns, water residence times, and proximity to regions of industrial activity. For example, mid-range regional estimates for the North Atlantic Ocean suggest a stable or declining future trend rather than an increase. The response time of the North Atlantic above 55° N to changes in atmospheric Hg concentrations is estimated to be 50 to 600 years, whereas in the North Pacific Ocean it may take 500 to 700 years for Hg concentrations to reach steady-state. Surface waters will naturally respond more rapidly than deep and intermediate water layers; for example, the surface Atlantic Ocean may reach equilibrium in just 10 to 30 years. More recent studies have not changed the seminal conclusions of Mason et al. (1998) that the biogeochemical cycling of Hg in the ocean is dominated by air-sea exchange at the sea surface, with removal of Hg to deep ocean sediments being analogous to that of carbon (i.e., only a small fraction of the Hg taken up by mixed-layer particulate matter is buried in deep water sediments). What is still clear is that the external inputs from different oceans to the Arctic Ocean will vary partly because of systematic differences in circulation patterns, residence times, and other abiotic and biotic processes.

The extent to which changes in these global reservoirs affect Hg levels in the Arctic environment depends on the degree of connectivity between the reservoir and the Arctic, which is a function of the speed of lateral transfer into the Arctic and the average residence time of Hg in the various environmental compartments and media. The amount of Hg present from natural sources within the Arctic (see Section 2.3) is also a factor, as the relative contribution of the external inputs to each environmental medium is greater if the local 'background' contamination is low and vice versa. The average residence times for Hg in the global atmosphere and upper oceans at the present time, which can be derived from the Sunderland and Mason (2007) model, are about 0.7 and about 27 years, respectively. Lateral transfer is likely to be significantly slower for seawater (of the order of centimetres per second) than for air (of the order of metres per second). However, given the long residence time of Hg in seawater it is likely that changes in global upper ocean and atmospheric Hg will both affect their Arctic counterparts but over differing time scales – relatively rapidly for the atmosphere and slowly for seawater. Recent best estimates of the net total Hg fluxes currently reaching the Arctic Ocean from global reservoirs via different pathways (ocean currents, atmosphere, rivers, coastal erosion), and the corresponding sizes of Hg reservoirs in the Arctic, are presented in Section 2.4.

### 2.1.2. **Mercury processing in the Arctic environment**

Inorganic Hg(II) is the key Hg 'feedstock' from which the more toxic and bioavailable monomethyl-Hg (MeHg) is formed in surficial environments (oceans, lakes, soils). One important difference between the atmospheric and aquatic transport pathways (see Figure 3.3) is that the dominant form of Hg present in the atmosphere and hence transported into the Arctic via the atmosphere is gaseous elemental Hg (GEM, Hg(0)). This must undergo chemical transformation to inorganic Hg(II) in the atmosphere in order for it to be deposited to Arctic surface environments. Unreacted GEM is simply transported out of the Arctic again by air mass movements. In contrast, Hg inputs via oceans, rivers, and coastal erosion already comprise mainly inorganic Hg(II), as well as small amounts of methylated Hg(II) and dissolved gaseous Hg(0), because of transformations that occurred in these reservoirs before the Hg reached the Arctic environment.

Because Arctic atmospheric transformations of Hg(0) to Hg(II) form such an integral part of the answer to the 'how does it get there' component of the main question addressed in this chapter, these transformations are discussed in detail here. The subsequent transformations, dynamics, and fate of Hg in Arctic waters, soils, sediments, and food webs are addressed in Chapter 3. As marine food webs (and especially marine mammals) appear to be the major exposure route of northern peoples to Hg (AMAP, 2009b; see also Chapter 8), the behavior and fate of Hg in the marine environment is a particular focus for Chapter 3.

Recent findings on Arctic atmospheric speciation and transformation of Hg, including wet and dry deposition processes and atmospheric mercury depletion events (AMDEs), are described in Section 2.5. The extent to which current understanding of these processes permits modeling to describe and quantify the fluxes of atmospheric Hg in the Arctic is evaluated in Section 2.6. The atmospheric Hg(II) is deposited into the upper ocean, into snowpacks, or into soil and freshwater environments, where it mixes with Hg(II) and other Hg species from global oceanic and local terrestrial geogenic sources (see Figure 3.3; Section 3.2). Thereafter, changes in chemical speciation occur via physical, chemical, and biological processing in marine, freshwater, and terrestrial environments, and result predominantly in three important forms of Hg: monomethyl mercury (MeHg), particulate-associated Hg(II) ($Hg_p$) and gaseous Hg(0). These Hg species are moved around, transformed into other Hg species, or recycled by internal processes in each environmental medium. Methylation of inorganic Hg(II) to MeHg (Section 3.3), and its uptake into Arctic food webs (Section 3.4), are two key steps in the exposure route between environmental Hg and Hg in human food chains. Mercury uptake into food webs is influenced by trophic processes that can affect the efficiency of MeHg transfer from lower to upper levels of food webs (Section 3.5), as well as by effects on Hg bioavailability by co-occurring materials such as organic carbon (Section 3.7). Ultimately, Hg is removed from the biologically-active Arctic environment to long-term storage in various archives such as ocean sediments, soils, and glacial ice (Section 3.8), or by transport out of the Arctic in air and seawater (see Figure 2.2).

## 2.2. What are the current rates of global anthropogenic emissions of mercury to air?

### 2.2.1. Global anthropogenic mercury emissions to air in 2005

Quantifying sources of Hg and its transport via atmospheric and aquatic pathways is fundamental to understanding the global fluxes and contamination of ecosystems by this metal. Due to the relatively long atmospheric-lifetime of GEM, Hg can be transported to the Arctic via the atmosphere from sources around the globe. Consequently, an assessment focusing on Arctic contamination needs to consider global emissions of Hg. Understanding global Hg emissions is also critical for the development of relevant and cost-efficient strategies aimed at reducing the negative impacts of this global pollutant. Emission inventories provide important input data for several types of atmospheric chemical-transport and source-receptor models that can provide information on Hg distribution and deposition rates. This section focuses on primary anthropogenic emissions to the atmosphere. For a full description of the atmospheric cycling of Hg, information on natural emissions as well as re-emissions of Hg deposited to land and water need to be considered and are presented in Sections 2.3 to 2.6.

The need for information on global emissions of Hg to the atmosphere to support work on Arctic Hg assessments has led to a strong connection between AMAP assessment activities and work by groups engaged in producing these global inventories. As a result, past AMAP assessments have integrated information on global anthropogenic emission inventories produced for the nominal years 1990 (AMAP, 1998) and 1995 and 2000 (Pacyna and Pacyna, 2002; AMAP, 2005). Most recently, an inventory of the global anthropogenic Hg emissions for 2005 (the '2005 v5' inventory) was prepared in a joint AMAP/UNEP project in 2008. Details on the methods, data sources and other information are reported by AMAP/UNEP (2008) and Pacyna et al. (2010a). Further work on the 2005 inventory was undertaken as part of the present assessment (see Section 2.2.2), resulting in the '2005 v6' inventory. The 2005 global anthropogenic emissions inventory was also used as a basis for developing some first order 'scenario' emissions inventories for 2020 (AMAP/UNEP, 2008). The scenario inventories and modeling work based on these inventories are presented in Chapter 7.

#### 2.2.1.1. Global emissions to air by industrial sectors

The largest anthropogenic emissions of Hg to the global atmosphere occur as a by-product of the combustion of fossil fuels, mainly coal in power plants and industrial and residential boilers. As much as 60% of the total emission of roughly 1450 tonnes of Hg emitted from 'by-product' sector sources, and 46% of the roughly 1921 tonnes of Hg emitted from all anthropogenic sources worldwide in 2005, came from the combustion of fossil fuels for energy and heat production (Table 2.1). Emissions of Hg from coal combustion are between one and two orders of magnitude higher than emissions from oil combustion, depending on the country. Some uncertainties remain about the magnitude of Hg emissions from natural gas and oil processing. Mercury is present in some natural gas deposits but is removed before distribution to avoid corrosion of aluminum equipment in the processing plants. The final fate of this Hg, and the potential emissions of Hg from crude oil processing and combustion, warrants further evaluation. Various factors affect the emission of Hg to the atmosphere during combustion of fuels. The most important are the Hg content of the coal and the type and efficiency of control equipment that can remove Hg from exhaust gases (as well as, naturally, the amount of fuel combusted).

Emissions from non-ferrous and ferrous metal industry (excluding Hg and gold production) are estimated to contribute about 10% to total anthropogenic Hg emissions. The content of Hg in ores varies substantially from one ore field to another (e.g., Pacyna, 1986; UN ECE, 2000) as does the Hg content in scrap metal. The Hg emissions from primary metal production (using ores) are between one and two orders of magnitude higher than the Hg emissions from secondary smelters (with scrap as the main raw material), depending on the country.

Table 2.1. Estimated global anthropogenic emissions of mercury to air in 2005 from various sectors (revised from AMAP/UNEP, 2008).

| Sector | Emissions in 2005[a], tonnes | Percentage contribution of total emissions to air |
|---|---|---|
| Coal combustion in power plants and industrial boilers | 498 (339-657) | 26 |
| Residential heating / other combustion | 382 (257-506) | 20 |
| Artisanal and small-scale gold production | 323 | 17 |
| Cement production | 189 (114-263) | 10 |
| Non-ferrous metals (Cu, Zn, Pb) | 132 (80-185) | 7 |
| Large-scale gold production | 111 (66-156) | 6 |
| Other waste | 74 | 4 |
| Pig iron and steel, secondary steel | 61 (35-74) | 3 |
| Waste incineration | 42 | 2 |
| Chlor-alkali industry | 47 (29-64) | 2 |
| Dental amalgam (cremation)[b] | 27 | 1 |
| Other | 26 | 1 |
| Mercury production | 9 (5-12) | 0.5 |
| Total | 1921 | |

[a] Represents best estimates: estimate (uncertainty interval), or conservative estimate (no associated range). See AMAP/UNEP (2008) for discussion on uncertainties; [b] does not include other releases from production, handling, use and disposal of dental amalgam.

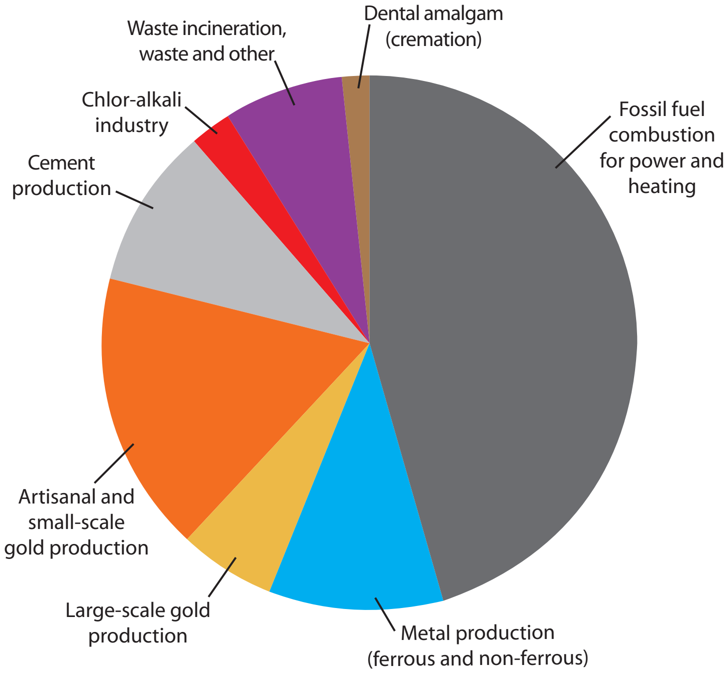


Figure 2.2. Proportion of global anthropogenic emissions of mercury to air in 2005 from various sectors. Source: revised after AMAP/UNEP (2008).

Pyro-metallurgical processes in primary production of non-ferrous metals, employing high temperature roasting and thermal smelting, emit Hg and other raw material impurities mostly to the atmosphere. Non-ferrous metal production with electrolytic extraction is more responsible for risks of water contamination.

Among various steel making technologies the electric arc process produces the largest amounts of trace elements, and their emission factors are about one order of magnitude higher than those for other techniques, for example, basic oxygen and open hearth processes. However, the major source of atmospheric Hg related to the iron and steel industry is the production of metallurgical coke.

The fuel-firing kiln system and the clinker-cooling and handling system are responsible for emissions of Hg in the cement industry. This industry contributes about 9.8% of the total anthropogenic Hg emissions (and 13% of 'by-product' Hg emissions) on a global scale. The content of Hg in fuel, limestone and other raw materials used in the kiln and the type and efficiency of control equipment are the main parameters affecting the size of Hg emissions.

Industrial (large-scale) gold production using Hg technology is another source of Hg to the atmosphere, contributing about 6% to the global Hg emissions.

The use of the mercury cell process to produce caustic soda in the chlor-alkali industry has decreased significantly over the past 15 years worldwide (www.eurochlor.org). The atmospheric chlor-alkali Hg emissions of 47 tonnes in 2005 account for less than 10% of Hg used in this production process and about 2.5% of the total anthropogenic Hg emissions worldwide. Major points of Hg release in the mercury cell process of chlor-alkali production include: by-product hydrogen stream, end box ventilation air, and cell room ventilation air. For long-term avoidance of emissions, safe storage of Hg-containing waste from these steps is required.

Mercury production for industrial uses contributes just over 0.5% to global Hg emissions.

The global product-related emissions of Hg (including all major uses of Hg in products) were estimated to be around 125 tonnes (6.5%) for the conservative estimate in the AMAP/UNEP (2008) study (Table 2.1). This estimate has subsequently been revised to 142 tonnes (7.4%). It is noteworthy that according to these calculations, around 30% of the product-related Hg emissions arises from waste incineration and another 52% from landfill waste.

Summing the Hg emissions from 'by-product' sectors, product use, cremation and artisanal / small-scale mining, results in a global inventory of Hg emissions to air from anthropogenic sources for 2005 of about 1920 tonnes. Table 2.1 and Figure 2.2 summarize the emissions attributed to various anthropogenic activities. The low- and high-end estimates are based on the uncertainties in emission estimates for the different sectors.

### 2.2.1.2. Emissions by geographical region

The combined global anthropogenic atmospheric Hg emissions inventory for by-product sectors, product use, cremation and artisanal mining of about 1920 tonnes for 2005 can be divided between the continents as summarized in Figure 2.3. From the compiled inventory data, it is possible to rank the countries by their emissions (see Figure 2.4). The sector-breakdown of emissions from the ten largest emitting countries is presented in Figure 2.5.

The Asian countries contributed about 65% to the global Hg emissions from anthropogenic sources in 2005, followed by North America and Europe. This pattern is similar if by-product emission sectors only are considered. Russia, with its contribution of about 4% to global emissions is considered separately due to its territories in both Europe and Asia.

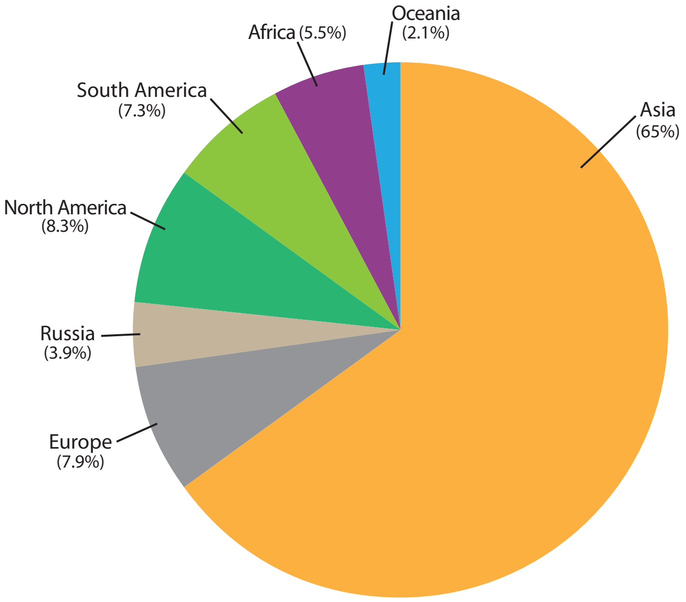


Figure 2.3. Proportion of global anthropogenic emissions of mercury to air in 2005 from different regions. Source: revised after AMAP/UNEP (2008).

Combustion of fuels to produce electricity and heat is the largest source of anthropogenic Hg emissions in Europe, North America, Asia, and Russia, and is responsible for about 35% to 50% of the anthropogenic emissions in Oceania and Africa. However, in South America, artisanal and small-scale gold mining (ASGM) is responsible for the largest proportion of the emissions (about 60%). Relatively large Hg emissions from ASGM in some Asian countries, as well as several countries in South America, explain why countries such as Indonesia, Brazil and Colombia appear in the top ten ranked Hg emitting countries, whereas if by-product emissions sectors alone are considered, no South American countries are represented and all other countries listed have a high degree of industrial development.

China is the largest single emitter of Hg worldwide, by a large margin. Power plant emissions are an important part of the total combustion emissions of Hg in China although the ongoing restructuring and improved emission control of air pollutants in the Chinese power sector may have reduced the importance of this sector in recent years. Equally significant are emissions from combustion of poor quality coal mixed with various kinds

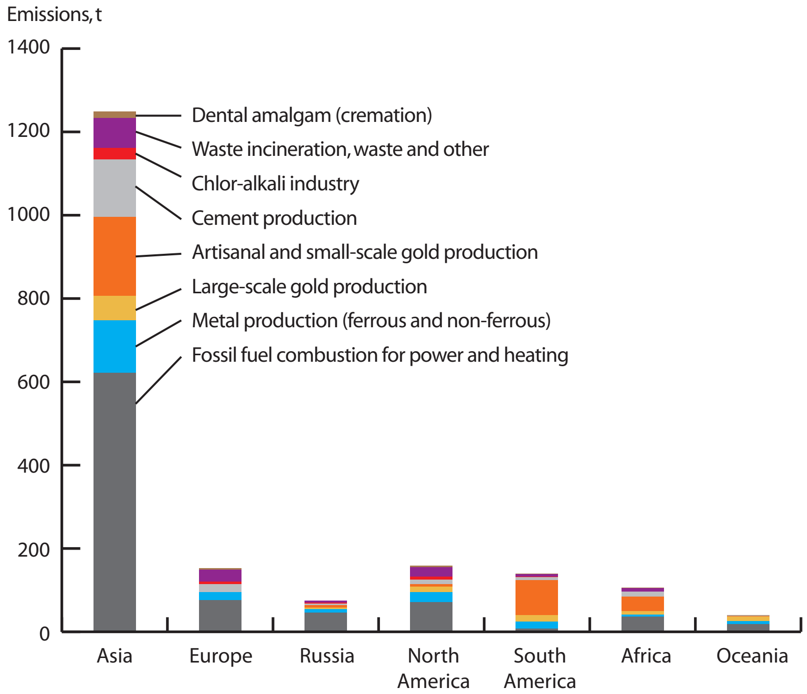


Figure 2.4. Global anthropogenic emissions of mercury to air in 2005 from different continents by sector. Source: revised after AMAP/UNEP (2008).

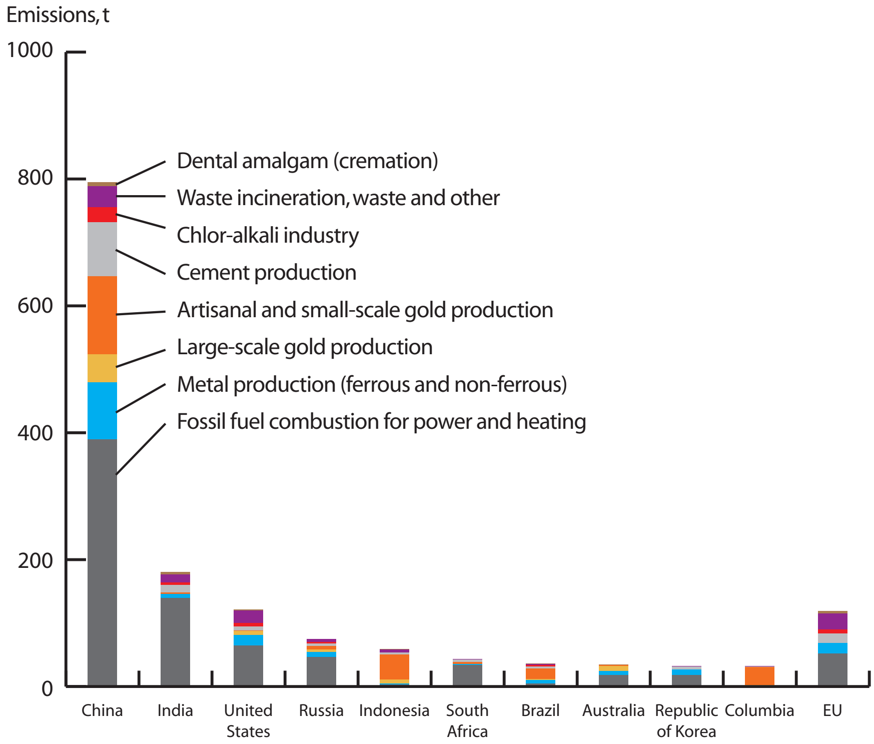


Figure 2.5. Emissions of mercury to air in 2005 from various anthropogenic sectors in the ten largest emitting countries. Source: revised after AMAP/UNEP (2008).

of wastes in small residential units to produce heat and cook food in rural areas. With estimated by-product sector emissions exceeding 600 tonnes, China contributes about 40% to the global Hg by-product emissions, and this contribution may be even higher because Hg emission factors for non-ferrous metal production in China may be underestimated. China also has significant emissions from ASGM.

Together, China, India, and the United States, are responsible for about 60% of the total global Hg emissions from by-product sectors (about 895 out of 1450 tonnes), and a similar percentage of the total estimated global emission inventory for 2005 (1095 out of 1920 tonnes).

### 2.2.2. Global emission trends 1990 to 2005

The 2005 (v5) global inventory of anthropogenic Hg emissions to air, described by AMAP/UNEP (2008) and summarized by UNEP (2008), was the most comprehensive such inventory published to date. Unlike previous global inventories, which essentially only addressed 'by-product' Hg emissions from main energy production and industrial sectors, the 2005 inventory also included estimates of emissions associated with a number of 'intentional-use' sectors, including artisanal and small-scale gold production.

The 2005 inventory was produced using a generally similar approach to that employed to compile (on the basis of 'by-product' sectors) Hg emission inventories for the nominal years 1990, 1995 and 2000 (Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010a; AMAP/UNEP, 2008), namely by combining reported national emissions for specific sectors with expert estimates for the remaining countries for the same range of sectors. The expert estimates were obtained using information on production and consumption of raw materials in relevant industries, in combination with applicable emission factors. However, since each inventory was compiled independently at about five-year intervals, the underlying source data used varied in terms of their sources, availability and quality. Furthermore, emission factors and the assumptions regarding technologies employed changed as knowledge was improved.

Each of the four available global inventories has also been geospatially distributed (gridded), again using similar but not identical methods (see Pacyna et al., 2003; Wilson et al., 2006; AMAP/UNEP, 2008). These inventories have been used to model the atmospheric transport of Hg, and investigate geographic source-receptor relationships (see Dastoor and Larocque, 2004; Christensen et al., 2004; Travnikov, 2005; AMAP/UNEP, 2008; Dastoor et al., 2008). Results of modeling using the 1990, 1995, 2000, and 2005(v6) global anthropogenic emissions inventories described here, and the 2005(v5) inventory presented in the previous section, are discussed in Section 2.6.

Figure 2.6 presents the global distribution of anthropogenic atmospheric emissions of Hg in 2005, following application of the geospatial distribution methodology described by Wilson et al. (2006) and Pacyna et al. (2010a) to the global anthropogenic (2005v5) inventory (AMAP/UNEP, 2008).

The AMAP/UNEP (2008) report included a preliminary discussion of the general trends in global emissions as implied from comparing the available 1990, 1995, 2000 and 2005 inventories. However, such a comparison may be compromised by methodological differences between years.

Consequently, and as part of its 2010 assessment of Hg in the Arctic, AMAP undertook a re-analysis of the 1990 to 2005 global Hg inventories in an attempt to prepare a series of more comparable historical emission inventories.

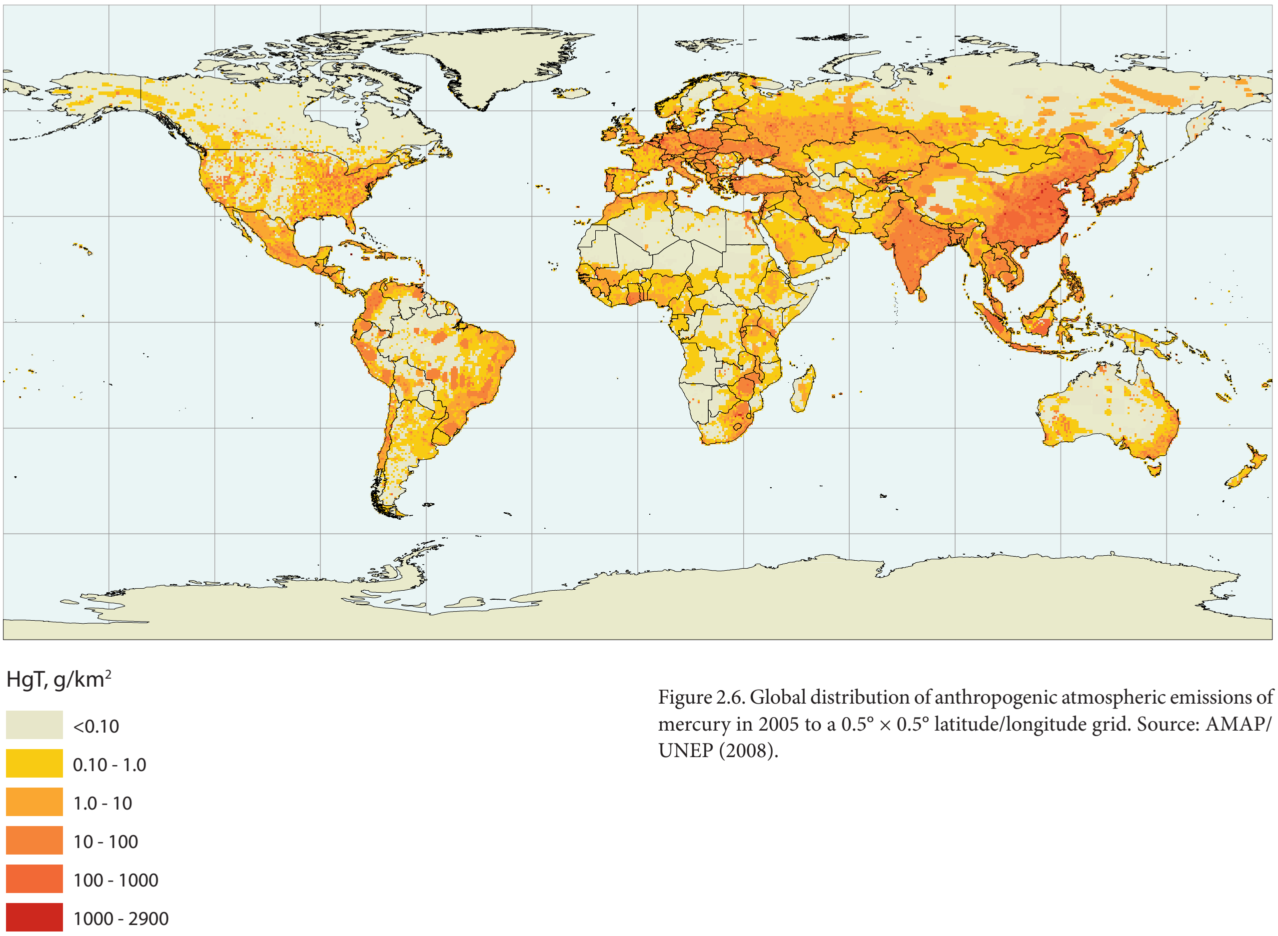


Figure 2.6. Global distribution of anthropogenic atmospheric emissions of mercury in 2005 to a 0.5° × 0.5° latitude/longitude grid. Source: AMAP/UNEP (2008).

This re-analysis employed a common methodology, a more consistent information base for estimating certain emissions, and updating of the earlier inventories to account for improved knowledge gained during the past 15 years or so. The re-analysis also involved correcting certain questionable estimates in older inventories according to updated information on practices and technologies, including a few apparent errors. It also involved further revising the 2005 inventory for newly available data on regional Hg consumption that form the basis for estimates of emissions associated with 'intentional-use' sectors. The main results of this re-analysis are presented as follows.

Revised estimates of total emissions of Hg to air in 1990, 1995, 2000 and 2005 from 'by-product' and 'intentional-use' sectors are presented in Figure 2.7. 'By-product' sectors comprise: stationary combustion of fossil fuels in power plants and for residential heating; pig iron and steel production; non-ferrous metal production; cement production; industrial-use mercury production; large-scale gold production; and minor 'other' sources. Mercury emissions from the chlor-alkali industry are accounted in the 'by-product' sector inventory. Intentional-use sectors include artisanal and small-scale gold mining; emissions from cremation; secondary steel production; and waste disposal (including waste incineration). The data for emissions from 'intentional-use' sectors are regarded as conservative estimates.

Regional trends in combined emissions from 'by-product' and 'intentional-use' sectors for 1990, 1995, 2000 and 2005 are summarized in Figure 2.8.

Revision of the 1990, 1995 and 2000 inventories resulted in a significant reduction in total 'by-product' sector emission estimates compared to those previously published (Pacyna and Pacyna, 2002, 2005; Pacyna et al., 2006, AMAP/UNEP, 2008) estimates (see Table 2.2). Newly compiled information on consumption and use of Hg allowed new inventories for emissions from 'intentional-use' sectors to be prepared for 1990, 1995 and 2000. These changed the sectoral patterns, and

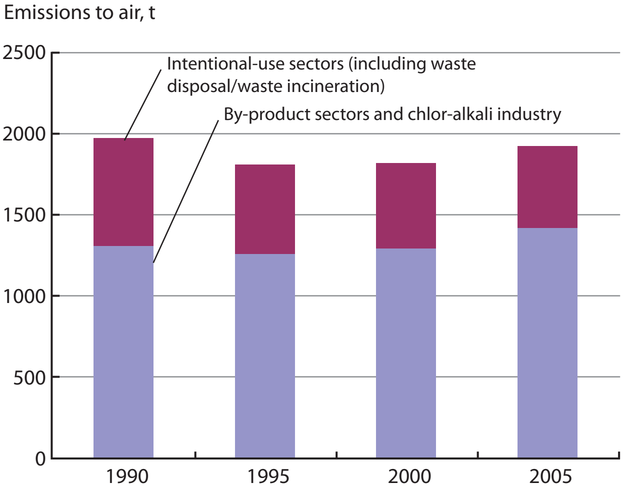


Figure 2.7. Revised estimates of total global anthropogenic mercury emissions to air from 'by-product' and 'intentional-use' emission sectors. Source: AMAP (2010); AMAP global mercury emission inventory v6.

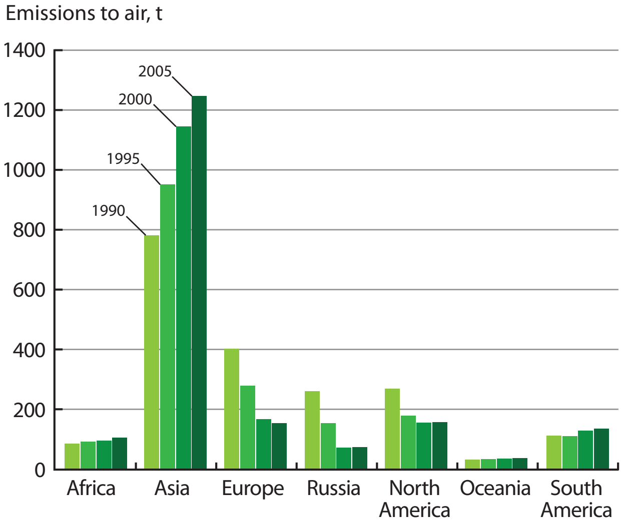


Figure 2.8. Revised estimates of annual anthropogenic mercury emissions to air from different continents/regions. Source: AMAP (2010).

to a lesser extent the magnitude of 'intentional-use' sector emissions in 2005.

The differences in the revised estimates for the emissions presented in Table 2.2 exceed the reported uncertainties associated with these estimates (which vary by about ± 20-40% for the main industrial sectors, depending on the region). See AMAP (2010) for a detailed description of the revision of the historical emission inventories.

The newly constructed emissions inventories for 1990, 1995, 2000 and 2005 represent a more consistent set of global inventories of Hg emissions to air than those previously available, in terms of the underlying data and the methods used to produce and compile the estimates for various countries and source sectors. For the revised emissions inventories, the same emission factors (expressed as emissions of mercury per industrial activity unit) used in preparing the 2005 inventory (AMAP/UNEP, 2008) were applied to activity data (e.g. statistical information on coal consumption, metal production, cement production) from the corresponding year. The revised inventories have also been geospatially distributed (to a 0.5 by 0.5 degree latitude/longitude grid) using a consistent approach. In practice this required ignoring information on emissions from specific point sources and geospatially distributing all emissions according to a series of 'surrogate' data distributions that reflect the geospatial distributions for the sectors concerned. The 'surrogate distributions' used are those employed for the 2005 inventory as reported by AMAP/UNEP (2008).

## 2.3. Are natural sources significant contributors of mercury to the Arctic environment?

### 2.3.1. Global natural emissions and re-emissions

Mercury occurs in the Earth's crust, especially as the mineral cinnabar (Hg(II) sulfide: HgS). The metal is released naturally via weathering of rocks and as a result of volcanic/geothermal activities that constitute primary natural sources of Hg. According to Sunderland and Mason (2007), the pre-industrial world carried about 1600 tonnes of Hg in the atmosphere, 107 000 tonnes in the upper ocean, 194 000 tonnes in the deep ocean, and about 900 000 tonnes in surface soil. In addition to primary sources, deposited oxidized Hg may be reduced via photochemical or biological processes and re-emitted to the atmosphere. Re-emission of Hg occurs from soil and vegetation as well as from sea surfaces and is considered significant in comparison to primary emissions. As a consequence, the Hg concentration in the atmosphere is determined not only by primary sources (both natural and anthropogenic) but also to a significant degree by re-emission from environmental reservoirs.

These re-emission cycles were also active in the pre-industrial environment, re-cycling Hg released from natural sources. It is likely that, prior to the industrial period, Hg in the environment was more or less in a steady-state with mobilization rates from geological reservoirs balanced by removal through long-term burial (in soils and sediments), and the various reservoir compartments (atmosphere, soils, oceans) were in equilibrium. Significant anthropogenic emissions since the start of the industrial period have disturbed this balance and the major environmental reservoirs are no longer in equilibrium.

Evaluations of natural emissions of Hg have been carried out as part of studies of global Hg budgets and fluxes using global Hg models (Shia et al., 1999; Seigneur et al., 2001, 2004; Lamborg et al., 2002a; Mason and Sheu, 2002; Selin et al., 2007). Flux estimates based on field measurements exist but represent only very limited geographical areas and limited time scales.

Some recent environmental Hg fluxes from global Hg models are shown in Table 2.3. Mercury sources in Table 2.3 are categorized into total emissions from land and total oceanic emissions. The land and oceanic sources are further separated into primary natural emissions and re-emissions. Natural sources correspond to estimates of fluxes in the 'pristine' (i.e., pre-industrial) environment, while re-emissions also include increases in emissions from natural surfaces caused

Table 2.2. Differences between the originally-published global inventories of anthropogenic mercury emissions to air and the revised inventories for 1990, 1995, 2000 and 2005 (original inventories from Pacyna and Pacyna, 2002, 2005; Pacyna et al., 2006, AMAP/UNEP, 2008; revised inventories from AMAP, 2010).

| | 1990 | 1995 | 2000 | 2005 (v6) |
|---|---|---|---|---|
| Original total inventory | 1732[a] | 2214[a] | 2190[a] | 1926[b] |
| Revised total inventory | 1967[b] | 1814[b] | 1819[b] | 1921[b] |
| Difference | 235 | -400 | -371 | -5 |

[a] By-product sectors only (plus waste incineration for Europe (EU countries), USA and Canada); [b] by-product and intentional use sectors combined.

Table 2.3. Environmental mercury fluxes estimated from global mercury models.

| Hg Fluxes (kt/y) | Lamborg et al., 2002a | Mason and Sheu, 2002 | Selin et al., 2007 | Mason, 2009 | Friedli et al., 2009a |
|---|---|---|---|---|---|
| Natural emissions from land | 1.0 | 0.81 | 0.5 | | |
| Re-emissions from land | | 0.79 | 1.5 | | |
| *Emissions from biomass burning* | | | | | 0.675 |
| *(A) Total emissions from land* | 1.0 | 1.6 | 2.0 | 1.85[a] | |
| Natural emissions from ocean | 0.4 | 1.3 | 0.4 | | |
| Re-emissions from ocean | 0.4 | 1.3 | 2.4 | | |
| *(B) Total oceanic emissions* | 0.8 | 2.6 | 2.8 | 2.6 | |
| *(C) Primary anthropogenic emissions* | 2.6 | 2.4 | 2.2 | | |
| Total sources (A+B+C) | 4.4 | 6.6 | 7.0 | | |
| *(D) Deposition to land* | 2.2 | 3.52 | | | |
| *(E) Deposition to ocean* | 2.0 | 3.08 | | | |
| Total deposition (D+E) | 4.2 | 6.6 | 7.0 | 6.4 | |
| Net load to land | 1.2 | 1.72 | | | |
| Net load to ocean (burial in sediments) | 1.2 (0.4) | 0.68 (0.2) | | | |
| Total net load (land + ocean) | 2.4 | 2.4 | 2.2 | | |
| Other parameters | | | | | |
| Mercury burden in the troposphere (kt) | 5.22 | 5.00 | 5.36 | | |
| GEM lifetime (y) | 1.3 | 0.76 | 0.79 | | |

[a] Including Hg(0) emissions (0.2 kt/y) in response to AMDEs in polar regions. Biomass burning is not included in the emissions from land in this table.

by anthropogenic emissions at present and in the past. Primary anthropogenic emissions correspond to direct emissions from human activities. The model results in Table 2.3 are based on similar primary anthropogenic emission values, i.e., 2.2 to 2.6 kt Hg per year. This is close to that from the original global anthropogenic Hg emissions inventory for 2000 (2.2 kt/y; Pacyna et al., 2006). However, the estimates of total flux vary among the models, because of how re-emissions are treated by the different models. For example, unlike earlier models, Selin et al. (2007) predicted that the re-emission flux from the ocean was relatively high, even slightly greater than primary anthropogenic emissions.

The difference in estimates of re-emissions also reflects the importance of primary anthropogenic sources in comparison to total sources. In the Lamborg et al. (2002a) model, primary anthropogenic sources constitute about 60% of the total Hg emissions, whereas it is only 31% in the Selin et al. (2007) model. The net Hg load to land and ocean is defined in Table 2.3 as [total deposition] - [total emission from land and ocean]. The net load constitutes an annual loss of Hg from cycling, and in all estimates this loss is of the same magnitude as the total emissions from anthropogenic sources. In the Lamborg et al. (2002a) model, the Hg net load to the surface of the oceans is 1.2 kt/y. About 1.8 kt of the Hg in the ocean's surface layer is scavenged by particles each year and removed to the deeper layers of the ocean, but is compensated by 0.6 kt/y upwelling. Hence, the net load of Hg to oceanic surface water is estimated to be zero at present. In contrast, Hg is accumulated in the deep ocean at a rate of about 1.2 kt/y, of which 0.4 kt/y is buried in sediments of the sea floor. In the Mason and Sheu (2002) model, the ocean is treated in a somewhat more simplified manner. The load to the ocean is 0.68 kt/y, of which 0.2 kt is buried in sediments each year. With regard to the net Hg load to land, Mason and Sheu (2002) predicted a larger load than Lamborg et al. (2002a). Divalent Hg bonds strongly to thiol ($SH^-$) groups in organic matter in soils, and is therefore to a large extent accumulated in the soil (Meili et al., 2003; Skyllberg, 2010).

One important aspect of the cycling of Hg in the environment is wildfires and biomass burning. Growing biomass and organic surface soils contain Hg originating from atmospheric deposition. When organic material is burned in accidental wildfires or intentional burning for forest clearance, the associated Hg is released back to the atmosphere. The global emission of Hg from this source category has been estimated at 675 ± 240 t/y (Friedl et al., 2009). This is a significant contribution to the atmospheric pool of Hg and needs to be taken into account when calculating global mass balances of Hg for atmospheric modeling. The largest emissions occur in regions where boreal and tropical forests are burned, whereas burning of agricultural residues are assumed to contribute very little Hg. The uncertainty in this estimate is large due to incomplete information on the occurrence of fires, the Hg content of the organic material, and the degree to which the Hg is released during the fire.

From a policy perspective, this Hg emission should be treated partly as a re-emission driven by natural processes (i.e., wildfires), and partly as an emission under human control (intentional burning, forest clearance). Reducing the global intensity of forest clearance and biomass burning would thus have the additional beneficial effect of reducing the remobilization of Hg.

### 2.3.2. Natural contributions of mercury to the Arctic environment

Globally the residence times of Hg in the global upper ocean (~70 y in the pre-industrial period and ~27 y now; Sunderland and Mason, 2007) and in air (~0.7 y in both pre-industrial and present times) are long relative to the time taken for these media to transport into the Arctic (decades and weeks, respectively). For this reason, natural Hg has historically been and continues to be delivered to the Arctic from regions outside the Arctic both through the atmosphere and the ocean. Within the Arctic itself, the natural Hg cycle also continues through the release of

Hg by weathering, and the transfer of Hg from soils, sediments and vegetation into aquatic systems through volatilization, fires, dust and sediment resuspension. Therefore, the natural Hg cycle (Figure 2.9), as inferred from records in ancient material, is significant and provides a ubiquitous base concentration of Hg in all environmental media to which has been added the Hg released by human activities during the past two centuries.

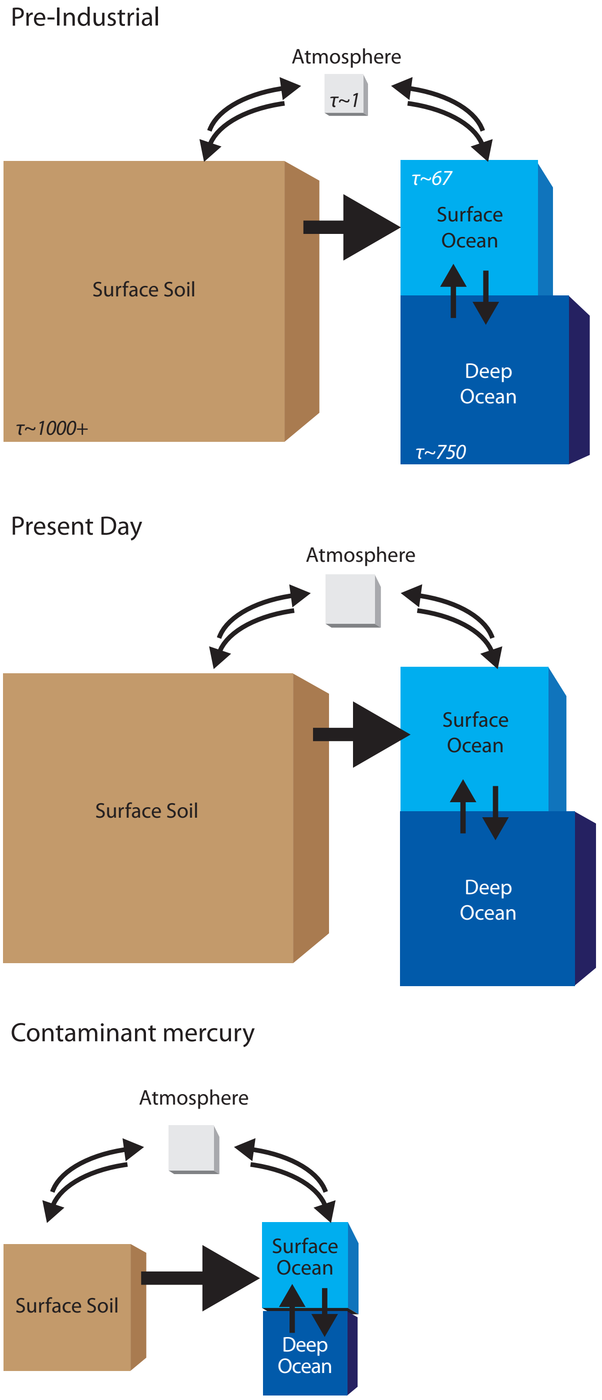


Figure 2.9. Major global mercury reservoirs and residence times in pre-industrial times. The sizes of the boxes reflect the relative amounts of mercury contained within each reservoir; values within boxes are average residence times in years. Adapted from Sunderland and Mason (2007).

## 2.4. What are the relative importance of and processes involved in atmospheric, oceanic, riverine and terrestrial inputs of mercury to the Arctic?

The Arctic Ocean and Hudson Bay are both semi-enclosed mediterranean seas, which provide the opportunity to calculate Hg budgets and therefore make direct comparisons of the relative importance of inputs to these systems (see Figure 2.10 and Figure 2.11). For Hudson Bay, Hare et al. (2008) also compared the modern Hg budget with one estimated for pre-industrial times. Detailed discussions of how the budget components were estimated and potential errors in the estimates are given in the respective publications. Briefly, the budgets depend upon reasonably well-balanced sediment and water budgets developed for both regions (Stein and Macdonald, 2004; Kuzyk et al., 2009). In the case of the Arctic Ocean, a modified version of the Global/Regional Atmospheric Heavy Metal (GRAHM; Dastoor and Larocque, 2004) model was used to arrive at an estimate of net atmospheric flux of Hg into the Arctic Ocean. The estimated fluxes for the various pathways are based on Hg concentrations and fluxes for media selected following comprehensive literature surveys (Table 2.4). For the Arctic Ocean as a whole (Figure 2.10), the largest single source of Hg was net atmospheric deposition, which contributed 48% (98 t/y) of the total annual Hg input (Outridge et al., 2008). The GRAHM model incorporates a re-emission term of 133 t/y and evasion of 12 t/y (thus, gross flux was 243 t/y). Of the net flux, 46% (45 t) occurred during springtime and 54% (53 t) during the rest of the year. Inflows from the Atlantic and Pacific Oceans (23%), and coastal erosion (23%) contributed most of the remaining total Hg to the system; rivers were collectively a minor source.

In contrast to the Arctic Ocean, for Hudson Bay, rivers were the largest single source (41%) followed in importance by the

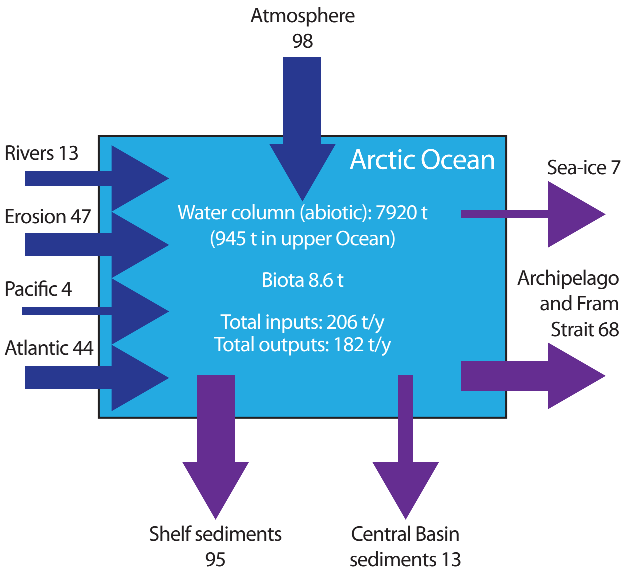


Figure 2.10. Mass balance model of total mercury in the Arctic Ocean with flux components estimated independently as described by Outridge et al. (2008). Flux units are t/y.

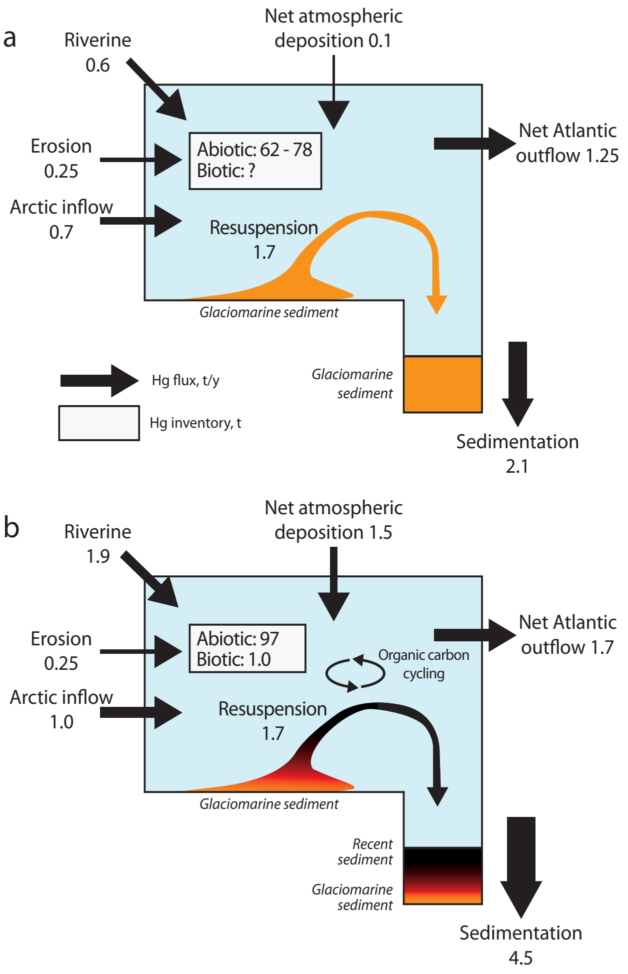


Figure 2.11. Mass balance model for total mercury in the Hudson Bay marine system; (a) for the pre-industrial period and (b) for the modern era. Source: Hare et al. (2008).

atmosphere (32%) and ocean inflow (22%) Hg fluxes (Hare et al., 2008). The difference between the Arctic Ocean and Hudson Bay can be partly attributed to the 'edge effect' of riverine inputs, which are relatively larger for smaller bodies of water. Another reason for differences between the two locations was that Hare et al. (2008) estimated the atmospheric deposition (1.5 t/y) from field measurements of atmospheric deposition, snowpack re-emission and seawater evasion, although the GRAHM model was used to set the maximum upper limit of 13.6 t/y.

The large difference between GRAHM model results and field measurements of atmospheric inputs in these budgets underscores what is widely regarded as the central uncertainty in Arctic Hg science – What is the actual net deposition from the atmosphere that accumulates in the water? Modeled deposition estimates incorporating gross flux including AMDE effects range from 100 t/y for areas north of 70° N (Banic et al., 2003), to 325 t/y comprising 100 t/y from AMDEs and 225 t/y from other processes (Ariya et al., 2004). Other model results fall within these limits (208 t/y for 'the Arctic' (Skov et al., 2004); and about 150 to 300 t/y in polar spring only (Lindberg et al., 2002)). None of these studies allowed for post-AMDE re-emission or oceanic evasion, nor have they been validated by actual flux measurements.

For the Arctic Ocean, an independent estimate of net atmospheric input, based on field measurements of parameters associated with atmospheric flux, was calculated by Outridge et al. (2008) as,

> net wet and dry deposition in winter/spring + wet and dry deposition during summer/autumn – evasion.

This approach, which employed data from direct measurements of wet deposition in the Arctic (Fitzgerald et al., 2005; Sanei et al., 2010), springtime snowmelt at many sites across the Arctic, and shipboard-based estimates of evasion from the ocean, produced a net atmospheric deposition to the Arctic Ocean of 8.4 t/y, over an order of magnitude lower than that provided by the GRAHM model. The net deposition rate (18.4 t/y), which was calculated without considering evasion, was similar to the 23 t/y calculated for the 'High Arctic Ocean' on the basis of snowpack sampling by Lu et al. (2001), and to the 27 ± 7 t/y calculated from a net atmospheric flux of 2.8 ± 0.7 μg/m$^2$/y for lakes in northern Alaska (Fitzgerald et al., 2005). More work using a variety of methodological approaches is essential to resolve the uncertainty in the atmospheric contribution to Arctic ecosystems, especially as it will be this term that should be most immediately affected by emission controls.

For the terrestrial Arctic (land and lakes), almost all of the Hg input will occur from the atmosphere via wet and dry deposition. Near the coast, Hg deposited from the atmosphere may also include a component that has recently been recycled out of the ocean as Hg(0) or dimethylmercury (DMHg) (e.g., St. Louis et al., 2007; Hammerschmidt et al., 2007). Some of the Arctic's drainage basins extend well beyond the Arctic Circle and, therefore, these southern drainage basins provide a source of Hg entering the Arctic as particulate or dissolved components in river flow. Mercury transported into the Arctic in this manner could include natural Hg as well as Hg from human activities within the southern drainage basins (e.g., mining, combustion), or Hg transported initially by the atmosphere and then deposited into these basins.

Table 2.4. Total mercury masses and the relative loadings from major input pathways into the Arctic Ocean and Hudson Bay: data from Outridge et al. (2008) and Hare et al. (2008), respectively. Mercury masses expressed as tonnes per year; relative loadings (in square brackets) are expressed as percentages of the total inputs. Hudson Bay data are for the modern era – see Figure 2.11b).

| Pathway | Arctic Ocean | Hudson Bay |
|---|---|---|
| Ocean currents | 48 [23%] | 1.0 [22%] |
| Net atmosphere | 98 [48%] | 1.5 [32%] |
| Rivers | 13 [6%] | 1.9 [41%] |
| Coastal erosion | 47 [23%] | 0.25 [5%] |
| Total inputs (t/y) | 206 | 4.65 |

Mercury input pathways to Arctic terrestrial ecosystems and lakes are poorly quantified. No work comparable to the oceanic mass studies has been done for Arctic terrestrial ecosystems, and only limited data are available for lakes. A Hg input and fate study by Fitzgerald et al. (2005) in a series of Alaskan lakes found that catchment soil erosion was the single most important total Hg input on average, followed by wet deposition and catchment runoff.

## 2.5. What is the influence of mercury speciation on total mercury transport by air?

### 2.5.1. Atmospheric transport and atmospheric chemistry – the status of present understanding

Mercury transported via the atmosphere can enter Arctic ecosystems following its deposition in aqueous, gas and particulate phases. Therefore the Hg species and mechanisms involved in transport through air, *in situ* chemical transformations, and the balance between deposition and re-emission at the surface, are important factors in the net atmospheric loading of Hg to the Arctic.

#### 2.5.1.1. Atmospheric mercury species

One of the most important properties of Hg regarding environmental concerns is its ability to exist as a gas in the atmosphere. Both anthropogenic and natural Hg emissions consist for the most part as Hg(0), i.e. gaseous elemental mercury (GEM), and in most circumstances approximately 98% of airborne Hg is GEM. The atmospheric residence time of Hg has been estimated at around 0.7 to 1.4 years (Schroeder and Munthe, 1998; Selin et al., 2007 and references therein), which is long enough for distribution on hemispherical scales before it is eventually oxidized and deposited to ground and water surfaces (Schroeder and Munthe, 1998). According to measurements, GEM is fairly uniformly distributed with concentrations of around 1.7 ng/m$^3$ in the Northern Hemisphere and 1.3 ng/m$^3$ in the Southern Hemisphere (Slemr et al., 2003). The higher values in the Northern Hemisphere are consistent with major industrial Hg sources being predominately located there. GEM is only to a small extent dry deposited to ground and vegetation or washed out by precipitation, but can be oxidized in the atmosphere forming divalent Hg species (Hg(II)) which are more easily removed from the atmosphere. Divalent Hg is found in both the gaseous and the particulate phase as well as in rainwater, however, the exact chemical compositions of these oxidation products are not yet known. The gaseous fraction of oxidized Hg is referred to as 'reactive gaseous mercury' (RGM) or 'gaseous oxidized mercury' (GOM). RGM is operationally defined as the fraction of gaseous Hg that can be sampled using a denuder measurement method (Landis et al., 2002; Steffen et al., 2008a), with species like $HgCl_2$(g) and $HgBr_2$(g) as likely candidates. The vapor pressures of Hg halides are relatively high, for example, P($HgCl_2$) = 0.017 Pa at 298 K (which corresponds to a saturation mixing ratio of 170 ppb). Due to the relatively high solubility of RGM, washout is an efficient removal process yet it is more readily dry deposited on water surfaces and on vegetation than Hg(0). Total gaseous mercury (TGM) is another operationally defined Hg fraction. TGM includes GEM plus other possible gaseous Hg species, such as RGM, that may also be detected when measuring gaseous Hg by the commonly used gold-trap method.

Mercury is also found in aerosols originating from direct emissions or adsorption of atmospheric Hg onto already existing particles in the atmosphere. The abbreviation TPM (total particulate mercury) is used in the literature and it normally denotes the concentration of particulate Hg obtained with open face air filter samplers. Total particulate Hg means that the sampling is not made in a size fractionated manner. If Hg in the fine mode (< 2.5 µm particle size) is sampled it is sometimes denoted as fine particulate mercury (FPM) or simply referred to as particulate mercury PHg.

Dimethylmercury ($CH_3HgCH_3$) is formed in the oceans and its presence in the atmosphere is believed to be due to emission from ocean surfaces (Pongratz and Heumann, 1999). Sewage plants and landfills (among others) also emit DMHg, although these sources are of minor importance in comparison to the oceans and, as well, the emitted DMHg does not travel long distances in the atmosphere to the Arctic. Monomethylmercury (MMHg) compounds are found in rainwater and have also been detected in the gas phase (Munthe et al., 1993).

#### 2.5.1.2. Atmospheric transport

Mercury is transported to the Arctic from source regions mainly during the winter and spring seasons (Raatz, 1984) and this transport is influenced by atmospheric circulation patterns including the Pacific North American (PNA) and the North Atlantic Oscillations (NAO) (Wallace and Gutzler, 1981; Barnston and Livezey, 1987; Macdonald et al., 2005). Long-range atmospheric transport of Hg consists mainly of GEM, because of its relatively long airborne residence time of 0.7 to 1.4 years (Schroeder and Munthe, 1998; Selin et al., 2007 and references therein). Global transport of GEM has been investigated in various modeling studies (Mason and Sheu, 2002; Lamborg, et al., 2002b; Seigneur et al., 2004; Selin et al., 2007; Stohl et al. 2007; Strode et al., 2009) but has also been verified by direct measurements. Long-range transport of GEM and other pollutants from Europe to the European Arctic was measured during an Arctic smoke event at Ny-Ålesund (Stohl et al., 2007). In winter and spring, transport of anthropogenic GEM emissions from Europe leads to the highest observed GEM concentrations at Ny-Ålesund (Hirdman et al., 2009). Similarly, long-range transport from Asia has been measured at observatories on the US West Coast and by airplane measurements (Jaffe et al., 2005; Weiss-Penzias et al., 2007). The origin of the air masses was inferred by measuring Hg:CO ratios and calculation of back-trajectories. Evidence for long-range transport of Hg(0) from Asian sources has also been reported from Storm Peak Laboratory in the Rocky Mountains, 1500 km inland from the Pacific Ocean (Obrist et al., 2008; Faïn et al., 2009b). Due to the shorter atmospheric residence time of RGM and particulate Hg, they may not be transported between continents (Schroeder and Munthe, 1998). On the other hand, particulate Hg, presumably associated with fine soot particles, seems to be a sensitive indicator of transport on the regional scale (Wängberg et al., 2003).

### 2.5.1.3. Oxidation of elemental mercury and formation of reactive gaseous mercury

Exactly how RGM is formed in the atmosphere remains a key question that is crucial to the understanding of atmospheric Hg chemistry and how atmospheric Hg enters other environmental media. The reactive capacity of the atmosphere is linked to photolysis reactions forming certain reactive radical species such as OH, $HO_2$ and Br. The reaction rates of mercury with atmospheric radicals and other atmospheric constituents, have been determined in laboratory experiments. This information has enabled the construction of chemical-meteorological models for Hg. With the help of these models, important chemical and physical processes can be studied and verified by comparison with field measurements. Several atmospheric models including descriptions of Hg chemistry have also been developed (see Section 2.6). However, critical kinetic information on Hg(0) gas phase reactions is still lacking, partly because kinetic investigations on Hg are experimentally difficult to perform. Despite these problems, the reactivity between Hg(0) and several oxidants in the atmosphere has been investigated. These studies have included the gas phase reactions between Hg(0) and $O_3$, OH, Cl, Br and $NO_3$ (Hall, 1995; Tokos et al., 1997; Sommar et al., 1999, 2001; Ariya et al., 2002; Bauer et al., 2003; Pal and Ariya, 2004a; Donohoue et al., 2005, 2006). The experimental results have also been reviewed recently (Simpson et al., 2007a; Ariya et al., 2008; Steffen et al., 2008a). In most of the studied reactions, no gaseous Hg-containing products were identified. The ability to identify products is, if not necessary, at least very helpful when trying to demonstrate a certain reaction. Some of the reaction rates obtained in early studies between Hg(0) and $O_3$, OH, Br and Cl may have been overestimated as a result of experimental difficulties (Bauer et al., 2003; Calvert and Lindberg, 2005).

Field measurements in polar regions indicate very fast atmospheric processes during springtime allowing GEM to be transformed and removed from the lower layer of the atmosphere on the scale of hours or days. This phenomenon, termed mercury depletion events, was first reported by Schroeder et al. (1998). Subsequently, AMDEs were confirmed to occur throughout the Arctic, sub-Arctic and Antarctic coasts (Lindberg et al., 2001; Ebinghaus et al., 2002; Berg et al., 2003, 2008a; Poissant and Pilote, 2003; Steffen et al., 2005). Concurrent with decreasing GEM, increasing concentrations of RGM are observed as well as increasing particulate Hg (Lindberg et al., 2001). Mercury is thus rapidly oxidized in the air producing RGM, some of which is quickly deposited onto the ice and snow surface.

These findings stimulated an intensive search for possible chemical reactions that are fast enough to explain the observations. Halogen chemistry is important during polar springtime. Ozone may become almost completely depleted in the atmospheric boundary layer (Bottenheim et al., 1986; Oltmans and Komhyr, 1986) because of its reactions with Br and Cl radicals (Reaction 1). The halogen radicals are recycled according to Reactions 2 and 3, making the ozone destruction very efficient (Barrie et al., 1988).

$O_3 + Br\ (Cl) \rightarrow BrO\ (ClO) + O_2$ (1)
$BrO\ (ClO) + HO_2 \rightarrow OHBr\ (OHCl) + O_2$ (2)
$OHBr\ (OHCl) + h\nu \rightarrow OH + Br\ (Cl)$ (3)

Recent Arctic and Antarctic field measurements showed an almost perfect match between removal of ozone and GEM (Schroeder et al., 1998; Lindberg et al., 2002; Temme et al., 2003; Gauchard et al., 2005; Sommar et al., 2007). Therefore, it has been suggested that Hg(0) also may react with halogen radicals (Simpson et al., 2007a and references therein; Steffen et al., 2009 and references therein). According to theoretical studies (Khalizov et al., 2003; Goodsite et al., 2004; Shepler et al., 2007), the Hg(0) + Br reaction may constitute an initial step in a chemical process leading to stable divalent oxidized Hg compounds. An excited intermediate, HgBr*, is initially predicted (Reaction 4). The HgBr molecule may decompose through Reaction 6 and 7 or further react according to Reaction 8 to form a stable gaseous Hg(II) compound.

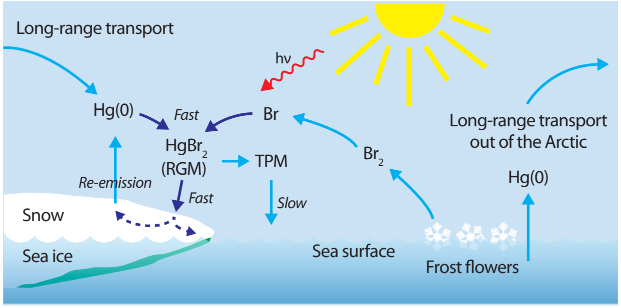
$Hg + Br \rightarrow HgBr^*$ (4)
$HgBr^* + M \rightarrow HgBr + M$ (5)
$HgBr^* \rightarrow Hg + Br$ (6)
$HgBr \rightarrow Hg + Br$ (7)
$HgBr + Y \rightarrow HgBrY\ (Y = Br, Cl, OH, Br_2, \text{etc.})$ (8)

Whether this path is significant depends critically on the stability of the intermediate HgBr radical. Reactions 4 and 5 have been recently verified experimentally by Donohoue et al. (2006), with the rate coefficient shown in equation (I) below. The stated accuracy of equation (I) was ± 50% (Donohoue et al., 2006).

$$k_{4\text{-}5}\ (243\text{-}293\ K) = (1.46 \pm 0.34) \cdot 10^{-32}\ (T/298)^{-(1.86 \pm 1.49)}\ cm^6\ molecule^{-2}\ s^{-1} \qquad (I)$$

The rate of Reaction 4-5 is $3.8 \times 10^{-13}$ $cm^3$ molecules per second at 293 K and atmospheric pressure. As yet, no experimental results have been reported on Reactions 7 and 8 which describe the fate of the intermediate HgBr. However, assuming peak concentrations of bromine atoms of $10^7$ to $10^8$ atoms/$cm^3$ under Arctic conditions, Donohoue et al. (2006) estimated the Hg(0) lifetime with respect to Reaction 4-5 to be in the range of 6 hours to 2.5 days, which is consistent with observations. Reactions 4 and 5 may also be important at much lower Br concentrations. Assuming an average concentration of Br radicals in the free troposphere of $1 \times 10^5$ molecules/$cm^3$, the lifetime of Hg(0) is then estimated to be about 220 days. According to theoretical studies, HgBr may form stable RGM compounds according to Reaction 8 (Goodsite et al., 2004; Shepler et al., 2007). Recent observations of elevated RGM concentrations in the free troposphere also support the idea that RGM formation through halogen radical reactions could be important (Swartzendruber et al., 2006; Faïn et al., 2009a). High concentrations of RGM were frequently observed in dry tropospheric air originating from the northern Pacific Ocean (Faïn et al., 2009a). Air masses containing elevated RGM were found to be low in CO and other anthropogenic air pollution tracers. It was thus concluded that RGM was formed *in situ* via photolytically-induced reactions in the free troposphere (Swartzendruber et al., 2006; Faïn et al., 2009a).

Bromine atoms can be produced from a number of sources: one is sea spray and is thus connected to the marine boundary layer; a second source during polar spring is refreezing leads (open water areas in sea ice or between sea ice and the shore in which are found bromine-enriched brine and frost flowers). Here, $Br_2$ is released from bromide-enriched sea-ice surfaces. A



Hg(0): gaseous elemental mercury
RGM (= $HgBr_2$): reactive gaseous mercury

Figure 2.12. A possible reaction scheme for the oxidation of gaseous elemental mercury leading to the formation of reactive gaseous mercury during an atmospheric mercury depletion event. Source: Henrik Skov, Aarhus University, Denmark, pers. comm.

third possibility is that Br may be produced in the upper part of the troposphere from the photolysis of organo-bromides. The production of atmospheric Br during polar spring is thought to be closely related to refreezing leads where bromide is pushed out to the surfaces during the refreezing of sea water (Figure 2.12; Simpson et al., 2007a). After entering the atmosphere, Br reacts mainly with ozone to form BrO. The abundance of reactive bromine in the Arctic during spring is a result of the documented 'bromine explosion' reaction sequence (Simpson et al., 2007a).

Other possible halogens involved in AMDEs are chlorine and iodine. Chlorine is present in the Arctic boundary layer during springtime, however, its concentration is too low to explain the observed AMDEs considering its reactivity with Hg (Skov et al., 2004; Simpson et al., 2007a; Steffen et al., 2008a). Relatively high concentrations of iodine oxide (IO) have been measured in Antarctic air (Saiz-Lopez et al., 2007). In general, iodine is much more reactive than bromine and thus iodine might also be an important reactant for the formation of RGM depending on the concentrations of IO in the Arctic.

### 2.5.2. Field observations of atmospheric mercury depletion events

Multi-year atmospheric datasets observing the AMDE phenomenon have been gathered for varying periods at several Arctic stations, including Alert, Nunavut, Barrow, Alaska; Amderma, Russia; Station Nord, Greenland; and Ny-Ålesund, Svalbard (Steffen et al., 2008a). Figure 2.13 shows the time series of GEM from 1995 to 2008 and the time series of GEM, RGM and particulate Hg from 2002 to 2009 at Alert, which are the longest datasets available for these atmospheric Hg species in the Arctic. These figures clearly demonstrate a reoccurrence of AMDEs in springtime. AMDEs result in significant changes in Hg speciation during Arctic springtime. Atmospheric Hg speciation in southern latitudes, outside polar regions, is dominated by GEM which represents about 98% of total Hg, with 1.6% RGM and 0.5% particulate Hg making up the balance (Peterson et al., 2009a). In contrast, during AMDEs the Arctic atmosphere is temporarily dominated by oxidized Hg species (Steffen et al., 2008a; see Figure 2.13, bottom panel) which have an average half-life of less than 1 day (Lindberg et al., 2007). This change in speciation is due to the oxidation of GEM to reactive Hg(II) species, as described in Section 2.5.1. Cobbett et al. (2007) reported that during spring 2005 the distribution of GEM, RGM and particulate Hg was 88.6%, 5.7% and 5.7%, respectively, at Alert. However, during the polar night the distribution of these species reflected a distribution similar to more southerly latitudes, i.e., 95%, 0.63% and 4.4%, respectively. Change of Hg speciation plays an important role in the deposition of Hg to the Arctic environment.

#### 2.5.2.1. Observation of mercury oxidation and conversion to the particulate phase

A unique series of photochemically initiated reactions involving ozone and halogen compounds (termed ozone depletion events – ODEs) and mercury depletion events, largely of marine origin, and especially bromine atoms and oxides ($BrO_x$, Br, BrO), lead to the destruction of ozone (Simpson et al., 2007a) and the depletion of GEM from the marine boundary layer (Steffen et al., 2008a). Surface based observations do not show a total removal of GEM from the atmosphere in the vertical column (Banic et al., 2003). In fact, the depletions appear to be limited vertically from the terrestrial or ocean surface up to usually less than 1 km height (Banic et al., 2003; Tackett et al., 2007).

The reported distribution of GEM, RGM and particulate Hg during AMDEs differs between measurement sites, times of the year and atmospheric conditions. For example, at Barrow in 2001, RGM was the dominant species during AMDEs (Lindberg et al., 2002). In Ny-Ålesund in 2003, the distribution was reported to vary throughout the study period but showed a predominance of RGM (Sprovieri et al., 2005; Gauchard et al., 2005), whereas during a more recent study at Ny-Ålesund, the distribution also varied but showed on the whole a predominance for particulate Hg (Steen et al., 2009). At Churchill, and Alert, Kirk et al. (2006) and Cobbett et al. (2007), respectively, showed a dominance of particulate Hg at the beginning of spring and a higher percentage of RGM towards the end of spring. Cobbett et al. (2007) suggested that a relationship existed between the stability of the atmosphere and the distribution of the Hg species, and reported a significant correlation between increases in particulate Hg and lower air temperatures and humidity. Observations from Alert indicate that atmospheric conditions are crucial in understanding when deposition of Hg to the snow surfaces occurs. Steffen et al. (2002) reported that not all the total Hg is lost from air during AMDEs, suggesting that although GEM may be depleted in the air there remains some RGM and particulate Hg. This implies that not all of the depleted GEM should be expected to be deposited onto the snowpack during an AMDE. Further, they observed a 'switch' in the predominant Hg species in air in the springtime each year (also observed by Cobbett et al., 2007). More recent work from Alert shows that the deposition of Hg from the air during AMDEs is dependent on the conditions of the atmosphere. Thus, in order to accurately understand the deposition processes of Hg from air to snow resulting from AMDEs, prevailing atmospheric conditions must be fully understood.

### 2.5.2.2. **Observations of deposition**

Mercury can be deposited onto snow surfaces through both wet and dry deposition processes. Dry deposition in coastal polar regions mainly corresponds to RGM formed during AMDEs (Lu et al., 2001; Lindberg et al., 2002; Ariya et al., 2004). However, the consequences of AMDE Hg deposition for Hg levels in the environment are still unclear. Brooks et al. (2006) published a mass balance for Hg at Barrow, Alaska, showing a net surface gain during a two-week AMDE period. Overall, the rate of deposition of Hg onto the snow is greater in Arctic coastal areas than in more southerly locations and inland areas (Lindberg et al., 2002; Douglas et al., 2005). The GRAHM model indicates springtime net deposition (both AMDE and non-AMDE processes) to the Arctic Ocean was about 45% of total (wet + dry) annual deposition (Outridge et al., 2008).

Mercury in surface snow following AMDEs is mainly found in its oxidized form (Hg(II)), with concentrations that can range from a few up to hundreds of ng/L (Lu et al., 2001; Lalonde et al., 2002; Lindberg et al., 2002; Steffen et al., 2002; Berg et al., 2003; Ferrari et al., 2004, 2005; Douglas et al., 2005; Lahoutifard et al., 2006; Steen et al., 2009, 2010). However, it has also been observed that, within a few days after each AMDE, about 80% on average of the deposited Hg in surface snow is re-emitted as GEM back to the atmosphere (see Section 2.6.2). It is important to point out that these results are based on the snowpack concentrations of total Hg, rather than on mass balance studies of the atmospheric concentration of GEM. In Svalbard, Ferrari et al. (2005) reported that during seven AMDEs no increase in the concentration of Hg in the surface snow was observed. The authors suggested that the origin of the air mass prevailing at the time of the AMDE may play a significant role in the amount of Hg deposition observed. Douglas et al. (2008) reported elevated concentrations in the surface snow following AMDEs, and suggested that the crystal structure of the surface hoar frost, diamond dust and frost flowers was important in determining the rate of Hg deposition and accumulation in snow from AMDEs. Thus, deposition of Hg onto the snow surfaces in the Arctic, as a result of AMDEs, is not spatially homogeneous and the factors affecting such deposition must be well understood to address the impacts of AMDEs on Hg levels in the Arctic environment. The possible impact of AMDEs on Hg bioavailability has also not been adequately addressed. At Barrow, Scott (2001) reported a post-polar sunrise increase in bioavailable Hg in surface snow and an increasing ratio of bioavailable Hg to THg as the springtime progressed to annual snowmelt.

In terms of the atmospheric contribution to Hg in the Arctic,

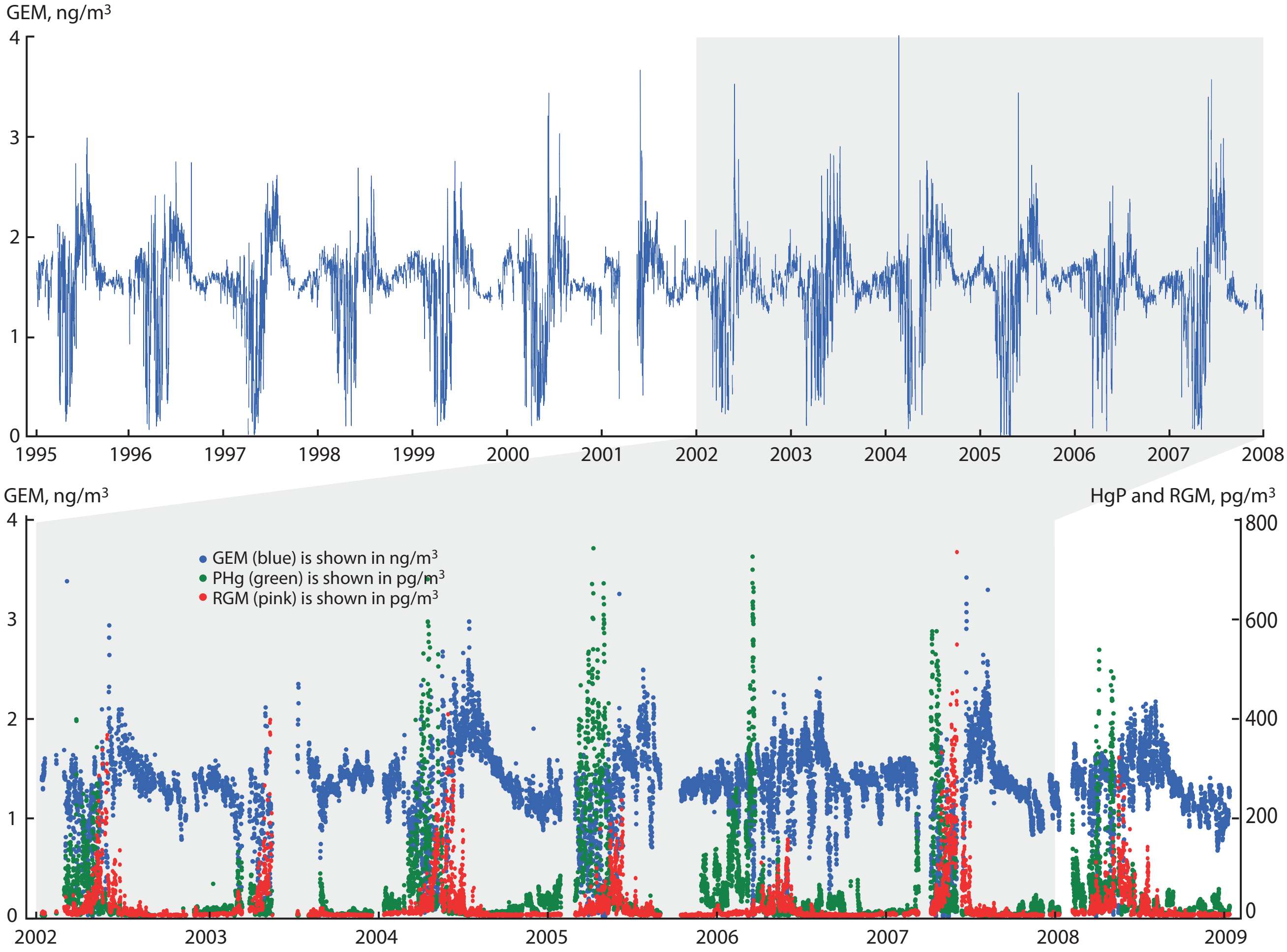


Figure 2.13. Time series for gaseous elemental mercury (six-hourly averaged data) concentrations at Alert, Nunavut, Canada from 1995 to 2008 (top) and time series of reactive gaseous mercury, particulate phase mercury and gaseous elemental mercury (three-hourly averaged data) concentrations from Alert 2002 to 2008 (bottom). Source: Alexandra Steffen, Environment Canada, pers. comm.

the largest limitation remains the paucity of knowledge of Hg speciation, and the net deposition rates of Hg. During a meeting of experts in 2003, the re-emission proportion of Hg from the surface after deposition from AMDEs, or release to other compartments, was identified as an essential missing component before true mass balance estimates could be made (Schroeder et al. 2003). Subsequently, an experts meeting in 2006 (Air Ice Chemical Interactions – AICI) determined that despite intense trans-Arctic springtime field campaigns this issue remained to be resolved. Model estimates of the atmospheric input to the Arctic region are discussed in Section 2.6.1.1. An updated summary of the snowpack-based literature concerning Hg re-emission after AMDEs in presented in Section 2.6.2.

### 2.5.3. Long term trends in gaseous elemental mercury

Worldwide atmospheric measurements up to the early 2000s suggested that GEM concentrations increased from the late 1970s to a peak in the 1980s and decreased to a plateau around 1996 to 2001 (Slemr et al., 2003). Data used in the reconstruction of the worldwide trend were collected at six sites in the Northern Hemisphere, two sites in the Southern Hemisphere and eight ship cruises over the Atlantic Ocean. More recently, a reconstruction of GEM levels in the air over Greenland Summit based on glacial firn sampling indicated that GEM increased from the 1940s to about the 1970s, decreased until the mid-1990s and has been stable since then (Faïn et al., 2009b).

Long-term datasets with at least five years of continuous instrumented measurements of atmospheric Hg concentrations are rare in polar regions. However, data have been consistently collected for at least five years from Alert, Canada (1995 to 2009 with automated monitors); Ny-Ålesund, Svalbard (1994 to 1999 with manual samplers, and 2000 to 2009 with automated monitors), and Amderma, Russia (2001 to 2002, and 2005 to 2009 with automated monitors). There are also multi-year datasets from Barrow, Alaska, and Station Nord, Greenland, however, they are not continuous or long-term.

To investigate annual trends in polar regions, it is important to take into account the strong seasonal variation caused by springtime decreases in GEM related to AMDEs, and summertime elevations in GEM levels caused by the re-emission of Hg deposited onto snow as well as evasion from oceans, freshwaters and the ground itself (see Chapter 3). These seasonal variations are much larger than any interannual changes and therefore it is challenging to discern statistically significant annual trends. A seasonal trends analysis of Alert data was undertaken and a statistically significant decrease was reported in the summer GEM concentrations (June – August) between 1995 and 2002 (Steffen et al., 2005). Temme et al. (2007) analyzed the same annual dataset, using a seasonal decomposition technique (in which annual trends are tested by sequentially removing seasonal data), and found the same summer declining trend up to 2002. However, no significant change for the overall period between 1995 and 2005 was found. Berg et al. (2004) reported no trends for GEM concentration at Ny-Ålesund for the period 1994 to 2002. When an extended time-series (1994 to 2005) was considered, Berg at al. (2008a) again reported no significant trend at Ny-Ålesund. In both studies from Ny-Ålesund, the manually collected data were included for 1994 to 1999. In the first study, annual averages were used, whereas in the second study the trends were analyzed on winter, spring, summer and autumn means. More recently, a small, but statistically significant decreasing trend (-0.6% per year) has been reported in the mean annual concentration of GEM at Alert for the 13 years between 1995 and 2007 (Cole and Steffen, 2010).

There could be several reasons for the reported weak or insignificant trends in Arctic atmospheric Hg. Most of the available time-series cover the period from 1995 to 2005 during which total global anthropogenic emissions of Hg have not changed markedly (see Section 2.2.2), although there have been significant changes in emissions from particular source regions during this period. Mercury emissions from East Asia increased by 50% from 1990 to 2005 whereas emissions from Europe and North America have declined over the same period, resulting in smaller emissions trends overall compared to the 1970s and 1980s. These small net changes in background GEM concentrations also may be masked by seasonal and interannual variability, particularly at sites with shorter records. In addition, changes in the major atmospheric circulation patterns (Kahl et al., 1999) may complicate the relationship between changes in emissions and trends in Arctic atmospheric GEM.

Other long-term atmospheric Hg trend studies based on Arctic observations include that of Li et al. (2009), who reported a decrease of 3% per year in airborne filterable (i.e. particulate) Hg in summer and autumn samples collected between 1974 and 2000 at Resolute, Canada. A similar decline in GEM concentrations after about 1970 was reported from a Greenland Summit firn core by Faïn et al. (2009b). This declining trend largely predates the start of instrumented gas phase Hg monitoring in the Arctic. The reported declines at Summit and Resolute may reflect the significant decreases in anthropogenic emissions of Hg between the 1970s and 1990s and possibly (in the case of Li et al., 2009) reductions in the proportion of particulate Hg resulting from the global introduction of control technology to remove particulates from industrial plant emissions (see Section 2.2.2).

Studies using sediment and peat cores have been used to estimate trends in depositional fluxes of Hg (see Section 2.7). However, trends based on direct measurements of Hg in wet and/or dry deposition are unavailable for most Arctic areas. Except for the recently initiated Kodiak station in Alaska, the Mercury Deposition Network (MDN) in North America does not include Arctic or sub-Arctic sites. At several Northern European stations, a comparison of wet deposition fluxes for the periods 1995-1998 with 1999-2002 showed an overall decrease of 10-30%, which was attributed to reduced emissions in industrial areas of Europe (Wängberg et al., 2007). A recent evaluation of deposition fluxes during three time periods (1995-1998, 1999-2002, 2003-2006) and also including the Pallas station (located in Finland above the Arctic Circle) indicated no significant trends in TGM or deposition at Pallas. However, a continued decrease in Hg deposition was found at most Northern European stations while trends in TGM were variable or insignificant (Wängberg et al., 2010).

As part of the present Assessment, statistical reanalyses of GEM data from all Arctic stations have been carried out using a consistent methodology. Figure 2.14 shows the time trends of median concentrations of GEM at the three long-term High Arctic monitoring sites for the autumn period (October to December). This period was selected because background GEM levels are least affected by fluctuations due to AMDEs and re-emissions of deposited Hg. The figure presents automated monitoring data only from Alert (1995 to 2008), Ny-Ålesund (2000 to 2009) and Amderma (2001 to 2002, 2005 to 2008) indicating the period of overlap of data from 2000 to 2008. Statistical runs were performed on these data sets using the PIA statistical application (Section 5.3.3.2). Runs were performed separately for each month using monthly (median) index values and also run for a combined October to December period.

Results from the October to December datasets did not reveal any statistically significant trends, although, a significant decreasing trend (-0.67% per year; $p<0.05$) was observed at Alert when considering data for the month of September alone. The time series indicated non-significant decreasing trends during autumn of about -0.6% per year at Alert (1995 to 2008) and -1% per year at Amderma (2001 to 2008), but an increasing trend (+1.5% per year) at Ny-Ålesund (2000 to 2009). The results from Alert are in keeping with those reported by Cole and Steffen (2010) on the annual data, indicating that the autumn period may be a good proxy for the annual trends. The results from Amderma should be interpreted with caution, since the site location changed in 2004; considering only the data since 2005 shows an increasing trend.

Clearly, many challenges exist in trying to ascertain long-term trends in GEM in the Arctic region. However, the availability of increasingly long-term time series, and the use of Hg samples archived in glacial ice or on particulate filters collected over the past few decades, has provided opportunities to elaborate trends that did not previously exist. Significant atmospheric processes affect GEM levels in polar regions, and further collection of data is required in the Arctic to truly discern long-term trends over the entire region.

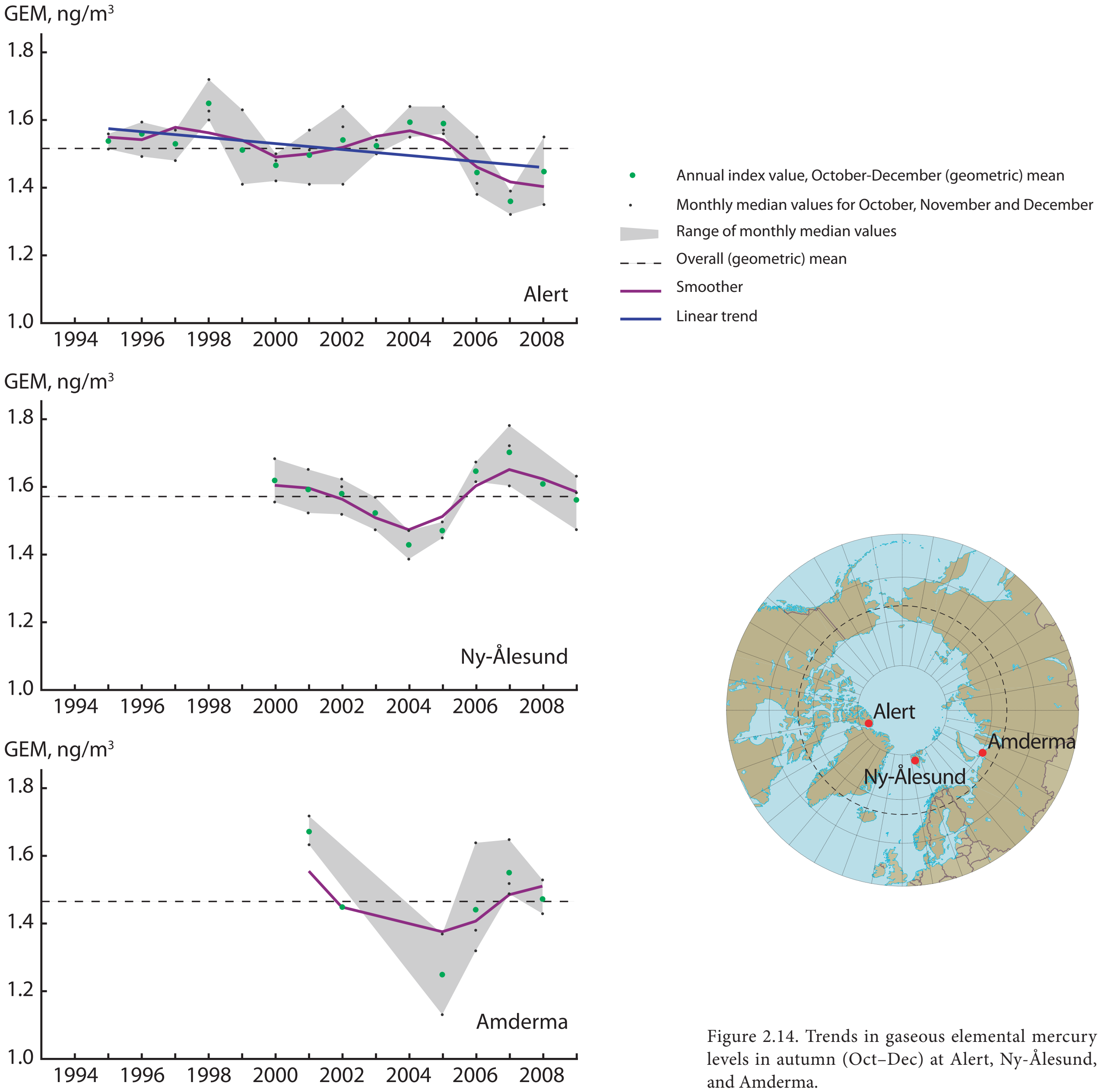


Figure 2.14. Trends in gaseous elemental mercury levels in autumn (Oct–Dec) at Alert, Ny-Ålesund, and Amderma.

## 2.6. What is known about the net atmospheric mass contribution of mercury to the Arctic?

### 2.6.1. Modeling atmospheric mercury transport to the Arctic

#### 2.6.1.1. Net deposition results from atmospheric modeling

In recent years, atmospheric chemical models have become powerful tools in assessing and understanding the level of contaminants in the environment, given the limited coverage of existing monitoring networks. Mercury models are employed to estimate Hg ambient concentrations and deposition, to estimate source attribution, explain long-term trends and to predict future levels of pollution. The models complement direct measurements by providing spatial coverage and detailed information on Hg budgets in the Arctic environment.

Atmospheric Hg models attempt to represent cycling of Hg in the atmosphere starting from Hg emissions to the air, including contemporary anthropogenic emissions, natural emissions, and re-emissions of Hg of both anthropogenic and natural origin, to its subsequent deposition to terrestrial and aquatic surfaces. Modeling atmospheric Hg requires extensive treatment of multiple Hg species (i.e. GEM, RGM and particulate Hg) that exhibit different properties and exist in multiple phases of the atmosphere. Main Hg processes implemented in the models are gas and aqueous phase chemistry, exchange processes in and below clouds, wet and dry deposition, boundary layer and cumulus cloud mixing and transport.

Owing to the global scale of Hg transport, hemispheric or global-scale atmospheric models are employed to estimate the atmospheric Hg mass contribution to the Arctic. Current Hg models are primarily constrained by measurements of surface air concentrations of GEM and wet deposition fluxes in North America and Europe, due to the lack of global measurements. Models also utilize a small number of available measurement data of RGM and particulate Hg ambient concentrations, vertical

Table 2.5. Characteristics of the participating atmospheric mercury models.

| Model | GRAHM (v1.2) | GLEMOS (v1.0) | GEOS-Chem (v8.2) | DEHM (v5.1) |
|---|---|---|---|---|
| Domain | Global | Global | Global | Hemisphere |
| Spatial resolution | | | | |
| Horizontal | 1° × 1° | 5° × 5° | 4° × 5° | 150 × 150 km |
| Vertical | 28 levels; top 10 hpa | | | |
| Emission | | | | |
| Anthropogenic, t/y | 1925 | 1925 | 1925 | 1469 [a] |
| Natural and re-emission, t/y | 3500 [b] | 4230 [b] | 6235-6770 [c] | Inflow from boundaries |
| Gaseous chemistry | | | | |
| Oxidation agents | $O_3$ | $O_3$, OH, $Cl_2$ | Br | $O_3$ |
| Oxidation rates [d] | $O_3$: $3 \times 10^{-20}$ [e] | $O_3$: $3 \times 10^{-20}$ [e]<br>OH: $8.7 \times 10^{-14}$ [e] | $8.1 \times 10^{-14}$ [e, f] | $O_3$: $3 \times 10^{-20}$ [e] |
| RGM/HgP partitioning | $O_{3o}$Oxidation product-1:1 | $O_3$ oxidation-HgP<br>OH oxidation-HgP<br>$Cl_2$ oxidation-RGM | Br Oxidation – 1:1<br>RGM adsorption to sea-salt aerosols parameterization | $O_3$Oxidation product-1:1;<br>RGM adsorption to black carbon |
| Reduction agents | none | none | none | none |
| Aqueous chemistry | | | | |
| Oxidation agents | $O_3$, OH, HOCl/$OCl^-$ | $O_3$, OH, HOCl/$OCl^-$ | none | $O_3$, OH, HOCl/$OCl^-$ |
| Reduction agents | hv, $SO_3^{=}$ | $SO_3^{=}$ | hν | $SO_3^{=}$ |
| AMDE | yes | yes | yes | yes |
| Chemistry [g] | over sea ice: Br, BrO, Cl, $Cl_2$, $O_3$ | Br, BrO, $Cl_2$, $O_3$ | over sea ice: Br | First order oxidation Over sea ice |
| RGM/HgP partitioning of Br oxidation | RGM | RGM | 1:1 | |
| Br oxidation rate [h] | $3.2 \times 10^{-12}$ [e] | $1.1 \times 10^{-12}$ [e] | $8.1 \times 10^{-14}$ [e, f] | |
| Br concentrations in Arctic boundary layer | From satellite data derived BrO conc. | From Satellite data derived BrO conc. | From fixed BrO conc. | Parameterization based on sea ice and temperature |
| Re-emission from snow | yes | no | yes | No |
| Wet deposition | | | | |
| In-cloud | RGM(rain/snow),<br>HgP(rain/snow) | RGM(rain/snow),<br>HgP(rain/snow) | RGM(rain), HgP(rain) | RGM(rain/snow),<br>HgP(rain/snow) |
| Below-cloud | RGM(rain/snow),<br>HgP(rain/snow) | RGM(rain/snow),<br>HgP(rain/snow) | RGM(rain), HgP(rain/snow) | RGM(rain/snow),<br>HgP(rain/snow) |
| Precipitation rates | Model predicted | Model predicted | Model predicted | Model predicted |
| Dry deposition | Hg(0), RGM, HgP | Hg(0), RGM, HgP | Hg(0), RGM, HgP | RGM, HgP |
| Source | Dastoor et al., 2008 | Travnikov et al., 2009 | Holmes et al., 2010 | Christensen et al., 2004 |

[a] Total value for the hemispheric model domain; [b] prescribed fluxes globally with dynamic seasonal and diurnal variation; [c] dynamic fluxes from oceans and terrestrial biosphere; [d] only major oxidant rates shown; [e] temperature and pressure dependence applied; [f] rate at 0.1 ppt Br, $1 \times 10^6$ $cm^3$ OH; [g] gas phase chemistry in the polar boundary layer; [h] units: $cm^3$ molecule per second; rate at 298 K; 1 atm.

Table 2.6. Summary of atmospheric deposition estimates in the Arctic region.

| Study location | Type of study | Gross or net deposition?[a] | Deposition, t/y | Model | Emissions inventory year | Source |
|---|---|---|---|---|---|---|
| Northern waters | Atmospheric | | 50 | | | Lu et al., 2001 |
| Arctic (north of Arctic Circle) | Atmospheric/model | Gross | 208 | | | Skov et al., 2004 |
| Arctic Ocean | Model | Net | 98 | GRAHM v1.1 | | Outridge et al., 2008 |
| | Field measurement (lit. review) | | 8.4 | | | |
| North of 66.5° N | Atmospheric /model | Net | 174 (range 150-181) | GRAHM v1.1 | 2005 v5 | Dastoor et al., 2008 |
| Barrow, Alaska | Atmospheric | | 100-300 (spring only) | | | Lindberg et al., 2002 |
| North of 70° N | Atmospheric | | 100 | | | Banic et al., 2003 |
| North of 60° N | Atmospheric/model | Gross | 325 (100 spring only) | GRAHM v1.0 | 2000 | Ariya et al., 2004 |
| North of 66.5° N | Atmospheric/model intercomparison study | Gross/net | 131 | GLEMOS v1.0 | 2005v5 | Travnikov et al., 2009; this report |
| North of 66.5° N | Atmospheric/model intercomparison study | Net | 143 | GRAHM v1.2 | 2005v5 | Dastoor et al., 2008; this report |
| North of 66.5° N | Atmospheric/model intercomparison study | Net | 80 | GEOS-Chem v8.2 | 2005v5 | Holmes et al., 2010; this report |
| North of 66.5° N | Atmospheric/model intercomparison study | Gross/net | 110 | DEHM v5.1 | 2005v5 | Christensen et al., 2004; this report |

[a] Net: deposition estimate from model that includes fast re-emissions from snow; Gross: deposition estimate from model that does not account for (fast) re-emissions from snow; Gross/net: gross deposition estimates from models that are constrained such that these estimates are comparable to net deposition estimates.

profiles of GEM and fluxes of Hg from terrestrial and oceanic surfaces. Mercury modeling in the Arctic is further complicated by the very dynamic exchange of GEM between air and snow because of AMDEs (see Section 2.5). Photochemical oxidation of GEM by halogens, speciation of products, deposition pathways and re-volatilization of GEM from snow must be parameterized to estimate the net accumulation of Hg in the Arctic. Using a Hg model that includes these processes, Durnford et al. (2010) showed consistent reproduction of the AMDE cycles at six Arctic air measurement sites. Their results indicate that the GEM transformations are generally governed by very similar processes throughout the Arctic, involving bromine photochemistry in air and re-emission mediated by solar insolation on surface snow.

A number of models are currently making use of the 2005 (v5) spatially distributed anthropogenic emissions inventory developed by AMAP (AMAP/UNEP, 2008, see Section 2.2.2). Published model results (Skov et al., 2004; Ariya et al. 2005; Travnikov, 2005; Dastoor and Larocque, 2004, 2008; Durnford et al., 2010) have utilized earlier versions of the global emission inventories, for example, the 2000 inventory (Pacyna et al., 2006; Wilson et al., 2006) that did not include the full range of source sectors included in the 2005 inventory. As part of the current AMAP assessment, models have now also been run using the consistent series of historical emissions inventories (1990 to 2005) discussed in Section 2.2.2.

Four atmospheric Hg models incorporating springtime AMDEs in the Arctic have been developed to date (DEHM: Christensen et al., 2004; GLEMOS: Travnikov et al., 2009; GEOS-Chem: Holmes et al., 2010; GRAHM: Dastoor et al., 2008). The main differences between the recent versions of these models are summarized in Table 2.5, with the largest differences in natural emissions and re-emissions. An important difference between model specification of natural and re-emission (not shown here) is that, due to a lack of knowledge, different approaches are used to distribute these emissions spatially. Other main differences are the major oxidants of GEM and the speciation of the reaction products included in the models. In the Arctic, the major differences are found in the GEM-Br oxidation rates, Br concentrations and spatial distribution and parameterization of re-emission of GEM from snow. Most recent versions of the four models were employed to estimate the Arctic Hg deposition and source attribution for 2005 using AMAP 2005 v5 anthropogenic emissions for this report.

The range of estimates of Arctic Hg deposition from the four model simulations performed for this Assessment, as well as previously published estimates and estimates from field measurements, are summarized in Table 2.6. The table distinguishes whether the estimates concern gross or net deposition (the latter including a re-emission term), and covers a variety of different models and emission inventories, which together account for the differences in the final estimates. Using DEHM, Skov et al. (2004) estimated a deposition of 208 t/y of Hg to the Arctic area north of the polar circle (66° 33’ 38” N), of which 120 t/y was attributed to AMDEs. Ariya et al. (2004) estimated that 325 t/y of Hg is deposited in the Arctic north of 60° N, including 100 t/y deposited as a result of AMDEs using an early version of GRAHM that did not incorporate post-AMDE re-emission. Dastoor et al. (2008) incorporated bi-directional exchange of Hg fluxes in the Arctic in GRAHM to account for the fast re-emission of Hg from snowpack following AMDEs. They estimated 174 t/y net accumulation of Hg in snow with an uncertainty range of 150 to 181 t/y for the region north of 66.5° N. Brooks et al. (2006) measured Hg deposition, re-emission and net surface gain fluxes of Hg at Barrow, Alaska during an intensive measurement campaign for a two week period in spring (March 25 to April 7, 2003) as 1.7 µg/m$^2$, 1.0 ± 0.2 µg/m$^2$ and 0.7 ± 0.2 µg/m$^2$, respectively. Dastoor et al. (2008) found excellent agreement between model-derived fluxes at Barrow

(1.8 µg/m$^2$ deposition, 1.0 µg/m$^2$ re-emission, and 0.8 µg/m$^2$ net surface gain of Hg) and the above study. The most recent modeling estimates are shown in the last four rows in Table 2.6. Although GLEMOS and DEHM do not model the re-emission of Hg from snow explicitly, the average ambient Hg concentration of GEM in these models is constrained by measurements. Their deposition estimates, therefore, could be considered net flux in some sense. The net deposition estimates from the recent simulations of GRAHM, GLEMOS, GEOS-Chem and DEHM range between 80 to 143 t/y for the Arctic north of 66.5° N.

The spatial distributions of net deposition of Hg (gross deposition for GEOS-Chem) simulated by the four models are presented in Figure 2.15. The impact of model resolution is evident in the simulation by GRAHM, which shows higher variability in deposition. All models, in general, portray an increasing north-to-south gradient in deposition that could be attributed to a coincident gradient in Br concentrations, proximity to emission sources and precipitation amounts. However, there are considerable differences between the deposition distributions within the Arctic and these mainly arise due to different approaches used in the models for Br activation in the Arctic boundary layer (Table 2.6). Large uncertainties associated with the production mechanism and concentrations of Br in the Arctic boundary layer, and an order of magnitude difference in GEM-Br reaction rates, result in significant differences in the springtime gross deposition of Hg simulated by GRAHM and

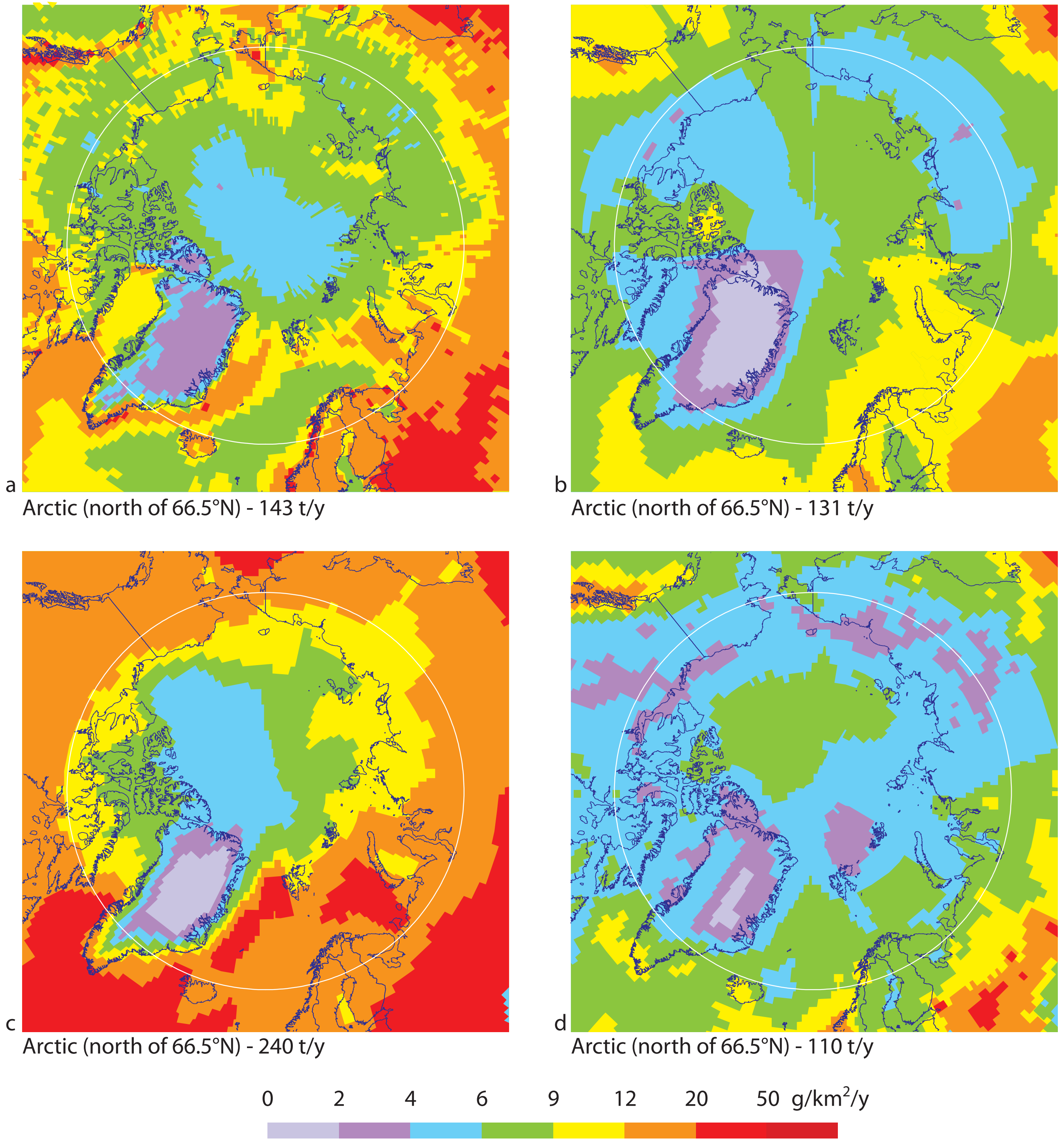


Figure 2.15. Spatial distribution of total mercury deposition to the Arctic simulated by (a) GRAHM (net), (b) GLEMOS (gross/net, see Table 2.6), (c) GEOS-Chem (gross), and (d) DEHM (gross/net, see Table 2.6) in 2005.

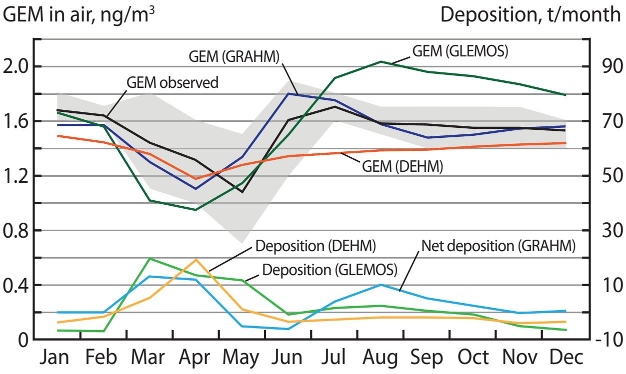


Figure 2.16. Monthly mean (north of 66.5° N) ambient concentrations of gaseous elemental mercury simulated by GRAHM, DEHM and GLEMOS and observed mean concentrations at six Arctic sites: Barrow, USA; Alert, Canada; Station Nord, Greenland; Ny-Alesund, Norway; Andoya, Norway; Amderma, Russia (left scale). Total monthly deposition and net deposition simulated respectively by GRAHM, DEHM and GLEMOS (right scale). Negative deposition indicates higher re-emission than deposition.

GEOS-Chem. However, the deviations are less pronounced in net deposition estimates from these models.

Figure 2.16 shows average monthly means of GEM ambient concentrations and deposition fluxes from DEHM, GRAHM and GLEMOS within the Arctic Circle along with measured monthly mean GEM concentrations estimated from six measurements sites (Barrow, USA; Alert, Canada; Station Nord, Greenland; Ny-Ålesund, Norway; Andoya, Norway; Amderma, Russia). The error bars show the extreme values of monthly means at the six sites. It should be noted that all measurement sites are coastal, and different years are combined to arrive at the measured seasonal cycle (some sites did not report data for all months; Durnford et al., 2010). The yearly averaged GEM concentrations for GRAHM, GLEMOS, DEHM and observation are 1.47, 1.61, 1.37 and 1.52 ng/m³, respectively. The model-estimated mean GEM concentrations and the seasonal cycles in the Arctic are well represented by the observed GEM concentrations at the six Arctic measurement sites, which suggests that similar Hg processes are occurring throughout the Arctic region.

The yearly net deposition fluxes for the four models (GRAHM, GLEMOS, DEHM, GEOS-Chem) in the Arctic are, respectively, 143, 131, 110 and 80 t/y (Table 2.6). The models estimate mean GEM concentration in the Arctic within a factor of 1.2, however, the annual accumulation of Hg in snow estimated by the models varies by a factor of 1.8. One of the major constraints used in all the Hg models, is the observed surface GEM concentration. Therefore close inter-model agreement of GEM concentration is not surprising. The uncertainties in Hg emission fluxes and removal rate constants have led to the inclusion of different plausible representations of these processes in the models so that observed GEM air concentrations can be reproduced. However, the differences in removal rate constants and the underlying parameterizations result in a relatively larger spread in model estimates of net deposition fluxes.

A few instrument-based wet Hg flux datasets are available to help constrain the model deposition estimates. These are from sub-Arctic precipitation collection stations at Churchill, Manitoba, Fort Vermilion, Alberta (a northern boreal forest station; Sanei et al., 2010), and Kodiak, on the Pacific coast of Alaska (Mercury Deposition Network – MDN; http://nadp.sws.uiuc.edu/mdn). Gross wet deposition fluxes from these stations were compared to model estimates (GEOS-Chem and GRAHM) at these sites (Sanei et al., 2010). The modeled wet Hg fluxes for these three sites ranged from 2.1 to 4.1 µg/m²/y compared to measurements of 0.54 to 5.3 µg/m²/y. The model estimates were closest to observed fluxes at Kodiak (GEOS-Chem -47% and GRAHM +23% compared to measurements). The largest discrepancy between observations and model estimates was at Churchill, where intense and recurring AMDEs were found to occur with springtime snow Hg levels temporarily reaching over 100 ng/L (Kirk et al. 2006). Both the wet deposition measurements by Sanei et al. (2010), and the earlier atmospheric and snow monitoring of AMDEs by Kirk et al. (2006), were carried out at the Northern Studies Centre near the western Hudson Bay shoreline. Here, GEOS-Chem and GRAHM overestimated the measured fluxes by 4.0-7.6 times and 6.5 times, respectively, and no evidence of elevated Hg concentrations or fluxes in precipitation was detected during springtime. Lu et al. (2001) found that the eastern shore of Hudson Bay exhibited almost two times higher Hg concentrations in snow compared to sites on the western shore. Tarasick and Bottenheim (2002) examined the frequency of ODEs that are highly correlated to AMDEs during spring. The authors found that severe ODEs occurred frequently at Alert, Eureka and Resolute, however, at Churchill such events were found less frequently. Another possible explanation for the model/measurement differences is that the model estimates represent average fluxes within a grid cell defined by the resolution of each model. The spatial resolution of the two models may not have been high enough to adequately resolve the strong gradient in AMDE-related processes in this region. Kirk et al. (2006) measured high concentrations of Hg in snow during AMDEs and Sanei et al. (2010) measured low wet deposition fluxes at Churchill. However, the relative contribution of wet and dry deposition at Arctic sites including Churchill is essentially unknown. Uncertainties in partitioning of dry and wet deposition in the models could thus be another source of discrepancies between measured and modeled estimates of wet deposition at Churchill. Dry deposition flux measurements and more wet deposition measurements are required to evaluate the models and the impact of AMDEs in the Arctic. Sanei et al. (2010) also found that the models' wet deposition estimates were within 5% of measured fluxes at southern Alberta MDN stations where annual fluxes were up to 10 times higher than at the sub-Arctic sites. Similarly, Travnikov et al. (2010) compared wet deposition estimates from five global/hemispheric-scale models with measured fluxes at MDN sites across temperate North America. They reported that the model predictions were within a factor of 2 of observed fluxes at 57% to 91% of the MDN sites.

Analysis of the sources of atmospheric Hg deposited in the Arctic was performed by estimating the contribution from eight source regions (shown in Figure 2.17) covering most of the global anthropogenic emissions, using GRAHM, GEOS-Chem and GLEMOS. Total anthropogenic Hg emissions and percentages to the global anthropogenic emissions in these regions for 2005 (AMAP/UNEP, 2008) are indicated in Figure 2.17. GRAHM and GLEMOS also estimated separately the contributions from combined natural sources and re-emissions from these regions. GEOS-Chem estimated the deposition contribution from combined recent anthropogenic emissions

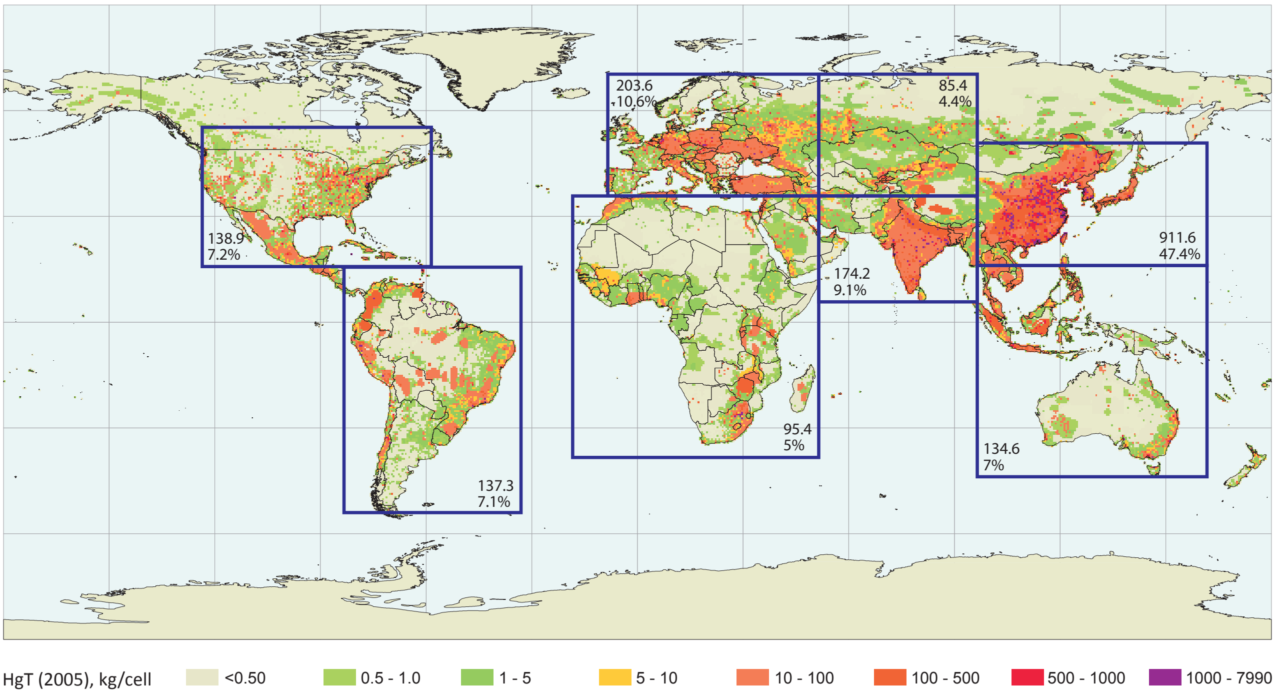


Figure 2.17. Location of source regions considered in the study, plus total anthropogenic emissions (t) and percentage global anthropogenic emissions of Hg in these regions for 2005.

and re-emissions from the eight source regions. All three models estimated the total contributions from global recent anthropogenic emissions (GEOS-Chem: anthropogenic and terrestrial re-emissions), oceanic emissions and terrestrial emissions (GRAHM and GLEMOS: natural and re-emissions; GEOS-Chem: natural emissions).

Figure 2.18 presents the model estimated contributions as well as total contributions from anthropogenic, terrestrial and oceanic emissions in 2005. The largest anthropogenic contribution is from East Asia followed by Europe, Central and South Asia, and North America. The most striking results of this analysis are that model estimates are close to each other with respect to the deposition contributions from recent anthropogenic emissions, and that the largest differences between model estimates of Arctic deposition are from the global natural sources and re-emissions. These results indicate that the largest differences in the model estimates of total deposition to the Arctic are due to the quantitative and spatial differences in natural emissions and re-emissions of Hg used by different models. The re-emissions estimates for Europe, North America and East Asia are significantly higher in GRAHM than in GLEMOS, which results in GRAHM estimating a larger overall contribution from these regions. GLEMOS and GEOS-Chem both included higher overall gas phase oxidation rates compared to GRAHM, which resulted in slightly shorter life times of Hg simulated by their models. On the contrary, a higher Br oxidation rate is used in GRAHM compared to GLEMOS and GEOS-Chem, leading to markedly higher gross deposition estimates by GRAHM which is mostly compensated by higher re-emission flux from the cryosphere. Natural and revolatilized emissions from land and ocean in GEOS-Chem are at least 50% higher (Table 2.6) than in GRAHM and GLEMOS, resulting in notably higher deposition contributions from these sources to the Arctic in GEOS-Chem. Overall, GRAHM estimates the highest contribution from natural sources and re-emissions over land (anthropogenic: 29%; terrestrial: 41%; ocean: 30%), while GLEMOS estimates the highest contribution from ocean (anthropogenic: 31%; terrestrial: 33%; ocean: 36%). Since the GEOS-Chem anthropogenic estimate includes terrestrial re-emission, it is not possible to estimate the contribution from terrestrial and oceanic emissions separately for GEOS-Chem (anthropogenic and re-emission: 32%; terrestrial natural: 29%; ocean: 39%). Based on the source attribution results from the models, the deposition input of Hg to the Arctic is found to be most efficient for emissions from Russia and Europe, followed by North America, East Asia, South Asia, Australia, South America and Africa.

Figure 2.19 depicts model ensemble average spatial distribution of the deposition contribution from four major source regions: Europe, North America, East Asia, and South

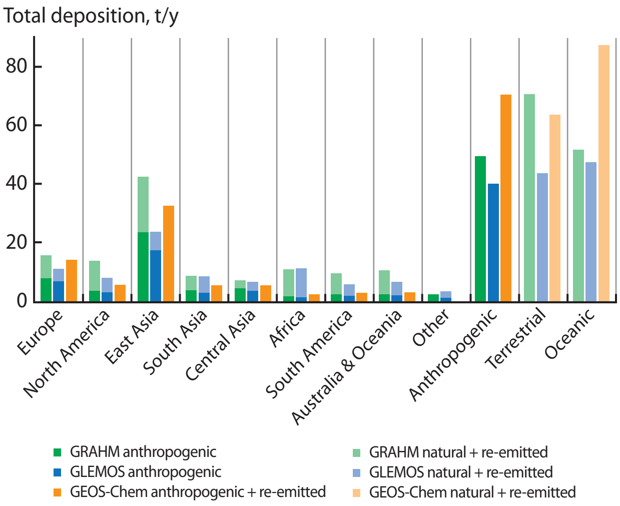


Figure 2.18. Contribution of the source regions to mercury deposition to the Arctic in 2005.

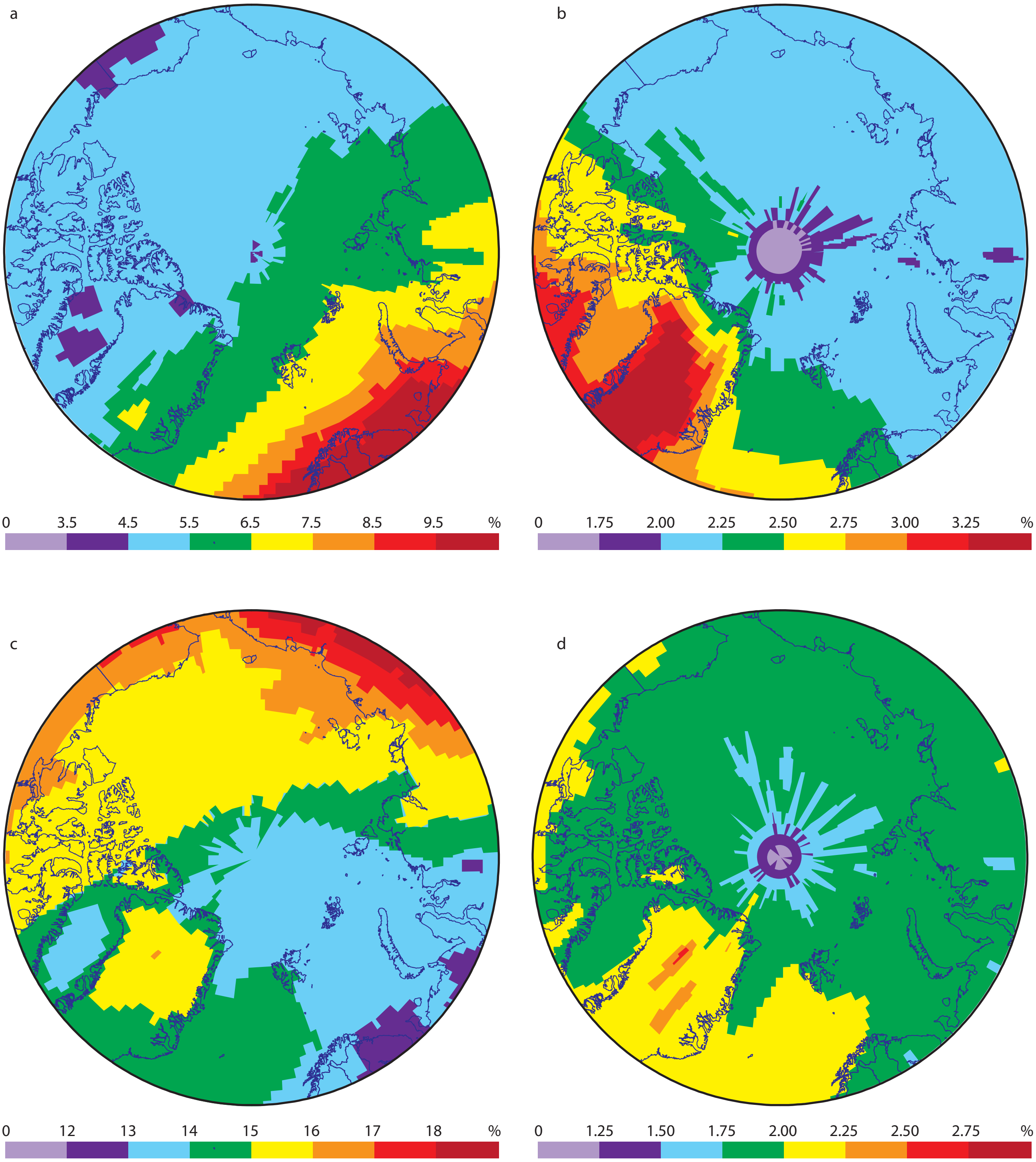


Figure 2.19. GLEMOS, GEOS-Chem and GRAHM model ensemble-mean spatial distribution of mercury deposition contribution to the Arctic from (a) Europe, (b) North America, (c) East Asia and (d) South Asia in 2005.

Asia. Since the lifetime of GEM in the atmosphere is between six and 24 months, the preferential long-range transport pathways from given source regions to the Arctic have a small impact on regional distribution of GEM transport and deposition to the Arctic. However as shown here, the North American and East Asian impact is somewhat higher in the western hemisphere, whereas the South Asian impact is slightly higher over Greenland and the adjacent ocean. European sources are closer to the Arctic therefore the regional variability of Hg contribution from this region is higher. These results suggest that relative changes in Hg emissions in these regions could affect the atmospheric deposition differentially in the Arctic. For example, increasing emissions in East Asia could increase deposition in the Canadian Arctic offsetting the decrease coming from reductions in North American emissions. Alternatively, a decrease in European emissions could decrease the deposition in the European Arctic in spite of increasing emissions in East Asia. Relative changes in Hg levels in the Arctic as a result of recent changes in emissions are discussed in Section 2.6.1.3. The main Hg transport pathways in the Arctic, Sub-Arctic and mid-latitudes from the major emission regions were analyzed by Durnford et al. (2010) based on an analysis of

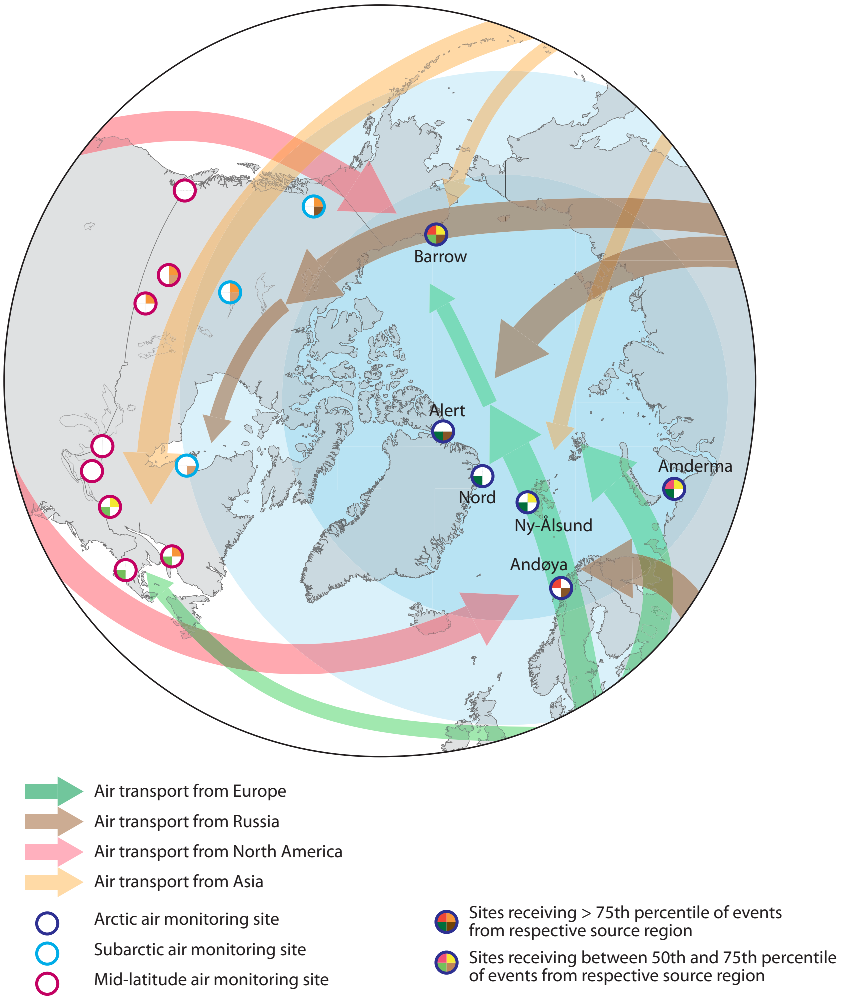


Figure 2.20. Dominant air transport pathways for mercury into the Arctic from major source regions, with an indication of the contribution from these source regions at specific monitoring locations. Source: after Durnford et al. (2010).

long-range transport events throughout the year, and on wind patterns that are shown in Figure 2.20. The figure identifies the transport pathways and the maximum, above the 75th percentile and between the 75th percentile and the median number of long-range transport events impacting on the Hg air measurement sites from Asia, North America, Russia and Europe. The study concluded that a higher percentage of long-range transport events are directed toward the Arctic from Europe and Russia compared to Asia and North America.

### 2.6.1.2. Uncertainties associated with Arctic deposition estimated by atmospheric models

The two most fundamental parameters that determine the exchange of Hg between the Earth's surface and the atmosphere, in areas remote from sources, are the airborne emissions of GEM, and its overall oxidation rate. Currently, estimates of anthropogenic emissions are considered to be far more reliable (Section 2.2) than estimates of the natural and revolatilized emissions of GEM from terrestrial and ocean surfaces, which are presently highly uncertain (Section 2.3). The latter emissions are roughly half to two-thirds of total global GEM emissions and therefore represent a significant source of uncertainty in the models. Uncertainty in the speciation of Hg emission has a profound impact on the simulated Hg deposition since Hg(0) is subject to long-range transport, while RGM and particulate Hg (to a lesser extent) deposit rapidly near emission sources.

Another major limitation of the current atmospheric Hg models is uncertainty in the chemical speciation and kinetics of Hg species in air (Section 2.5). These are currently extrapolated from limited laboratory investigations. The uncertainties in the gaseous Hg chemistry are mainly associated with the reported kinetic constants, and the lack of deterministic product identification of Hg reaction. The existing Hg kinetic parameters for gas and aqueous phases, obtained from theoretical calculations and laboratory measurements, vary significantly, and the application of these data to the real atmosphere has been questioned (Calvert and Lindberg, 2005).

Given both that emissions and atmospheric oxidation rates of GEM have significant knowledge gaps, the models must rely upon observational data constraints to ascertain the appropriateness of parameterizations of Hg processes. However, GEM surface air measurements and wet deposition fluxes, mostly from mid-latitude North America and Europe, are almost the only reliable sources of observational data available to date. Measurements of oxidized Hg concentrations and dry deposition fluxes are severely limited and highly uncertain. In addition, present-day techniques cannot determine the speciation of oxidized Hg. The uncertainties, particularly in natural and re-emitted Hg fluxes (see Table 2.5), chemical mechanisms, reaction rates, speciation and GEM dry deposition could be considered in generally descending order in models. Other important sources of uncertainties are associated with the lack of knowledge of seasonal variation of anthropogenic emissions, scavenging characteristics of Hg in liquid and solid condensate, precipitation rates and model resolution.

Large uncertainties both in Hg emissions and chemistry on the one hand and lack of adequate and reliable observations on the other, lead to a range of representations of non-anthropogenic Hg emissions, chemical mechanisms, Hg speciation and dry deposition in the models (Table 2.6). The four models applied to Arctic deposition and source attribution represent the full spectrum of parameters related to Hg processes. At the same time, all the models are constrained with common sets of Hg measurements. Therefore these models represent an ensemble that together provides a reasonable measure of the sensitivity of deposition estimates to various configurations and parameters of Hg processes available in the literature.

### 2.6.1.3. Impact of changing anthropogenic emissions from 1990-2005 on Arctic atmospheric mercury inputs

One of the measures of the impact of changes in Hg emissions worldwide is the temporal changes in atmospheric Hg levels in the Arctic. Long-term monitoring records for GEM concentrations at several Arctic sites have been analyzed in Section 2.5.2. However, it is challenging to relate the observed trends to the heterogeneous variations in anthropogenic Hg emissions on the globe. At the same time as anthropogenic emissions have changed, the observed changes in Arctic Hg may be also impacted by variations in weather patterns and in natural and revolatilized emissions, atmospheric chemical composition, land-use and climate. Modeling the impact of these factors independently and in combination on global Hg transport can illuminate the relationship of these changes to the measured trend in Hg levels in the Arctic.

Modeling studies have been conducted using global Hg inventories for 1990, 1995, 2000 and 2005 that were previously developed by AMAP. Recently, AMAP re-analyzed the 1990 to 2005 global anthropogenic emission inventories and developed more comparable historical inventories that are better suited for modeling the impact of changing Hg emissions in the Arctic over recent decades. The re-analyzed inventories use a common methodology and a more consistent information base for estimating certain emissions. Details are discussed in Section 2.2.2. Briefly, emissions in Europe and North America declined most rapidly from 1990 to 2000 and declined only slowly from 2000 to 2005 (see Figure 2.8). The emissions from other continents, most notably Asia, steadily increased from 1990 to 2005. Overall, global anthropogenic Hg emissions declined from 1990 to 1995 by 7.8% and increased between 1995 and 2000, and 2000 and 2005, by 0.3% and 5.6%, respectively.

As part of the current Assessment the GLEMOS, DEHM and GRAHM models were applied to assess the impact of changing anthropogenic emissions since 1990 on Hg concentrations in and deposition from the Arctic atmosphere. All three models used the four new emission inventories (1990 to 2005) while keeping the meteorology and all other variables identical in the model runs. Table 2.7 and Figure 2.21 illustrate the average simulated changes in Hg surface air concentrations and net deposition fluxes in the Arctic from 1990 to 2005.

The model results showed a decline in average surface air concentrations of GEM in the Arctic between 1990 and 1995 that was roughly half of the decline in anthropogenic emissions over this period, because over half of the total global GEM emissions are from natural and re-emission sources. Although anthropogenic emissions increased between 1995 and 2000, the simulated GEM concentrations and deposition in the Arctic and sub-Arctic continued to decline until 2000, mainly due to the larger impact of reductions in European and North American emissions. Durnford et al. (2010) found that the relative efficiency of Hg transport to the Arctic from Europe was higher than from Asia. For a similar reason, GEM concentrations and deposition in the Arctic increased more slowly from 2000 to 2005 than the increase in global emissions because of the off-setting effect of decreasing European and North American emissions. The model simulations also pointed to regional differences within the Arctic in response to changes in emissions from global industrial sources. The smallest reductions were predicted to occur in the North American Arctic, because of the impact of increasing emissions from Asia on this region that offset the emission reductions in North America. Further modeling studies are needed to investigate the potential impact of coincidental changes in meteorological, environmental and climatic variables (listed earlier) on the temporal trends of Hg in the Arctic atmosphere.

Table 2.7. Annual mercury deposition from 1990 to 2005 and percentage change relative to preceding year (1995 *vs* 1990, 2000 *vs* 1995, 2005 *vs* 2000) for various Arctic and Sub-Arctic regions.

| Mercury emission and deposition | 1990 | 1995 | | 2000 | | 2005 | |
|---|---|---|---|---|---|---|---|
| | t/y | t/y | % | t/y | % | t/y | % |
| Global anthropogenic mercury emissions | 1967.27 | 1813.88 | -7.8 | 1818.57 | 0.3 | 1920.57 | 5.6 |
| **Arctic 66.5° N – 90° N** | **133.12** | **122.79** | **-7.8** | **117.39** | **-4.4** | **119.34** | **1.7** |
| European Arctic 10° W – 60° E | 37.04 | 33.33 | -10.0 | 31.36 | -5.9 | 31.71 | 1.1 |
| Asian Arctic 60° E – 170° W | 49.41 | 44.82 | -9.3 | 42.53 | -5.1 | 43.46 | 2.2 |
| North American Arctic 170° W – 10° W | 45.95 | 43.87 | -4.5 | 42.76 | -2.5 | 43.44 | 1.6 |
| **Sub-Arctic 60° N – 66.5° N** | **134.32** | **114.86** | **-14.5** | **105.40** | **-8.2** | **106.94** | **1.5** |
| West European sub-Arctic 10° W – 20° E | 16.03 | 13.57 | -15.4 | 12.34 | -9.1 | 12.12 | -1.7 |
| East European sub-Arctic 20° E – 60° E | 30.08 | 22.95 | -23.7 | 19.19 | -16.4 | 19.49 | 1.6 |
| West Asian sub-Arctic 60° E – 100° E | 19.57 | 16.16 | -17.4 | 14.31 | -11.4 | 14.73 | 3.0 |
| East Asian sub-Arctic 100° E – 170° W | 25.87 | 21.21 | -18.0 | 19.45 | -8.3 | 20.04 | 3.1 |
| West North American sub-Arctic 170° W – 100° W | 17.51 | 16.95 | -3.2 | 16.62 | -1.9 | 16.83 | 1.2 |
| East North American sub-Arctic 100° W – 10° W | 25.54 | 24.14 | -5.5 | 23.50 | -2.6 | 23.78 | 1.2 |

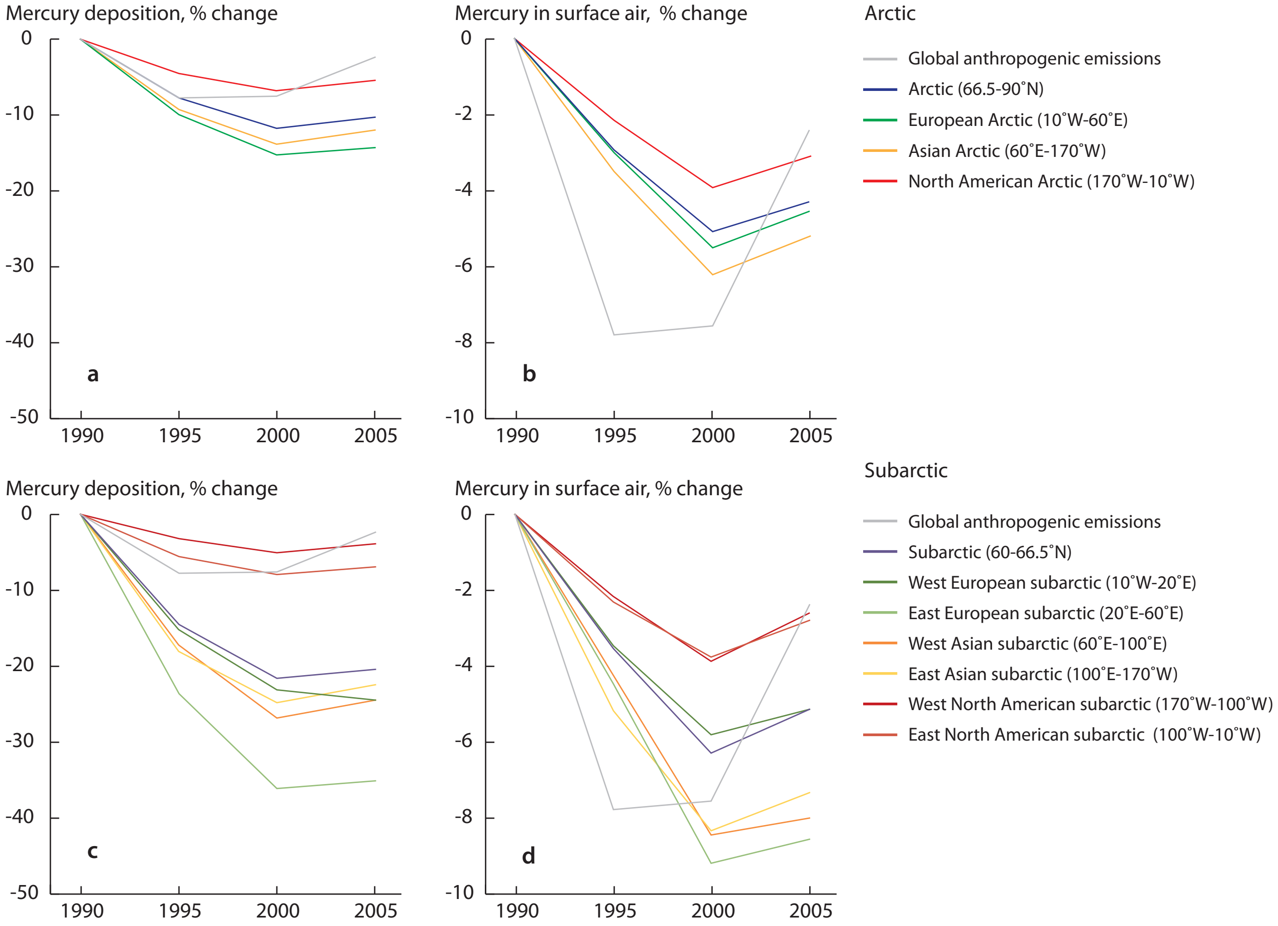


Figure 2.21. Relative change in annual mercury deposition between 1990 and 2005 in (a) Arctic and (c) sub-Arctic regions, and relative changes in surface air mercury concentrations in (b) Arctic and (d) sub-Arctic regions.

## 2.6.2. Field observations of re-emission of deposited mercury from snow surfaces

Mercury transformations at the interface between air and snow are a key component of the Arctic Hg cycle because atmospheric deposition is a major source of Hg (Skov et al., 2004; Ariya et al., 2004) and much of the Arctic surface is covered by snow for most of the year. The fate of Hg in snow is of fundamental importance because of its potential to enter aquatic ecosystems during spring melt and stimulate methylmercury production, followed by its bioaccumulation in food webs (Lindberg et al., 2002; Ebinghaus, 2008). Snow surfaces and ice crystals can become concentrated with Hg following the rapid oxidation of GEM during springtime AMDEs, reaching THg levels as much as 100 to 1000 ng/L (Lu et al., 2001; Kirk et al., 2006; Douglas et al., 2008; Johnson et al., 2008; Dommergue et al., 2010).

Freshly deposited Hg on snow is highly reactive (Lalonde et al., 2002), and a large portion of the Hg deposited during AMDEs is quickly revolatilized (re-emitted) to the atmosphere because of photo-reduction of Hg(II) to GEM within the surface snowpack (Lalonde et al., 2002; Poulain et al., 2004). A review of studies on snow Hg concentrations suggests that this rapid loss in surface snow is a common feature across the circumpolar Arctic (Table 2.8 and Figure 2.22). Approximately 80% of newly deposited mercury from AMDEs is typically lost from the snow surface after two days or longer. GEM flux measurements at the snow-air interface support the hypothesis that Hg loss is primarily due to re-emission to the atmosphere (Lahoutifard et al., 2005; Ferrari et al., 2005; Brooks et al., 2006; Johnson et al., 2008; Dommergue et al., 2010), although some loss may also result from movement into deeper layers of the snowpack or horizontal transfer from blowing snow.

Certain environmental conditions can promote retention of Hg within the snowpack. Low light energy, particularly in layers deeper than 10 cm, may prevent photo-reduction (King and Simpson, 2001). Moreover, changes in the incoming light energy regime can result in re-oxidation of the newly produced Hg(0) (Poulain et al., 2004). The presence of halogens in snow can help retain Hg by favoring a photo-oxidation reaction (Amyot et al., 2003), and indeed, elevated snow Hg concentrations are more often found in Arctic ocean or coastal environments where a deposition of sea-salt may be expected (Douglas and Sturm, 2004; Poulain et al., 2007a; St. Louis et al., 2007). Conversely, these higher concentrations may occur primarily because AMDEs are a result of photochemical reactions involving marine halogens and ozone (Lindberg et al., 2002; Simpson et al., 2007a). Burial through snow accumulation, sublimation, condensation and ice layer formation are other processes that promote retention of Hg in the snowpack (Douglas et al., 2008).

While deposition occurs at the snow surface, Hg can also be redistributed within the snow accumulation. Migration of GEM within the snowpack and subsequent oxidation could result in accumulation of Hg within deeper layers (Dommergue et al.,

Table 2.8. Percentage loss of total mercury (THg) concentrations in surface snow shortly following atmospheric mercury depletion events (AMDEs) at various Arctic locations. Concentrations are mean ± 1 SD, maximum (during AMDE only), range or single observation depending on the study (n in parentheses). Percentage loss of snow THg determined by measurements of gaseous elemental mercury (GEM) fluxes is also provided as a comparison.

| Location | Date of AMDE | Sampling site | THg in snow during and after AMDE, ng/L | | Number of days after AMDE | Percentage loss in snow | Depth sampled in snowpack, cm | Source |
|---|---|---|---|---|---|---|---|---|
| | | | During | After | | | | |
| Alert, Canada | 11-14 April 2002 | Over sea ice | 5.7 (1) | ~1 (1) | 1 | ~82 | surface | St. Louis et al., 2005 |
| | 23-25 April 2002 | Over land | 7.3 (1) | <2 (1) | 5 | >73 | surface | St. Louis et al., 2005 |
| Barrow, Alaska | May 2000 | Over land | >90 (1) | <20 (1) | 6 or more | **92**[a] | 0-10 | Lindberg et al., 2002 |
| | 22-31 March 2006 | Site 1, over land | 194 ± 22 (14) | 53 (1) | 2 | 73 | 0-1 | Johnson et al., 2008 |
| | | Site 2, over land | 147 (17) | 41 (1) | 2 | 72 | 0-1 | Johnson et al., 2008 |
| Churchill, Canada | 19 March to 3 June 2004[b] | Over sea ice | 67.7 ± 97.7 | 36.5 ± 16.3 | 1 | 46 | surface | Kirk et al., 2006 |
| | | Over sea ice | 67.7 ± 97.7 | 15.8 ± 8.1 | 2 | 77 | surface | Kirk et al., 2006 |
| | | Over sea ice | 67.7 ± 97.7 | 22.3 ± 12.3 | 3 | 67 | surface | Kirk et al., 2006 |
| | | Over sea ice | 67.7 ± 97.7 | 4.3 ± 1.9 | 4 or more | 94 | surface | Kirk et al., 2006 |
| Kuujjuarapik, Canada | 10-11 April 2002 | Over land | ~20-24 (4) | 17.2 (2) | 1 | ~14-28 | surface | Dommergue et al., 2003b |
| | | Over land | ~20-24 (4) | 2.3 (2) | 1.5 | ~89-90[a] | surface | Dommergue et al., 2003b |
| | 13 March 2004 | Over land | 12-16 (6) | 10-16 (6) | 2 | ~0[c] | 0-10 | Constant et al., 2007 |
| | 16 March 2004 | Over land | ~12 (2) | ~3 (2) | 0.5 | **78** | 0-10 | Constant et al., 2007 |
| Ny-Ålesund, Norway | 21-23 April 2002 | Over land | ~40 (1)[d] | <10 (1) | 6 | >75 | surface | Sommar et al., 2007 |
| | 24-27 April 2005 | Over land | 44.1 ± 19.0 (6) | 28.4 ± 18.5 (15) | 7 or more | 36[e] | surface | Ferrari et al., 2008 |
| Resolute, Canada | 7-14 May 2003 | Over land | 29.2 ± 1.5 | <15 | 3 | >49 | 0-10 | Lahoutifard et al., 2005 |
| | 7 June 2003 | Over land | 17.7 ± 7.8 (3) | 1.5 (3) | 2 | **92** | 0-1 | Poulain et al., 2004 |
| | | | GEM fluxes between air and snow (μg Hg/m²) | | | | | |
| | | | Deposition | Re-emission | | | | |
| Barrow, Alaska | 25 March to 7 April 2003[b] | Over land | 1.7 | 1.0 | | 59 | n.a. | Brooks et al., 2006 |

Percentage loss values in bold were calculated by the authors of the respective study. na; not applicable. [a] Losses during snowmelt; [b] multiple AMDEs occurred between those dates; [c] essentially no loss in snow THg concentration was observed; [d] maximum snow THg concentration measured during GEM recovery phase (24 April 2004); [e] Ferrari et al. (2008) reported an 80% loss relative to pre-AMDE THg concentrations in snow (instead of relative to mean THg concentration during the AMDE as calculated here).

2003a; Faïn et al., 2006a,b). Melt events may redistribute Hg toward deeper layers away from the high energy surface of the snowpack. A review of Arctic studies on the depth distribution of THg within the snowpack suggests that the highest THg concentrations are most commonly found in the surface layer (Table 2.9). However, the middle stratum and depth hoar can also be dominant reservoirs of Hg in some settings, emphasizing the fact that post-depositional processes over the entire depth of the snowpack may influence Hg accumulation.

The onset of spring melt results in a rapid flushing of THg from the snowpack; Hg(II) is transported by melt waters and photo-reduction also returns some of the Hg to the atmosphere (Lindberg et al., 2002; Dommergue et al., 2003b; Aspmo et al., 2006). Studies of THg concentrations in snowmelt water in the Canadian and Greenland Arctic generally display a range from 0.3 to 10 ng/L, with an average of about 3 ng/L (Outridge et al., 2008), although high Hg concentrations may occur briefly in the surface meltwater from a snowpack during the earliest melt period (e.g., up to 24 ng/L for 1 day; Dommergue et al., 2010).

A few studies have estimated the net impact of snowmelt Hg loadings from springtime AMDEs on receiving waterbodies. At Ny-Ålesund (Svalbard, Norway), Dommergue et al. (2010) found that because most Hg deposited on snow was photo-reduced and re-emitted back to the atmosphere, snowmelt contributed 8-21% of the annual THg loading to a fjord. Similarly, Kirk et al. (2006) estimated that AMDEs resulted in only a small net loading of Hg to Hudson Bay, Canada (equivalent to 2.1 ± 1.7 mg/ha; 0.21 ± 0.07 μg/m²) because of high re-emission rates. St. Louis et al. (2007) estimated snowpack contributions of 5.2 mg /ha for the Canadian High Arctic and concluded that Arctic snow contributes relatively little to marine pools of Hg. These observations suggest that, for at least most marine waters, the

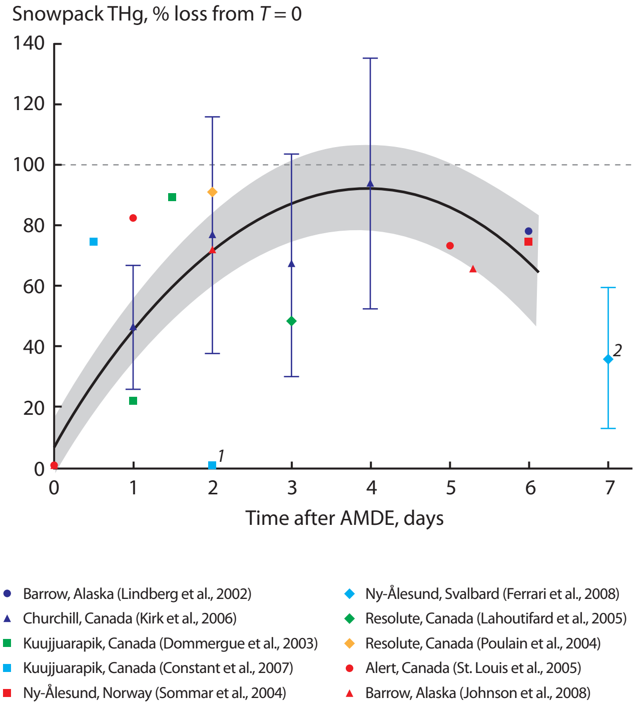


Figure 2.22. Rate of total mercury loss from Arctic surface snow (0 to 10 cm depth) after atmospheric mercury depletion events (AMDEs). (Data from Kirk et al. (2006) represent mean ± 1 SD, for other studies, the median values are used. Polynomial quadratic regression: THg (ng/L) = $5.77 + 44.7x - 5.75x^2$ ($r^2 = 0.78$, $p<0.0001$, total df = 26); shaded area indicates 95% confidence intervals around regression. Data points 1 and 2 were excluded; 1: see note 'c' in Table 2.8., 2: see note 'e' in Table 2.8.).

overall contributions of Hg following springtime AMDEs are less significant than previously thought (e.g., Lu et al., 2001; Lindberg et al., 2002), probably because of the dominant effect of photo-reduction. However, there may be differences between different kinds of environments in the net snowmelt contribution. Poulain et al. (2007a) reported that surface seawater sampled from a sea-ice lead during the time of ice melt temporarily exhibited THg concentrations that were 5 to 10 times greater than those at depth. Photo-reduction is hampered in seawater due to its high halogen content and consequently once Hg(II) enters marine ecosystems it may have a longer residence time than in freshwater (Poulain et al., 2007b). It is also possible that Hg contained in marine snow and ice may be more directly available to ice algae communities that represent a key part of the Arctic marine food web.

## 2.7. Can atmospheric fate models reproduce historical mercury deposition rates recorded in sediments, peat or by instruments?

To understand future effects, it is necessary to understand past processes. Environmental archives provide a means of doing so, because they are widely believed to accurately preserve the deposition history of Hg through time, either as a direct record or modulated by some type of focusing. All environmental archives by their nature involve an annual or seasonal accumulation process, which allows a chronology to be established. Studies on Hg deposition in environmental archives in the Arctic and sub-Arctic include records preserved in glacial ice and firn (perennial snowpack) (e.g., Faïn et al., 2006a,b, 2007, 2008, 2009b), lake sediments (Landers et al., 1995, 1998, 2008; Hermanson 1998; Bindler et al., 2001a,b; Lindeberg et al., 2006, 2007; Outridge et al., 2007; Muir et al., 2009), marine sediments (Siegel et al., 2001), and peat (Shotyk et al., 2003, 2005b; Givelet et al., 2004b; Bindler et al., 2005). Aside from lake sediments, there is limited spatial coverage across the Arctic of environmental archives, and the geographical representativeness of the other records is still under debate. Chronological resolution of the investigated archives was sometimes limited given the uncertainty associated with sampling and dating techniques.

Human activities have perturbed the natural biogeochemical cycling of Hg as well as other elements emitted through anthropogenic processes. It is essential that this perturbation is understood, so that future deposition and subsequent impacts given a warming climate and changing global atmospheric Hg concentrations may be reasonably predicted by atmospheric deposition models. This type of historical information is also required for effective environmental management (Hylander and Goodsite, 2006; Renberg et al., 2009), which requires a good knowledge of past accumulation rates as a basis for comparison with current accumulation rates and possibly future predictions given climate and global emission trends.

Owing to the paucity of real-time, instrumental atmospheric flux data for the Arctic, environmental archives of Hg deposition are particularly important sources of data for checking against atmospheric model outputs. There are advantages and limitations to any archive, and each type of archive should be seen as providing biogeochemical information that is supplementary and complementary to each other. This section attempts to address whether one, all, or any of the non-biological archives can accurately reproduce historical trends in Hg deposition in the Arctic, and if so, can atmospheric fate and transport models then reproduce these trends.

The trends in Arctic atmospheric Hg concentrations and deposition over recent decades represent the empirical basis for answering these questions. Recent work on GEM trapped in snow and firn layers at Greenland Summit (Faïn et al., 2009b) and a series of airborne particulate Hg samples collected at Resolute, Nunavut (Li et al., 2009) has now provided a database extending back several decades, while GEM monitoring at Alert, Nunavut, since 1995 (Temme et al., 2007) provides the longest, real-time instrumental dataset of GEM trends in the Arctic. Collectively, this body of work reveals that there was an approximate two-fold rise in atmospheric GEM concentrations before the 1970s, largely due to increased anthropogenic Hg emissions during the 20th century (Faïn et al., 2009b). Subsequently, a large-scale decline in atmospheric gaseous and particulate Hg levels occurred during the 1970s to 1990s in northern Canada and Greenland, probably due to implementation of air pollution regulations, especially on coal-fired power plants (Faïn et al., 2009b; Li et al., 2009). This decline is consistent with global emission inventories (Faïn et al., 2009b; see also Section 2.2.2). GEM concentrations in Greenland Summit snow, and in air at Resolute, have been largely stable or possibly slowly declining since the 1990s (Temme et al., 2007; Faïn et al., 2009b; see also Section 2.6.1).

Table 2.9. Comparison of total mercury (THg) concentrations in different layers of the snowpack (surface, middle stratum, depth hoar) at various Arctic locations. Observations are presented in order of increasing concentration (mean ± 1 SD, n in parentheses) in the surface layer.

| Location | Date | Sampling site | THg in snow, ng/L | | | Rank of THg comcentration in snow strata | Source |
|---|---|---|---|---|---|---|---|
| | | | Surface | Middle stratum | Depth hoar | | |
| Resolute, Canada | 14 June 2003 | Over land | <1 (3) | <1 (6) | <1 (3) | --- | Poulain et al., 2004 |
| Resolute, Canada | 9 June 2004 | Over lake ice | 0.9 ± 0.02 (3) | 0.4-2.7 (6) | 0.6 ± 0.4 (3) | M > S > D | Poulain et al., 2007a |
| Colville, Alaska | March/April 2002 | Over land | 1.1 ± 0.7 (3) | 0.5 ± 0.2 (3) | 0.8 ± 0.5 (3) | S > D > M | Douglas and Sturm, 2004 |
| Council, Alaska | March/April 2002 | Over land | 1.4 ± 0.2 (3) | 1.2 ± 0.2 (3) | 1.0 ± 0.1 (3) | S > M > D | Douglas and Sturm, 2004 |
| Selawik, Alaska | March/April 2002 | Over land | 1.4 ± 0.5 (3) | 1.3 ± 0.0 (3) | 1.7 ± 0.5 (3) | D > S > M | Douglas and Sturm, 2004 |
| Brooks Range, Alaska | March/April 2002 | Over land | 1.7 ± 0.1 (3) | 1.1 ± 0.2 (3) | 1.0 ± 0.5 (3) | S > M > D | Douglas and Sturm, 2004 |
| Resolute, Canada | 9 June 2004 | Over sea ice | 1.8 ± 0.6 (3) | 4.9 ± 0.5 (3) | 45.2 ± 13.1 (3) | D > M > S | Poulain et al., 2007a |
| Axel Heiberg Island, Canada | 16 May 2004 | Over land | 2.5 (1) | 0.3 (1) | 0.1 (1) | S > M > D | St. Louis et al., 2007 |
| John Evans Glacier, Canada | 10 May 2004 | Over land | 2.6 (1) | 0.4 (1) | 0.2 (1) | S > M > D | St. Louis et al., 2007 |
| Allman Bay, Canada | 10 May 2004 | Over sea ice | 3.6 (1) | 0.3 (1) | 0.6 (1) | S > D > M | St. Louis et al., 2007 |
| Talbot Inlet, Canada | 10 May 2004 | Over sea ice | 4.5 (1) | 0.4 (1) | 7.9 (1) | D > S > M | St. Louis et al., 2007 |
| Alert, Canada | 12 April 2002 | Over sea ice | 5.7 (1) | 0.4 (1) | 2.5 (1) | S > D > M | St. Louis et al., 2005 |
| Kuujjuarapik, Canada | 14 April 2002 | Over land | ~6 (2) | 2.6 (4) | ~4 (2) | S > D > M | Dommergue et al., 2003b |
| Buchannan Bay, Canada | 10 May 2004 | Over sea ice | 6.1 (1) | 1.3 (1) | 5.4 (1) | S > D > M | St. Louis et al., 2007 |
| Alert, Canada | 31 May 2004 | Over land | 6.2 (1) | 1.2 (1) | 1.4 (1) | S > D > M | St. Louis et al., 2007 |
| Atqasuk, Alaska | March/April 2002 | Over land | 6.6 ± 0.2 (3) | 3.3 ± 1.5 (3) | ~1 (3) | S > M > D | Douglas and Sturm, 2004 |
| Alert, Canada | 25 April 2002 | Over land | 7.3 (1) | 19.2 (1) | <2 (1) | M > S > D | St. Louis et al., 2005 |
| Norwegian Bay, Canada | 16 May 2004 | Over sea ice | 8.0 (1) | 8.1 (1) | 1.2 (1) | M > S > D | St. Louis et al., 2007 |
| Kuujjuarapik, Canada | 6 April 2002 | Over land | ~10 (2) | 14.3 (4) | ~4 (2) | M > S > D | Dommergue et al., 2003b |
| Alert, Canada | 22 April 2002 | Over sea ice | 11.1 (1) | 21.1 (1) | 1.3 (1) | M > S > D | St. Louis et al., 2005 |
| Eureka Sound, Canada | 16 May 2004 | Over sea ice | 15.9 (1) | 1.4 (1) | 9.8 (1) | S > D > M | St. Louis et al., 2007 |
| Resolute, Canada | 7 June 2003 | Over land | 17.7 ± 7.8 (3) | ~2 (6) | <1 (3) | S > M > D | Poulain et al., 2004 |
| Bay Fiord, Canada | 16 May 2004 | Over sea ice | 19.8 (1) | 18.1 (1) | 48.6 (1) | D > S > M | St. Louis et al., 2007 |
| Churchill, Canada | 31 March, 16 April, 22-23 May 2004 | 3 sites over sea ice | 21.4 ± 27.2 (9) | 15.2 ± 13.8 (9) | 10.6 ± 9.6 (9) | S > M > D | Kirk et al., 2006 |
| Wellington Channel, Canada | 16 May 2004 | Over sea ice | 66.4 (1) | 3.3 (1) | 2.3 (1) | S > M > D | St. Louis et al., 2007 |
| Jones Sound, Canada | 11 May 2004 | Over sea ice | 78.2 (1) | 8.0 (1) | 17.1 (1) | S > D > M | St. Louis et al., 2007 |
| Makinson Inlet, Canada | 10 May 2004 | Over sea ice | 150 (1) | 253 (1) | 281 (1) | D > M > S | St. Louis et al., 2007 |
| Barrow, Alaska | June 2000 | Over land | --- | 21 ± 10 | 50-90 | D > M | Lindberg et al., 2002 |
| | | | No. observations with highest [THg] at: | | | surface | 16 |
| | | | | | | middle stratum | 5 |
| | | | | | | depth hoar | 6 |

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

With respect to Hg deposition data, at northern European stations a comparison of deposition fluxes for the period 1995-1998 with those for 1999-2002 showed a decrease of 10-30%, which was attributed to reduced emissions in industrial areas of Europe (Wängberg et al., 2007). In a more recent comparison between three time periods (1995-1998, 1999-2002, 2003-2006), which also included the Pallas station (northern Finland), no significant trends in TGM or bulk deposition of Hg were found at Pallas, consistent with the previously-discussed studies on GEM trends at Alert and Greenland Summit. A continued decrease in Hg in bulk deposition was however found at most northern European stations, while trends in TGM were variable or insignificant (Wängberg et al., 2010). In North America, no deposition monitoring stations have been active in Arctic regions long enough to establish a time trend.

Major comparative studies have been conducted between instrument-based measurement of Hg deposition and atmospheric modeling results covering areas outside the Arctic (e.g., Bullock et al., 2008, 2009), discussion of which is beyond the scope of this report. To date, however, there has only been one such study relevant to the Arctic (Sanei et al., 2010). Sanei et al. (2010) reported wet deposition Hg fluxes measured over two years using precipitation collectors operated at Churchill on Hudson Bay, and at a second site in the western Canadian boreal forest. Because of typically low precipitation rates, measured Hg fluxes (0.5 to 1.3 μg/m$^2$/y) at these sub-Arctic sites were lower than those reported for temperate North American stations and for a station at Kodiak, Alaska, recently established by the Mercury Deposition Network (nadp.sws.uiuc.edu/mdn). GRAHM and GEOS-Chem model estimates for these locations were supplied by A. Dastoor (Environment Canada) and C. Holmes (Harvard University), respectively. For the Canadian sub-Arctic stations, both models consistently over-estimated wet Hg fluxes relative to field measurements. The largest discrepancy with both models was for Churchill, where AMDEs occur during spring (March to May; Kirk et al., 2006). Here, the model annual flux values were up to 7.6 times higher than measurements for GEOS-Chem, and 6.5 times higher for GRAHM. However, much better agreement was obtained for Kodiak, which experiences 4-fold higher annual precipitation rates (and an almost 10-fold higher annual Hg flux) than the Canadian sub-Arctic sites. GRAHM model wet flux estimates at Kodiak were only 23% higher than measured (based on 2007 modeled *vs* 2008 MDN measured data). GEOS-Chem gave an estimate 47% lower than measured at Kodiak.

GEOS-Chem is designed to resolve fluxes on relatively coarse, global scales, and is particularly not intended to provide accurate predictions for coastal sites such as Churchill (C. Holmes, Harvard University, pers. comm., Nov 11, 2009). Sanei et al. (2010) suggested that the closer agreement for the Kodiak and other MDN stations could be interpreted to mean that larger wet Hg fluxes, due either to elevated Hg concentrations or precipitation rates, may be modeled more accurately than are the fluxes in low precipitation, low Hg concentration settings such as the Canadian sub-Arctic. It is possible that precipitation type as well as amount may be an issue in relation to the model calculations. The relative scavenging effect of snow *vs* rain on the flux of atmospheric Hg is a research area needing attention.

In general, the snow and ice records have demonstrated the most consistent representations of historical Hg accumulation. However they are in air masses that are away from the coastlines and thus potentially not affected by AMDEs. They are also difficult to sample and analyze owing to their typically very low Hg concentrations. Sediments, whether lacustrine or marine, are the archives with the greatest spatial resolution so far in the Arctic, but physical, chemical and biological sources of perturbation to the signal that they present are a source of great discussion in the scientific community. Efforts are being made to better address issues such as focusing of Hg (Van Metre et al., 2009), as the lake dataset may provide the most robust and compelling insight into the past deposition of Hg across the Arctic.

### 2.7.1. Lake sediments

Lake sediments collectively tell a compelling story about the accumulation of Hg from the long-range transport of Hg emitted by human activities outside the Arctic, to local sensitive environments in the Arctic. When evaluating lake sediments (and any other archive), it is important to examine the chronology and the way it was determined. For example, the dating models employed to obtain a chronology rely on an estimation of excess $^{210}$Pb activity which may be based on subtracting a background level, rather than measuring supported $^{210}$Pb separately.

Landers et al. (1998), as well as Lockhart et al. (1998), Bindler et al. (2001a), Outridge et al. (2007), Lindeberg et al. (2007) and Muir et al. (2009), reported pre-industrial Hg fluxes in a combined total of 57 Arctic and sub-Arctic lakes (north of 53° N) ranging from 0.7 to 54 μg/m$^2$/y (geometric mean 6.7 μg/m$^2$/y), and 'post-industrial' (around 1960 to late 1990s) fluxes ranging from 2.3 to 52 μg/m$^2$/y (geometric mean 13.9 μg/m$^2$/y). Increases of Hg flux in recent decades were observed in 53 of 57 cores. In some cases the results were corrected for particle focusing (Lockhart et al., 1998) but not for other processes such as increased sedimentation. Anthropogenic Hg inputs to the lakes (ΔF = recent flux – pre-industrial flux) were presented by these authors or have been calculated from their published data. ΔF ranged from -14 to 35 μg/m$^2$/y (geometric mean 7.4 μg/m$^2$/y). Latitudinal and longitudinal trends of ΔF for the 57 lakes are shown in Figure 2.23. ΔF declined weakly with latitude (log ΔF *vs* latitude; $r^2 = 0.10$, $p = 0.015$) but was not significantly correlated with longitude.

Recent studies have examined the various factors influencing Hg profiles in Arctic lake sediments. Much of the emphasis has been on the effect of historical variations in sedimentation rates estimated by dating the cores using $^{210}$Pb. Understanding this variation is critical to assessment of Hg fluxes and therefore key findings from recent papers are briefly summarized here. Fitzgerald et al. (2005) found that whole-lake Hg sedimentation determined from 15 $^{210}$Pb-dated cores from five small Alaskan lakes (north of the tree line), showed a 3-fold increase in atmospheric Hg deposition since the start of the Industrial Revolution. They concluded that between 11% and 64% of Hg in recent sediments was from soil erosion and that another source term was needed to balance the evasional and sedimentation sinks. They noted that the additional flux needed (1.21 ± 0.74 μg/m$^2$/y) was similar in magnitude to direct wet Hg deposition. They suggested that the missing input may be some combination of springtime Arctic depletion and more generalized deposition of reactive gaseous Hg species. Outridge et al. (2005b) found significant correlations between Al and Hg in the DV-09 (Devon Island Canada) post-1854 stratigraphy and attributed a significant fraction of Hg input to local geological sources via weathering and runoff. Lindeberg et al. (2007) found that large fluctuations in Hg concentrations in pre-19th century sediments of lakes in West Greenland were related to changes in the influx of material from regional aeolian activity. Muir et al. (2009) also found higher recent sedimentation rates in 16 of 31 Arctic and sub-Arctic lakes. They concluded that the increased sedimentation did not appear to have a large lithogenic component (i.e. from erosion or aeolian inputs), because concentrations of lithogenic elements Al and Zn were not correlated with sedimentation rate. The higher recent sedimentation rates could also be due to the flattening of the slope of the $^{210}$Pb activity profile near the sediment surface due to bioturbation or to diagenetic dilution of the $^{210}$Pb due to accumulation of iron oxides at the surface (Gubala et al., 1990). Fitzgerald et al. (2005) noted iron oxide enrichment at the surface in their cores but Muir et al. (2009) found that iron concentrations were positively correlated with sedimentation rate in only 4 of 31 Arctic and sub-Arctic lakes.

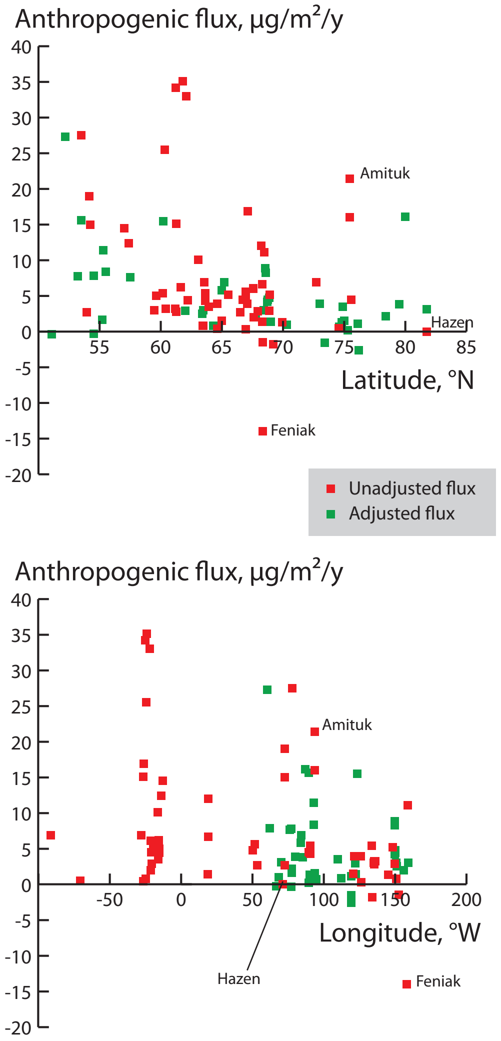


Figure 2.23. Anthropogenic fluxes (ΔF) of mercury in dated sediment cores from Arctic and sub-Arctic lakes. Unadjusted fluxes are from results presented by Landers et al. (1998), Lockhart et al. (1998), Bindler et al. (2001a), Outridge et al. (2007) and Lindeberg et al. (2007). Adjusted fluxes ($\Delta F_{adj}$) are from Fitzgerald et al. (2005), Landers et al. (2008) and Muir et al. (2009).

To adjust for effects of erosional inputs on Hg fluxes, Fitzgerald et al. (2005) and Landers et al. (2008) adjusted Hg fluxes using Mg and Ti, respectively, while Muir et al. (2009) adjusted for sedimentation rate as described by Perry et al. (2005). These adjusted anthropogenic fluxes for 39 lakes ($\Delta F_{adj}$) are plotted with latitude and longitude in Figure 2.23. $\Delta F_{adj}$ ranged from -2.6 to 27 µg/m$^2$/y (geometric mean 4.5 µg/m$^2$/y) and declined weakly with latitude (log $\Delta F_{adj}$ *vs* latitude; $r^2$ = 0.17, $p$ = 0.01) but not with longitude. These adjusted fluxes apply only to Arctic Canada and Alaska because there are no comparable data available for the rest of the circumpolar Arctic.

Whether adjusted or unadjusted fluxes are used, the geographic trends based on the lake sediment record suggest relatively uniform flux patterns of Hg in Arctic regions (Figure 2.23). In North America, $\Delta F_{adj}$ is predicted to decline from about 6 µg/m$^2$/y at 60° N to 0.5 µg/m$^2$/y at 83° N. By comparison, the GRAHM model predicted Hg depositional fluxes ranging from about 9.5 to 2.2 µg/m$^2$/y over this latitude range (from 60° to 83° N) in the Canadian Arctic, thus apparently corroborating the lake sediment data (Muir et al., 2009). The Danish Eulerian Hemispheric model (DEHM) predicted annual Hg deposition with AMDEs included ranging from 12 to 6 µg/m$^2$/y in the Canadian Arctic Archipelago (Christensen et al., 2004). Thus, there is relatively good agreement between the spatial trends of modeled terrestrial Hg fluxes and (measured) anthropogenic fluxes to freshwaters. This modeled result is in the same relative magnitude of Hg flux measured in peat from southern Greenland and around the Faroe Islands (Shotyk et al., 2003, 2005b). However, as DEHM does not presently account for re-emission after AMDEs, further model development is required to determine the degree to which DEHM can be used to support the notion that models are matching observed spatial trends.

The role that climate change has played in modifying Hg fluxes into lake sediments has been an area of recently active research. Two of the possible mechanisms by which this climatic influence may be exerted include increasing algal scavenging of Hg which increases the rate of Hg transfer from the water column to sediments, and inputs of Hg from thawing of adjacent permafrost peatlands. Rydberg et al. (2010) reported that during warm periods in pre-industrial times, Hg export from a thawing sub-Arctic mire in northern Sweden significantly increased Hg flux into an adjacent lake. The impact of the thawing peatland on sedimentary Hg fluxes was as large as that of airborne anthropogenic Hg deposition in the 20th century. Large increases in algal productivity have occurred over recent decades in Arctic lakes (Gajewski et al., 1997; Michelutti et al., 2005). There is evidence that these increases may have markedly increased the rate of organic particle scavenging and transfer of Hg into lake sediments (Outridge et al., 2005b, 2007), in a process analogous to the well-established phytoplankton 'biological pump' for vertical Hg flux in oceans (Cossa et al., 2009; Sunderland et al., 2009). To date, significant Hg-algal carbon flux and/or concentration relationships (with correlation $r^2$ values >0.75) have been found in all four of the lakes (Amituk, DV-09, Kusawa, Hare Indian Lake) which have been investigated in this way (Outridge et al., 2007; Carrie et al., 2010; Stern et al., 2009). It was estimated for Kusawa Lake, Yukon, and Lake DV-09 on Devon Island, Nunvut, that because of this climate-related effect no more than 22-29% of the 20th century increase in Hg concentrations was attributable to anthropogenic Hg inputs (Outridge et al., 2007; Stern et al., 2009). These recent findings, although requiring further investigation and testing, have implications if lake sediments are used to test the validity of atmospheric models.

Sediment total organic carbon (TOC) has occasionally been used to normalize Hg concentrations because it is assumed that most Hg enters lake sediments associated with organic matter. Bindler et al. (2001a,b) and Lindeberg et al. (2006) found that TOC increased over time in dated cores from West Greenland, and Muir et al. (2009) found that TOC increased over time in nine of 31 Canadian Arctic and sub-Arctic lakes. However, Bindler et al. (2001a,b) found that total carbon-normalized Hg concentrations still showed comparable increases in the Hg concentration of recent sediments, indicating that the Hg increases were not related to changes in the total carbon content of the sediment. On the other hand, total carbon data may not be an appropriate measure of the labile, thiol-rich algal organic matter which is believed to be involved in Hg scavenging. Organic matter is a biochemically complex material. Outridge et al. (2005b, 2007) reported increasing TOC in Amituk Lake, and

Lake DV09, but that the relative increase in algal-derived carbon, using a kerogen carbon parameter ('S2'), was markedly greater – 760% since 1854. These S2 carbon increases were highly correlated with diatom valve abundances, suggesting good preservation of the historical organic matter. The increased TOC could be partly due to greater autochthonus organic carbon production or other production in the littoral zone of the lake, as primary production in the littoral zone of lakes is densely concentrated in a considerably narrower space than that in the pelagic zone (Nozaki, 2002). Smol et al. (2005) and Michelutti et al. (2005) have also documented increased production in the pelagic zone. Progressive loss of carbon following burial, as shown by Gälman et al. (2008) for varved lake sediment in northern Sweden is another process that could generate the increase in TOC profiles in recent horizons. However, based on careful characterization of the organic matter using organic geochemistry and petrographic techniques, as well as the agreement between trends in Hg and in diatom abundances, decomposition is unlikely to explain the similar down-core profiles of algal carbon and Hg in the Arctic and sub-Arctic lakes studied by Outridge et al. (2005b, 2007), Carrie et al. (2010) and Stern et al. (2009). Other algal productivity indicators, such as total diatom valve abundance, and total pigment and biogenic silica concentrations, corroborate the occurrence of profound, widespread Arctic lake productivity increases as a consequence of earlier melting and ice-out under warming conditions (Gajewski et al., 1997; Michelutti et al., 2005; Smol et al., 2005).

### 2.7.2. Glacial ice

The state-of-the-art regarding records in glacial ice is the Faïn et al. (2009b) article on the trends in atmospheric levels of GEM in northern latitudes, reconstructed from the interstitial air of firn at Summit, Greenland. The study found that GEM concentrations increased rapidly from ~1.5 ng/m$^3$ after the Second World War, reached a maximum of about 3 ng/m$^3$ around 1970, and then decreased until stabilizing at about 1.7 ng/m$^3$ by around 1995 until the end of the record at 2003 (Figure 2.24b). The later part of their reconstruction agreed with instrument-based measurements of stable GEM concentrations in the Arctic since 1995 (e.g., at Alert; Temme et al., 2007). Overall, the ice core record matched the general trend in estimated global atmospheric emissions and global industrial Hg use (Figure 2.24a). The post-1970 decline in GEM at Greenland Summit was corroborated by coincident and significant declines in particulate Hg concentrations during summer and autumn at Resolute, Nunavut (Li et al., 2009). Spring particulate Hg levels also declined during those three decades, but the decline was not statistically significant because of high intra-seasonal variability possibly related to AMDEs (Li et al., 2009). Readers are cautioned not to place too much emphasis on industrial Hg production figures as a 'surrogate' for atmospheric emissions. The former are based on mining / production statistics and do not (generally) take into account that this has to some extent been offset by recovery / re-use of Hg. For example, cinnabar mines may cut production on a tonne-for-tonne basis as Hg recovered from EU chlor-alkali plants is brought back into circulation. Major atmospheric sources such as coal burning, which are unrelated to industrial Hg uses, add to the difficulty in making direct interpretations (see Section 2.2, for more information). Also, the 1980 global anthropogenic emissions data shown in Figure 2.24a may be an uncertain estimate, although emissions were almost certainly higher than in the 1990s and 2000s (Pacyna et al., 2006; see Section 2.2).

The atmospheric Hg trend results reported from the Greenland ice core and Resolute airborne aerosols are not consistent with the lake sediment Hg profiles in the Canadian Arctic and sub-Arctic after 1970 (see Figure 2.24). The trends move in opposite directions: declining significantly in air, and rising several-fold in sediment profiles relative to 1900-1910. Section 2.2 discusses changes in global emissions from 1990 to 2005. Global emissions are changing regionally, with relatively greater outputs from Asia during the past 20 years (Pacyna et al., 2006). However, it is unclear how polluted Asian air masses might impact on Hg levels in Canadian Arctic lake sediments, but not in the coinciding Canadian and Greenland atmosphere, particularly when the atmospheric study sites bracket the triangular region of Arctic lake sediments – Resolute (Li et al., 2009) to the west, Greenland (Faïn et al., 2009b) to the east, and Alert (Temme et al., 2007) to the north.

After reviewing the lake sediment- and peat-based Hg literature, Biester et al. (2007) stated that lake sediments appear to be a more reliable archive for estimating historical Hg accumulation rates than peat. This conclusion is not yet generally accepted across the scientific community, although there are many highly cited studies of Hg in lake sediments in the Arctic. However, what seemed (as recently as a few years ago) like very compelling interpretations from Arctic lake sediment studies with respect to their ability to reproduce Hg emission and deposition trends, must now be questioned in the light of recent evidence about the apparent effects of warming perturbing sedimentary Hg records. How these records in lake sediments are now interpreted, particularly given the contradictory atmospheric data from Faïn et al. (2009b), Li et al. (2009) and Temme et al. (2007) is an issue of ongoing debate. From examining the body of literature, scientific consensus has not yet been reached as to whether lake sediments do or do not accurately represent atmospheric Hg deposition in the Arctic, or which models best reproduce historical Hg accumulation.

### 2.7.3. Marine sediments

There have been few additional studies on records in marine sediments since that by Gobeil et al. (1999). The crucial factors governing surface Hg enrichment in Arctic basin sediments were shown to be diagenesis related to the low sedimentation rates (<1 cm ka(-1)) and sediment mixing rates (<0.03/cm$^2$/y) which redistributed Hg in the sediment profile. In all seven cores they investigated, strong similarities were observed between the Hg and reactive iron (Fe) profiles, implying that a proportion of the total Hg deposited is recycled along with Fe during redox changes. Intense redox processing in these cores was demonstrated by sharp decreases in organic content with depth and by vertical profiles showing surface enrichment of reactive elements. Thus, Gobeil et al. (1999) demonstrated that because of post-depositional processes, Arctic marine sediment archives are not generally reliable archives of Hg deposition.

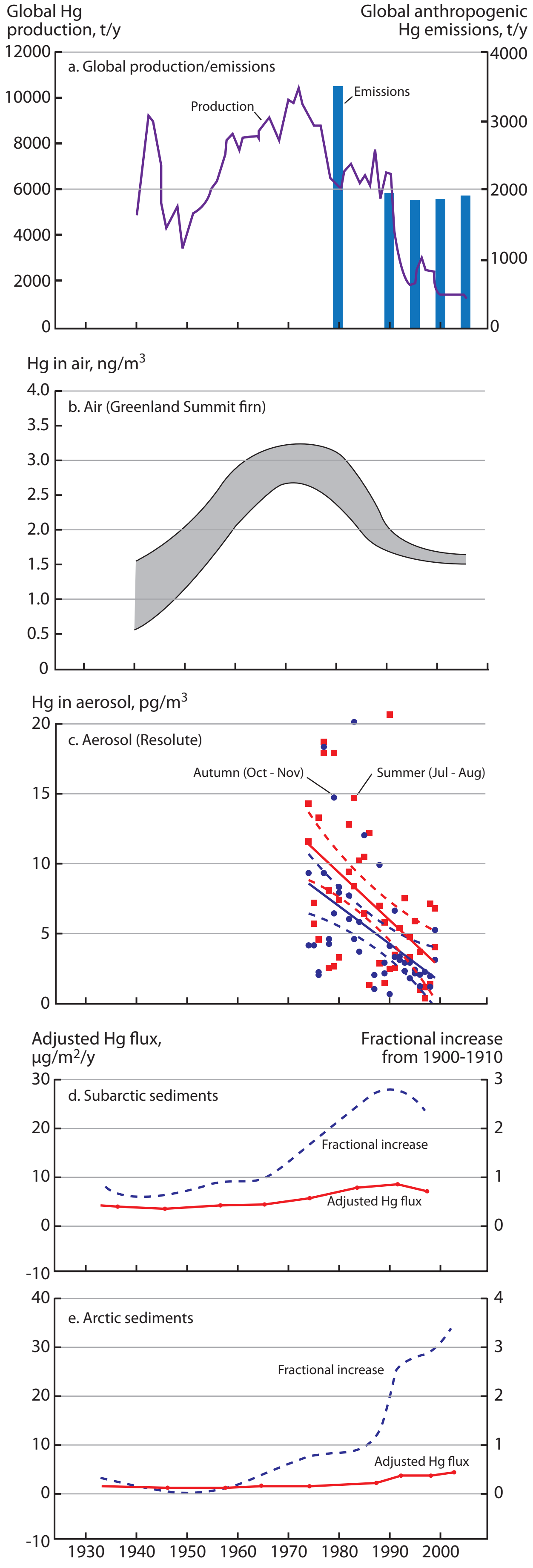


Figure 2.24. Comparison of published trends since 1940 in (a) global industrial mercury production (line; USGS, 2006) and global atmospheric emissions (bars; 1980 – Nriagu and Pacyna (1988), 1990 to 2005 – this report Section 2.2.2), (b) gaseous elemental mercury concentrations in Greenland Summit firn (Faïn et al., 2009b), (c) aerosol mercury at Resolute (Li et al., 2009), and in (d) Canadian sub-Arctic and (e) Arctic lake sediments (Muir et al., 2009).

### 2.7.4. Peat bogs

While ombrotrophic peat bogs are widely accepted as reproducing the atmospheric deposition of Hg (e.g., Steinnes and Sjobakk, 2005; Farmer et al., 2009) and there is good agreement between the measured accumulation rates and the modeled rates for lead (e.g., von Storch et al., 2002), the case is not as straightforward for Hg in peat types other than ombrotrophic deposits. Further complications arise when considering peat bogs subject to freeze-thaw cycles and other physical and chemical processes specific to the Arctic. The Biester et al. (2007) review started a debate in the environmental archive community regarding the overall validity of peat archives of Hg, especially those in the Arctic (see Givelet et al., 2004b; with subsequent critical comment and response: Bindler et al., 2005; Shotyk et al., 2005a). Studies of the historical Hg record in peat bogs suggested higher modern increases (9- to 400-fold, median 40-fold) than in lake sediments. Biester et al. (2007) compared published data of background and modern Hg accumulation rates derived from globally distributed lake sediments and peat bogs and discussed reasons for the differences observed in absolute values and in the relative increase in the industrial age. Direct measurements of modern wet Hg deposition rates in remote areas of the Northern Hemisphere presently coalesce around the range of about 1 to 4 µg/m²/y, but were possibly as high as 20 µg/m²/y during the 1980s. Values on the same order of magnitude were determined from lake sediments, thus suggesting that modern Hg accumulation rates derived from peat bogs tended to overestimate deposition. Biester et al. (2007) attributed this to the smearing of $^{210}$Pb in the uppermost peat sections and thus an underestimation of peat ages, and attributed the lower background Hg accumulation rates in peat as compared to lake sediments to non-quantitative retention and loss of Hg during peat diagenesis. Both points are contentious given the reliable Pb isotopic profiles retrieved from peat bogs as well as the lack of association between direct measures of peat humification and Hg accumulation rates (Shotyk et al., 2005b; Zaccone et al., 2009).

### 2.7.5. Summary comments on records in environmental archives

At least in part, the lack of agreement concerning the reliability of environmental archives is due to difficulties in establishing reliable chronologies, and in the present limits of geographical coverage of most archive types. Reconstructing archive data requires a reliable chronology of the archive. Producing this chronology is not trivial and generally this is one of the sources of uncertainty when interpreting the archive. Another source is the lack of geo-spatial coverage. Each archive type represents the transfer of Hg by various processes from the atmosphere to its ultimate deposited form, where at least a proportion of the original deposited amount is ultimately preserved. The transfer functions from air to ultimate accumulation in an archive, and the subsequent post-depositional processes, are still not well described in any of the archives, although there have been positive efforts to model the ultimate fate of Hg in a lake (Gandhi et al., 2007; Knightes et al., 2009). Post-depositional processes are likely to account for some of the non-correlation observed between the measured trends in archives and the modeled values.

The only historical environmental archives of Hg with enough data to reasonably statistically compare the results with the models, besides the ice cores, are the lake sediments. There are simply not enough studies in peat to reliably test for a compelling correlation. Nevertheless, additional studies in all archives are needed as the historical records may reflect different air masses and terrestrial catchments.

Although the number of studies of environmental archives has increased and systematically attempted to address known scientific gaps, there are still significant gaps that must be investigated to allow these past records of Hg deposition to be effectively used to help parameterize models to predict future concentrations in the various environmental archives. The answer to the question *Can atmospheric fate models reproduce historical Hg deposition rates recorded in sediments, peat or by instruments?* based on the available peer reviewed literature and state of the art is *a qualified yes*. The recent ice records are presently providing the most unequivocally reliable records with an excellent correlation between the measured trends and global anthropogenic emission records, but there is not yet a consensus among the authors of the present report as to whether lake sediments do or do not accurately represent rates of atmospheric Hg accumulation in the Arctic.

## 2.8. Conclusions and recommendations

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

### What are the current rates of global anthropogenic emissions of mercury to air?

1. Recent inventories of the global anthropogenic emissions of Hg to air for 2005 indicate annual emissions of 1921 tonnes. Emissions occur both from 'unintentional' sources (i.e., where Hg is present as a contaminant in fuels and raw materials) and from intentional use of Hg. Stationary combustion is the largest single source sector at 880 tonnes, mainly from the use of coal for energy production and thus also the largest 'unintentional' source. Artisanal gold production is the second largest source at 330 tonnes and also the largest intentional use source. Metal production and cement manufacturing are also large contributors to the global emissions.

2. Asia is by far the region with the largest emissions of Hg to air with about 65% of the total emissions, followed by North America and Europe.

3. A reanalysis of global emission inventories from 1990 to 2000 has produced a new set of consistent emissions data. The analysis shows that global emissions have been fairly constant during the period 1990 to 2005. During this period, emissions have decreased in Europe and North America but have increased in Asia. The re-analysis also includes an estimate of emissions from intentional use of Hg for the same period.

4. Once released to the environment, Hg can be recirculated between different compartments. Re-emissions of Hg to air will occur via evasion from natural surfaces (water, snow, soil, vegetation) as well as anthropogenically induced emissions via, for example, biomass burning.

5. Natural emissions result from the presence of Hg in the Earth's crust and can occur from, for example, volcanoes or soils enriched in Hg-containing minerals. Once released, naturally emitted Hg is indistinguishable from anthropogenic Hg and will follow the same atmospheric pathways i.e. transport, transformation, deposition and re-emissions from natural surfaces.

6. Available estimates of natural and re-emissions are within the range 2000 to 5000 tonnes per year and are thus of the same magnitude or larger than anthropogenic emissions. For modeling of atmospheric transport and for assessment of environmental contamination it is thus necessary to include these fluxes.

*For assessment of global transport and impacts of Hg and for the development of strategies for reducing the impacts, it is necessary to reduce the uncertainty of emission inventories. Information on Hg contents in fuels and raw materials as well as information on the current technical status of industrial sectors is lacking. Emission estimates from some sectors notably intentional use and waste handling are associated with large uncertainties and need to be better characterized.*

*Estimates of natural emissions and re-emissions are often based on a very limited number of measurements and models using a mass balance approach. Further research into the transfer of Hg from different environmental compartments to air is a high priority.*

### Are natural sources significant contributors of mercury to the Arctic environment?

7. Despite the absence of any known natural sources within the Arctic, natural emissions of Hg to air are estimated to contribute between 1000 to 2000 tonnes per year globally and are thus an important factor in the global atmospheric cycling of Hg including deposition to the Arctic.

### What are the relative importance of and processes involved in atmospheric, oceanic, riverine and terrestrial inputs of mercury to the Arctic?

8. The main input source of Hg to the Arctic is the atmosphere, which contributes slightly less than half of the annual input. Oceanic transport mainly from the Atlantic makes up around 23% as does erosion. The remaining fraction originates from riverine input.

### What is the influence of mercury speciation on total mercury transport by air?

9. Atmospheric chemistry and changes in speciation are key processes determining the transport of Hg from global sources to the Arctic and other remote ecosystems. The bulk of the atmospheric Hg is in the form of elemental Hg vapor which can be oxidized to form divalent forms which are more water soluble and thus more prone to deposition via wet or dry processes. Divalent gaseous Hg is often operationally defined as RGM (reactive gaseous mercury) or GOM (gaseous oxidized mercury).

10. RGM is formed continuously in the troposphere via reactions between elemental Hg and oxidants such as OH and Br. The exact reaction mechanisms are somewhat uncertain mainly due to experimental difficulties in determining reaction rates and product formation.

11. Operationally defined measurement techniques for RGM have been extensively applied in the Arctic for measurements of atmospheric mercury depletion events (AMDEs), where a very rapid oxidation of Hg occurs during the Arctic spring. These AMDEs lead to deposition of Hg from the atmosphere. In subsequent photochemically induced reactions, a fraction of the oxidized Hg can be reduced back to the elemental form and volatilized to the atmosphere again.

12. An analysis of long-term measurement data of atmospheric Hg in the Arctic indicates stable conditions. A slight decrease has been observed in Alert (Canada), but results from other sites do not show any significant trends.

13. Very few time series of atmospheric deposition measurements exist in the Arctic. Bulk deposition data from Pallas (Finland) indicate some variability but no significant trend.

### What is known about the net atmospheric mass contribution of mercury to the Arctic?

14. The transport processes in the Hg models are well represented; these have been developed and extensively evaluated for better known atmospheric chemical species. Model estimates of source attribution of Hg in the Arctic are remarkably consistent, and this provides evidence for the robustness of model dynamics in simulating transport.

15. The model-simulated annual mean GEM concentrations in the Arctic are within a factor of 1.1 of measured values at six monitoring sites. Model estimates of yearly wet deposition differ from measured values at three sites (two sub-Arctic, one Arctic) by a factor of 1.2 to 7.6.

16. Models are generally capable of simulating the depletion / re-emission cycles of Hg during springtime AMDEs in the Arctic, implying the role of halogen photochemistry; however there remains considerable uncertainty in Hg chemical kinetics parameters in air and at snow surfaces which limits precise determination of net deposition fluxes.

17. The most recent estimates of the net deposition of atmospheric Hg to the Arctic (north of 66.5° N) are provided by the four Hg models presented in this report. The model net deposition estimates range from 80 to 143 tonnes per year with a mean value of 116 tonnes per year. Net deposition is found to be highest in the region north of Europe and lowest in the region north of North America. Maximum net deposition is found to occur in the months of March, April and May and is attributed to enhanced deposition during AMDEs. The model mean net deposition during spring (March to May) is 42.8% of the yearly net deposition.

18. Anthropogenic emissions, terrestrial emissions (natural and revolatilized) and oceanic emissions (natural and revolatilized) each contribute approximately one third of the total deposition to the Arctic. The total deposition contribution (anthropogenic, natural, revolatilized) is highest from East Asia (21.4%), followed by Europe (8.7%), Africa (7.4%), North America (7%), South Asia (5.7%), Australia and Oceania (5.4%), South America (5%) and Central Asia (includes Russia) (4.6%). The contribution from anthropogenic sources alone is highest from East Asia (13.6%), followed by Europe (4.8%), Central Asia (includes Russia) (2.6%), North America (2.2%), South Asia (2.2%), Australia and Oceania (1.5%), South America (1.4%) and Africa (1%). The anthropogenic source attributions of Hg deposition to the Arctic estimated by different models are very close, and more reliable compared to the non-anthropogenic source attributions.

19. Geographic distribution of the Hg contributions to the Arctic from major emission source regions shows small but definite correlation with the direct transport pathways; a result of long lifetime (6 to 24 months) of elemental Hg in the atmosphere. The North American and East Asian emissions impact is somewhat higher in the western hemisphere, whereas the South Asian impact is slightly higher over Greenland and the adjacent ocean. The contribution from European sources has the strongest regional variability. These results suggest that relative changes in global emissions from these regions have a small differential impact on the atmospheric deposition rates in the Arctic.

20. Changes in anthropogenic global emissions between 1990 and 2005 led to generally corresponding changes in deposition to the Arctic. However, the impact of emissions reductions in Europe and North America is found to be larger compared to the impact of increases in emissions in other regions between 1995 and 2000. The smallest changes in deposition are simulated for the sub-Arctic and Arctic regions north of North America and the largest changes are found for the sub-Arctic and Arctic regions north of Europe. These regional differences are attributed to the relatively larger impact of East Asian emissions to the Arctic region of North America and the larger impact of European emissions to the Arctic region north of Europe.

21. There are significant differences between current Hg model configurations, most notably in natural and revolatilized Hg emissions, chemical mechanisms and reaction rate constants. The models represented in this report cover a comprehensive range of uncertainties in Hg emissions and processes found in the literature. Therefore the results reported here provide

a reasonable estimate of the uncertainty in the current ability to determine the atmospheric Hg input to the Arctic using models.

*Model estimates of the source attribution and temporal trends of Hg in the Arctic depend highly on the reliability of anthropogenic emissions data and on the speciation of Hg emissions. Therefore, further improvements of global Hg emission inventories are needed.*

*Studies are required for quantitative and mechanistic understanding of natural and revolatilized Hg emissions from various surfaces (soils, water, snow, vegetation) for constraining the models uncertainties.*

*Improved understanding of Hg chemical mechanisms, reaction rates and products in gas, aqueous and heterogeneous phases in global and Arctic environment is needed through laboratory and field measurement studies. Better understanding of bromine reaction rate constants in air and Hg reduction chemistry in snow are of particularly importance for the Arctic.*

*The models are generally consistent with each other for quantities that are better measured such as GEM, however the differences are large for quantities lacking observations such as wet and dry deposition in the Arctic. Measurements over the Arctic basin are largely missing which severely restricts the evaluation of the models over the Arctic Ocean. There is a need for a comprehensive network of measurements in the Arctic that includes concentrations of speciated Hg and chemical reactants in air, as well as wet and dry deposition.*

*Modelers need to explore the use of surface measurements such as Hg concentrations in snowpacks, streams and sediments to constrain the models.*

*Comprehensive parameterizations for Hg exchange between air and cryosphere need to be developed to limit the uncertainty in net deposition estimates to the Arctic.*

*Although, the atmospheric reservoir of mercury is comparatively much smaller, the atmosphere serves as an efficient mechanism for exchanging Hg between the two large reservoirs of Hg in the terrestrial and oceanic systems. Biogeochemical models linking atmosphere, ocean and terrestrial systems are needed to take into account the entire cycling of Hg in the environment for an adequate assessment of Hg inputs to the Arctic. It is particularly relevant for the evaluation of long-term trends, future scenarios and the impact of climate change on Hg pollution in the Arctic.*

*Modeling studies are needed to investigate the impact of changes in meteorology, atmospheric chemical composition, land-use and climate on Hg budgets in the Arctic.*

### Can atmospheric fate models reproduce historical mercury deposition rates recorded in sediments, peat or by instruments?

22. Reconstructing archive data is restricted due to difficulties in establishing reliable chronologies, and in the present limits of geographical coverage of most archive types. The transfer functions from air to ultimate accumulation in an archive, and the subsequent post-depositional processes, are still not well described in any of the archives. Additional studies in all archives are needed as the historical records may reflect different air masses and terrestrial catchments.

23. The answer to the section question is *a qualified yes,* based on the available peer reviewed literature and state of the art. The recent ice records are presently providing the most unequivocally reliable records with an excellent correlation between the measured trends and global anthropogenic emission records, but there is not yet a consensus among the authors of the present report as to whether lake sediments do or do not accurately represent rates of atmospheric Hg accumulation in the Arctic.

*It is possible that precipitation type as well as amount may be an issue in relation to the model calculations. The relative scavenging effect of snow vs rain on the flux of atmospheric Hg is a research area needing attention.*

*Sampling both dry and wet deposition under Arctic conditions is an important area requiring further research and development; sampling snowfall is a particular challenge in this respect. These measurements are important for improved parameterization of models.*

*Depositional and flux measurement techniques and campaigns are needed as wet deposition may be similar at different times and locations yet re-volatilization may be quite different.*

*It is of the utmost importance that better techniques be developed for measuring the geographical and temporal dynamics of Hg deposition and the concomitant re-emission of atmospheric Hg to the Arctic and the rest of the World. Because of the global cycling of Hg it is not possible to develop an accurate model of the Arctic portion of the global cycle in regional isolation. Therefore, technological development of measurement techniques is needed so that the concentrations of Hg species in the atmosphere can be measured rather than only the fractionation of Hg. Furthermore, there is only one published study of the fluxes of RGM and a few studies of the fluxes of GEM in the Arctic.*

*Further studies to investigate the possible over-estimation of atmospheric wet deposition fluxes by lake sediments and atmospheric models, and the reasons for any over-estimation are needed. These studies must be corroborated with studies of Hg in annually deposited snow and ice where possible, using uniformly agreed sampling and analysis methods.*

*One of the gaps in knowledge for future studies is the need to develop and accept common sampling and dating routines, as best practice, to allow better intercomparison of the data sets.*

*AMAP should recommend the creation of an expert working group to address the question of exactly what studies and data are needed ensure that the models are properly parameterized to predict the future deposition and likely re-emission of Hg and its ultimate fate in future Arctic ecosystems.*

*There is a need for standardized best practices for sampling and later biogeochemical analysis in environmental archives, as such protocols do not exist in the literature except for peat (see Givelet et al., 2004a). Studies presenting Hg as stand alone data generally therefore do not advance overall understanding.*

# Chapter 3

# What is the Fate of Mercury Entering the Arctic Environment?

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## 3.1. Introduction

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

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

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

### 3.1.1. The Arctic as a unique location

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

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

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

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

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

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

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

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

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

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

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

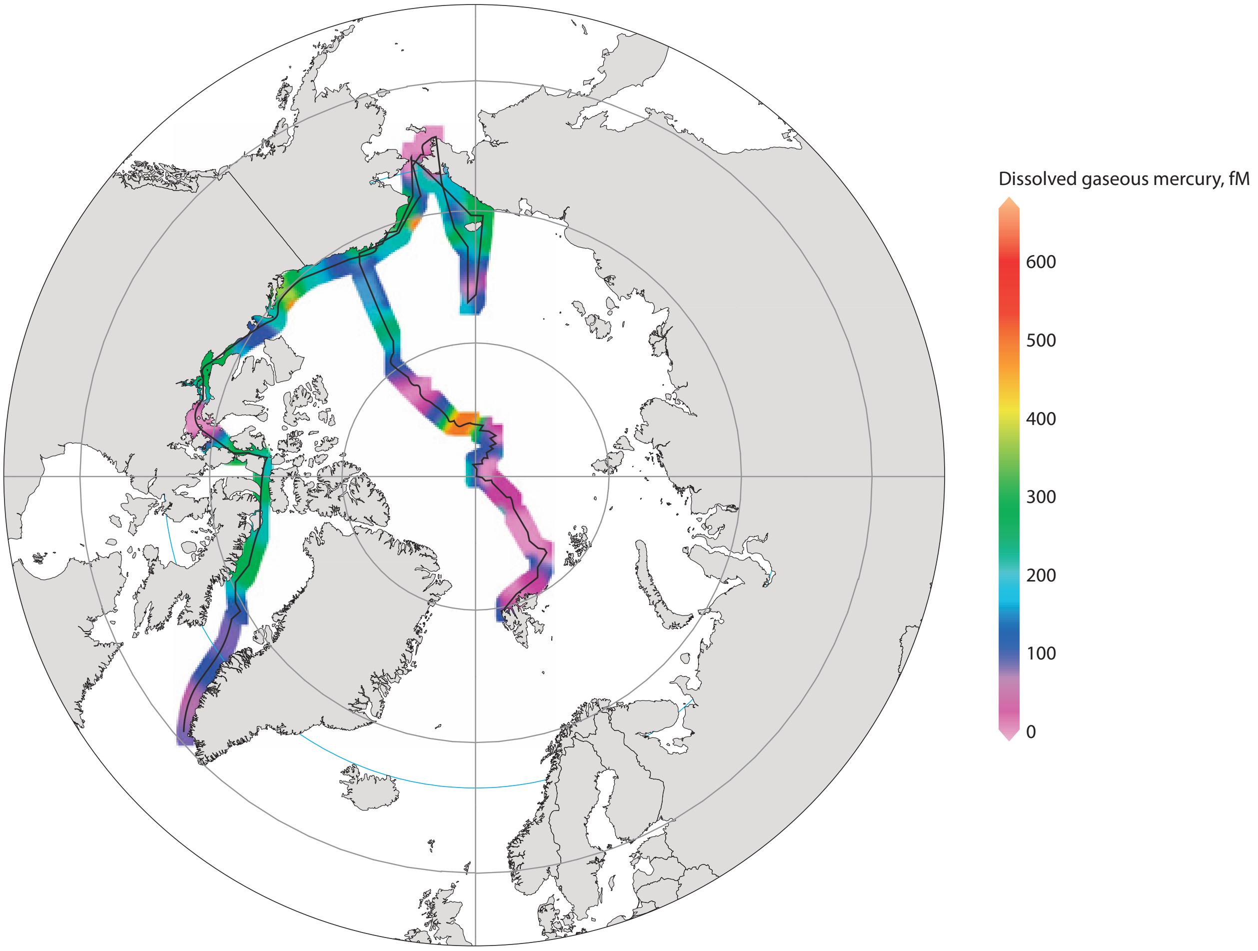

Figure 3.1. Dissolved gaseous mercury (DGM) in surface water along the *Beringia* 2005 cruise track showing predominant supersaturation in the water, with generally higher DGM concentrations found under locations covered with sea ice. Modified from Andersson et al. (2008).

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

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

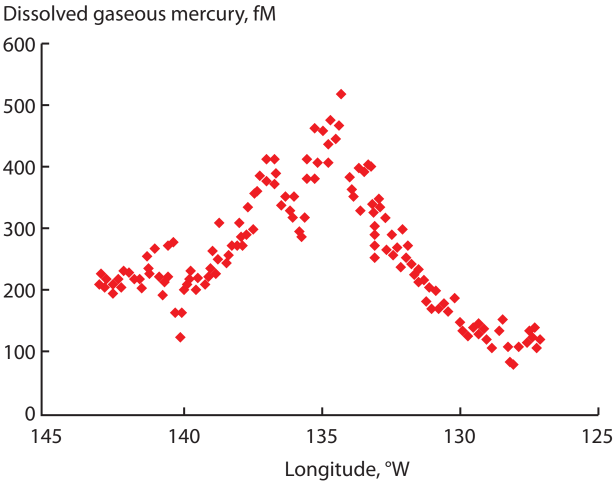

Figure 3.2. Dissolved gaseous mercury (DGM) in surface water along the *Beringia* 2005 cruise track as it crossed the Mackenzie River plume. The high DGM concentrations in plume waters may indicate direct supply from the river, or enhanced production of DGM facilitated by riverine dissolved organic carbon.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

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

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

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

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

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

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

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

### 3.2.2. Microbial carbon processing and mercury in the Arctic

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

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

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

### 3.2.3. The fate of mercury in the Arctic Ocean

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

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

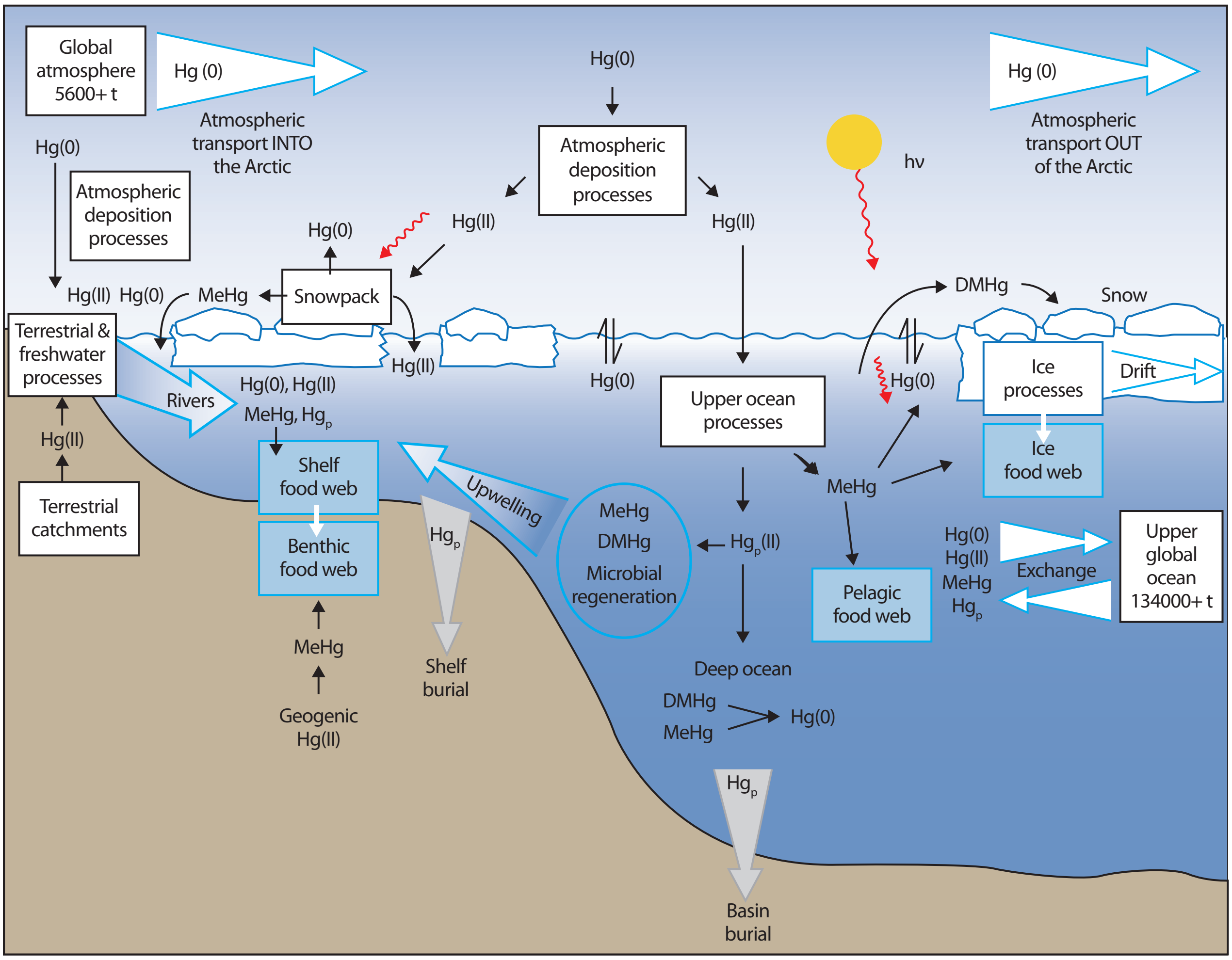

Figure 3.3. The mercury cycle in the Arctic Ocean. Rectangular boxes show system processes, like food webs or atmospheric deposition chemistry, that have detailed schematics and discussion presented elsewhere. Large shaded arrows refer to atmospheric or oceanic transport processes that exchange Hg with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

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

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

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

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

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

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

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

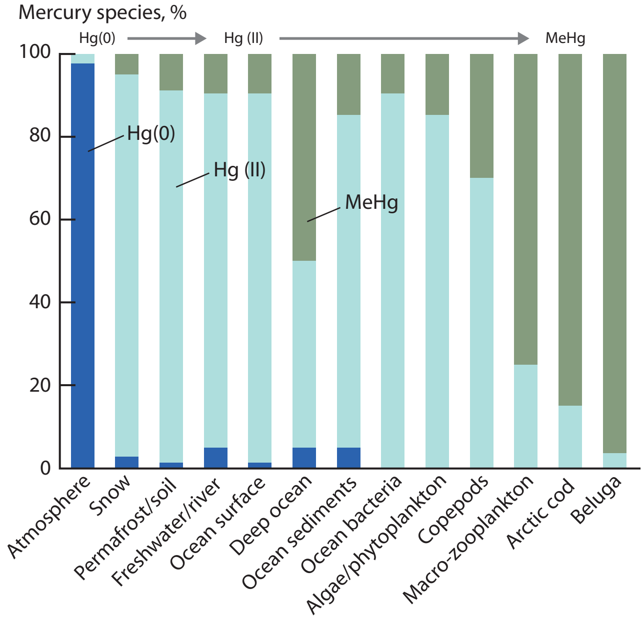

Figure 3.4. To present a risk, the predominant form of Hg transported in the atmosphere, Hg(0), must undergo oxidation to Hg(II) and then methylation to MeHg. Risk to top aquatic predators, therefore, is a consequence not only of the amount of Hg(0) cycling in the atmosphere, but also of the balance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

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

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

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

### 3.3.1. Bioavailability of mercury

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

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

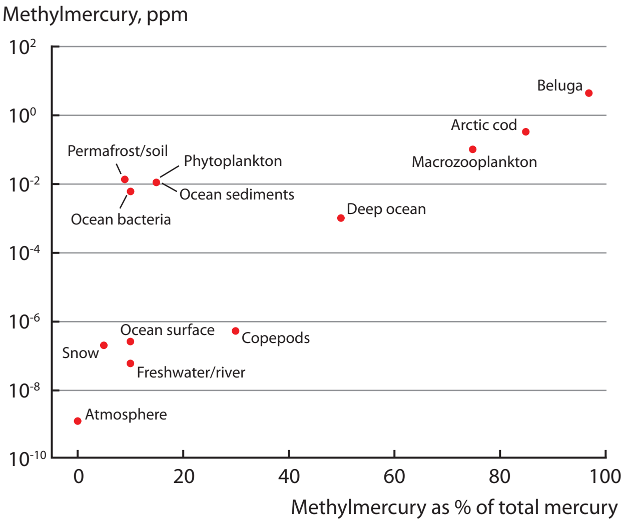

Figure 3.5. Methylmercury bioconcentrates and biomagnifies. In inorganic media, MeHg tends to represent a minor proportion of the total mercury (about 20% or less), but progressively increases upward through aquatic food webs to become the predominant form of Hg at trophic levels 2 and above.

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

### 3.3.2. Transfer pathways for mercury into Arctic food webs

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

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

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

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

### 3.4.1. Methylmercury production pathways

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

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

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

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

### 3.4.2. Methylmercury destruction pathways

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

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

### 3.5.1. Introduction

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

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

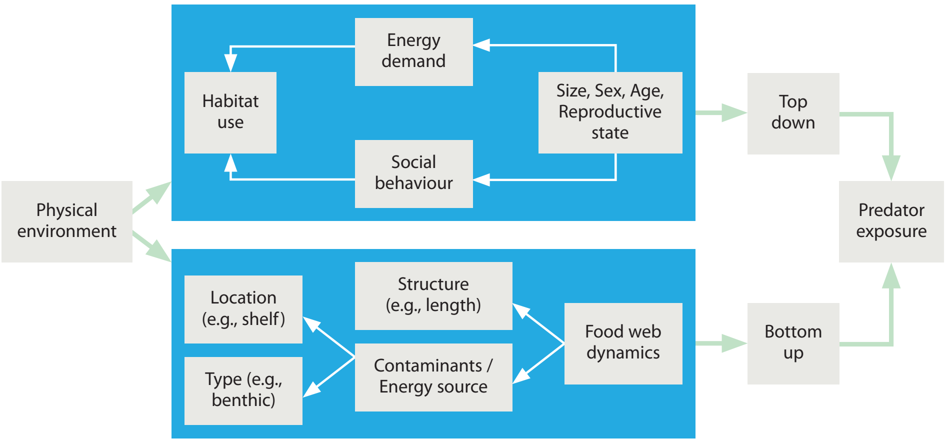

Figure 3.6. The processes affecting Hg concentrations in a high trophic level species. Food web interactions determine the sources, bioaccumulation and biomagnification of Hg (in the form of MeHg). Dietary preferences are shaped by many factors including the sex, size, age, and reproductive status of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

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

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

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

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

### 3.5.2.1. Marine food webs

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

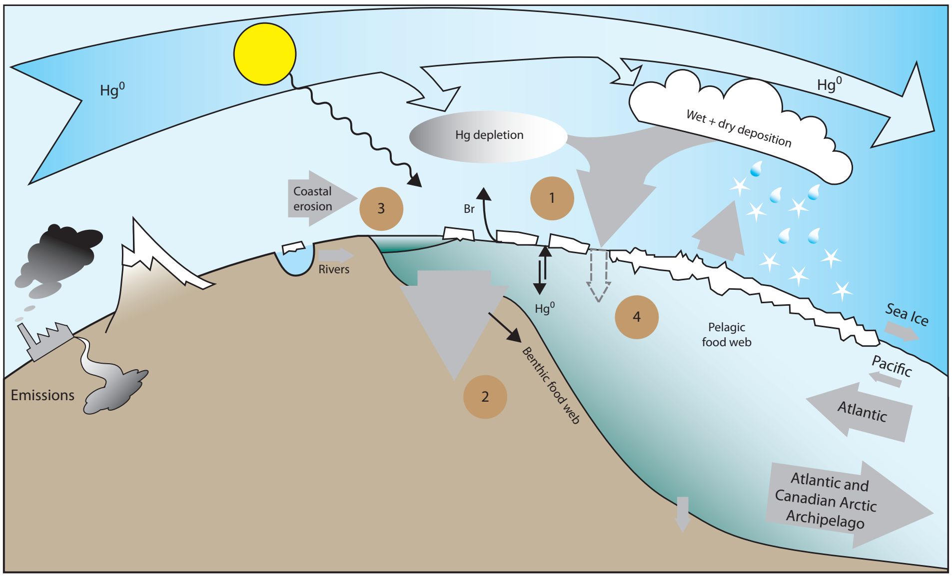

Figure 3.7. Potential inorganic Hg input pathways underpinning Hg methylation and bio-uptake in distinct Arctic marine food webs. Circled numbers represent atmospheric deposition to the ocean surface (1), sediment methylation processes (2), riverine and terrestrial sources (3), and ocean water column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

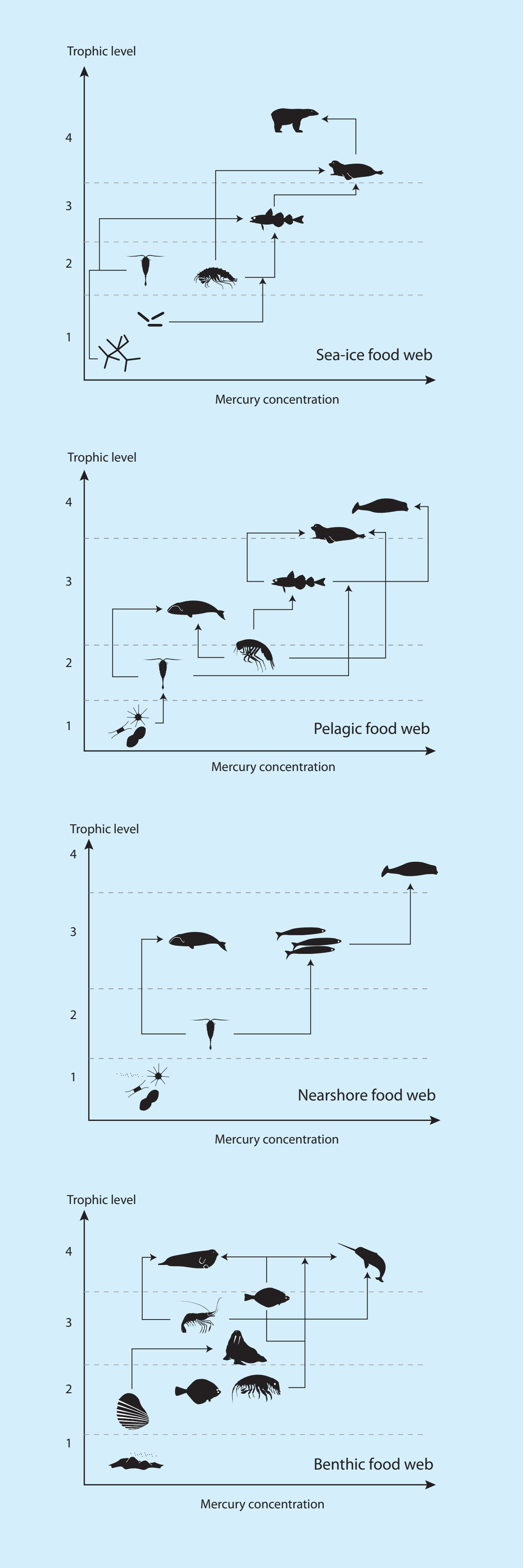

Figure 3.8. Mercury flow through marine food webs in the Beaufort Sea, northern Canada (seabirds and humans not included).

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

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

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

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

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

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

#### 3.5.2.1.2. ***Pelagic food webs***

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

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

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

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

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

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

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

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

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

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

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

### 3.5.2.2. Freshwater food webs

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

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

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

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

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

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

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

### 3.5.3.1. Eastern Beaufort Sea beluga

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

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

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

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

### 3.5.3.2. Landlocked Arctic char

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

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

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

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

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

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

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

### 3.5.4. Physiological factors determining dietary mercury exposure in predators

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## 3.9. Conclusions and recommendations

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

# Chapter 4
# How Does Climate Change Influence Arctic Mercury?

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## 4.1. Introduction

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

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

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

This chapter focuses specifically on how the Arctic's Hg cycle has been and is likely to be impacted by climate change. It can be inferred from detailed schematics of the Hg cycle (see Chapters 2 and 3) that climate-related variables may act on Hg transport, transfer and transformation processes anywhere between global emissions and the accumulation of monomethylmercury (MeHg) in top Arctic predators. Broadly speaking, the Hg cycle can be affected by change in the physical and biological systems or in the carbon cycle. There is better understanding about the physical components of the system and, thus, it is easier to propose how alteration of, for example, temperature, precipitation, and ice cover, would affect the volatility, deposition and air-water exchange of Hg in the Arctic. In contrast, for the biological and carbon systems, there is still insufficient understanding of their coupling with the Hg cycle to construct plausible descriptive or predictive models of climate effects.

The chapter begins (Section 4.2) by briefly summarizing the present state of knowledge about change in the physical components of the Arctic. Subsequent sections discuss the connections between these physical changes resulting from climate change and the Arctic Hg cycle.

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

### 4.2.1. Atmosphere

Arctic air temperature is increasing (Overland et al., 2008) and the weather becoming less predictable. Indeed, large variation in environmental parameters, frequently alluded to by northerners (Krupnik and Dyanna, 2002), is likely to be an important manifestation of the changing climate. The loss of sea-ice cover for extensive areas of the Arctic Ocean has allowed radiation to penetrate the water during summer, thus storing heat in the upper ocean. This heat later feeds back to the lower atmosphere with the consequence that autumn temperatures in the Arctic have recently been as much as 4 °C above average with an Arctic-wide anomaly above +1 °C. Altering ice cover and heat balance over the Arctic Ocean in this manner then changes atmospheric connections between the Arctic and southern latitudes (Francis et al., 2009; Honda et al., 2009). During the past decade, the Arctic atmospheric pressure pattern has been characterized by anomalously high sea-level pressure on the North American side of the Arctic and low pressure on the Eurasian side (Overland et al., 2008), which has then supported more southerly winds. Altered atmospheric pressure fields imply the possibility of altered patterns of atmospheric transport of Hg into and out of the Arctic (Macdonald et al., 2005). Deposition of Hg within the Arctic, including through AMDE (atmospheric mercury depletion events) chemistry, may also be affected by precipitation and temperature changes (see Chapter 2 and Section 4.3).

### 4.2.2. Arctic freshwater and terrestrial systems

Change in terrestrial systems is complex because it may manifest in snow and ice cover, glaciers, permafrost, vegetation, river discharge and timing, moisture balance, incidence of forest fire, migration pathways and invasive species (e.g., Hinzman et al., 2005; Wrona et al., 2005; Prowse and Furgal, 2009). To some degree, all of these system components have been undergoing change, but not at the same rate or in the same way everywhere, and trends are frequently masked by large seasonal and inter-annual variations. This variation will, of course, lead to change in components of the Hg cycle both spatially and temporally. The lower atmospheric warming trends, supported by loss of sea ice (as described in Section 4.2.3), have led to declines in the length of snow seasons during the past three decades (Peterson and Baringer, 2009), loss of lake ice (Smol and Douglas, 2007b), earlier break-up in rivers (Schindler and Smol, 2006; Prowse and Furgal, 2009) and feedbacks between marine and terrestrial systems (e.g., Lawrence et al., 2008).

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

Permafrost temperatures have generally increased (Walker, 2007), with recent observations suggesting that temperatures have risen by 1 to 2 °C during the past three decades (Smith et al., 2005a; Oberman, 2008; Osterkamp, 2008). Thawing leads to the release of old carbon (Guo and Macdonald, 2006; Schuur et al., 2009; Roehm et al., 2009) and Hg (Klaminder et al., 2008) from organic-rich soils. The process of release during thawing may be particularly pertinent for Hg deposited from the atmosphere and stored at the surface of frozen ground, as this Hg has been shown to 'fast track' to the biota (Harris et al., 2007). Permafrost soils slumping into lakes as a consequence of thaw may also provide a pathway to increase Hg methylation in affected lakes. A widespread desiccation of small Arctic ponds has been observed (Smith et al., 2005b; Riordan et al., 2006; Smol and Douglas, 2007b), and with this the demise of an aquatic food source (zooplankton), which could result in a change in MeHg exposure for animals such as aquatic birds that can switch prey.

Lakes in the Arctic have been losing their ice cover, in some cases for the first time in millennia Schindler and Smol, 2006; Smol and Douglas, 2007b). Given the collective area of lakes in the Arctic (see Section 3.8), changes in lake ecosystems consequent to warming have the leverage to widely alter the systematics of carbon production and metabolism and thereby impact the Hg cycle. It is clear that the earlier opening of lakes to light in spring has changed phytoplankton production, perhaps beyond critical thresholds (Michelutti et al., 2005; Smol and Douglas, 2007a,b). The impacts of these changes have been recorded in Arctic lake sediments, in both the organic carbon and Hg profiles (e.g., Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2010). What these changes mean for biological uptake is less clear. Enhanced productivity could lead to bio-dilution of Hg (e.g., Pickhardt et al., 2002; Larsson et al., 2007), whereas greater light exposure could lead to greater photo-demethylation. Conversely, greater productivity and carbon supply could drive higher methylation rates in lake waters as it does in the ocean (Sunderland et al., 2009). Carrie et al. (2010) reported an apparent relationship between warmer temperatures during recent decades and increasing tissue Hg concentrations in burbot (*Lota lota*) in the Mackenzie River, Canada, and suggested that one possible explanation was increased MeHg supply from a warming tributary lake where organic productivity had increased concurrently with fish and sediment Hg concentrations.

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

River discharge from the Arctic's drainage basins has been generally increasing in the Russian Arctic since the 1930s at a rate of about 2 to 3 km$^3$/y (Peterson et al., 2002; Shiklomanov et al., 2006). For North America, the more limited records suggest that trends are neutral or even declining slightly during recent decades (Déry and Wood, 2005; McClelland et al., 2006). Arctic rivers provide a significant source of particulate and dissolved inorganic Hg and smaller amounts of MeHg to the Arctic Ocean (Coquery et al., 1995; Leitch et al., 2007). An important feature of river hydrology is that the concentration of Hg is positively correlated with discharge (Stanley et al., 2002; Balogh et al., 2004; Leitch et al., 2007). Therefore, projections of altered river flows, and frequencies of extreme flow events, imply changed riverine Hg inputs to the Arctic Ocean and lakes.

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

### 4.2.3. The Arctic Ocean

In October 2009, the United Nations Environment Programme (UNEP) released an updated summary of the 2007 IPCC Assessment report (UNEP, 2009). In this Climate Change

Science Compendium, the authors warned that many of the IPCC forecasted changes were underestimated and that the scale and pace of effects such as sea level rise, ocean acidification, freshening ocean waters and sea-ice extent have and will continue to accelerate.

The extensive loss of sea ice which has occurred over recent decades is, undoubtedly, the most obvious recent change witnessed in the Arctic (Serreze et al., 2000; Stroeve et al., 2007, 2008). Between 1979 and 2006, average sea-ice extent in September (the annual sea-ice minimum) declined by about 20% or 1.60 million km$^2$, which corresponds to about 7.5% per decade (Figure 4.1). Remarkably, in September 2007, the minimum sea-ice extent reached a record low of 4.13 million km$^2$ corresponding to a 30% decrease compared to the September average for the period 1979 to 2000. In subsequent years, sea-ice extent has rebounded somewhat but the average rate of decline has reached 11.2% per decade, and average summer sea-ice cover in 2009 was over 25% below the 1979 to 2000 average (Figure 4.1). Of possibly even greater significance is the loss of multi-year (thick) ice, which provides the year-to-year resilience of the permanent pack (Giles et al., 2008; Kwok and Rothrock, 2009). The images shown in Figure 4.2 compare ice age (a proxy for ice thickness) in 2007, 2008, 2009, 2010, and the 1981 to 2000 average. The amount of multi-year Arctic sea ice in 2009 was the lowest on record even though the overall ice extent was greater than in 2007 and 2008. In autumn 2009, 32% of the ice was 2nd year ice and only 19% was 3rd year ice and older, the lowest in the satellite record (data from National Snow and Ice Data Center, http://nsidc.org/, courtesy C. Fowler and J. Maslanik, University of Colorado at Boulder). The overall mean winter thickness of the Arctic sea ice, based on submarine data, declined from about 3.6 m in 1980 to 1.9 m in 2007 (Rothrock et al., 2008). Loss of so much permanent ice moves the Arctic Ocean toward a seasonally ice-free state (Lindsay and Zhang, 2005; Maslanik et al., 2007), which will have consequences for primary production, habitat and range for large animals like bears, walrus and whales and, of course, the Arctic seas as shipping corridors between Asia and Europe. All of these factors have the potential to alter Hg concentrations and geochemistry in the Arctic Ocean and adjoining seas.

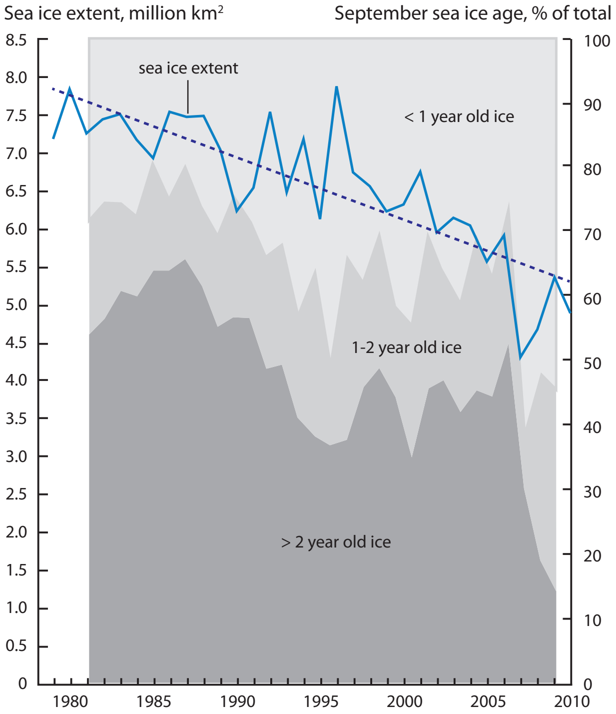

Figure 4.1. September sea-ice extent in the Arctic Ocean from 1979 to 2010. The rate of decline since September 1979 has now reached an all time high of 11.2% per decade. Source: National Snow and Ice Data Center, Colorado.

Based on the regression line shown in Figure 4.1, it can be projected that the Arctic Ocean will be ice free in summer by around 2080. Sou and Flato (2009) modeled future change in sea ice in the Canadian Arctic Archipelago and reported that, during the period 2041 to 2060, a 45% decrease may be expected in summer sea-ice concentrations relative to the period 1950 to 2004. Their model also predicted that ice thickness would decline by 36% and 17% in summer and winter, respectively. Based on the results, the authors projected that the Archipelago may be ice free in summer by about 2050.

The biogeochemical status of the Arctic Ocean itself is changing, partly due to the loss of sea ice and partly due to change in the properties of water imported from the Atlantic and Pacific Oceans, and discharge from rivers. Recently, the surface waters of the Arctic Ocean have been anomalously fresh, implying greater stratification (McPhee et al., 2009; Proshutinsky et al., 2009). The source of much of the freshening appears to be sea-ice melt, and Arctic Ocean ice shelves (i.e., the marine terminal ends of glaciers) (England et al., 2005; Mueller et al., 2008). Clearly this is not a sustainable freshening as the fresh surface water will be flushed from the Arctic Ocean within years to a decade, and eventually the supply of melting glacier and multi-year ice will run out (Lavoie et al., 2010). The general loss of ice cover within the Arctic Ocean affects wind mixing, up-welling and the light climate. Changes in these parameters then alter the spatial and temporal intensity of primary production (Carmack and Chapman, 2003; Lavoie et al., 2010), and the bacterial regeneration of organic carbon contained in sinking particles. This latter process may be important for Hg in marine food webs considering that Hg methylation is associated with regeneration (Sunderland et al., 2009) and may be a factor in the spatial variation of zooplankton MeHg concentrations within the Beaufort-Chukchi Seas (Stern and Macdonald, 2005). Presently, there are no data with which to assess the importance of these processes in the Arctic or the changes in them that are likely to be occurring.

Global ocean acidification due to anthropogenic $CO_2$ invasion is becoming a widely-recognized problem (Doney et al., 2009). From a Hg perspective, this may be a profound change because, as the oceans become more acidic and forams and other shell makers can no longer produce shells, then the transfer of carbon from the surface ocean into the deep waters, the so-called 'biological pump', will change thus affecting the cycling of Hg. Presently, it is known that the vertical flux of carbon can affect Hg cycling in two very different ways. First, like many elements, Hg is entrained into the rain of particulate organic carbon (Cossa et al., 2009) and thus Hg can be removed from the mixed layer and delivered to the deep ocean through remineralization and aggregation processes. Second, the remineralization of organic carbon at depth provides the means by which Hg can be methylated (Cossa et al., 2009; Sunderland et al., 2009), which may well

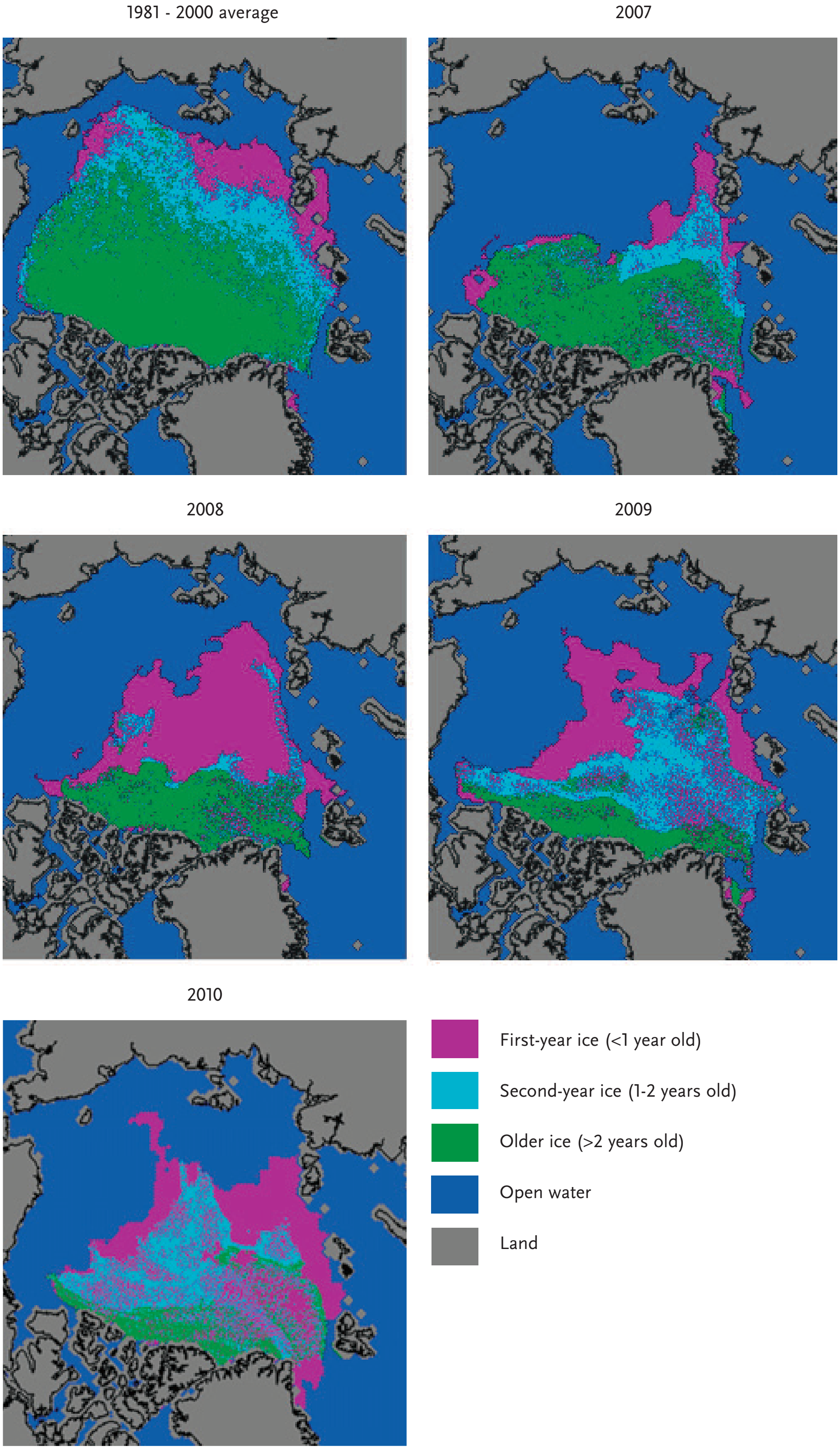

Figure 4.2. Arctic sea-ice age at the end of the melt season. Source: National Snow and Ice Data Center, courtesy of C. Fowler and J. Maslanik, University of Colorado at Boulder.

be the critical process in terms of ecosystem exposure to Hg. Low pH environments also favor the production of MeHg. The Arctic Ocean is probably particularly vulnerable because of its cold, relatively fresh surface waters (Bates and Mathis, 2009), which can take up more $CO_2$ than warmer, saltier oceans. Furthermore, the recent loss of ice cover will allow surface waters to 'catch up' with other regions through enhanced air-sea exchange because the Arctic Ocean historically has lagged behind in the uptake of anthropogenic $CO_2$ (Anderson et al., 1998; Steinacher et al., 2008). Given that climate change is reducing ice cover (increasing air-sea exchange) and increasing the primary production causing increased regeneration at depth (producing $CO_2$), accompanying pH declines can be expected. The problem of acidification is manifest in water up-welled over continental shelves (Feely et al., 2008). In the Arctic Ocean, upwelling is also likely to increase systematically in response to withdrawal of the ice edge beyond the shelf (Carmack and Chapman, 2003), thus it might be anticipated that the effects of lowered pH are first seen over the Arctic's shelves (Yamamoto-Kawai et al., 2009).

## 4.3. How do rising temperatures affect atmospheric mercury chemistry?

Mercury is transported to the Arctic from lower latitudes via atmospheric pathways largely in the form of gaseous elemental Hg (GEM, or Hg(0)). The deposition of Hg involves the chemical oxidation of GEM to the much more reactive gaseous Hg(II) compounds (RGM) and particle-bound Hg, although particle-bound Hg can also be transported from sub-Arctic sources directly. The oxidation of GEM to RGM is particularly enhanced in episodic AMDEs during polar spring (see Chapter 2). These are estimated to contribute as much as 10% to 55% of the total atmospheric Hg deposited to the Arctic annually (Ariya et al., 2004; Christensen et al., 2004; Skov et al., 2004; Outridge et al., 2008). Therefore, it is crucial to understand how climate change may affect the frequency and magnitude of AMDEs in the future in order to predict the future inputs of Hg to the Arctic.

### 4.3.1. Temperature effects on mercury oxidation reactions

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

### 4.3.2. Temperature effects on bromine generation

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

Temperature may also have indirect effects on bromine activation through changes in the Arctic cryosphere (ice and snow) (Piot and von Glasow, 2008). Frost flowers (intricate ice crystals formed on the surface of new ice) are thought to be a source of halogen-enriched aerosol (Rankin et al., 2000), and areas where they are likely to be present have been linked to high levels of BrO (Kaleschke et al., 2004). However, high BrO events at Barrow, Alaska, were not correlated with air traversing areas of potential frost flowers but rather with air that simply came into contact with first-year sea ice (Simpson et al., 2007b). Either way, if multi-year sea ice in the Arctic Ocean is being replaced by annual ice, as is suggested by decreases in multi-year ice (see Section 4.2.3), this may provide a mechanism for increased springtime reactive halogen concentrations in the near future. Finally, it also seems that reactions on snow are key to sustaining atmospheric Br levels (Simpson et al., 2005; Piot and von Glasow, 2008). Potential changes to the Arctic snowpack with temperature are likely to be region-specific and are as yet highly uncertain, as are potential impacts on air-snow chemistry. This uncertainty, coupled with the unknown relative contributions of frost flowers and first-year sea ice, makes it difficult to even qualitatively predict how rising average temperatures will impact on reactive bromine levels, and thus atmospheric Hg chemistry, in the future. Further research into the mechanism of the bromine explosion is needed, at which point a modeling study is likely to be necessary to predict the net effect of temperature changes on all the different components.

### 4.3.3. Field observations of temperature effects

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

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

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

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

There are few Arctic data directly relevant to this question, and those that do exist mainly concern the three processes discussed in the following sections (water discharge, timing of spring freshet, forest fires). However, considerations of the known interactions of the Hg cycle with other freshwater and terrestrial processes or features (such as primary productivity, soil characteristics, permafrost thaw) suggest the potential for significant future changes under a warming climate (Macdonald et al., 2005). For example, the water-column concentrations of nutrients, dissolved organic matter (DOM) and particulate organic matter (POM) in lakes and rivers are expected to increase because of greater export from watersheds (Prowse et al., 2006), partly due to higher rates of microbial decomposition in soils (Xu et al., 2009). In this context, the empirical relationship between catchment-to-lake area ratios and fish Hg levels in Arctic lakes (Gantner et al., 2010b) may be suggestive of future climate effects on Hg delivery to freshwater ecosystems. Movement of Hg from catchment soils into receiving waters has been shown to be strongly influenced by soil DOM and POM, which act as Hg carriers (Grigal, 2002; see Section 4.6.2 for more discussion on this point). Increased nutrient loading may enhance phytoplankton and algal productivity, which has been shown to affect carbon and Hg dynamics in Arctic lakes (Outridge et al., 2007; Stern et al., 2009). Warmer air temperatures have already increased the active layer depth and period in Arctic permafrost soils, thereby releasing long-retained Hg and carbon (Klaminder et al., 2008), and may tend to increase catchment geochemical weathering rates.

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

### 4.5.1. Water discharge

The Mackenzie River, Canada, has been intensively studied with respect to its Hg dynamics (Leitch et al., 2007). Water discharge has an amplifying effect on Hg flux in the Mackenzie River with particulate Hg concentrations increasing disproportionately as discharge increases (Figure 4.3a). This results in considerably greater Hg flux in high flow years; for example, a 30% increase in discharge produces almost a doubling of particulate Hg concentrations. By contrast, dissolved Hg levels are lower than particulate Hg levels and not strongly related to discharge (Figure 4.3b). The correlation between particulate Hg concentration and discharge is due to increased land inundation and bank erosion during high water level years. Therefore, changes in the average discharge or number of extreme flow events of the Mackenzie River are likely to be accompanied by a magnification of Hg flux from the Mackenzie River Basin. On average, the discharge of the Mackenzie River has been increasing at a rate of 0.6 km$^3$/y over the past 35 years (Peterson et al., 2002), which is predicted to have been accompanied by only a modest increase in Hg flux. However, the strong dependence of Hg flux on discharge indicates that increasing frequency and severity of major storm events would potentially be a more important process than variations of average discharge. The approximate 7% increase in Russian river discharge into the Arctic Ocean since the mid-1930s (Peterson and Baringer, 2009) may also have resulted in an increased Hg flux to the Arctic Ocean. However, as their sediment discharge rates are an order of magnitude less than that of the Mackenzie River (Outridge et al., 2008) a corresponding increase in Hg flux will also be less pronounced.

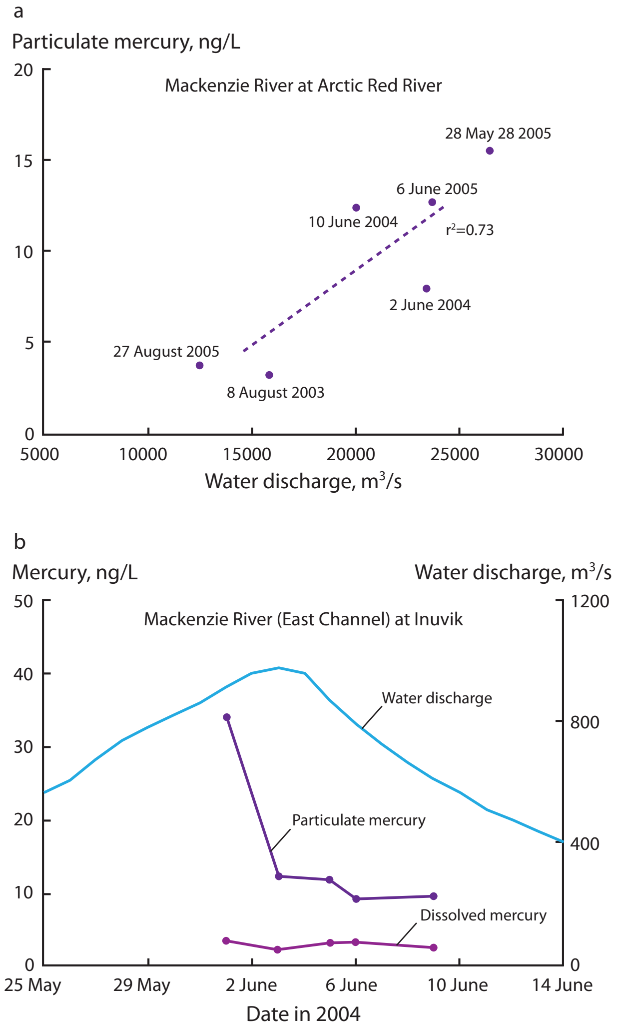

Figure 4.3. Relationship between (a) particulate mercury concentration and water discharge for the Mackenzie River at Arctic Red River, and (b) changes in particulate and dissolved mercury concentrations and water discharge for the Mackenzie River during the spring freshet 2004. Source: Leitch et al. (2007).

### 4.5.2. Timing of spring freshet

The warming of the Arctic is advancing the dates of snowmelt and spring break-up. Spring break-up on the Mackenzie River has already advanced by an average of three days per decade since 1973 (Woo and Thorne, 2003). Leitch et al. (2007) have shown that the freshet season discharges more than 50% of the total annual Hg flux from the Mackenzie River (see also Figure 4.3b). An advance in the freshet season would change the seasonal pattern of the Hg flux, and could potentially better align the peak Hg outflow timing with the season of rapid growth of marine biota in the Mackenzie Delta and Beaufort Sea.

### 4.5.3. Forest fires

Inertinitic carbon fragments (i.e., oxidized or fossilized charcoal) of forest fire origin are commonly present in sediments from the Mackenzie River (Carrie et al., 2009). Enhanced forest and ground fires are likely to be a consequence of climate change in the north partly due to desiccation and partly to increased incidence of convective storms and lightning (Kochtubajda et al., 2006; Wrona et al., 2005). Not only does fire in a drainage basin alter the flow of carbon in rivers and lakes (Czimczik et al., 2003), but it also has the consequence of releasing Hg sequestered in foliage and soil (Biswas et al., 2008). Global forest fires have been estimated to contribute in the order of 675 ± 240 t/y to the global atmosphere (Friedli et al., 2009b; see Section 2.3).

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

One of the potentially most important impacts of climate change may be on net MeHg formation in Arctic aquatic ecosystems (Outridge et al., 2008). As stated in the preceding chapters (Chapters 2 and 3), there is some uncertainty about the relative importance of the different sites, sources and processes of MeHg production generally. However, it is useful to consider general insights gleaned from research in temperate regions.

### 4.6.1. Temperature-related effects

Most of the methylation capacity linked to bacteria is found in sediments. Methylmercury production is highly correlated to bacterial activity, which in turn is generally enhanced at elevated temperatures. It is therefore not surprising that higher temperatures often promote sedimentary Hg methylation

(Bodaly et al., 1993). Usually, epilimnetic sediments produce more MeHg during warm summer months compared to colder winter months (Canário et al., 2007). However, demethylation in sediments is also clearly a microbial process, and more demethylation is expected at higher temperature. That being said, methylation rates significantly increase with rising temperatures (e.g., by 37% with a temperature increase of about 20 °C) while demethylation rates are already fairly high (often up to 80% per day) regardless of the temperature regime (Canário et al., 2007). Hence, one would expect the net methylation rate in sediments to generally increase with temperature. The impact of climate change on water column MeHg levels, however, can be unpredictable; one example results from the effect of climate-induced changes in the thermocline depths of lakes with anoxic hypolimnia. In temperate lakes, oxygen changes related to climate change may result in a depth reduction of the anoxic hypolimnion, which is critical for the overall produced mass of MeHg in seasonally anoxic lakes. As a consequence, the total mass and concentration of MeHg in epilimnetic waters, and fish MeHg concentrations, decrease because in those lakes a significant proportion of the MeHg is formed in the anoxic hypolimnion and later mobilized into the epilimnion (Rask et al., 2010; Verta et al., 2010). The effect of warmer temperatures on the thermocline depths in Arctic lakes is still uncertain. For example, Arctic lakes often lack an anoxic hypolimnion. However, inputs of more nutrients and DOC as a result of permafrost thawing in combination with stronger thermal stratification through warming of the epilimnion may allow the development of anoxia. This could cause an increase in MeHg production relative to previously completely oxic lakes.

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

As noted in Section 4.5, climate change is likely to increase the export of total Hg (Klaminder et al., 2008), DOM and nutrients from watersheds to Arctic lakes and oceans. Considering that DOM is one of the most important factors controlling the bioavailability of Hg(II) (e.g., Gorski et al., 2008; Driscoll et al., 1995), its increased export may have a profound effect on methylation rates. Dissolved organic matter appears to affect MeHg formation in at least three ways: (i) fresh DOM enhances bacterial activity, serving as an organic substrate for microbes (Hammerschmidt and Fitzgerald, 2004; Lambertsson and Nilsson, 2006); (ii) DOM is a carrier of Hg(II) (Skyllberg et al., 2003; Chadwick et al., 2006), delivering it to sites of methylation; and (iii) binding of Hg(II) and MeHg by large DOM molecules decreases Hg(II) bioavailability for methylation, and may reduce the availability of MeHg for bioaccumulation (Barkay et al., 1997; Drexel et al., 2002). However, the overall response is difficult to predict and field measurements are sometimes contradictory (Ravichandran, 2004). There is probably an optimum range of DOM concentrations, at which Hg methylation and MeHg bioavailability peak, but this level is unknown for Arctic systems. Dissolved organic matter also complexes MeHg, making it more mobile and elevating its total concentration in water (Regnell and Hammar, 2004). The relative importance of watershed inputs compared to *in situ* production depends on the specific ecosystem. The direct export of MeHg from watersheds is often only a minor contribution to MeHg in freshwater lakes, unless the watershed to lake area ratio is very large or the lake is surrounded by wetlands with direct connection to the lake. It can also be a major source for systems with relatively little *in situ* production, such as large lakes (Rolfhus et al., 2003) or the continental shelf (Hammerschmidt and Fitzgerald, 2006c; Hollweg et al., 2009). Wetlands are often a net source of MeHg and suggested to be its principal source to lakes, in particular when wetland runoff dominates the catchment hydrology (Krabbenhoft et al., 1995; Rudd, 1995; Driscoll et al., 1998; Branfireun et al., 2005; Hall et al., 2008). Arctic lakes with wetlands in their catchments would therefore be expected in general to exhibit increased concentrations of MeHg in lake water compared to those without wetlands (Loseto et al., 2004a); MeHg levels may be correlated to the wetland area in the catchment (Lindqvist et al., 1991; Porvari and Verta, 2003). Enhanced formation rates will most certainly lead to higher concentrations of standing pools of MeHg in wetlands but this will only be of importance for aquatic systems if the wetland is also hydrologically connected to a lake, that is, produced MeHg must also be mobilized and exported from the wetland (Watras et al., 2005). Otherwise, MeHg may only undergo fast internal recycling (methylation/demethylation cycle). But even if MeHg is confined to an isolated wetland, it may still expose local wildlife and biota living in the wetland to elevated concentrations of MeHg. This is of concern for Arctic freshwater ecosystems, which often serve as breeding grounds for migratory birds, possibly exposing them to harmful levels of MeHg.

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

### 4.6.3. Ice-free season length and methylation/demethylation

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

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

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

### 4.6.4. Photochemical demethylation

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

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

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

### 4.7.1. Environmental drivers and ecological responses associated with climate warming

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

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

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

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

Empirical evidence is currently lacking for interactions between climate warming and Hg bioaccumulation in Arctic freshwater food webs, with the exception of a small number of studies (see Section 4.7.2.1). In this section, potential mechanisms are presented, based on anticipated changes to food web structure and dynamics that are also key determinants of Hg bioaccumulation in fish: diet resources, growth, and ecosystem productivity. Some impacts on food webs may enhance Hg bioaccumulation while others may reduce it; the net effect is likely to vary geographically due to regional differences in the structure of aquatic food webs and their responses to environmental change.

#### 4.7.2.1. Dietary changes of fish

Change in available food for fish, such as shifts in the composition or dominance of invertebrate prey species, may affect Hg bioaccumulation in fish if these food sources have altered Hg concentrations. For example, the waterflea (*Daphnia* spp.) has elevated MeHg concentrations compared to other zooplankton species in the High Arctic, and its density in lakes is related to ecosystem productivity (Chételat and Amyot, 2009). An expansion of *Daphnia*'s distribution driven by climate warming could result in a greater transfer of Hg to fish that consume them, similar to temperate lakes where *Daphnia* are a key vector for Hg transfer in pelagic food chains (Pickhardt et al., 2002). *Daphnia* are primary consumer invertebrates that graze on algae and bacteria in the water column (Bertilsson et al., 2003), and therefore, consumption of *Daphnia* by fish could enhance their accumulation of Hg without increasing their trophic level. However, a recent comparison of Arctic char (*Salvelinus alpinus*) food webs in 18 lakes of variable productivities and species compositions along a ~20° latitudinal gradient did not find evidence for this effect (Gantner et al., 2010a). The Hg concentrations in Arctic char in southerly, more productive and diverse food webs were not greater than in the lower productivity High Arctic lakes in Nunavut.

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

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

Climate change may affect the extent to which fish feed by anadromy (Reist et al., 2006b), which could affect their exposure to and bioaccumulation of Hg. Lakes in the Canadian High Arctic support populations of anadromous and landlocked Arctic char, with lower Hg concentrations generally observed in the latter strain (Lockhart et al., 2005a, Section 6.3.6). This difference is likely to be related to the Hg content of fish diets in lakes versus the ocean, or to variable growth rates (anadromous individuals tend to grow faster). There are also other facultative anadromous species in the Arctic (e.g., Dolly Varden (*Salvelinus malma miyabei*), brown trout (*Salmo trutta morpha* sp.), brook trout (*Salvelinus fontinalis*) (Reist et al., 2006b)) for which changes in the extent of anadromous feeding could be a relevant factor in Hg bioaccumulation.

#### 4.7.2.2. Metabolic effects on fish

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

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

#### 4.7.2.3. **Bio-dilution of mercury**

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

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

Climate-driven changes in the physical environment can both directly and indirectly alter the structure and dynamics of Arctic marine food webs thereby affecting the Hg concentrations of Arctic marine species. Many of the impacts predicted for food webs and Arctic biota are associated with a reduction in sea-ice concentration and thickness, a significant feature of change and a prominent feature defining Arctic marine ecosystems (see Section 4.2.3).

Moore and Huntington (2008) developed a conceptual model which predicted the impacts of changes in sea ice on marine mammals based on the resilience of ice-obligate, ice-associated and seasonally migrant species. Ice-obligate species are defined as those that depend on sea ice as a platform for hunting, breeding and resting. Reduction in sea-ice extent, for example, will negatively affect polar bears (*Ursus maritimus*) by reducing their opportunities for using ice as a platform from which to prey on ringed seal (*Phoca hispida*), as well as by reducing the survival of the ringed seals themselves as these require sea ice for birthing. These relationships can be very dynamic as the effects of changing sea ice will impact on ecosystem structure and productivity. Similarly, effects on sea-ice associated species such as beluga (*Delphinapterus leucas*), narwhal (*Monodon monoceros*) and bowhead whales (*Balaena mysticetes*) will vary depending on their ability to adapt to ecosystem shifts. Net loss of sea ice, for example, may result in enhanced access and feeding opportunities in previously inaccessible regionally productive areas or by increased foraging opportunities on both prey produced in, or advected to their summer and autumn habitat that may alter Hg exposure. For example, a switch in the diet of polar bears from sympagic-based food webs to pelagic food webs resulted in an increase in Hg levels (Horton et al., 2010). Specific bottom-up and top-down processes (see Figure 3.6) are described in the following sections.

### 4.8.1. **Bottom-up processes: dynamics of energy flow in food webs**

Bottom-up processes are described as those which result in changes in the physical environment that will alter the onset, duration, and biomass/quantity and/or quality of primary productivity. These alterations may increase or decrease the amount of energy or carbon available for a species to grow and reproduce and sustain a food web. Overlying the direction of these processes is the potential for changes in trophic transfer of energy across space and time that can lead to food web or predator-prey mismatching. The four Arctic marine food webs described in Chapter 3 (sea ice, shelf, pelagic, benthic) do not exist independently of one another and are directly or indirectly influenced by sea ice and its role in productivity and impacts on carbon sources (Carmack et al., 2006). Thus, changes in sea ice will influence the coupling between food webs which, in turn, will alter food web structure and energy transfer up food webs. Sea ice impacts on the Arctic marine ecosystem may be driven by (i) bottom-up shifts in carbon/energy sources to food webs; (ii) changes at the species level in terms of growth rates and biomass driven by temperature and energy availability/quality; and (iii) change in food web structure and length by the removal or addition of species.

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

Table 4.1. Types of impacts on Arctic ecosystems expected as a result of bottom-up changes.

| Impact level | Impacts on marine Arctic ecosystem | Affected Hg processes |
|---|---|---|
| Source | Shifts in carbon/energy/productivity | Hg input at the bottom of the food web |
| Species | Growth rates: bio-dilution, accumulation | Bioaccumulation rates |
| Food web | Food web size (introduction or loss of species) | Extent of biomagnification |

#### 4.8.1.1. Implications of bottom-up processes on marine mercury

Mercury concentrations in the lowest levels of marine food webs, as well as food web structure, govern Hg concentrations in the higher trophic level species, principally through bioaccumulation and biomagnification processes (Cabana and Rasmussen, 1994). A warming climate will result in reductions in Arctic sea ice that will have a range of bottom-up impacts on Arctic marine food webs. Bottom up impacts will act on the productivity/energy available for food webs that parallel processes of Hg trophic transfer in food webs (Table 4.1). Methylmercury increases approximately $10^4$-fold between water and algae with increases of four to six times at each subsequent trophic level (i.e., algae to zooplankton; invertebrates to small fish; small fish to big fish; and big fish to top predators including man). Uptake is through their food with the fraction of MeHg relative to THg progressively increasing from about 1% to 10% (water to algae), to 30% (invertebrates) and ultimately to 90% in top predator fish and marine mammals (Morel et al., 1998; Lockhart et al., 2005a).

A strong understanding of ecosystem dynamics along with a baseline of Hg trends is required in order to test for climate change impacts on food web structure and Hg processes. Food web processes defining Hg levels in higher trophic species are presented in Chapter 3 and are discussed in Section 4.8.2 in connection with climate predictions.

### 4.8.2. Top down: habitat removal

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

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

#### 4.8.2.1. Implications of top-down processes on marine mercury

As described in Chapter 3, predators and other high trophic level species exert a top-down influence on food web Hg levels due to their feeding ecology and diet preferences. Social behavior such as habitat selection, dictated to some extent by size, age, sex and reproductive status (Loseto et al., 2008b) will affect dietary exposure to Hg (Loseto et al., 2008a; Gaden et al., 2009; Young et al., 2010). Although most of these studies consider predator behavior in relation to the environment and Hg body burdens only, Gaden et al. (2009) have shown the direct impacts of climate warming-induced sea ice variations on the feeding behavior, diet and thus Hg exposure of ringed seals, an upper trophic level species. Seal muscle Hg levels were found to be significantly higher during periods following relatively short and long sea-ice years, because of ice-induced changes in feeding behavior (for a case study on polar bear see Section 5.4.2, Case Study 8).

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

### 4.9.1. Potential release of mercury from melting Arctic glaciers

Glaciers and ice caps represent transient reservoirs for atmospheric contaminants, including Hg. Present-day concentrations of THg in Canadian Arctic ice caps are low, of the order of 0.5 to 2 ng/L (St. Louis et al., 2005; Zdanowicz et al., 2009; Zheng et al., 2009). Depending on the size and turnover time of glaciers, this Hg can remain trapped inside for decades to millennia before being released by melt. However as climate warms and glaciers melt, contaminants that have accumulated over decades or millennia may be prematurely released from ice, adding to contemporary fluxes to aquatic ecosystems (e.g., Blais et al., 2001).

Atmospheric Hg deposited in the past on Arctic glaciers and ice caps is only preserved in their net accumulation area, that is, the area where there is a net addition of ice every year. The net accumulation area typically represents 50% to 80% of the total area of glaciers or ice caps. Any Hg deposited outside this area, in the ablation area, is lost in melt and runoff during the same year. This is a seasonal flux that can be estimated from the concentration of Hg in runoff produced by snowmelt (St. Louis et al., 2005). However, just as in ice-free areas, Hg stored in the supra-glacial snowpack is quickly released in early melt. As summer progresses, the contribution of water from glacial ice wastage becomes larger and the flux of Hg in snow meltwater is diluted by this comparatively clean glacial water.

An anticipated effect of the current warming trend will be to increase the ablation area of circum-Arctic glaciers, leading to an overall loss of ice mass (Bahr et al., 2009) and associated Hg. This ice loss is already observable in Greenland (Abdalati and Steffen, 2001; AMAP, 2009a). However, in large polar ice caps like the Greenland Ice Sheet, only a fraction of this ice volume may contain anthropogenic Hg, and the total quantity to be released cannot simply be scaled up from the total ice wastage. Predicting the timing of Hg release from melting glaciers is equally difficult. First, the reduction in glacial volume is expected to accelerate over time as rates of meltdown increase. Furthermore, the amount of Hg released will vary over time if the concentrations are greater, for example, in deeper ice layers formed in previous decades when atmospheric Hg levels in the Arctic were higher (e.g., Boutron et al., 1998; Faïn et al., 2009b; Zheng et al., 2009). Hence, future Hg fluxes in glacial meltwater are likely to increase, before declining again. When these fluxes will attain their maxima depends on the Hg concentration depth-age profile, turnover time, and wastage rate of individual glaciers.

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

### 4.9.2. Release of mercury from thawing permafrost

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

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

A few studies have suggested that the flux of Hg released from thawing permafrost to Arctic lakes (Klaminder et al., 2008) and marine ecosystems (Leitch, 2006; Hare et al., 2008; Outridge et al., 2008) could be significant, even higher than the atmospheric depositional flux. For instance, Klaminder et al. (2008) studied Hg concentrations and fluxes in the surface active layers and sediments from a large palsa mire complex in the Stordalen valley, northern Sweden. The study sites were covered with various types of vegetation along a thermokarst erosion gradient, and results revealed that hummock peat experiencing subsidence and submergence released 40% to 95% of its Hg pool (Figure 4.4). The annual average flux of Hg released from the thawing permafrost was estimated to be about 200 $\mu g/m^2/y$ for the period 1970 to 2000, which was about an order of magnitude higher than the estimated atmospheric depositional flux in the region. The importance of THg flux from thawing coastal permafrost and erosion to the Arctic marine environment is smaller, but still significant. The flux of Hg released to the Arctic Ocean from eroding coastal permafrost was estimated to be 47 t/y (range 26 to 47 t/y), half that of the estimated atmospheric flux (Outridge et al., 2008). In Hudson Bay, the best estimate for the erosional Hg input was 0.25 t/y (range 0.25 to 0.38 t/y), compared to 1.5 t/y (range 3.4 to 13.6 t/y) from the atmosphere (Hare et al., 2008).

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

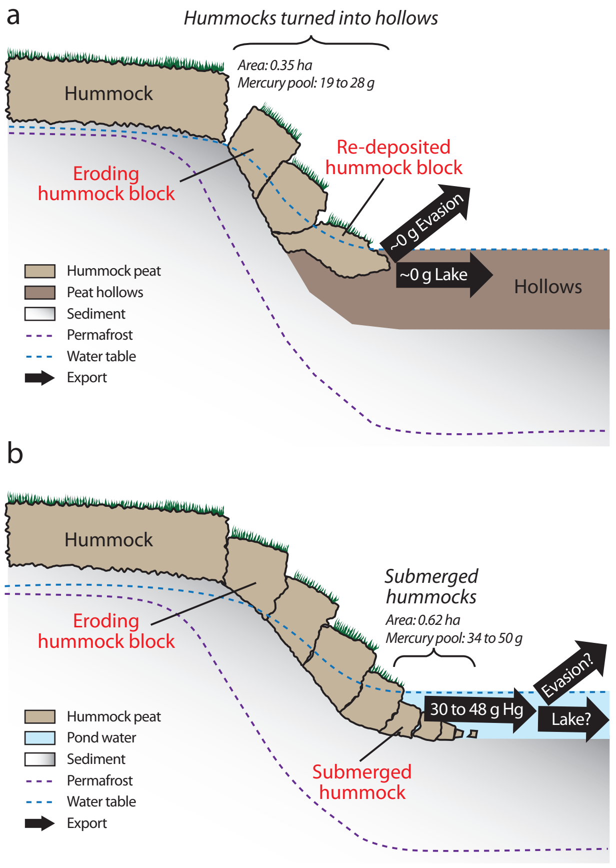

Figure 4.4. Conceptual illustration of the collapse of a hummock palsa into (a) peat hollows and (b) pond water. Text in italics indicate the areal change between 1970 and 2000 within the Stordalen palsa mire and the estimated mercury pools affected by this change. Red texts indicate eroding peat feature, and black arrows indicate the pool of mercury that is estimated to be lost over a period of a few decades. Source: Klaminder et al. (2008).

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

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

One of the key findings from these compilations was that, like global oceans in general (Mason and Sheu, 2002; Fitzgerald et al., 2007; Sunderland and Mason, 2007), Arctic marine ecosystems are currently believed to contain relatively large total (inorganic) Hg reservoirs in seawater as a result both of significant anthropogenic inputs over the past roughly 200 years as well as large naturally-occurring background Hg inventories. Furthermore, the biologically-unassimilated inorganic Hg reservoir (about 8000 t in the Arctic Ocean, 98 t in Hudson Bay) is at least two orders of magnitude greater than the small inventory contained in Arctic marine biota (comprising less than 0.1% of THg mass in the ocean and about 1% in Hudson Bay). There is no suggestion in these data that the present or future production rates and bio-uptake rates of MeHg by Arctic marine food webs are in general limited by the availability of inorganic Hg in seawater, although additional work in this area is called for. These findings also imply that if the net methylation rate in Arctic marine systems significantly increased in the future, because of climate-related or other factors, there is a potential for significantly more of the large inorganic Hg reservoir to be transferred into the more toxic and bioaccumulative MeHg form, which may translate into higher MeHg levels throughout Arctic marine food webs. However, it is presently unclear whether or by what mechanisms the increased methylation may occur.

As described earlier in this chapter, climate warming has the potential to alter the rate and geographic extent of a number of environmental, ecological and geochemical processes that can rapidly work on and transform the large abiotic inorganic Hg reservoir presently in seawater to bioavailable MeHg, or otherwise alter the capacity of food webs to assimilate MeHg. On the basis of current understanding, it is difficult to quantitatively predict which processes are likely to be most influential on future biotic Hg trends, or what the overall net effect will be. Table 4.2 qualitatively summarizes the available evidence on these questions as reviewed by earlier sections in this Chapter and provides direction for future marine Hg research priorities in this area. Possibly a modeling approach incorporating all known geophysical, biogeochemical and ecological factors may be informative. However, such an ambitious project has not yet been attempted, and would face the challenge of the presently limited understanding of some key processes and their relationship to climate factors.

Outridge et al. (2008) tentatively concluded that the overall effect of a warming Arctic Ocean may be a future slow decline in seawater THg concentrations and subsequently of marine food web Hg levels. However, recent papers by Sunderland et al. (2009) and Cossa et al. (2009), which related Hg methylation rates in seawater to marine algal organic matter productivity, suggest that a warmer and more productive Arctic Ocean may in fact lead to higher methylation rates of the available inorganic Hg in seawater, and thus to higher biotic Hg levels. Simultaneously, increased sedimentation rates associated with higher productivity may act to lower inorganic Hg concentrations in seawater (see Table 4.2).

In freshwater systems, although climate-related effects on Hg fate, methylation and bioaccumulation (e.g., Outridge et al., 2007; Chételat and Amyot, 2009; Chételat et al., 2008; Stern et al., 2009) may be at least as profound as in marine systems, there is evidence that the role of inputs from the atmosphere may be more important simply because freshwater Hg methylation rates often appear to be inorganic Hg-limited, and surface area/volume ratios (i.e., atmospheric inputs relative to volume) are higher than in marine systems. There is abundant evidence for the atmosphere's important role in temperate regions (e.g.,

Table 4.2. Summary of likely impacts of climate warming on Arctic marine biota Hg levels.

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

Source: Outridge et al. (2008), except that marine productivity increases are now believed to promote increased methylation rates and so higher biotic Hg levels (see Sunderland et al., 2009 and Cossa et al., 2009). Likely changes in most processes are summarized from ACIA (2005), for methylation and demethylation see Section 4.6. '+' indicates increases in process rates and impact on biotic Hg levels; '-' indicates decreases in rates and impacts; '±' indicates no change.

Orihel et al., 2007; Hammerschmidt and Fitzgerald, 2006b), and limited evidence from the Arctic. Methylmercury mass balance studies on a series of Alaskan lakes showed that *in situ* MeHg production (most of which occurred in sediments), was inorganic Hg-limited, thus suggesting that atmospheric Hg(II) loadings were a major controller on methylation rates (Hammerschmidt et al., 2006). The findings also highlighted the importance of Hg loading from watershed soil during summer. Therefore, climate change impacts on soil and permafrost seem highly relevant in settings like these. Photo-decomposition was the major MeHg loss process, accounting for about 75% of annual MeHg production. Climate warming is predicted to reduce photo-demethylation and enhance methylation rates due to increased organic carbon and inorganic Hg loadings from catchments, and higher temperatures and autochthonous productivity (Hammerschmidt et al., 2006).

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

## 4.11. Conclusions and recommendations

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

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

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

### How do rising temperatures affect atmospheric mercury chemistry?

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

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

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

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

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

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

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

*Additional research is warranted on this processes, as well as other processes which could be important: release of Hg, nutrients and labile carbon into lakes and the ocean as a result of thawing of permafrost soils and peatlands; the 'greening' of the Arctic tundra with grasses and woody plants which may add more carbon to aquatic systems; and altered hydrological regimes which will probably see reduced lake water levels, lower snowpacks and so reduced spring freshets.*

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

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

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

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

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

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

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

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

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

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

8. Future trends in Hg fluxes from glaciers will increase under a warming climate, before ultimately declining as archived pollutant Hg in upper ice layers is flushed out. In comparison to permafrost; however, the overall fluxes will be insignificant except possibly in ice-margin environments. Thawing permafrost is already releasing significant masses of largely inorganic Hg to lakes and the Arctic Ocean which approach or even exceed atmospheric inputs depending on the setting. Concurrent release of ancient organic

matter which may serve as a substrate and physical focus for bacterial methylation activity will increase the risk to ecosystems.

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

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

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

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

## Chapter 5

# Are Mercury Levels in Arctic Biota Increasing or Decreasing, and Why?

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## 5.1. Introduction

An analysis of the temporal trends for mercury in Arctic biota is important for scientists and managers concerned with making sound science-based policy with respect to changes in Hg in the Arctic environment. Long-term datasets (i.e., comparing modern with historical or pre-industrial Hg concentrations) can be used to estimate the relative importance of natural and anthropogenic Hg inputs in modern biota and the environment, while short-term datasets (i.e., covering the past one to three decades) illustrate how Hg concentrations have changed in recent times and suggest likely trends in the near-term future.

In the previous AMAP assessment of Hg in the Arctic environment (AMAP, 2005), evidence of increasing Hg concentrations from pre-industrial or historical to more recent times was presented for Arctic marine biota. Those trends were shown to continue in recent (short-term) datasets, primarily in higher-order marine biota from Canada and West Greenland. In contrast, time series for lower-order marine biota for Iceland and the European Arctic showed a general pattern of recently stable or declining Hg concentrations. The reasons for this spatial difference in trend patterns were not clear. Data for higher-order marine biota from Europe and Iceland were lacking as were temporal trend datasets for biota from Russia and Finland. One of the recommendations resulting from the previous AMAP assessment was that temporal trend monitoring of Hg concentrations should be continued in order to obtain longer and more statistically reliable trend analyses.

This chapter presents an update of the information available for both long-term and short-term trends, including a statistical meta-analysis of recent temporal trends in Hg concentrations in Arctic biota. The final section presents a discussion, using case studies, of the possible mechanisms driving the temporal trends observed.

## 5.2. How much higher are current mercury levels in Arctic biota than in the pre-industrial period, and thus what is the anthropogenic contribution to mercury in modern biota?

Information in this section is based on Dietz et al. (2009a).

### 5.2.1. Introduction

Although Hg is a naturally occurring element and, as such, has always been present in the environment, global human activity has led to a several-fold increase in Hg emissions to the atmosphere and inputs to oceans and rivers (Nriagu and Pacyna, 1988; Pacyna et al., 2006). In some areas of the Arctic, Hg concentrations in marine food webs have significantly increased in recent decades (Braune et al., 2005; see also Section 5.3), causing levels in some marine mammals, birds, and fish to reach the point where adverse biological effects might be expected (AMAP, 2003; see also Chapter 6). The question remains as to what extent global anthropogenic Hg emissions since the pre-industrial period have increased Hg concentrations in Arctic biota, and thus the exposure of humans who continue to use this wildlife as food. Calcified and keratinaceous hard tissues such as teeth, hair and feathers have the potential to help answer this question, because they tend to preserve well in dry, cold climates like polar regions (Outridge, 2005a) and are well represented at Arctic archeological sites and in museum collections. Also, work on laboratory and wild animal populations indicates that Hg concentrations in mammalian hair and teeth and bird feathers are correlated with the intake of organic and inorganic Hg and with organ Hg levels (Born et al., 1991; Eide and Wesenberg, 1993; Eide et al., 1995; Outridge et al., 2000; Bearhop et al., 2000a). Thus, analysis of historical and modern samples of hard tissues can be informative about the long-term changes in Hg intake and body burdens in wildlife.

The literature on this subject is not extensive. Several early studies reported data on biotic Hg concentrations spanning several centuries: in human teeth from Norway (Eide et al., 1993; Tvinnereim et al., 2000), human and seal hair from Greenland (Hansen et al., 1989), and human hair from Arctic Canada (Wheatley and Wheatley, 1988). These studies compared two time periods (pre-industrial and modern), and were based on relatively few samples; data on age and possible dietary differences between time periods were not available. More recently, Hg concentrations were examined in Greenland polar bear (*Ursus maritimus*) hair collected at intervals during the period 1892 to 2001 as well as in two pre-industrial samples dated 1300 AD from northwestern Greenland (Dietz et al., 2006a). The tooth Hg content of scores of Canadian beluga (*Delphinapterus leucas*), walrus (*Odobenus rosmarus*) and ringed seals (*Phoca hispida*) from pre-industrial, historical (19th and early to mid-20th century) and modern populations were examined by Outridge et al. (2002, 2005a, 2009), and the long-term changes were assessed within the context of animal age structure and dietary information inferred from tooth stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope data. Time trends in Hg concentrations in primary feathers of West Greenland gyrfalcons (*Falco rusticulus*), peregrine falcons (*F. peregrinus*), and white-tailed sea eagles (*Haliaeetus albicilla*) for the period 1850 to 2004 have also been reported (Dietz et al., 2006b). This section combines the various published time series to calculate the average anthropogenic contribution to present-day Hg concentrations in Arctic biota, and to determine the historical timing of any changes. Note that the modern values used are the maximum annual mean values, which generally fell within the period 1973 to 2003, for specific species and locations. The caveats for these interpretations are also discussed, especially the effects of possible changes in feeding behavior (diet and location) as extrapolated from $\delta^{13}C$ and $\delta^{15}N$ measurements, and potential contamination or loss of Hg in archaeological and museum collections of ancient biological tissues.

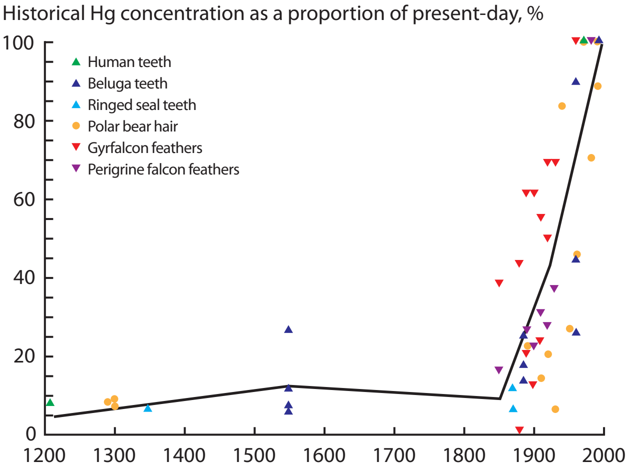


Figure 5.1. Historical trends in Hg concentration in hard tissues of various Arctic biota, expressed as a percentage of modern maximum annual average concentrations. Most points plotted represent mean values of multiple samples; for beluga and seal teeth, these are presented for different age classes (see Dietz et al., 2009a). Original data sources: beluga teeth (Outridge et al., 2002, 2005a, 2009); ringed seal teeth (Outridge et al., 2009); human teeth (Eide et al., 1993; Tvinnereim et al., 2000); polar bear hair (Wheatley and Wheatley, 1988; Dietz et al., 2006a); gyrfalcon and peregrine falcon feathers (Dietz et al., 2006b). Regions covered by these datasets include parts of the Canadian Arctic, Greenland Arctic, and northern Norway.

### 5.2.2. The anthropogenic mercury contribution in modern Arctic biota

Similar to other long-term archives such as lake sediments and peat bogs, estimating the anthropogenic Hg contribution to modern biota requires a comparison of modern Hg concentrations (Hg concentrations denoted as [Hg]) in hard tissues against those from the pre-industrial period (taken to be pre-1800 AD) in a given animal population from a defined region. The modern [Hg] increase, if any, in the population is taken to be the anthropogenic contribution, which was calculated in two ways by Dietz et al. (2009a). First, however, the published Hg data need to be represented in a consistent and comparable manner across tissues and species, because absolute concentrations in the hard tissues of various species varied by three to four orders of magnitude both in the pre- and post-industrial period (Dietz et al., 2009a). Therefore, the maximum present-day annual median concentration in each dataset was initially set to 100%, and the median historical and pre-industrial concentrations are given as percentages of the recent maximum, using the following formula:

***Historic proportion of present-day [Hg] (%) = (median historic [Hg] / median recent maximum [Hg]) × 100***

The resulting data distribution, which extends back over eight centuries, is shown in Figure 5.1.

The conversion of absolute concentrations to percentages of the modern maxima indicates a similar overall pattern across species and regions. Pre-industrial period hard tissues contained a median of 7.6% (range: 5.6% to 25.8%) of the maximum annual average Hg levels recorded for the same species in the same areas during recent decades. This finding means that, on average, 92.4% (range: 74.2% to 94.4%) of the present-day Hg in Arctic wildlife is likely to be of anthropogenic origin. This conclusion assumes that the long-term increase in Hg concentrations in Arctic biota occurred solely as a result of increased inputs of Hg from pollution sources, and that other potentially important factors such as changes in the cryosphere, biogeochemical processes or ecological factors (see Section 5.4) did not significantly affect the long-term increasing trend of biotic Hg levels. The possible effect of many of these other processes is difficult to assess within this context, first because of a lack of long-term data concerning how these processes have changed since pre-industrial times in the specific areas in which the long-term biotic studies were conducted, and second because of uncertainty as to how exactly and to what degree these types of change affect Hg levels in Arctic biota (see Chapter 4).

The possible effect of dietary changes on long-term trends in Hg concentration were assessed in beluga and ringed seal in the Canadian Arctic using stable carbon (C) and nitrogen (N) isotope data by Outridge et al. (2002, 2005a, 2009), and discussed in greater detail by Dietz et al. (2009a) (see also Section 5.2.5). Briefly, the Beaufort beluga trends (Outridge et al., 2002, 2009) were not accompanied by significant changes in C and N isotope ratios; which indicates that dietary changes do not explain the order of magnitude Hg increases in that population since pre-industrial times. The trophic position of Amundsen Gulf ringed seals, inferred from stable N isotopes, did not change over time, but feeding location inferred from stable C isotopes may have changed. $\delta^{13}C$ values in modern seals were significantly lower than in those from the 14th and 19th centuries, which could indicate a recent shift to more pelagic, offshore feeding (Outridge et al., 2009). A shift to more pelagic feeding over the centuries may have exposed the modern population to prey items with a lower average Hg content than inshore, benthic prey (Stern and Macdonald, 2005). If this was the case, then this shift would have caused the anthropogenic contribution to modern seal Hg to have been under-estimated rather than over-estimated. Section 5.2.5 includes an example in which a slight change in trophic position ($\delta^{15}N$) resulted in an over-estimate of the anthropogenic component of a central Arctic beluga population. However, there is no *a priori* reason to believe that adjustments for long-term dietary changes across the entire long-term biotic dataset, covering several species in different Arctic regions, would consistently bias the Hg trend results in one particular direction (higher or lower) compared to analyses of the unadjusted trends.

The only Arctic species studied so far that did not show a significant modern increase was walrus near Igloolik, Canada (Outridge et al., 2002). It is also the only species in this compilation which usually feeds at a very low trophic level (on clams and other bivalves). Low trophic-level species were predicted to be relatively immune to increases in environmental Hg levels compared to higher trophic-level species, because biomagnification would have little effect on Hg concentrations in these species or their prey in response to elevated environmental levels (Bernhard and Andreae, 1984). The results reported here support this prediction and so the walrus data were not included in the above calculations.

Although there are no long-term studies close to developed areas of the world, recent findings from Antarctica indicate that both the Arctic and the Antarctic have experienced significant increases in biotic Hg levels since the Industrial Revolution, with the increases in Antarctic biota markedly less than those in the Arctic. Hair of southern elephant seal (*Mirounga leonine*) retrieved from an Antarctic lake sediment core displayed considerable variation in [Hg] in the pre-industrial period (Sun et al., 2006). However, the minimum values (~ 1 µg/g) were on average about 60% of those in the uppermost sediment layer (1.7 µg/g), which would suggest an anthropogenic contribution of about 40% in modern elephant seals.

The long-term increases found by Hansen et al. (1989) in seal and human hair between 15th century Qilakitsoq Inuit mummies and 1970 were less pronounced (pre-industrial levels 23.1% of present [4.3-fold increase] and 31.6% [3.2-fold increase], respectively) than the above studies. Likewise, Wheatley and Wheatley (1988) reported that modern Hg levels in human hair from the Canadian Arctic were only several times higher than in pre-industrial samples. Both studies were excluded from the calculations above, but the effect was minimal; including these datasets would have only increased the median pre-industrial baseline value to 12.6% from 7.6% (with a resulting anthropogenic contribution of 87.4%). They were excluded because of the possibility of confounding factors which may have decreased the calculated anthropogenic component in the samples. A lower intake of high trophic-level marine foods by present-day Inuit compared to their forebears could explain the lower than expected modern increase in hair Hg (see Kinghorn et al., 2006). Also, modern hunting pressures may have significantly reduced the average age of harvested seals (and other human food items) compared to historic times when hunting pressure was presumably lower (R. Dietz, National Environmental Research Institute, Denmark, unpubl. data). This would have tended to reduce the Hg increases in harvested seal hair and the modern human Hg intake from those seals (as well as Hg levels in modern human hair). To what extent diagenetic contamination could have increased the historic hair Hg concentrations is difficult to assess, although the fact that the Qilakitsoq mummies and their clothing were lying on dry rock and not in soil (Hansen et al., 1989) may make it unlikely. Alternatively, the ancient light and heating technique of burning blubber oil lamps in small enclosed spaces may have created a substantial external Hg contamination of the hair of the Inuit and their seal-skin clothing which resulted in higher than normal, and inaccurate, hair Hg concentrations.

### 5.2.3. Timing of mercury increases over the past 150 years

Dietz et al. (2009a) used two separate calculations of the long-term change in the anthropogenic Hg component in Arctic biota. While both formulas agreed on the average input in modern biota (i.e., 92.4%), there were subtle differences in the rate of change between 1850 and recent decades. However, these differences are minor and do not detract from the overall picture. As is clear from Figure 5.2, both measures indicated that the 20th century showed a steep increase in biotic Hg compared to relatively constant values over the previous four to six centuries. As no Hg data were available from the period between the 16th century and about 1850, it is not possible to precisely identify the onset of the steep industrial era increase. However, based on the shape of the curves, it seems plausible that Hg started to increase somewhere between 1850 and 1900, with a clear acceleration in the rate of increase after 1900. The overall pattern is clearly seen in several individual studies. When assessing the temporal trends for two adjacent and complementary datasets – beluga in the Beaufort Sea and ringed seal in the Amundsen Gulf – Outridge et al. (2009) concluded that Hg levels in marine biota in this region had

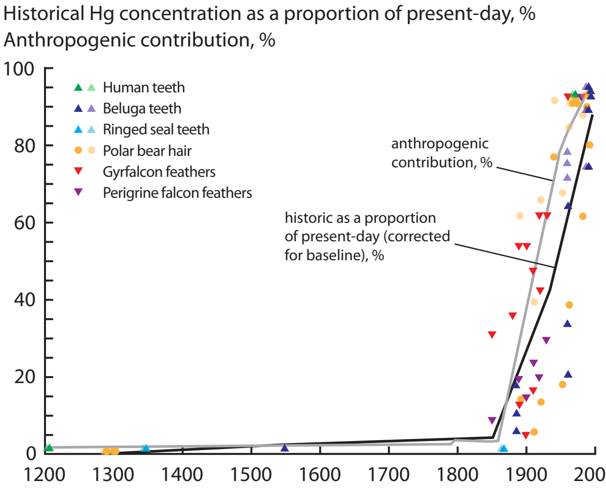


Figure 5.2. Change in the anthropogenic contribution to Hg levels in Arctic biota since the pre-industrial period, calculated from the data presented in Figure 5.1. The figure shows the historic proportion of the present level corrected for the baseline percentage (black line and darker symbols) and the percentage contribution of anthropogenically-derived Hg (grey line and lighter symbols). See Dietz et al. (2009a) for details.

not increased from pre-industrial times up to at least the late 19th century, with the most substantial increases occurring between then and 1960/61. Beluga teeth collected around Somerset Island during 1894 to 1998 showed Hg increases of 4.1- to 7.7-fold overall, but with no change between the late 19th century and the 1920s to 1940s, indicating that most or all of the increase has taken place after the early 20th century (Outridge et al., 2005a). Similarly, Hg trends in polar bear hair from eastern and northwestern Greenland displayed minimal increases until as late as 1950 (Dietz et al., 2006a). However, Hg trends in Greenlandic birds of prey since the 1850s (Dietz et al., 2006b) generally increased earlier and more rapidly than the previously discussed marine mammal datasets. As the bird species exploited a mixed terrestrial and aquatic food chain, the dichotomy between species with different food-chain bases suggests the possibility of systematic differences between marine- and land-based food webs in terms of the immediacy and effectiveness of atmospheric Hg deposition as a rapid forcer of biological Hg trends (Outridge et al., 2009).

The average rate of Hg increase over the past 150 years was usually within the range of 1% to 4% per year, based on linear regressions of tissue Hg concentration versus time. Polar bear hair showed a significant average 2.1% per year increase in Hg concentration from 1920 to 1991 in northwestern Greenland, and a 3.1% per year increase in the period 1892 to 1973 in northeastern Greenland (Dietz et al., 2006a). Mercury in primary feathers of western Greenland gyrfalcons, peregrine falcons, and white-tailed sea eagles from the period 1880 to 1935 showed average increases in the range 1.1% to 4.5% per year, whereas for 1880 to 1960 the average increase was slower, at 0.4% to 0.9% per year (Dietz et al., 2006b).

### 5.2.4. Preservation of the original mercury concentration in pre-industrial samples

Pre-industrial samples were invariably retrieved from archaeological sites, and both pre-industrial and historical era specimens were often stored for many decades in museums or other facilities prior to their recent analysis, sometimes open to the ambient air or in poorly-sealed bags and boxes. Archaeological material, which may have been in contact with soil, sediment or moisture for extended periods, can potentially experience physical, chemical or biochemical changes ('diagenesis'; Jackson, 1997) that may increase or decrease the original biogenic Hg concentration. Two additional preservation issues are: exposure to inorganic Hg contamination in museums which employed elemental Hg sublimate as a fungicide, and possible Hg volatilization from specimens over long periods at typical Arctic soil temperatures. The consequences of diagenesis and inadequate preservation can be bi-directional: either over-estimation of the modern increase and thus the anthropogenic contribution (i.e., when Hg was lost from the historical material) or under-estimation (when Hg contamination occurred). Outridge (2005a) and Dietz et al. (2009a) addressed these issues in detail. This section briefly reviews the evidence for the stability of Hg in the bioarchives included in this review.

Empirical evidence for the stability of Hg in hard tissues over any time span is very limited. However, Dietz et al. (2009a) concluded that over-estimation of the anthropogenic component in modern biota (because of losses of Hg from historical material) was extremely unlikely. Keratin-based samples such as hair and feathers exhibit surprising resistance to Hg loss. After up to eight months exposure to various harsh treatments including continuous ultraviolet (UV) light, heating to 100 °C, *in situ* exposure at various northern sites, and freezing, bird feathers lost less than 10% of their Hg content (Appelquist et al., 1984). Tanning of skins significantly alters the inorganic Hg and methylmercury (MeHg) content of hair (Newman et al., 2005), but none of the datasets included here used tanned skins.

Two alternative tests for the effect of diagenetic alteration of Hg in hard tissues were proposed by Outridge (2005a): evaluation of hard tissue Hg–age relationships, and of C:N concentration ratios. The first test is based on the premise that Hg concentrations in modern animal hard tissues are almost universally correlated with age. If diagenesis was absent in a historical group of samples, then a significant tissue Hg–age correlation should also be found in the group. However, if diagenetic alteration of tissue Hg levels had occurred, then the measured Hg values in the historical group should not be correlated with animal age. This test assumes that sample diagenesis or Hg volatilization from samples is independent of the original Hg concentration. This assumption is reasonable because elemental Hg(0), which is the only Hg form exhibiting marked volatilization at normal environmental temperatures, does not occur in significant quantities in biological tissues because of its rapid biological reactivity. Methylmercury, a non-volatile Hg species, dominates in hair and feathers (Bearhop et al., 2000b; FAO/WHO, 2003), and may also in teeth (Eide et al., 1994). When this test was applied (i.e., in the beluga tooth studies by Outridge et al. 2002, 2005a, 2009), significant tooth Hg–age regressions were found in pre-industrial or historical groups, suggesting that the baseline beluga Hg data were reliable. Mercury levels in the pre-industrial and 19th century ringed seal teeth studied by Outridge et al. (2009) were below detection, thus invalidating this test. However, the second test involving elemental C:N concentration ratios can be applied in cases like this. This test is based on the preferential metabolism by bacteria of carbon over nitrogen during diagenetic alteration of ancient calcified material, which results in a decrease of C:N values (DeNiro, 1985). In historical Somerset Island beluga teeth (Outridge et al., 2005a), no evidence of diagenetic alteration was found; C:N ratios were virtually identical between modern (3.1 ± 0.1) and historical (3.3 ± 0.1) samples. Similarly good preservation of ringed seal teeth was reported by Outridge et al. (2009), with 14th and 19th century samples having C:N values (3.2 ± 0.06 and 3.2 ± 0.02, respectively) similar to modern teeth (3.2 ± 0.06; 1-way ANOVA $p > 0.10$).

### 5.2.5. Using stable carbon and nitrogen isotopes in long-term trend studies

Another factor which could influence the interpretation of long-term biotic Hg trends is the possibility that feeding behavior (dietary trophic level and location) of the animal population changed significantly during the study period. One means of assessing this possibility, and of correcting [Hg] for any changes, involves the concurrent measurement of different stable isotopes along with Hg concentrations in animal hard tissues.

Food web stable isotope measurements, especially using stable isotope assays of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$), can provide a time-integrated assessment of the source of feeding and relative trophic level of animals, respectively. Since source of feeding determines the exposure of organisms to Hg, and trophic level influences the degree of bioaccumulation or biomagnification of Hg in an organism's tissues, stable isotope measurements can assist in the interpretation of trend data to a degree previously unavailable, by ruling out the possibility of, or correcting for, concomitant changes in population feeding behavior (e.g., Braune et al., 2001, 2002; Outridge et al., 2002, 2005a, 2009). This is especially true for organisms which can markedly alter their trophic level or migratory or feeding origin. An in-depth discussion of the application of stable isotope systems to contaminant trend interpretation is provided by Dietz et al. (2009a). As discussed in Section 5.2.2, most of the beluga and seal long-term datasets were either not accompanied by dietary changes, or evidenced dietary changes which would, if anything, result in an under-estimation of the anthropogenic input.

As an example of how a relatively subtle shift in trophic position over the long term can result in over-estimation of the anthropogenic component, the paper by Outridge et al. (2005a) which reported historical changes in Hg levels in teeth of beluga at Somerset Island, Northwest Territories, Canada was revisited. That study determined that tooth Hg levels increased with age for both late 19th century and mid-1990s animals but that this relationship was much more pronounced in the modern animals ($r^2 = 0.63$ *vs* 0.17). Tooth $\delta^{15}N$ values of modern animals were slightly higher than those of historical samples (18.5 ± 0.4‰ *vs* 17.8 ± 1.3‰). This corresponds to a mean trophic level increase of 0.18 (using the trophic enrichment value of 3.8‰ for Arctic marine food webs, see Campbell et al., 2005). Although it is not clearly understood how changes in the mean trophic level of beluga alters its average Hg content, Loseto (2007) estimated a total Hg (THg) biomagnification factor (BMF) of 12.8 to 16.0 for beluga feeding primarily on a fish diet. Thus, a trophic increase over time of 0.18 should correspond to a correction (subtraction) of the Hg increase from the 1890s to 1990s of about 2.2 to 2.9 (i.e., 0.18 times the BMF of 12.8 to 16.0). Using an average correction factor of 2.5, corrected [Hg] increases in Somerset beluga teeth from the 1890s to the 1990s ranged from a factor of 1.6 in younger animals to 5.2 in older animals, which are smaller than indicated by the isotopically-uncorrected data (Table 5.1). Corrections like these rely on assumptions including no temporal variation in food web stable isotopic values.

Changes in food web $\delta^{13}C$ values can occur due to changes in nutrients available to primary producers or other factors influencing plant growth rates (e.g., Laws et al., 1995). Another factor of interest regarding $\delta^{13}C$ is the isotopic change in atmospheric carbon dioxide ($CO_2$) that has occurred due to anthropogenic burning of fossil fuels. Normalizing terrestrial or freshwater food webs for this effect is relatively straightforward due to the well-mixed atmosphere and fast equilibrium with lakes (e.g., Bada et al., 1990). However, it has proven to be much more difficult to predict the consequences of this effect in the world's oceans (but see Hilton et al., 2006). This phenomenon, known as the 'Seuss effect' (Quay et al., 1992), is complicated because of the differential effects of deep ocean upwelling and mixing processes that may not be in equilibrium with atmospheric $CO_2$. Certainly at high latitudes, upwelling and lack of mixing may depress the Seuss effect in marine biota (Schell, 2000; but see Cullen et al., 2001). Recently, based on a long-term isotopic record of teeth from northern fur seals (*Callorhinus ursinus*), Newsome et al. (2007) provided more convincing evidence that the Seuss effect has been responsible for decreases in $\delta^{13}C$ of animal tissues over that period. However, unlike the model used to correct for trophic level changes using $\delta^{15}N$ measurements, quantitative corrections to Hg trends using $\delta^{13}C$ values are not yet possible because it is not known how Hg levels vary across a benthic-to-pelagic gradient of beluga prey. Better use of $\delta^{13}C$ values in future studies of Hg trends will be possible when the isotopic and Hg benthic-pelagic effect is better described for areas of interest (e.g., Stern and Macdonald, 2005; Loseto, 2007; Loseto et al., 2008a).

## 5.3. In which areas and species have mercury levels recently increased or decreased?

In the previous AMAP Hg assessment (AMAP, 2005), compelling evidence was presented for increasing trends in Hg concentration in recent decades, primarily for marine birds and mammals from the Canadian and West Greenland Arctic. In contrast, Hg concentrations in the European Arctic in lower-order marine biota and terrestrial mammals were either stable or declining. Furthermore, based on the analysis of 42 datasets with 4 to 29 years of data for Hg in Arctic biota, Bignert et al. (2004) concluded that only 10% of the 42 time series were 'adequate' with respect to the number of years of data required to meet reasonable standards of statistical power. For this assessment, a review of Hg trends reported in the recent literature was undertaken followed by an updated meta-analysis of time-series datasets for Hg concentrations in Arctic biota.

Table 5.1. Changes in geometric mean mercury concentrations in teeth of beluga at Somerset Island, Northwest Territories, Canada between the late 19th century and the 1990s, with and without normalization using $\delta^{15}N$ values. The analysis is based on data provided by Outridge et al. (2005a), except that the ages have been doubled because of a change in beluga ageing technique (Stewart et al., 2006). The assumed increase in beluga mercury concentration and trophic level was a factor of 12.8 to 16 based on Loseto (2007).

| Sample | [Hg] 19th century, ng/g dw | [Hg] 1990s, ng/g dw | Uncorrected factor increase | Corrected factor increase |
|---|---|---|---|---|
| 10y old | 6.6 | 26.8 | 4.1 | 1.2 – 1.9 |
| 20y old | 13.4 | 78.4 | 5.9 | 3.0 – 3.7 |
| 30y old | 23.0 | 178 | 7.7 | 4.8 – 5.5 |

### 5.3.1. Selection of tissues and chemical forms of mercury for monitoring

The chemical form of Hg and the tissues in which it is measured varies among monitoring programs. The most bioavailable and toxic form of Hg is MeHg (Wiener et al., 2003). In seabirds, concentrations of MeHg appear to be less variable across tissues than THg with a rank order of MeHg concentrations in various tissues as follows: liver > kidney > muscle (Kim et al., 1996). The rank order for concentrations of THg across tissues seems to be similar for marine mammals: liver > kidney > muscle > *muktuk* (Lockhart et al., 2005b) or in the case of polar bear: kidney > liver > muscle > adipose (Dietz et al., 1995, 2000a). In birds, nearly 100% of the Hg transferred by breeding female birds to their eggs is in the form of MeHg (Wiener et al., 2003), making eggs a valuable, non-intrusive monitoring matrix for Hg. However, interpretation of Hg concentrations measured in biota is a complex issue requiring an understanding of sources and chemical forms of Hg in the environment, food web biomagnification, and animal physiology. For a detailed discussion of these factors, see Chapter 3.

It has been shown that the percentage of THg present as MeHg in liver decreases as concentrations of THg increase in some higher trophic-level species (Dietz et al., 1990). This has also been documented for seabird liver (Kim et al., 1996). This may be due, in part, to the capability of some seabirds, as well as marine mammals, to demethylate MeHg into tiemanite in the liver (Dietz et al., 1990; Wagemann et al., 1998; Chapter 6). Given this potential for changing concentrations of MeHg in some tissues, it is perhaps best to monitor concentrations of THg rather than MeHg for tracking environmental trends.

### 5.3.2. Mercury trends in the recent literature

A summary of recently published temporal trends in THg in Arctic biota is presented in Table 5.2. The literature contains many datasets which include only two or three years of data. This table includes only those datasets with at least three years of data. The majority of such datasets were from Canada and Greenland with only one dataset from Alaska, three from Norway, and four from the Faroe Islands.

Table 5.2 includes datasets ranging from 3 to 14 years of data and covering variable time periods between 1973 and 2007. Of the four published time series for terrestrial biota, two showed a decreasing Hg trend and two showed no change. All except one of the recently published time series for freshwater fish were from Canada. Of the 18 datasets reported for freshwater fish, none were significant; one showed a non-significant increasing trend, three showed a decreasing tendency, and 14 showed no trends at all. However, of 167 short time series for

Table 5.2. Summary of temporal trends for total mercury in Arctic biota from the recent literature.

| Area | Species[a] | Tissue | Period (n)[b] | Trend | Trend significance according to author[c] | |
|---|---|---|---|---|---|---|
| **Terrestrial** | | | | | | |
| Faroe Islands | Mountain hare | liver | 1997-2006 (5) | → | Ns | Hoydal and Dam, 2009 |
| Central West Greenland | Caribou | liver | 1995-1999 (4) | → | Ns | Rigét et al., 2004 |
| Yukon, Canada | Caribou | kidney | 1994-2003 (10) | ↓ | * | Gamberg et al., 2005 |
| Yukon, Canada | Moose | kidney | 1994-2003 (10) | ↓ | * | Gamberg et al., 2005 |
| **Freshwater** | | | | | | |
| Lake Á Mýrunum, Faroe Islands | Arctic char (landlocked) | muscle | 2002-2007 (3) | → | Ns | Hoydal and Dam, 2009 |
| Lake Hazen, Canada | Arctic char (landlocked) | muscle | 1990-2006 (7) | → | Ns | Gantner et al., 2009 |
| Amituk Lake, Canada | Arctic char (landlocked) | muscle | 1989-2003 (5) | → | Ns | Muir et al., 2005 |
| Char Lake, Canada | Arctic char (landlocked) | muscle | 1993-2003 (5) | → | Ns | Muir et al., 2005 |
| Resolute Lake, Canada | Arctic char (landlocked) | muscle | 1993-2003 (7) | → | Ns | Muir et al., 2005 |
| Lac Ste. Therese, Canada | Lake trout | muscle | 1980-2002 (4) | → | Ns | Evans et al., 2005a |
| Lac Ste. Therese, Canada | Walleye | muscle | 1975-2002 (5) | → | Ns | Evans et al., 2005a |
| Lac Ste. Therese, Canada | Pike | muscle | 1980-2002 (4) | → | Ns | Evans et al., 2005a |
| Lac Ste. Therese, Canada | Whitefish | muscle | 1992-2002 (3) | → | Ns | Evans et al., 2005a |
| Mackenzie River, Canada | Burbot (males) | muscle | 1985-2001 (6) | ↑ | Ns | Evans et al., 2005a |
| Mackenzie River, Canada | Burbot (females) | muscle | 1985-2001 (6) | → | Ns | Evans et al., 2005a |
| Great Slave Lake, Canada | Pike | muscle | 1976-2002 (12) | → | Ns | Evans et al., 2005a |
| Great Slave Lake, Canada | Lake trout | muscle | 1979-2002 (9) | → | Ns | Evans et al., 2005a |
| Great Slave Lake, Canada | Burbot | muscle | 1975-2002 (10) | → | Ns | Evans et al., 2005a |
| Slave River, Canada | Burbot | muscle | 1991-2002 (8) | → | Ns | Evans et al., 2005a |
| Lake Laberge, Canada | Lake trout | muscle | 1993-2002 (6) | ↓ | Ns | Evans et al., 2005a |
| Kusawa Lake, Canada | Lake trout | muscle | 1993-2002 (4) | ↓ | Ns | Evans et al., 2005a |
| Quiet Lake, Canada | Lake trout | muscle | 1992-2002 (4) | ↓ | Ns | Evans et al., 2005a |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Marine** | | | | | | |
| Northwest Greenland | Shorthorn sculpin (large) | liver | 1987-2004 (4) | → | Ns | Rigét et al., 2007 |
| Central West Greenland | Shorthorn sculpin (small) | liver | 1994-2002 (5) | → | Ns | Rigét et al., 2007 |
| Central West Greenland | Shorthorn sculpin (large) | liver | 1994-2004 (7) | → | Ns | Rigét et al., 2007 |
| Northern Norway | Herring gull | egg | 1983-2003 (3) | → | Ns | Helgason et al., 2008 |
| Northern Norway | Atlantic puffin | egg | 1983-2003 (3) | → | Ns | Helgason et al., 2008 |
| Northern Norway | Black-legged kittiwake | egg | 1983-2003 (3) | → | Ns | Helgason et al., 2008 |
| Koltur, Faroe Islands | Black guillemot | egg | 1999-2006 (6) | → | Ns | Hoydal and Dam, 2009 |
| Skúvoy, Faroe Islands | Black guillemot | egg | 1999-2006 (6) | ↑ | Ns | Hoydal and Dam, 2009 |
| Seymour Island, Canada | Ivory gull | egg | 1976-2004 (3) | ↑ | Ns | Braune et al., 2006 |
| Lancaster Sound, Canada | Thick-billed murre | egg | 1975-2003 (8) | ↑ | * | Braune, 2007 |
| Lancaster Sound, Canada | Northern fulmar | egg | 1975-2003 (7) | ↑ | * | Braune, 2007 |
| Lancaster Sound, Canada | Black-legged kittiwake | egg | 1975-2003 (6) | → | Ns | Braune, 2007 |
| Northwest Greenland | Walrus | liver | 1977-2003 (7) | → | Ns | Rigét et al., 2007 |
| Northwest Greenland | Ringed seal | liver | 1984-2004 (5) | ↑ | Ns | Rigét et al., 2007 |
| Central West Greenland | Ringed seal | liver | 1994-2004 (7) | → | Ns | Rigét et al., 2007 |
| Central West Greenland | Ringed seal | liver | 1999-2004 (6) | ↑ | * | Rigét et al., 2007 |
| Hudson Strait, Canada | Ringed seal | liver | 1989-2002 (4) | ↑ | Ns | Braune et al., 2005 |
| Ungava Bay, Canada | Ringed seal | liver | 1989-2002 (3) | ↓ | Ns | Braune et al., 2005 |
| Qausuittuq, Canada | Ringed seal | liver | 1976-2000 (3) | ↓ | Ns | Braune et al., 2005 |
| Ulukhaktok, Canada | Ringed seal | muscle | 1973-2007 (10) | → | Ns | Gaden et al., 2009 |
| Faroe Islands | Pilot whale | muscle | 2001-2007 (6) | → | Ns | Hoydal and Dam, 2009 |
| Mackenzie Delta, Canada | Beluga | liver | 1981-2002 (8) | ↑ | Ns | Lockhart et al., 2005b |
| Pangnirtung, Canada | Beluga | liver | 1984-2002 (5) | → | Ns | Lockhart et al., 2005b |
| Coral Harbour, Canada | Beluga | liver | 1993-2000 (3) | → | Ns | Lockhart et al., 2005b |
| Lake Harbour, Canada | Beluga | liver | 1994-2001 (3) | → | Ns | Lockhart et al., 2005b |
| Central East Greenland | Polar bear | liver | 1983-2000 (9) | → | Ns | Rigét et al., 2004 |
| Central East Greenland | Polar bear | hair | 1973-2001 (14) | ↓ | * | Dietz et al., 2006a |
| Canada | Polar bear | liver | 1982-2002 (3) | ↑ | Ns | Rush et al., 2008 |
| Alaska | Polar bear | liver | 1993-2002 (8) | ↓ | Ns | Kannan et al., 2007 |

[a] Mountain hare (*Lepus timidus*); caribou (*Rangifer tarandus*); moose (*Alces alces*); Arctic char (*Salvelinus alpinus*); lake trout (*Salvelinus namaycush*); walleye (*Stizostedion vitreum*); pike (*Esox lucius*); whitefish (*Coregonus clupeaformis*); burbot (*Lota lota*); shorthorn sculpin (*Myoxocephalus scorpius*); herring gull (*Larus argentatus*); Atlantic puffin (*Fratercula arctica*); black-legged kittiwake (*Rissa tridactyla*); black guillemot (*Cepphus grylle*); ivory gull (*Pagophila eburnea*); thick-billed murre (*Uria lomvia*); northern fulmar (*Fulmarus glacialis*); walrus (*Odobenus rosmarus*); ringed seal (*Phoca hispida*); pilot whale (*Globicephala melas*); beluga (*Delphinapterus leucas*); polar bear (*Ursus maritimus*); [b] 'n' represents number of sample years during time period; [c] statistically significant (*) and non-significant (Ns) time trends.

fish from 45 Canadian lakes and rivers covering variable periods between 1971 and 2002, and which had been measured for Hg on more than one occasion, 34 comparisons (20%) suggested that Hg levels had increased while 22 (13%) indicated decreases when two years were compared (Lockhart et al., 2005a). The majority showed no statistically significant changes with time. The highest number of increasing trends in Hg concentration was seen in marine biota. Of the 29 datasets reported in the literature for the marine environment, nine (31%) suggested increasing trends (only three of those were significant), and only four (14%) showed decreasing concentrations (one was significant). The other 16 (55%) datasets showed no trend.

The following section presents the results of an updated meta-analysis of available time series datasets. Some of the datasets included in the meta-analysis are based on the datasets presented in Table 5.2 which have been updated with more recent data. In some cases, data subsets have been created for analysis based on size, age, or sex. Inclusion / exclusion of co-variables may also differ between the published Hg trends and the meta-analysis presented here. The objective was to analyze Hg time-series datasets in a consistent and comparable manner.

### 5.3.3. Meta-analysis of recent temporal trends of mercury in Arctic biota

The present 'meta-analysis' of recent temporal trends in Hg concentration in Arctic biota is a part of the AMAP Hg assessment process. Previous temporal trend workshops were held in Copenhagen in 2001 and Stockholm in 2006 (see AMAP, 2007).

### 5.3.3.1. Available data

At the AMAP Mercury Expert Group meeting held in Quebec City in December 2008, it was decided that only time series with at least six years of data, and including years both before and after 2000, be included in the meta-analysis of temporal trends. The inclusion of pre-2000 data was intended to ensure that the time series were representative of a time period sufficiently long to detect any change. A total of 83 time series fulfilling these requirements were available as follows: Canada (30), Faroe Islands (7), Denmark (Greenland) (15), Iceland (15), Norway (9), Sweden (6), and the United States (Alaska) (1). The datasets included time series of Hg levels in various tissues and organs of a range of species (including shellfish, freshwater and marine fish, marine mammals, terrestrial mammals, and seabirds). In a few cases, Hg was analyzed in different tissues or organs of the same animals and these were treated as separate time series. No time series were available from Russia or Finland, and so the geographical coverage was essentially semi-circumpolar. The time series covered periods ranging from 7 to 38 years (average time span 17.3 years), with data available for an average of 11.0 years. However, within this overall pattern, datasets were generally characterized either by series based on annual sampling, or by non-contiguous series of samples representing different time periods with gaps of several years between them.

### 5.3.3.2. Statistical application

The statistical application used was PIA developed by Anders Bignert – a custom application based on Fortran code and developed to run on Windows systems. A 'PIA distribution package' (a zip file containing the program, documentation and examples) is available on the public area of the AMAP website (www.amap.no).

The PIA application applies a trend assessment on 'index values' (by default, the annual geometric mean concentration) for each data year and employs a running-mean smoother (default, 3 years) to test for non-linear trend components (as described by Bignert, 2001 and Bignert et al., 2004). The application can also analyze trends in concentrations adjusted for a single selected covariate. In addition to the statistical results, the application output includes a trend plot and a simplified 'trend interpretation'. A directive file specifies options for the analysis to be conducted, including options to vary the power and alpha values used in the statistical tests, and to apply an analysis based on median or geometric mean index values. The categorization of trends by the software is based on a robust regression-based analysis to detect trends, described in detail by Nicholson et al. (1998), as well as an ordinary log-linear regression. The two methods differ slightly when testing for a log-linear trend component and, in a few cases, these results conflicted (one showed a *p*-value just below and the other just above 5%). In these few cases, the ultimate trend evaluation was based on closer examination of the detailed results, such as how well the smoother described the trend compared to a log-linear regression (comparing the standard deviation of the residuals from the two trend lines), and visual inspection of the PIA trend plot to check for dubious points.

### 5.3.3.3. Trend analyses

At the AMAP Mercury Expert Group meeting held in Quebec City in December 2008, it was decided that the trend analyses should be run using annual geometric means and the 3-year running-mean smoother. However, in two cases, annual median values were applied instead because of the occurrence of several data points below the analytical detection limit. Medians are less influenced than means by the assumptions necessary to deal with below detection values.

It was the intention of this exercise to perform the temporal trend analyses in as consistent a manner as the available data allowed. However, the data providers are the scientists most familiar with their data, and their advice for treatment of covariates and the basis of concentrations (wet weight or dry weight) has been followed. During the AMAP Workshop on Statistical Analysis of Temporal Trends of Mercury in Arctic Biota held in November 2006, valuable experience was gained in making adjustments for covariates in trend analyses of Arctic Hg time series. Results from the workshop (AMAP, 2007) demonstrated that age and length or weight were powerful covariates, and the data runs also indicated the need to transform Hg data (e.g., using log transformations) prior to conducting trend analysis. Stable isotope values ($\delta^{13}C$, $\delta^{15}N$) can also be used to adjust Hg concentrations for species known to undergo shifts in diet (see Chapter 3). However, stable isotope values were not included as a covariate in the statistical analyses; rather they were used prior to PIA analysis to group some populations into sub-groups according to feeding behavior.

### 5.3.3.4. Data adjustment for covariables

The procedures of data adjustment for covariates used in this assessment are described here. Time-series of Hg in blue mussels (Iceland and Norway) involved the collection of animals in specific length / weight classes; additionally, the limited size ranges available made it difficult to establish relationships between the covariates and Hg concentrations. For these reasons, no adjustment for biological covariates in these samples was performed. Furthermore, the trend analyses were carried out using dry weight concentrations to address potential problems related to variable water content.

It is well known that Hg concentrations in fish muscle (freshwater and marine) are related to the size of the fish (AMAP, 1998). Therefore, most of the fish trend analyses were based on length-adjusted data using log-transformed length as a covariate (one case used log-transformed weight, and one square-root transformed age). In a few cases, fish were divided into two length intervals. Stable isotope data were available for a landlocked Arctic char (*Salvelinus alpinus*) population, which was separated into two well-defined morphs with different feeding behavior according to the $\delta^{15}N$ value. Trend analyses were carried out separately for the two morphs.

For seabird eggs, no adjustment was applied. The Canadian Hg time series for seabird eggs were based on dry weight concentrations while the Faroe Islands time series were based on wet weight concentrations.

Terrestrial mammal Hg data were available from Sweden and Canada. The Swedish monitoring program is based on

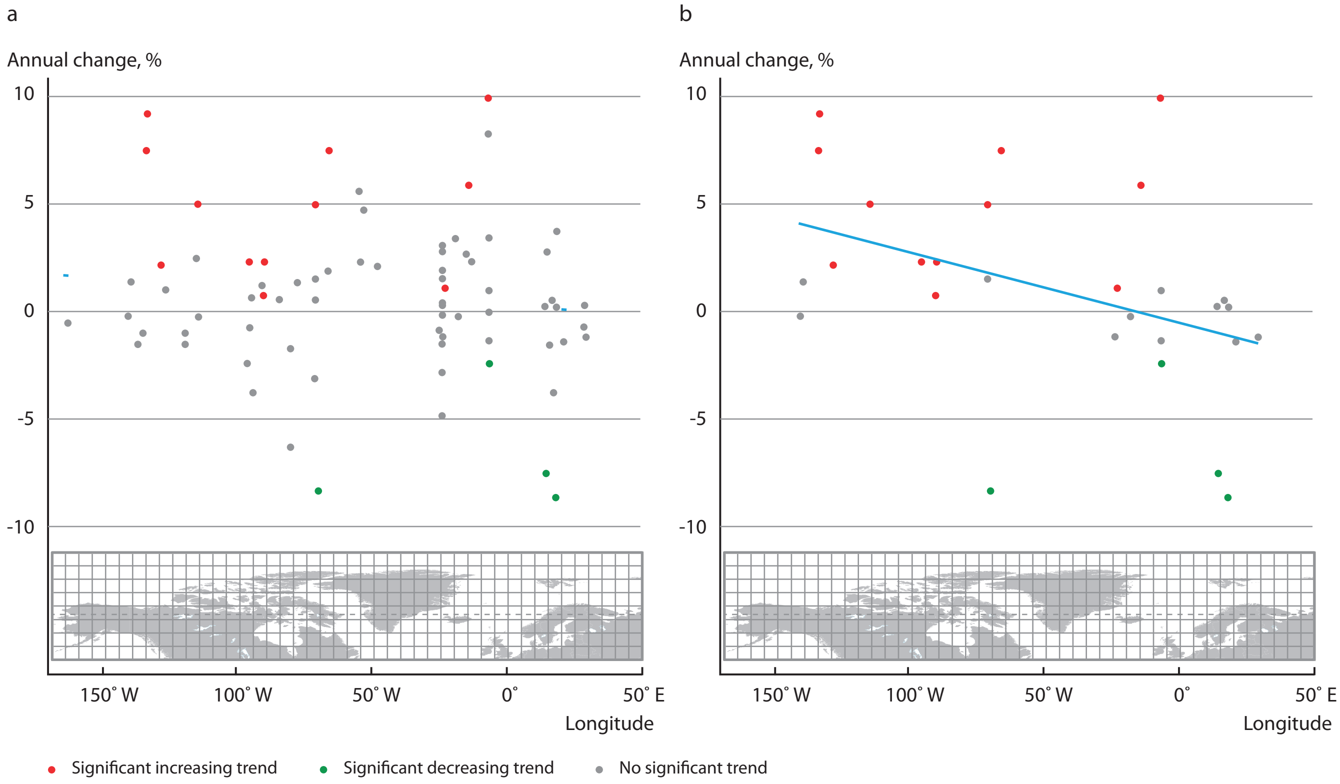


Figure 5.3. Annual change estimated (a) for all 83 analyzed time series versus longitude, and (b) for only those time series (n = 28) showing linear statistical significance or which meet the data adequacy requirements. The blue line indicated a significant linear regression ($R^2 = 0.2$, $p = 0.02$).

reindeer of specific age and gender, and thus no adjustment for covariates was done. The Canadian caribou kidney time series were separated by sex, and the square root of age was applied as a covariate according to the guidelines of the data providers.

It is well known that Hg in marine mammals is positively correlated to animal age (AMAP, 1998). In some cases, data were separated into age groups (e.g., juveniles and adults) and by sex, and no further adjustment for covariates was done. In other datasets, square-root transformed ages were applied as a covariate. In the case of Canadian beluga, data were separated into two time series above and below the overall mean age, and in addition, square-root transformed age was applied as a covariate. This procedure was chosen because the age range of beluga was very large (0 to 84 years old), and the assumption that there was a linear relationship between square-root transformed age and log-transformed Hg concentration over the total age span created unreliable results. In the case of polar bears from Alaska, only male adults and sub-adults were included (i.e., cubs were excluded) and the data were analyzed with square-root transformed age as a covariate. In one case, no covariate adjustment was applied due to missing data.

### 5.3.3.5. Adequacy of time series

In the Stockholm Workshop Report (AMAP, 2007), a concept termed 'Adequacy' was used which is closely related to, yet distinct from, the 'statistical power' of datasets. 'Adequacy' (expressed as a percentage or a proportion) is defined as the number of actual monitoring years in a time series divided by the number of years of sampling required to detect a 5% annual change in Hg concentration, with a significance level of $p < 0.05$ and 80% statistical power (see Bignert et al., 2004). Adequacy should not be confused with the concept of power, which is only one component of adequacy, albeit a very important one. Statistical power is defined as 1.0 minus the probability of a false positive result (β or Type II Error) (Sokal and Rohlf, 1981); it is affected by factors such as the number of samples taken each year, variability in Hg concentrations within and between years of sampling, and the desired detectable rate of change in Hg levels. The desired power level can also be pre-set (in these analyses, a conventional value of 80% was used). When this is done, other parameters of practical interest can be calculated, such as the number of years of data required to statistically detect a 5% annual change in Hg concentration (i.e., used in this measure of adequacy). Time series which have fewer than the minimum number of years required to detect a 5% annual rate of change are classed as 'inadequate', while those with years of data equal to or more than the minimum required are 'adequate'.

### 5.3.3.6. Annual change

The annual change in average Hg concentration ranged from -8.6% to 10% across all time series, with a median value of 0.5%. The annual change showed no apparent trend with longitude (linear regression, $p = 0.20$) (Figure 5.3a) or latitude (linear regression, $p = 0.65$) (Figure 5.4a). Considering only those datasets with significant linear trends, or which met the data adequacy requirements, the median annual rate of change was 2.4%. The annual rate of change decreased significantly from west to east ($p = 0.02$) (Figure 5.3b) but showed no trend with latitude ($p = 0.54$) (Figure 5.4b).

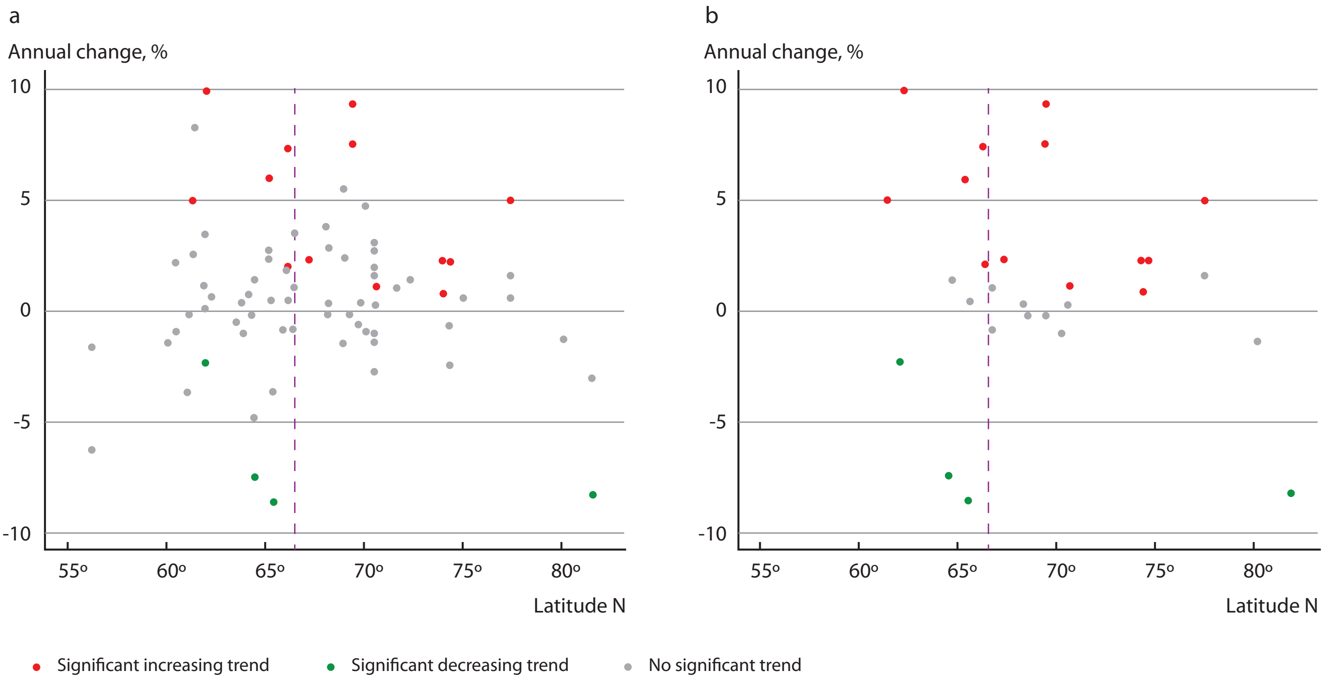


Figure 5.4. Annual change estimated (a) for all 83 analyzed time series versus latitude, and (b) for only those time trends (n = 28) which show linear statistical significance or which meet the adequacy requirements. The Arctic Circle is indicated by the dashed line.

One of the outputs of the temporal trend analysis is an estimation of the statistically detectable annual trend, assuming a sampling period of ten years, a significance level of 0.05 and a statistical power of 80%. The minimum detectable annual change ranged from 1.9% to 100% with a median value of 11% (Figure 5.5). Based on the datasets available for the previous AMAP Hg assessment (the 'Phase II' Assessment), and using the same criteria as above, Bignert et al. (2004) determined that the minimum detectable annual change in datasets available at that time ranged from 2.2% to 57% with a median value of 12%.

The utility of different taxa or biotic media for monitoring Hg can also be evaluated using the magnitude of the residual standard deviation from the trend; i.e., linear or non-linear. The

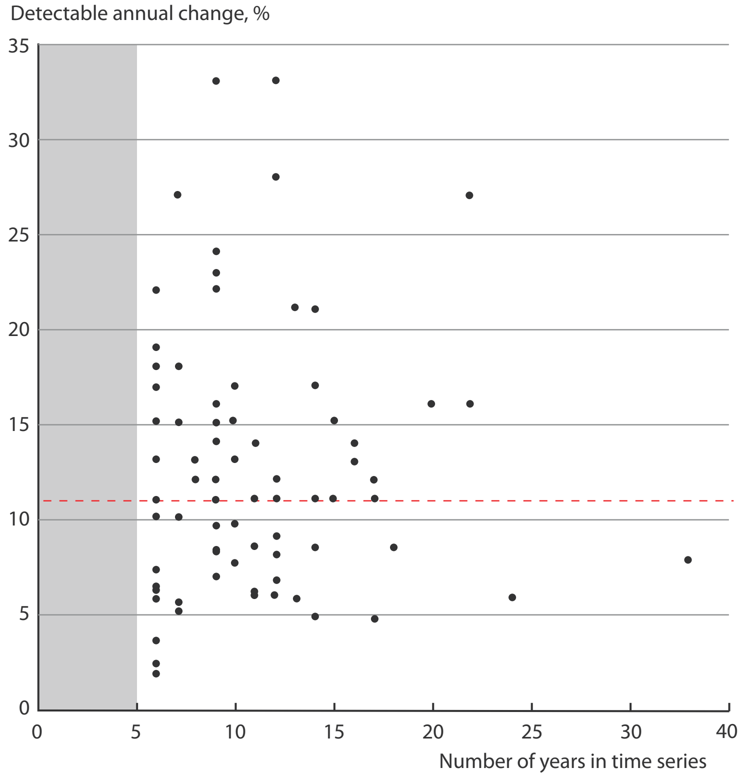


Figure 5.5. Statistically detectable annual change in Hg concentrations (assuming a sampling period of ten years, α = 0.05, power = 80%) plotted against number of years in available time series. Time series with less than six years of data were not included. Horizontal dashed line indicates the median detectable change.

lower the residual standard deviation, the more powerful the dataset. Seabird eggs had the lowest residual standard deviations (median = 0.17), while terrestrial and marine mammals had the highest (median = 0.41 and 0.40, respectively). The other groups fell within this range.

### 5.3.3.7. Evaluation of temporal trends

A summary of results from analysis of all 83 datasets included in this assessment is found in Table 5.3 and a summary of the statistical outputs resulting from analysis of the 45 time series with adequate data or which were statistically significant is presented in Table 5.4. It is outside the scope of this assessment to evaluate the individual time series; these are considered in far greater detail in related scientific papers and publications. The aim of this meta-analysis is to deduce possible general geographical patterns in Hg trends within the Arctic, or any similarities or dissimilarities between freshwater, terrestrial and marine ecosystems. The results have been categorized into four groups: significant increasing or decreasing trends (log-linear

Table 5.3. Results of trend analysis of mercury time series for all datasets (n = 83) analyzed using the PIA program.

| Ecosystem/ Country/Species[a] | Tissue | Location | Range of years | No. years | Temporal trend | Annual change, % | Adequacy of data |
|---|---|---|---|---|---|---|---|
| **Terrestrial Animals** | | | | | | | |
| Sweden | | | | | | | |
| Reindeer | muscle | Abiskojaura | 1983-2005 | 22 | Significant non-linear trend | 3.8 | 0.81 |
| Reindeer | liver | Ammarnäs | 1996-2005 | 10 | Significant decreasing trend | -8.6 | 0.50 |
| Reindeer | liver | Abiskojaura | 1983-2005 | 22 | No trend | 0.2 | 1.05 |
| Reindeer | muscle | Ammarnäs | 1996-2005 | 10 | Significant non-linear trend | -3.8 | 0.48 |
| Canada | | | | | | | |
| Caribou (female) | kidney | Yukon | 1994-2007 | 14 | No trend | -0.3 | 1.00 |
| Caribou (male) | kidney | Yukon | 1994-2007 | 12 | No trend | 1.3 | 1.00 |
| **Freshwater Fish** | | | | | | | |
| Sweden | | | | | | | |
| Pike | muscle | Storvindeln | 1968-2006 | 33 | Significant non-linear trend | 0.4 | 2.54 |
| Arctic char, landlocked | muscle | Abiskojaura | 1981-2006 | 24 | Significant non-linear trend | -0.3 | 2.18 |
| Faroe Islands | | | | | | | |
| Arctic char, landlocked | muscle | Á Mýrunum | 2000-2007 | 6 | Significant increasing trend | 10.0 | 0.50 |
| Greenland | | | | | | | |
| Arctic char, landlocked | muscle | Isortoq | 1994-2008 | 6 | Significant non-linear trend | 2.1 | 0.55 |
| Canada | | | | | | | |
| Arctic char, landlocked | muscle | Char Lake | 2000-2008 | 6 | Significant increasing trend | 2.3 | 0.86 |
| Arctic char, landlocked (small morph) | muscle | Lake Hazen | 1990-2008 | 9 | Significant decreasing trend | -4.4 | 0.82 |
| Arctic char, landlocked (large morph) | muscle | Lake Hazen | 1990-2008 | 9 | No trend | 1.3 | 0.50 |
| Arctic char, landlocked | muscle | Amituk Lake | 1989-2008 | 9 | Significant non-linear trend | 0.5 | 0.47 |
| Arctic char, landlocked | muscle | Resolute Lake | 1997-2008 | 11 | Significant non-linear trend | -0.7 | 0.69 |
| Burbot | muscle | West Basin | 1996-2007 | 9 | Significant increasing trend | 5.1 | 0.75 |
| Burbot | liver | Fort Good Hope | 1985-2008 | 12 | Significant increasing trend | 2.2 | 0.86 |
| Burbot | muscle | Fort Good Hope | 1985-2008 | 13 | Significant increasing trend | 2.4 | 1.18 |
| Lake trout | muscle | Kusawa | 1993-2008 | 9 | No trend | -1.6 | 0.45 |
| Lake trout | muscle | West Basin- Hay River | 1999-2007 | 7 | No trend | 2.5 | 0.64 |
| Lake trout | muscle | East Arm Great Slave | 1995-2007 | 9 | No trend | -0.3 | 0.64 |
| Lake trout | muscle | Laberge | 1993-2008 | 11 | No trend | -1.0 | 0.79 |
| **Marine Invertebrates** | | | | | | | |
| Norway | | | | | | | |
| Blue mussels | soft tissue | Brashavn | 1998-2007 | 9 | No trend | 0.2 | 0.64 |
| Blue mussels | soft tissue | Fensneset Grytoya | 1994-2007 | 6 | No trend | -1.6 | 0.67 |
| Blue mussels | soft tissue | Skallneset | 1994-2007 | 14 | No trend | -1.0 | 1.40 |
| Blue mussels | soft tissue | Elenheimsundet | 1994-2007 | 6 | Significant non-linear trend | 0.3 | 1.00 |
| Iceland | | | | | | | |
| Blue mussels | soft tissue | Mjoifjordur Hofs | 1995-2007 | 12 | Significant increasing trend | 6.1 | 0.75 |
| Blue mussels | soft tissue | Mjoifjordur Dalatangi | 1997-2007 | 9 | No trend | 2.4 | 0.56 |
| Blue mussels | soft tissue | Ulfsa Skutulsfjordur | 1997-2007 | 9 | No trend | 0.4 | 0.60 |
| Blue mussels | soft tissue | Dvergasteinn Alftafjordur | 1996-2006 | 10 | No trend | -0.9 | 0.77 |
| Blue mussels | soft tissue | Hvassahraun | 1992-2007 | 15 | No trend | 0.4 | 0.79 |
| Blue mussels | soft tissue | Eyri Hvalfjordur | 1992-2007 | 16 | No trend | 0.7 | 0.84 |
| Blue mussels | soft tissue | Grimsey | 1992-2007 | 14 | No trend | 3.5 | 0.88 |
| Blue mussels | soft tissue | Hvalstod Hvalfjordur | 1992-2007 | 16 | No trend | -0.3 | 0.89 |
| Blue mussels | soft tissue | Mjoifjordur head | 1996-2007 | 11 | No trend | 2.6 | 0.92 |
| Blue mussels | soft tissue | Straumur Straumsvik | 1992-2007 | 15 | Significant non-linear trend | -1.0 | 0.75 |
| Blue mussels | soft tissue | Hvitanes Hvalfjordur | 1992-2007 | 16 | Significant non-linear trend | 0.8 | 0.89 |

Table 5.3 (continued).

| Ecosystem/ Country/Species[a] | Tissue | Location | Range of years | No. years | Temporal trend | Annual change, % | Adequacy of data |
|---|---|---|---|---|---|---|---|
| **Marine Fish** | | | | | | | |
| Norway | | | | | | | |
| Plaice | muscle | Lille Mola/Husholmen | 1993-2006 | 11 | No trend | 2.8 | 0.58 |
| Plaice | muscle | Skogerøy | 1997-2007 | 9 | No trend | -1.1 | 0.75 |
| Atlantic cod | muscle | Lille Mola/bjørnerøya | 1993-2006 | 12 | No trend | 0.3 | 0.71 |
| Atlantic cod | muscle | Varangerfjorden | 1994-2007 | 14 | Significant non-linear trend | -0.8 | 0.58 |
| Faroe Islands | | | | | | | |
| Atlantic cod (≤73 cm) | muscle | Faroe Islands | 1979-2007 | 20 | Significant decreasing trend | -2.4 | 1.00 |
| Iceland | | | | | | | |
| Atlantic cod | muscle | Southeast | 1990-2003 | 7 | Significant decreasing trend | -7.4 | 0.64 |
| Atlantic cod | muscle | Southwest | 1990-2001 | 6 | Significant non-linear trend | -4.9 | 0.33 |
| Atlantic cod | muscle | Northeast | 1990-2007 | 17 | No trend | 1.0 | 1.00 |
| Atlantic cod | muscle | Northwest | 1990-2007 | 17 | Significant non-linear trend | -0.9 | 1.00 |
| Greenland | | | | | | | |
| Sculpin (<27 cm) | liver | Qeqertarsuaq | 1994-2006 | 7 | No trend | 4.8 | 0.26 |
| Sculpin (>27 cm) | liver | Qeqertarsuaq | 1994-2008 | 9 | No trend | 5.5 | 0.38 |
| Sculpin | liver | Ittoqqortoormiit | 1995-2008 | 6 | Significant non-linear trend | 2.7 | 0.46 |
| **Marine Mammals** | | | | | | | |
| Norway | | | | | | | |
| Polar bear (>2 yrs) | hair | Svalbard | 1995-2008 | 12 | No trend | -1.3 | 1.09 |
| Faroe Islands | | | | | | | |
| Pilot whale (adult male) | muscle | Faroe Islands | 1979-2006 | 13 | No trend | 1.0 | 0.54 |
| Pilot whale (immature) | muscle | Faroe Islands | 1979-2007 | 14 | No trend | 3.4 | 0.67 |
| Pilot whale (adult female) | muscle | Faroe Islands | 1979-2007 | 15 | No trend | 0.1 | 0.94 |
| Greenland | | | | | | | |
| Polar bear (>2 yrs) | hair | Ittoqqortoormiit | 1984-2008 | 17 | Significant increasing trend | 1.2 | 1.70 |
| Polar bear (adult) | kidney | Ittoqqortoormiit | 1984-2001 | 6 | No trend | -1.4 | 0.25 |
| Polar bear (juvenile) | kidney | Ittoqqortoormiit | 1983-2001 | 9 | No trend | -2.8 | 0.47 |
| Polar bear (juvenile) | liver | Ittoqqortoormiit | 1983-2006 | 10 | No trend | 1.8 | 0.67 |
| Polar bear (>2 yrs) | hair | Avanersuaq | 1987-2006 | 18 | No trend | 1.6 | 1.29 |
| Polar bear (adult) | liver | Ittoqqortoormiit | 1984-2006 | 8 | Significant non-linear trend | 1.8 | 0.44 |
| Ringed seal (juvenile) | liver | Avanersuaq | 1984-2008 | 7 | Significant increasing trend | 5.0 | 0.32 |
| Ringed seal (juvenile) | liver | Ittoqqortoormiit | 1986-2008 | 9 | No trend | 2.9 | 0.36 |
| Ringed seal (adult) | liver | Ittoqqortoormiit | 1986-2008 | 9 | No trend | 1.4 | 0.53 |
| Ringed seal (juvenile) | liver | Qeqertarsuaq | 1994-2008 | 9 | Significant non-linear trend | 2.3 | 0.53 |
| Walrus (9-16 yrs) | liver | Avanersuaq | 1977-2003 | 7 | No trend | 0.6 | 0.37 |
| Canada | | | | | | | |
| Beluga (≤30 yrs) | liver | Hendrickson Island | 1981-2006 | 12 | Significant increasing trend | 9.4 | 0.43 |
| Beluga (>30 yrs) | liver | Hendrickson Island | 1981-2006 | 12 | Significant increasing trend | 7.7 | 0.40 |
| Beluga (≤20 yrs) | liver | Pangnirtung | 1984-2002 | 10 | Significant increasing trend | 7.5 | 0.53 |
| Beluga (>20 yrs) | liver | Pangnirtung | 1984-2002 | 9 | No trend | 1.9 | 0.36 |
| Beluga (≤27 yrs) | liver | Sanikiluaq | 1994-2004 | 6 | Significant non-linear trend | -1.7 | 0.29 |
| Beluga (>27 yrs) | liver | Sanikiluaq | 1994-2004 | 6 | Significant non-linear trend | -6.3 | 0.32 |
| Narwhal | liver | Pond Inlet | 1978-2004 | 8 | No trend | 1.3 | 0.44 |
| Ringed seal | liver | Arviat | 1992-2007 | 6 | No trend | -3.7 | 0.26 |
| Ringed seal | liver | Sachs Harbour | 1987-2007 | 6 | No trend | 1.0 | 0.38 |
| Ringed seal | muscle | Holman | 1973-2007 | 10 | No trend | -1.1 | 0.56 |
| Ringed seal | liver | Holman | 1973-2007 | 12 | No trend | -1.3 | 0.86 |
| Ringed seal | liver | Resolute | 1993-2007 | 6 | Significant non-linear trend | -2.5 | 0.29 |
| Alaska | | | | | | | |
| Polar bear (male) | liver | Chucki/Bering Sea | 1987-2007 | 13 | No trend | -0.6 | 0.22 |
| **Marine Birds** | | | | | | | |
| Faroe Islands | | | | | | | |
| Black guillemot | egg | Koltur | 1999-2006 | 6 | No trend | -1.3 | 0.50 |
| Black guillemot | egg | Skuvoy | 1999-2006 | 6 | Significant non-linear trend | 8.3 | 0.38 |
| Canada | | | | | | | |
| Black-legged kittiwake | egg | Prince Leopold Island | 1975-2008 | 7 | No trend | 1.0 | 0.44 |
| Northern fulmar | egg | Prince Leopold Island | 1975-2008 | 11 | Significant increasing trend | 0.9 | 1.00 |
| Thick-billed murre | egg | Prince Leopold Island | 1975-2008 | 12 | Significant increasing trend | 2.4 | 1.00 |
| Thick-billed murre | egg | Coats Island | 1993-2008 | 7 | Significant non-linear trend | 0.5 | 0.64 |

[a] Caribou, reindeer (*Rangifer tarandus*); pike (*Esox lucius*); Arctic char (*Salvelinus alpinus*); burbot (*Lota lota*); lake trout (*Salvelinus namaycush*); blue mussels (*Mytilus edulis*); plaice (*Pleuronectes platessa*); Atlantic cod (*Gadus morhua*); sculpin (*Myoxocephalus scorpius*); ringed seal (*Phoca hispida*); walrus (*Odobenus rosmarus*); pilot whale (*Globicephala melas*); narwhal (*Monodon monocerus*); beluga (*Delphinapterus leucas*); polar bear (*Ursus maritimus*); black guillemot (*Cepphus grylle*); black-legged kittiwake (*Rissa tridactyla*); northern fulmar (*Fulmarus glacialis*); thick-billed murre (*Uria lomvia*).

Table 5.4. Summary of statistical results for all 83 mercury time series analyzed and for the 45 time series showing significantly increasing/decreasing/non-linear trends or with adequate datasets.

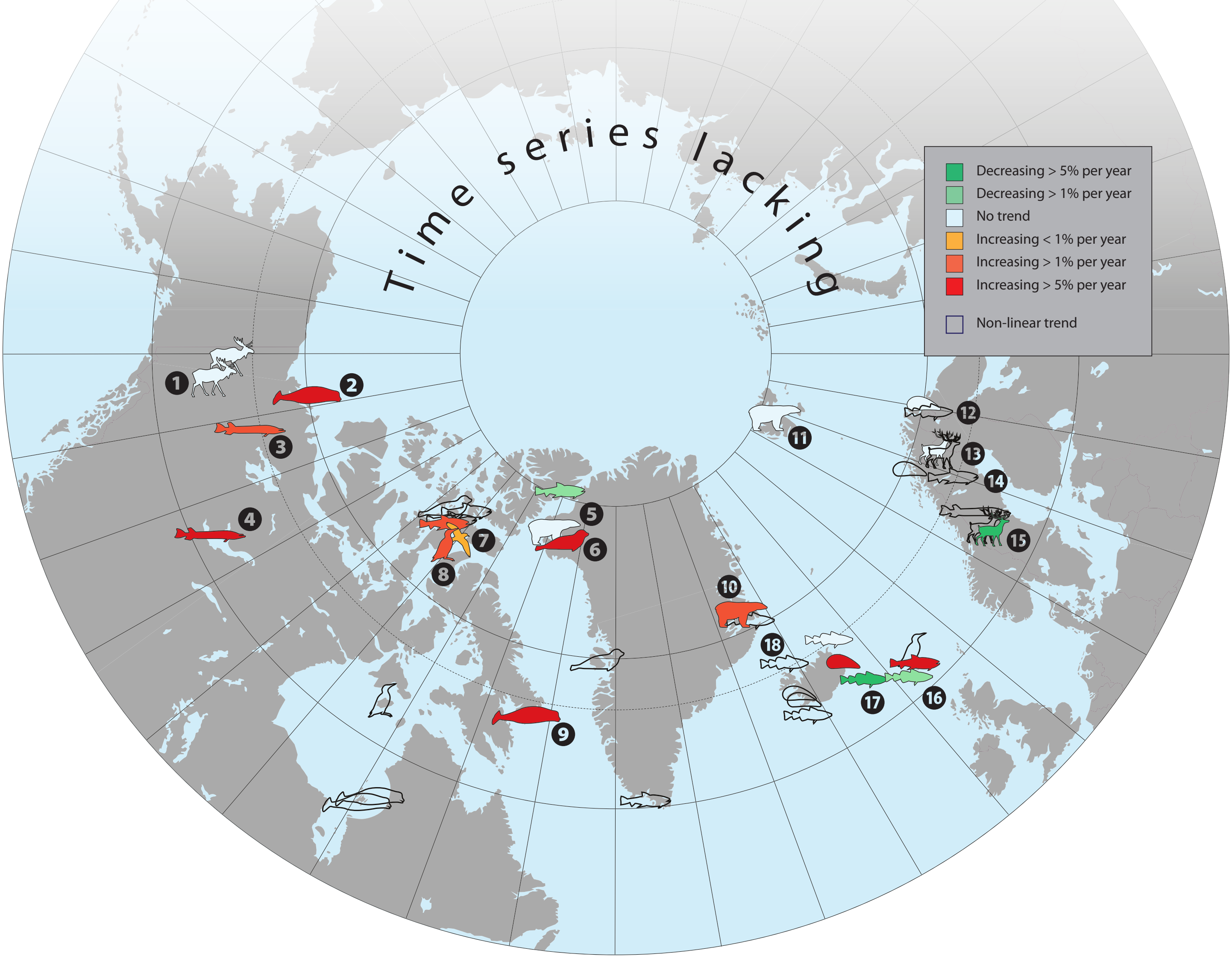
| Significant increasing trend | Significant decreasing trend | No trend | Significant non-linear trend | Median annual percentage change | Median lowest detectable trend (%) in 10 years with α = 5% and a power of 80% | Median power (%) in 10 years to detect 5% with α = 5% and a power of 80% |
|---|---|---|---|---|---|---|
| All 83 time series | | | | | | |
| 13 (16%) | 4 (5%) | 45 (54%) | 21 (25%) | 0.6 | 11.0 | 24 |
| 45 times series with increasing/decreasing/non-linear trend or adequate datasets | | | | | | |
| 13 (29%) | 4 (9%) | 7 (16%) | 21 (47%) | 0.8 | 11.0 | 27 |

trend component is significant), significant non-linear trends (non-linear trend component is significant) and no trend.

Of the 83 time-series analyzed, 13 (16%) showed a significantly ($p < 0.05$) increasing linear trend and one of these also had a significant non-linear trend component within the overall trend. Two of the significant datasets were from the same animals but different tissues. Four time series (5%) showed a significantly decreasing linear trend and one of these also had a significant non-linear component. Twenty-one time series showed a significant non-linear trend. If the required α level of significance is weakened from 5% to 10%, then the number of time series showing an increasing trend would increase slightly, from 13 to 16, and the number showing a decreasing trend would increase from 4 to 5.

The average annual increases for the 13 significantly increasing datasets ranged between 0.9% and 10% (median 5.0%). Breaking the results down by country, nine significantly increasing time series were found for Canada (30% of the Canadian datasets), two for Greenland (13%), and one each for the Faroe Islands (14%) and Iceland (7%) (Figure 5.6, see next page spread). Broken down by taxonomic grouping, increasing trends were found in marine invertebrates (1; 8% of the significantly increasing datasets), seabirds (2; 15%), marine mammals (5; 38%) and freshwater fish (5; 38%). Only four (5%) of the time series showed a significantly decreasing trend and one of these also had a significant non-linear trend component. The annual decreases ranged between -2.4% and -8.6% (median -5.9%). Two of these were for Atlantic cod (*Gadus morhua*) from the Faroe Islands and Iceland, one was for Arctic char from Canada, and one was for reindeer (*Rangifer tarandus*) from Sweden. None of the Arctic marine mammal or seabird datasets showed a significantly declining trend. The remaining 66 Hg time series showed either no trend or a significant non-linear trend component. The overall median annual rate of change of these time series was 0.4%.

These overall results are, as expected, similar to those obtained during the Stockholm Workshop in 2006 (AMAP, 2007), particularly as the majority of the significant time series are identical except for a few additional years of data in some cases.


Time series lacking
Decreasing > 5% per year
Decreasing > 1% per year
No trend
Increasing < 1% per year
Increasing > 1% per year
Increasing > 5% per year
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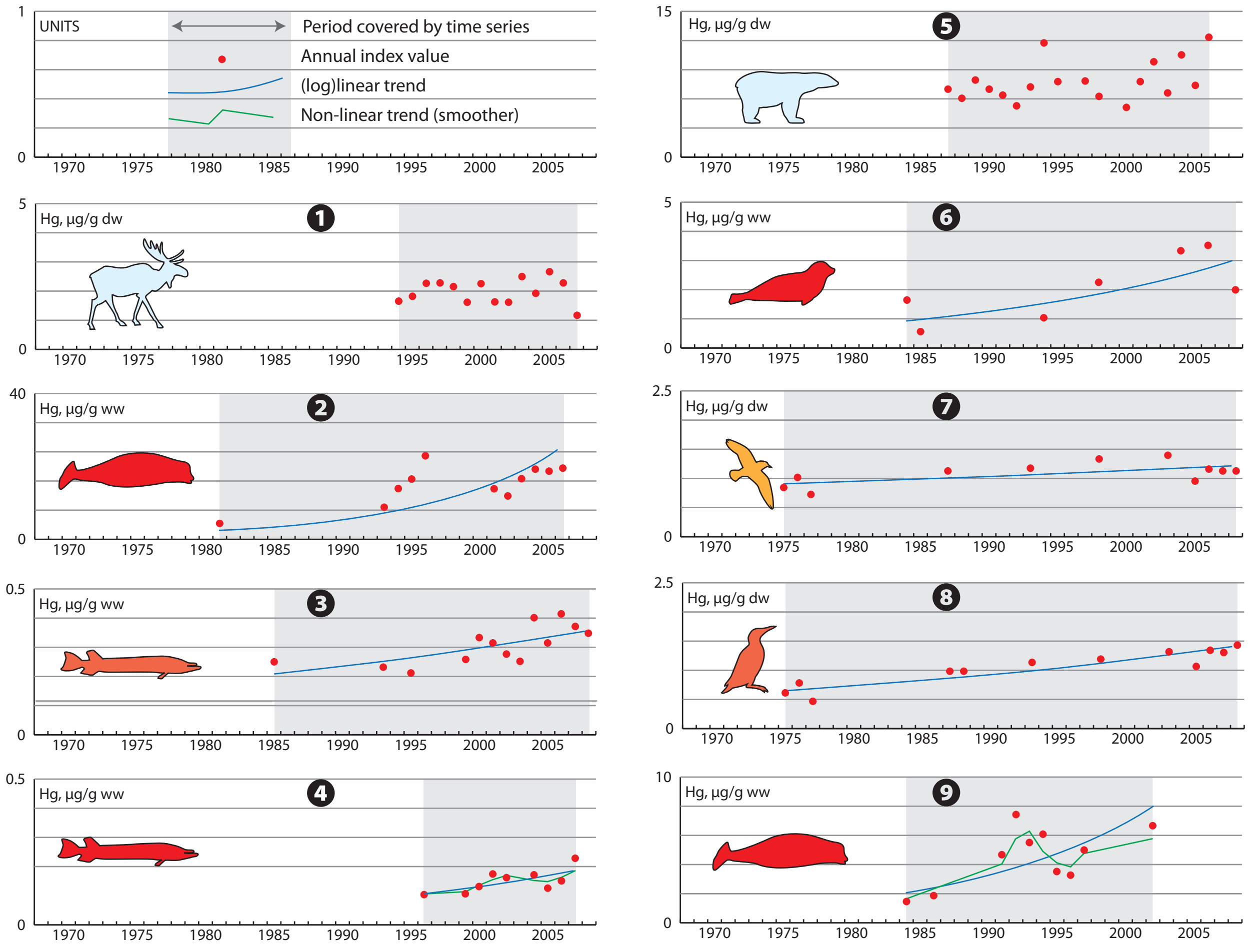
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UNITS
Period covered by time series
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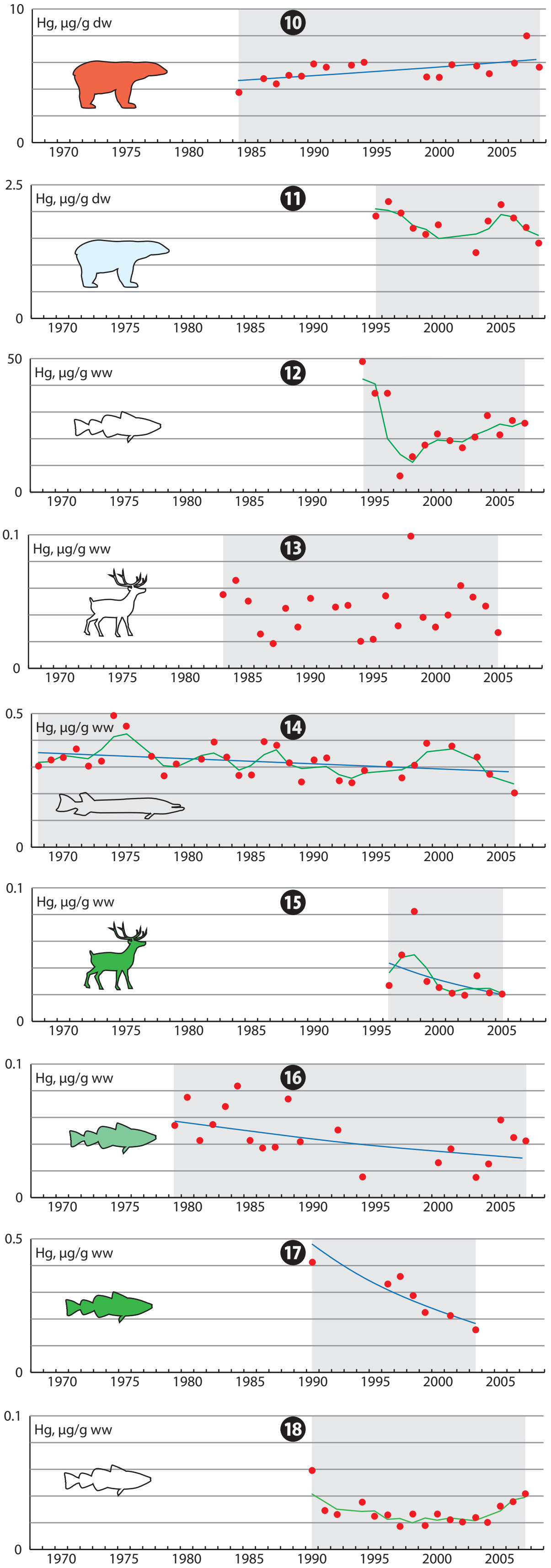

Figure 5.6. Summary of trends which are statistically significant or meet the data adequacy requirements, with details of trends for selected time series from Canada and West Greenland (1-9) and East Greenland and the European Arctic (10-18).

### 5.3.3.8. Evaluation of adequacy of time series to detect trends

At the Stockholm workshop in 2006, only five time series were found to be 'adequate'. Four of those are also classified as 'adequate' in this update, whereas the fifth (Finnish freshwater fish influenced by construction of hydroelectric reservoirs) is not included in this update. Here, a total of 16 (19%) of the 83 time series were classified as 'adequate' (Figure 5.7). These included seven datasets showing no trend, four showing a significant non-linear trend, four showing a significantly increasing trend, and one showing a significantly decreasing trend (see Table 5.3). It was predicted in 2006 that a larger number of time series would be classified as 'adequate' in this updated assessment because of the additional years of data. However, in some cases, adequacy may have declined or remained constant, largely attributed to increased between-year variability in the extended time series. Overall, however, the results from this assessment represent an increase from 10% to 19% of datasets deemed 'adequate' relative to the previous AMAP Hg assessment (Bignert et al., 2004).

If an additional five years of data were to be added to the time series, it is predicted that 44 of the 83 time series would meet the criteria for adequacy defined here (as indicated by the broken line in Figure 5.7). However, this assumes that other factors, such as between-year variability, remain the same.

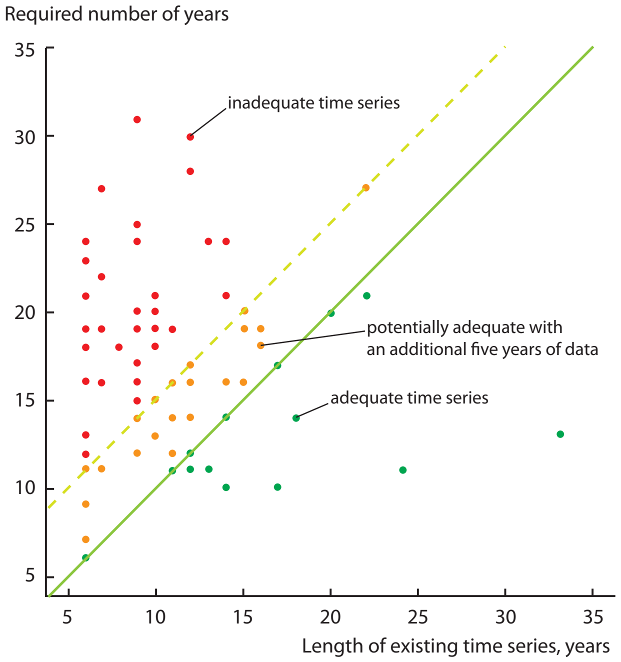

Figure 5.7. Statistical adequacy of the datasets analyzed. Points at or below the solid line have an adequacy of ≥ 1 and points above the solid line have an adequacy of < 1. The dashed line predicts the situation if the time series are extended with an additional five years of data (assuming unchanged between-year variation).

### 5.3.4. Comparison of meta-analysis results with mercury trends published in the recent literature

In both the published literature (Table 5.2) and this meta-analysis (Table 5.3), Hg concentrations in terrestrial biota showed either no trend (this includes significant non-linear trends) or a decreasing trend. Of the time series for freshwater fish, none of the published time series showed statistically significant trends (Table 5.2). However, of the 16 time series for freshwater fish included in the meta-analysis, five of the time series (31%) showed significant increases in Hg concentration (although two of those were for different tissues from the same fish), and one (6%) showed a significant decrease. The highest number of increasing trends in Hg concentration was seen in marine biota. Of the 29 datasets reported in the literature for the marine environment (Table 5.2), 31% suggested increasing trends while the other 69% showed either no trend or decreasing concentrations. Of the 61 time series for marine biota included in the meta-analysis, a similar percentage compared to those in the literature (13% *vs* 10%) showed significantly increasing trends.

Since there was a geographical bias in the time series represented, it is difficult to evaluate with great confidence the meaning of the overall spatial / circumpolar distribution of increasing or decreasing trends. However, the seabird egg datasets provide an opportunity to do so since there are data available from Canada, the Faroe Islands and Norway (Table 5.5). Three of the five Canadian egg datasets showed increasing Hg trends and one of two datasets from the Faroe Islands showed a significant non-linear trend which included a recently increasing trend component, whereas none of the three datasets from Norway nor the remaining datasets from Canada or the Faroe Islands showed any linear trend. Although few in number, these egg datasets support the general pattern of higher numbers of time series showing an increasing trend in Canada and Greenland compared with northern Europe (see Figures. 5.3 and 5.6).

Factors that may be driving the Hg trends observed, both spatially and across ecosystems, are discussed in Section 5.4.

## 5.4. Why are mercury levels in Arctic biota increasing or decreasing?

It becomes clear from Sections 5.2 and 5.3 that, while Hg concentrations in some Arctic populations have increased more than 10-fold on average compared to pre-industrial times, no consistent trend can be generalized across tissues and species of the entire circumpolar Arctic for the past 30 years or so. There was, however, a clear west-to-east gradient in the occurrence of recent increasing Hg trends, with larger numbers and a higher proportion of biotic datasets in the Canadian and West Greenland region of the Arctic showing significant increases than in the North Atlantic Arctic. Most of the increasing datasets were for marine-based species, especially marine mammals.

Since the potential biases of important biological covariates such as age and (in some cases) trophic change have been accounted for in the statistical analyses, the biotic Hg increases and decreases, or lack of change, presumably approximate real variations (or lack thereof) in Hg levels in the animals' environments and food webs. A clearer picture of the variability and consistencies in Hg trends in Arctic biota over time spans of recent centuries and decades is now emerging. This section discusses the possible drivers of these trends, grouped under the general categories of sources (anthropogenic and natural emissions) and environmental processes (mainly but not exclusively climate-driven).

### 5.4.1. Sources- vs. processes-driven mercury bioaccumulation in the Arctic

As detailed in Section 5.2, the significant increase in Hg concentrations in present-day Arctic animals compared to their pre-industrial counterparts is most likely to have been driven primarily by the increase in anthropogenic Hg influx to the Arctic ecosystems. This is supported by the significant increase in anthropogenic Hg depositional flux recorded in Arctic lake sediments and peat bogs (Bindler et al., 2001b; Shotyk et al., 2003, 2005a; Fitzgerald et al., 2005; Lindeberg et al., 2006, 2007; Outridge et al., 2007; Landers et al., 2008; Muir et al.,

Table 5.5. Mercury trends in seabird eggs.

| Location/species | Published trend[a] | Meta-analysis trend[b] |
|---|---|---|
| Northern Norway | | |
| Herring gull | No trend | n/a[c] |
| Atlantic puffin | No trend | n/a |
| Black-legged kittiwake | No trend | n/a |
| Faroe Islands (Koltur) | | |
| Black guillemot | No trend | No trend |
| Faroe Island (Skúvoy) | | |
| Black guillemot | Increasing trend since 2000 | Significant non-linear trend |
| Canada (Prince Leopold Island) | | |
| Black-legged kittiwake | No trend | No trend |
| Northern fulmar | Significant increasing trend | Significant increasing trend |
| Thick-billed murre | Significant increasing trend | Significant increasing trend |
| Canada (Coats Island) | | |
| Thick-billed murre | No published trend | Significant non-linear trend |
| Canada (Seymour Island) | | |
| Ivory gull | Non-significant increasing trend | n/a |

[a] See Table 5.2.; [b] see Table 5.3.; [c] n/a not analyzed because dataset did not meet criteria for meta-analysis.

2009), by global Hg emission inventories (see Chapter 2), and by evidence of significant amounts of Hg contamination in the world's oceans (Sunderland and Mason, 2007) (see Chapter 3).

However, this anthropogenic source-driven scenario appears not to be the sole explanation for biotic trends in recent decades (Wang et al., 2010). Although there has been a regional shift in Hg emission to the atmosphere, the global size of the atmospheric pool of Hg has been either stable since the mid-1970s or may have decreased (Pacyna et al., 2003; Lindberg et al., 2007; Fain et al., 2009b; Streets et al., 2009). *In situ*, high resolution measurements at Alert, Canada, have shown no significant trend in the annual average concentration of gaseous elemental Hg (GEM) in High Arctic air since 1995 (Steffen et al., 2005). Prior to 1995, a reconstructed GEM history from Greenland Summit firn snow showed a decline in atmospheric Hg levels from the early 1970s to early 1990s (Faïn et al., 2009b). Similarly, analysis of particulate Hg in archived air filters collected from Resolute, Canada, has shown a significant declining trend for summer/autumn during the period 1974 to 2000 (Li et al., 2009). These constant or declining trends in Arctic atmospheric Hg do not explain the continued recent increasing trends of Hg in Arctic wildlife (see Section 5.3). As some of the case studies in Section 5.4.2 illustrate, the lack of a direct atmosphere-biota 'dose-response' relationship for Hg in the Arctic has precipitated several recent studies on alternative drivers for Hg bioaccumulation in the Arctic. These alternative drivers include additional Hg sources, as well as cryospheric, biogeochemical and ecological processes that control the movement of Hg from the abiotic environment to Arctic animals (see Chapter 3).

### 5.4.1.1. Mercury sources other than atmospheric deposition

Atmospheric deposition is often the dominant source of Hg to Arctic lakes. However, migratory seabirds have also been shown to contribute Hg via their guano locally in a few small, isolated Arctic ponds that are visited by a large number of seabirds (Blais et al., 2005, 2007). Transport of Hg to the Arctic marine environment also occurs via riverine discharge, thawing permafrost, coastal erosion, and oceanic circulation (Macdonald et al., 2005; Leitch et al., 2007; Outridge et al., 2008). Recent studies on the mass budget of Hg in the Arctic Ocean (Outridge et al., 2008) and Hudson Bay (Hare et al., 2008) suggested that the atmospheric influx of Hg to the Arctic Ocean may have been significantly overestimated and that the contribution of atmospherically deposited Hg needs to be considered within the context of the total Hg flux including terrestrial and marine sources.

### 5.4.1.2. Cryospheric processes that control the timing, speciation, and net flux of atmospheric mercury deposition

Although the annual average concentration of GEM has stayed essentially unchanged since at least 1995 (Steffen et al., 2005), the discovery of the tropospheric atmospheric Hg depletion events (AMDEs; see Chapter 2) during polar sunrise (Schroeder et al., 1998) raises the question of the significance of photochemically oxidized Hg during AMDEs in Hg uptake in Arctic ecosystems. This is, however, complicated by the fact that most of the surfaces of Arctic marine and coastal systems are frozen at the time of AMDEs. A time lag thus exists between when the Hg is deposited onto the frozen surface and when it is transported to the underlying aquatic or terrestrial ecosystems, during which post-depositional changes in concentration and speciation are known to occur. Therefore, the net contribution of atmospherically transported Hg to the Hg flux in the Arctic ecosystem is highly modified by cryospheric conditions, which is reflected in the large uncertainty in the estimate of atmospheric Hg flux to the Arctic Ocean (8 to 300 t/y; Outridge et al., 2008).

### 5.4.1.3. Biogeochemical processes that control the methylation of mercury

Although uptake of inorganic Hg is possible, it has been well established that Hg uptake and accumulation in Arctic aquatic animals occurs mainly in the form of MeHg (see Chapters 3 and 6). No mass budget is currently available for MeHg in the Arctic Ocean, but the majority of MeHg is believed to be formed by methylation of the existing pool of inorganic Hg in the aquatic environment. Mercury methylation can occur in deep sediments (Kraepiel et al., 2003; Hammerschmidt and Fitzgerald, 2005) as well as in the water column (Kirk et al., 2008; Cossa et al., 2009; Sunderland et al., 2009) of the ocean, and is controlled by biogeochemical processes that affect the influx of inorganic Hg and organic matter, and the presence and activity of Hg methylators. Any change in these processes will thus change the locality and pool of MeHg available for uptake by Arctic ecosystems.

### 5.4.1.4. Biological and ecological processes that control the transport of methylmercury in food webs

Because MeHg biomagnifies in food webs, any change in the foraging behavior (e.g., habitat use, diet preferences) of an Arctic animal, and in the structure and dynamics of Arctic food webs in general, would result in a change in the Hg concentration in the animal.

Therefore, to better understand the temporal and spatial variation in Hg concentrations in Arctic animals, changes both in Hg sources and post-depositional Hg processes need to be considered (Wang et al., 2010). This requires an understanding of changes in anthropogenic activities and the effects of climate change which has occurred in the Arctic over recent decades (Post et al., 2009).

## 5.4.2. Case studies

This section presents eight case studies as examples for discussing the relative importance of different drivers that may be responsible for the temporal variations in Hg concentration in Arctic animals. These case studies demonstrate that the interactions between the various factors are complex, with atmospheric Hg deposition, and environmental and ecological processes, in some cases coupled with climate change, playing a role, as does the biology and behavior of the species.

### Case Study 1. Landlocked Arctic char from Lake Hazen

Muscle tissue of landlocked Arctic char (*Salvenlius alpinus*) from Lake Hazen was used to investigate temporal trends in Hg concentration using recent data in addition to data published by Gantner et al. (2009). Lake Hazen is the largest lake in the Canadian High Arctic and Arctic char from this lake have been relatively well studied compared to most other lakes in the Canadian Arctic Archipelago. Up to three different morphotypes of Arctic char are present in Lake Hazen (Reist et al., 1995; Guiguer et al., 2002). All the char are considered to be non-anadromous (resident) (Babaluk et al., 1997). Archived and newly collected char consisting of two morphotypes (large piscivores and smaller insectivores) were analyzed by Gantner et al. (2009). The morphotypes differed in Hg concentration, and the resulting variability was accounted for by adjusting the Hg concentrations using their nitrogen stable isotope ratio ($\delta^{15}N$) values. The adjustment using $\delta^{15}N$ was justified by the fact that the relationship of $\delta^{15}N$ with Hg was the same each year (parallel slopes of the $\delta^{15}N$–Hg concentrations). Adjusted Hg concentrations showed no significant change over the 16-year study period (1990 to 2006) (Gantner et al., 2009).

More recent measurements (2007 and 2008) were added to the original dataset from Gantner et al. (2009) and contributed to the meta-analyses described in Section 5.3.3. Results show a significant decreasing trend (-4.4%) for the small morphotype (Table 5.3) and no trend (1.3%) for the large morphotype. Combining both morphotypes into a single dataset and adjusting for $\delta^{15}N$, as done by Gantner et al. (2009) showed an overall non-significant trend (+17%) for Hg in Lake Hazen char using PIA. The lowest detectable change in the time series is 16% (with a power of 80% and one-sided test, $\alpha = 0.05$). The non-significant trend and relatively high variation among char result in statistical inadequacy for the combined dataset (50%) or the individual morphotypes (50% and 82%, Table 5.3). The unadjusted values and geometric mean concentrations in Lake Hazen char are shown in Figure 5.8.

One explanation for the different Hg trends in small and large morphotypes could be that small morphotypes may respond more immediately to changes in Hg (deposited in the lake) associated with sediments. Small char in Lake Hazen feed mainly on sediment-dwelling organisms (chironomids) and therefore feed closer to the 'source' of bioavailable Hg (i.e., the site of methylation). While large char that feed on juvenile char have greater Hg concentrations owing to greater biomagnification, their Hg concentrations also are more variable, making trend analysis more difficult. Unfortunately, the available sediment record (Muir et al., 2009) does not extend past 2004, making a parallel examination of the trends in sediment and small char impossible. Another explanation may be that the statistical approach for this assessment was different from the original trend (Gantner et al., 2009). While the two groups were separated using a $\delta^{15}N$ cut-off, unadjusted Hg values were used in the PIA analysis here. The overall decline in Hg at Lake Hazen of -5.4% appears to be greater than the modest declines estimated by PIA for landlocked char in Resolute Lake and in Lake Abiskojaure (Sweden) (Table 5.3). In two other lakes in the Canadian Arctic and also in Lakes Á Mýrunum (Faroe Islands) and Isortoq (Greenland), the Hg trend in char increased or showed a non-significant positive trend (Table 5.3).

The reason for the apparent decline in Hg concentration in small morphotype char in Lake Hazen is unknown. With a surface area of 537.5 km², Lake Hazen is the tenth largest Arctic lake and the world's largest lake north of 74° N. It is much larger than all the other landlocked char lakes with Hg time series, it is also the most remote from global anthropogenic sources and the only one that is glacier fed. Several indicators of the physical environment of Lake Hazen point to the stability of the system. Basic water chemistry data from multi-year monitoring indicated little change over time (Babaluk, 1999; Babaluk et al., 2009), and Hg fluxes in a dated sediment core from Lake Hazen collected in 2005 showed only an overall modest increase in recent horizons compared to the pre-industrial era (flux ratio = 1.13; compared with an average flux ratio of 2.2 for 16 other Arctic lakes) (Muir et al., 2009). The Hg trends in char and the recent trend in the anthropogenic Hg flux in sediment are compared in Figure 5.8. Nearby measurements of GEM at Alert, Nunavut, Canada show no significant decline to mid-decade (Temme et al., 2007). Thus three different lines of investigation of Hg trends from northern Ellesmere Island are not entirely in agreement although, given inter-annual variation, they suggest very little overall change.

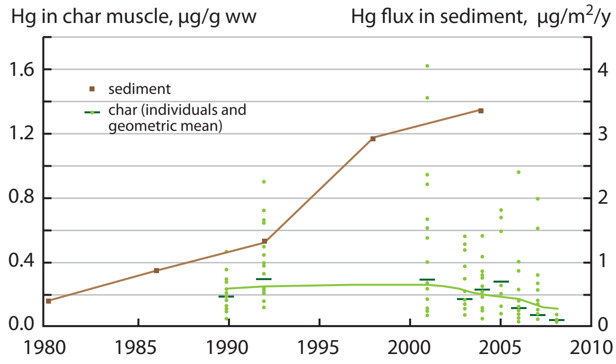

Figure 5.8. Trend in Hg in landlocked Arctic char and a dated sediment core from Lake Hazen, Canada, over the period 1980 to 2008. For char, the plot shows the individual data, annual geometric means, and the 3-point running mean. For sediments, the plot shows the anthropogenic flux, estimated from the average recent (1998 to 2004) flux minus the pre-industrial (1830 to 1840) flux. Symbols represent mid-points of 0.5 cm thick sediment horizons. Data from Gantner et al. (2009) and Muir et al. (2009).

### Case Study 2. Canadian Arctic seabirds

Eggs of thick-billed murres (*Uria lomvia*), northern fulmars (*Fulmarus glacialis*) and black-legged kittiwakes (*Rissa tridactyla*) from Prince Leopold Island in Lancaster Sound in the Canadian High Arctic have been monitored for contaminants since 1975 (Braune, 2007). Significant increases in concentrations of THg in eggs of northern fulmars and thick-billed murres were documented between 1975 and 2008, whereas the increase of THg in eggs of blacklegged kittiwakes was not significant over the study period (Figure 5.9, Table 5.3). Mercury concentrations in eggs of ivory gulls (*Pagophila eburnea*) from Seymour Island in the Canadian High Arctic also increased between 1976 and 2004 although the trend was not statistically significant (Braune et al., 2006).

The ivory gull is a resident Arctic species whereas the other three species are migratory, dispersing to various areas throughout the North Atlantic for the winter. Interpretation of

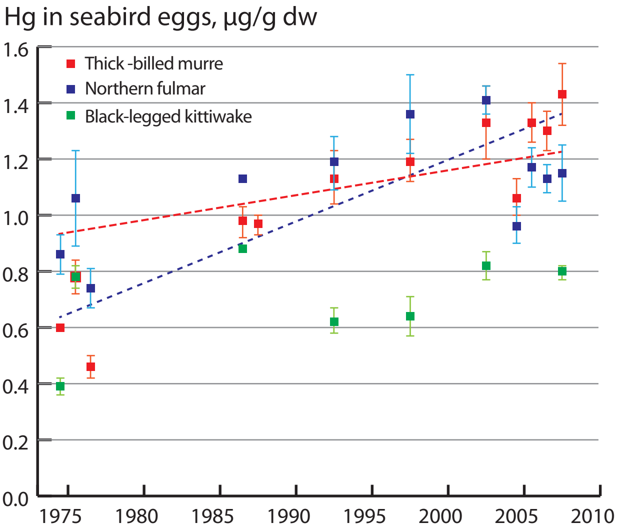

Figure 5.9. Annual mean concentrations (± standard error) of THg in eggs of thick-billed murres, northern fulmars and black-legged kittiwakes from Prince Leopold Island (Canada) for 1975 to 2008. Linear regression lines are shown for statistically significant relationships (*p*<0.05).

Hg levels and trends must include consideration of the year-round distribution of these birds since the components of each egg will contain materials gained from food items obtained at the breeding colony as well as those obtained over the winter and on migration. The kittiwakes probably overwinter on the Grand Banks off Newfoundland and possibly further south along the eastern seaboard of North America (Baird, 1994), whereas band return data suggest that the thick-billed murres from Prince Leopold Island overwinter in open waters off southwestern Greenland (Donaldson et al., 1997). The northern fulmars from the Canadian Arctic appear to overwinter anywhere from the Labrador Sea to the North East Atlantic (Hatch and Nettleship, 1998; Mallory, 2005). In general, then, the overwintering range of the kittiwakes breeding at Prince Leopold Island extends further south than that of the murres and fulmars (Figure 5.10).

The lack of a significant trend in THg concentrations in eggs of kittiwakes is similar to time series data showing no change or decreasing Hg concentrations in seabirds at lower latitudes such as herring gulls from the Great Lakes (Koster et al., 1996), common terns from the New Jersey coast (Burger and Gochfeld, 2004) and the Wadden Sea (Becker et al., 2001), and little terns from the Baltic Sea (Thyen et al., 2000). This is in agreement with the declining Hg emissions in North America (Lindberg et al., 2007), suggesting that, by overwintering at lower latitudes, kittiwakes may be exposed to less Hg over the year and are less impacted by the changing Hg bioavailability in the Arctic. In contrast, since the ivory gulls, murres and fulmars spend extended periods of time at higher latitudes, the trend of increasing Hg concentrations in their eggs may reflect different atmospheric sources and/or deposition processes in higher latitude regions when compared to lower latitude regions. Although there has not been a net change in the size of the atmospheric pool of Hg in the Northern Hemisphere since the mid-1970s (Lindberg et al., 2007), the proportionate emissions attributed to the various source regions have changed, with Hg emissions from Asia increasing, and those from Europe and North America decreasing (Lindberg et al., 2007). Further studies are needed to investigate changes in the bioavailability of Hg in the Arctic and to what extent changes in regional emission patterns are affecting the Hg concentrations in High Arctic seabirds.

### Case Study 3. Non-predatory and predatory fish from Arctic reservoirs

A specific source for MeHg in freshwater biota is the construction of man-made reservoirs and river diversion systems. The process of decomposition of flooded organic material (in soil and in vegetation) appears to promote Hg methylation, but the physical parameters of reservoirs may also be important. Rates of Hg methylation are far greater in anaerobic-aerobic transition zones with enhanced activity of sulfate-reducing bacteria which are the main methylators of Hg (see Section 3.3). In Arctic and sub-Arctic regions, this has been shown in Canada (e.g., Bodaly et al., 1984) and Finland (Lodenius et al., 1983; Verta et al., 1985). Increases in MeHg were found in all compartments of the reservoirs: water, zooplankton, benthic invertebrates, and fish; downstream effects were reported (e.g., Bodaly et al., 1997; Lucotte et al.,

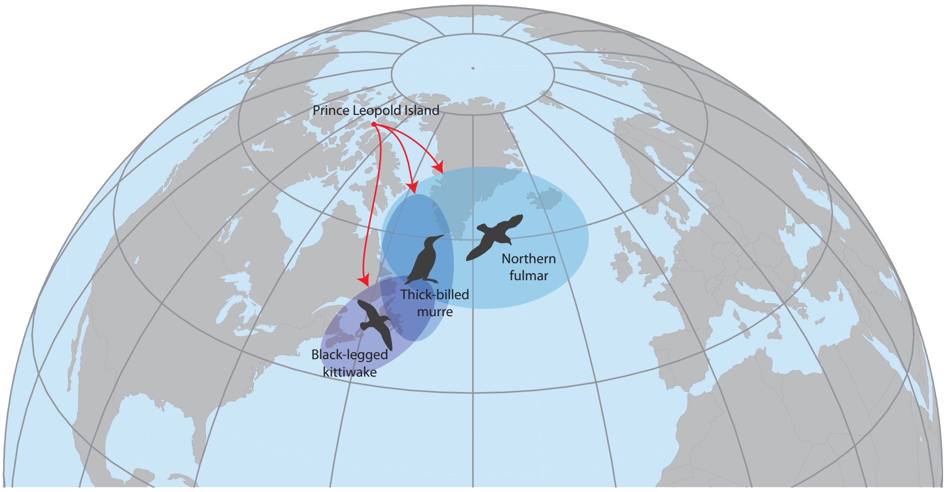

Figure 5.10. Assumed overwintering areas based on best available information for thick-billed murres, northern fulmars and black-legged kittiwakes breeding on Prince Leopold Island, Canada.

1999; Schetagne et al., 2000; St. Louis et al., 2004). In most cases, the MeHg concentration in water and in fish eventually decreases, with a typical recovery time of more than 10 years for water and more than 20 years for fish.

The post impoundment time trends for MeHg concentrations in non-piscivorous whitefish (*Coregonus clupeaformis*) and in piscivorous fish, walleye (*Sander vitreus*) and northern pike (*Esox lucius*), from some hydroelectric reservoirs in northern Manitoba and the Finnish Arctic are presented in Figure 5.11. These reservoirs were constructed in the late 1960s to mid-1970s. The muscle Hg concentration in all the fish increased shortly after the impoundment, with higher Hg concentrations in the predatory fish than the non-predatory fish. The Hg concentration in the fish peaked in the first ten years after the impoundment and then started to decline. By the 2000s (20 to 30 years after the impoundment) the Hg concentration in fish had recovered to background levels. Atmospheric Hg deposition plays a negligible role in the fish MeHg concentration in these reservoirs.

### Case Study 4. Burbot and lake trout from the Mackenzie River basin, Canada

Long-term monitoring of THg in burbot (*Lota lota*) has been ongoing at the Rampart Rapids of the Mackenzie River near Fort Good Hope since 1985 and in Great Slave Lake since 1998

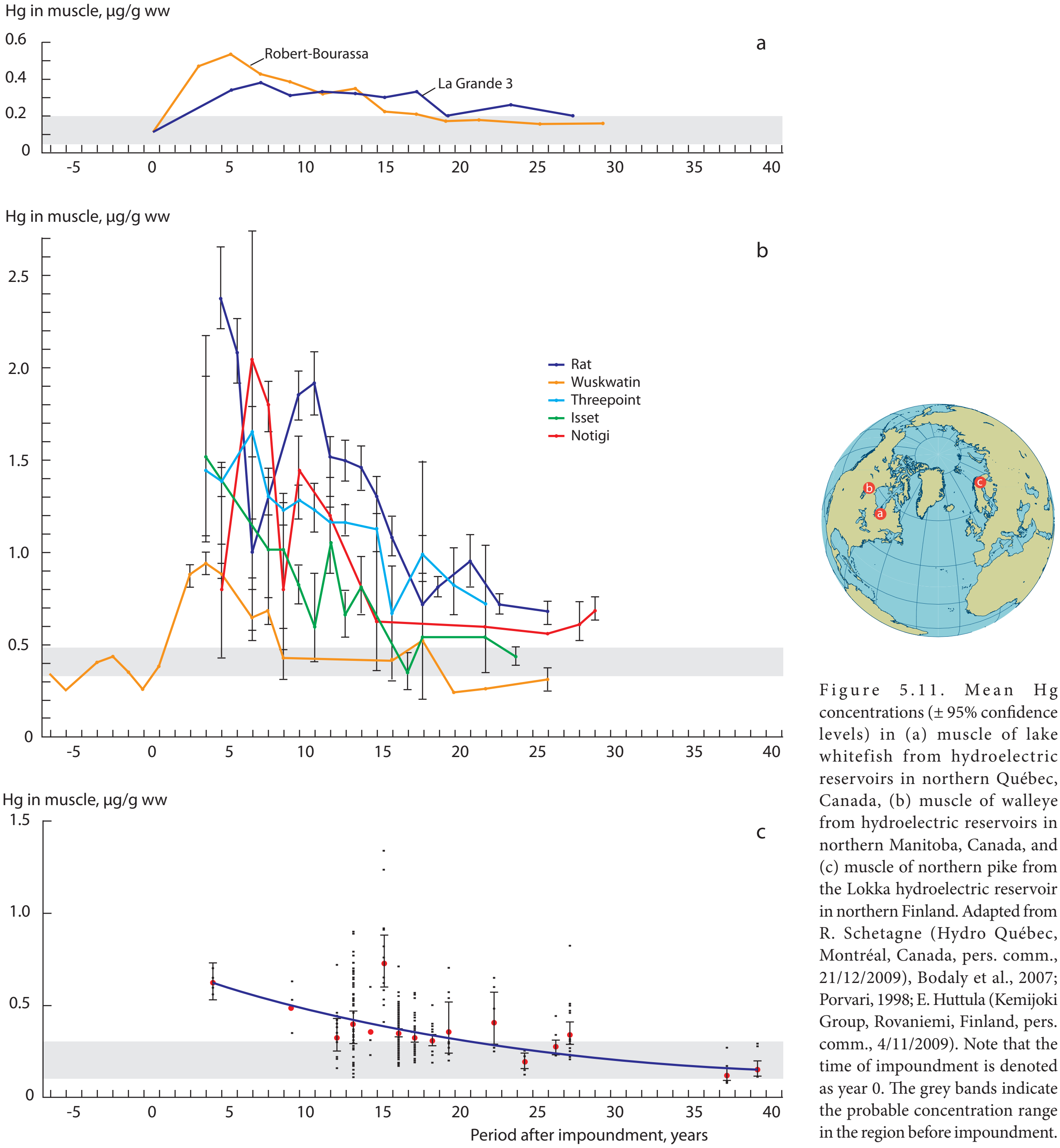

Figure 5.11. Mean Hg concentrations (± 95% confidence levels) in (a) muscle of lake whitefish from hydroelectric reservoirs in northern Québec, Canada, (b) muscle of walleye from hydroelectric reservoirs in northern Manitoba, Canada, and (c) muscle of northern pike from the Lokka hydroelectric reservoir in northern Finland. Adapted from R. Schetagne (Hydro Québec, Montréal, Canada, pers. comm., 21/12/2009), Bodaly et al., 2007; Porvari, 1998; E. Huttula (Kemijoki Group, Rovaniemi, Finland, pers. comm., 4/11/2009). Note that the time of impoundment is denoted as year 0. The grey bands indicate the probable concentration range in the region before impoundment.

(Evans et al., 2005a; Lockhart et al., 2005a; see Figure 5.12). Mercury levels have also been periodically monitored in lake trout (*Salvelinus namaycush*) in lakes along the Mackenzie River (Evans et al., 2005a; Lockhart et al., 2005a).

Burbot is a top predator freshwater fish and an important staple for northern Canadian communities. Carrie et al. (2010) recently examined the temporal trend for THg in muscle of burbot from the Fort Good Hope area and the causes for such a trend. The fish were collected in winter (December to January) by the local residents and analyzed for age (*via* otoliths), sex, morphometry, contaminants (THg and PCBs), and stable isotopes ($\delta^{13}C$, $\delta^{15}N$). Overall, Carrie et al. (2010) reported data for 13 time points over the 24-year period from 1985 to 2008. Over this period, muscle Hg concentrations increased around 2-fold (Figure 5.13) and cannot be explained by differing physiological characteristics or changes in feeding behavior. There is no significant change in $\delta^{15}N$ and $\delta^{13}C$ data over the period 1995 to 2005, implying that burbot have not been feeding differently; nor are there significant differences for $\delta^{15}N$ between years of lower Hg concentration (1999: 0.24 ± 0.06 µg/g; mean ± SD) and higher Hg concentration (2004: 0.40 ± 0.09 µg/g; mean ± SD). Additionally, no correlation was noted between muscle Hg concentration and $\delta^{15}N$ or $\delta^{13}C$. There is also no correlation between muscle Hg concentration and fish size (weight or length), with the exception of a weak, although statistically significant, correlation with age. This last finding is contrary to observations for other fish species (e.g., Evans et al., 2005b; Gantner et al., 2009) and may be attributed to a relatively short half-life of Hg in burbot muscle and liver (Carrie et al., 2010). The overall increasing trend in burbot Hg concentration and its associated large degree of temporal variability (Figure 5.13) cannot be explained by the atmospheric Hg trend either, as atmospheric Hg concentrations have been stable or falling in the Arctic over the past 25 years (Chapter 2).

Using a dated sediment core from Hare Indian Lake, a tributary lake near the Mackenzie River sampling site (Figure 5.12), Carrie et al. (2010) showed striking temporal similarities between Hg concentration in burbot muscle and in Hare Indian Lake sediment core slices when plotted against year of collection and median year of deposition, respectively (Figure 5.13). Furthermore, there is an almost perfect point-by-point co-variation between the Hg concentration (normalized against the conservative element titanium (Ti) to correct for potential geogenic inputs of Hg) in the sediment core and labile, algal-derived organic matter (measured as S1 and S2 carbon by Rock-Eval pyrolysis; Sanei and Goodarzi, 2006) over the past 150 years, similar to what has been reported in two High Arctic lakes (Outridge et al., 2007). While tagging data on Mackenzie River burbot are scarce, the results of a study conducted in Aklavik (450 km away in the Mackenzie Delta) found that burbot for the most part stayed within 15 km of their tagging point (Stein et al, 1973). Also, Hare Indian Lake is characteristic of burbot feeding habitat (McPhail and Lindsey, 1970; Scott and Crossman, 1973). Based on these results, Carrie et al. (2010) suggested that the significant increase in Hg concentration in burbot muscle since the 1980s may be strongly influenced by increased concentrations of algal-derived organic matter in the water column. This is possible as algal blooms are efficient scavengers, concentrators, and possibly producers, of MeHg from and to the water column and hence sources

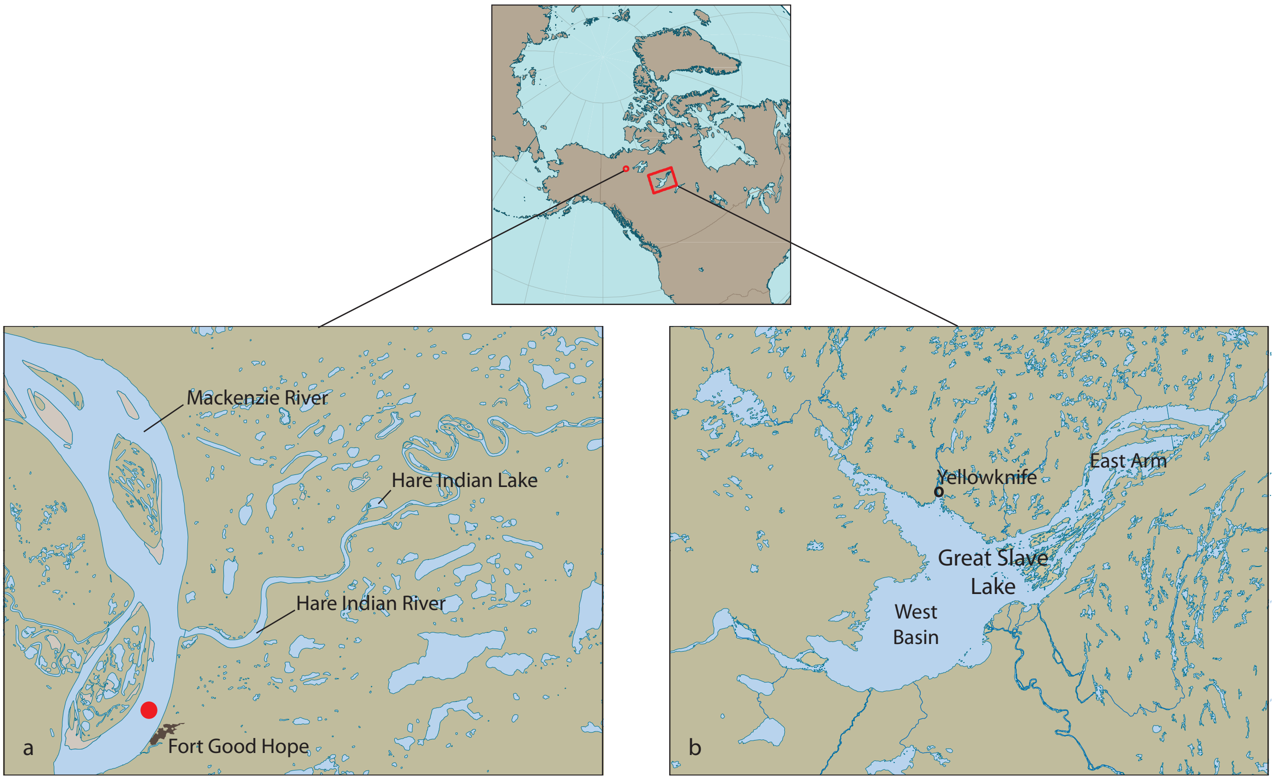

Figure 5.12. (a) Fort Good Hope region, showing the fish collection site (red dot) and the lake sediment core site (Hare Indian Lake), and (b) Great Slave Lake showing the West Basin and East Arm. Modified from Carrie et al. (2010).

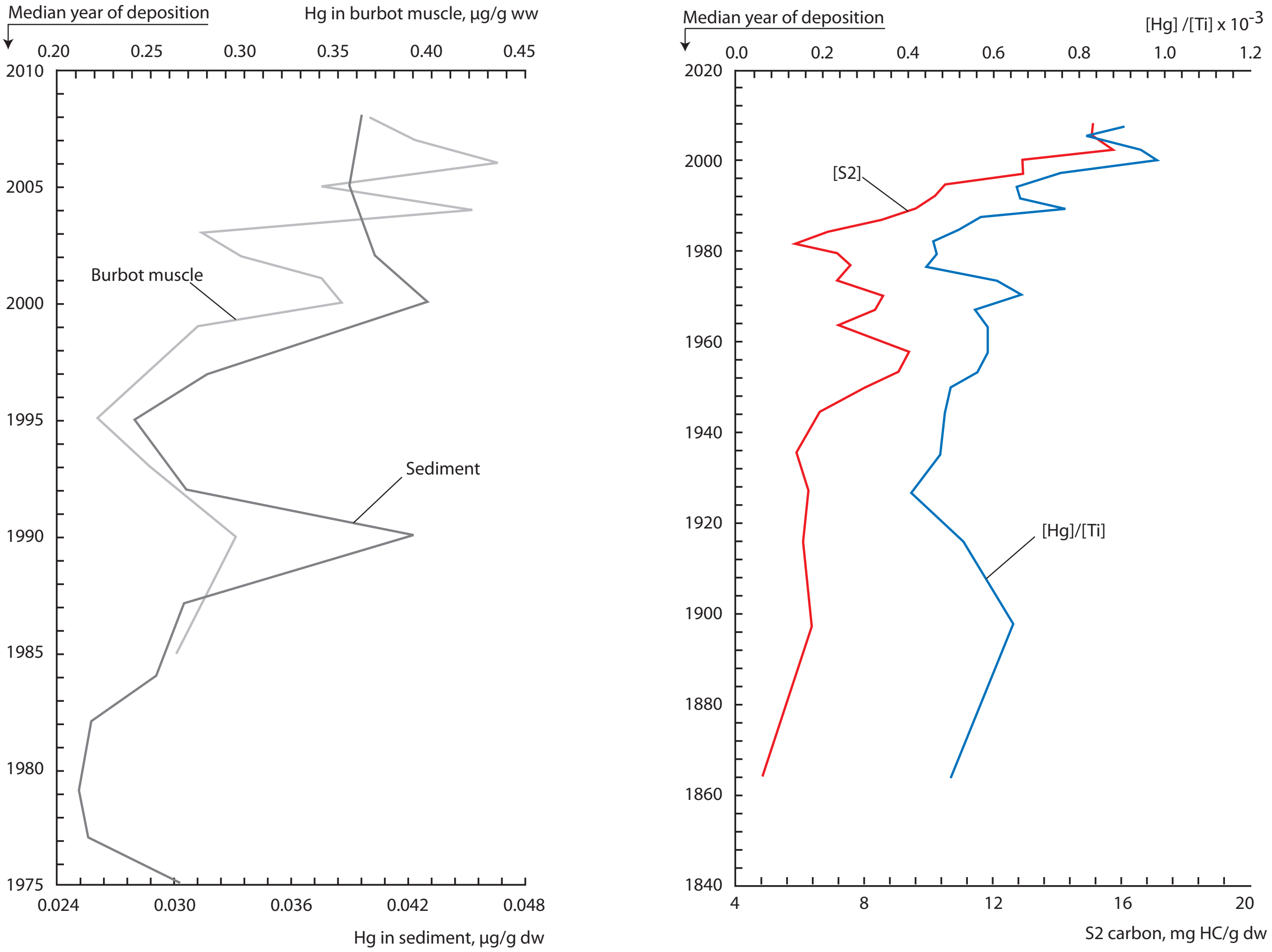

Figure 5.13. Chronological variations (a) in total mercury concentration in Hare Indian Lake sediment core and in Mackenzie River burbot and (b) by point comparison between [THg]/[Ti] and S2 carbon concentrations in the Hare Indian lake sediment core. Source: Carrie et al. (2010).

of bioaccumulative Hg to larger biota (Balogh et al., 2002; Pickhardt et al., 2002; Luengen and Flegal, 2009).

The significant increase in algal-derived organic matter as indicated from the sediment core is also consistent with the climatic record of the Mackenzie Basin. The mean annual air temperature for the nearby Norman Wells, for instance, has seen a statistically significant increase of about 1.9 °C since the early 1970s. This region has also seen a significant decrease in snow cover over the same period. Reduction in ice-season length, and consequent improvement in the light regime for algal growth, is thus a plausible explanation for the coincidence among rising air temperature, algal productivity, and increasing Hg in Hare Indian Lake sediment in Mackenzie River burbot.

A generally increasing trend, although not always statistically significant, has also been observed in burbot and lake trout in a broader range of lakes in the Mackenzie River Basin with different physical features and watersheds (Evans et al., 2005b). The greatest increases in Hg concentration in lake trout are observed in warmer, smaller, and shallower lakes with large watersheds. Small lakes with large watersheds have a proportionately larger littoral zone relative to the pelagic zone, a closer connection to watershed inputs of Hg and dissolved organic carbon, warm to a greater extent in summer, and thus potentially experience a higher rate of increase in algal productivity.

Furthermore, different time trends in different fish species in a given lake from this region suggest that the biology of the fish is also important (Evans et al., 2005b). This is most evident for Great Slave Lake which has two distinct sub-basins (see Figure 5.12): the West Basin is strongly influenced by the Slave River, while the East Arm is deeper and less productive. In the West Basin, burbot have shown a pronounced trend in Hg concentration, while trends are less evident for lake trout (Table 5.3). This is possibly because the lake trout is a coldwater stenotherm and thus more associated with deeper waters, whereas burbot is a nearshore fish that is exposed more to the littoral zone. Mercury concentrations are lower in both species in the East Arm where watershed influences are weaker and the waters deeper.

### Case Study 5. Ringed seals from Ulukhaktok

Total Hg concentration in muscle tissue from ringed seals (*Phoca hispida*) sampled at Ulukhaktok (Holman), NWT, in the western Canadian Arctic was recently reported for ten years from the period 1973 to 2007 (Gaden et al., 2009). All samples were taken during the subsistence harvests primarily during June and prior to break-up of the sea ice. In total, 214 samples of muscle tissue from adult seals ranging in age from 7 to 36 yrs were analyzed for THg. Stable isotope ratios of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) were also analyzed for 117 of the muscle tissue samples. These biomarkers, together with biological data (age and sex) and climate data (length of the ice-free season in the Eastern Amundsen Gulf), were examined for trends.

No significant difference was found in Hg concentration between the sexes ($p = 0.31$), therefore male and female seal samples were pooled for subsequent analysis. No temporal trends in THg were observed for the study period from 1973 to 2007 ($p = 0.24$), but a significant association of the muscle Hg concentration was found with the length of the ice-free season in the previous year to seal harvest. The THg concentrations displayed a 2nd-order polynomial trend in which concentrations increased from about 140 ice-free days onward and about 110 days and under (Figure 5.14), suggesting that the muscle Hg concentration in seals may have been influenced by the previous year's environmental conditions which affect the types and/or amounts of prey eaten by the ringed seals. This reasoning is based upon (i) the turnover of stable isotope ratios and Hg in muscle tissue, (ii) the seal population's seasonal distribution and diet and (iii) biological and ecological responses to shifts in climate parameters.

By knowing the turnover times of elements in certain tissues, the timeframe of prey consumption and subsequent deposition into tissues can be identified. In this study, the turnover of THg in seal muscle was found to be about twice as long (seven months) as the typical replacement time of tissue nitrogen and carbon (three months) (Gyrd-Hansen, 1981; Baumann et al., 1994). Since the seals were harvested during June–July, the turnover times of the $\delta^{15}N$ and $\delta^{13}C$ signatures correspond to the seal diet in March (late winter) and November (late autumn to early winter) for the THg concentrations. This mismatch in turnover times may explain why THg was strongly associated with the previous ice-free season but that $\delta^{15}N$ and $\delta^{13}C$ were not. It is likely that the length of the ice-free season in the previous year may have affected the seal diet in the consecutive autumn, reflecting the measured THg concentrations, in comparison to late winter (associated with the $\delta^{15}N$ and $\delta^{13}C$ signatures).

The next step, then, was to consider the diet of the study population during late autumn to early winter. Ringed seals are opportunistic foragers and have a varied diet that changes seasonally. Work by Smith (1987) showed that adults in the study population remain near Ulukhaktok in the Prince Albert Sound from late autumn to ice break-up. Throughout the ice-covered period, ringed seals primarily consume Arctic cod (*Boreogadus saida*) (Smith, 1987). Therefore, variation in the length of the ice-free season may have influenced the overall exposure of seals to Hg by means of changes in the cod

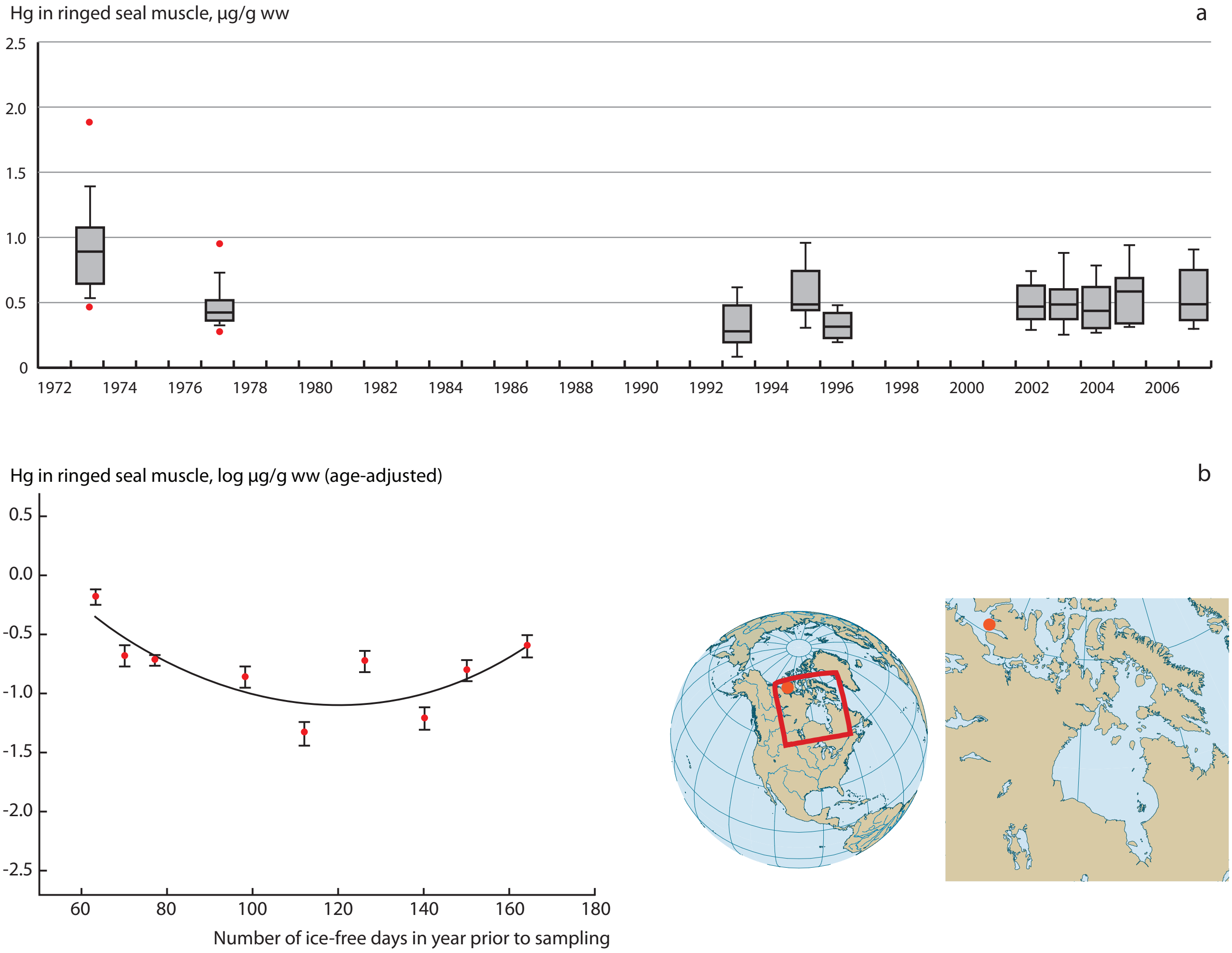

Figure 5.14. (a) Box and whisker plot of total Hg concentrations in muscle of adult (7+ yrs) ringed seals (males and females) sampled during the period 1973 to 2007, Ulukhaktok (Holman), NWT, Canada. Lines in boxes represent mean concentrations; whiskers represent 5th and 95th percentiles. (b) Log-transformed, age-adjusted mean total Hg concentration in muscle of adult (7+ yrs) ringed seals (males and females) plotted against ice-free days in the year prior to sampling. Source: Gaden et al. (2009).

population structure or abundance available to seals in the late autumn to early winter.

Gaden et al. (2009) postulated that during short ice-free seasons there may have been shifts in the cohort composition of the Arctic cod population, whereas long ice-free seasons could have resulted in higher numbers of the prey species. Young Arctic cod are particularly vulnerable to the harsh conditions imposed by the ice-covered period (Michaud et al., 1996). In years with long winters and shorter ice-free seasons, a majority of older, more contaminated cod may have out-lived the younger cohorts, exposing predators like the seals to a higher Hg intake (Lockhart and Evans, 2000). Alternatively, longer ice-free seasons are likely to have favored the survival and abundance of the cod via the longer growing season, enhanced ecological productivity and overall increased food availability in the pelagic food web. With the higher abundance of Arctic cod, ringed seals could have fulfilled a larger proportion of their diet with cod and subsequently accumulated higher Hg loads.

Findings suggest that shifts in climate over the study period indirectly influenced Hg uptake in ringed seals in the western Canadian Arctic. The length of the ice-free season in the Arctic is predicted to increase in the future (Walsh, 2008), and therefore it is plausible that Hg concentrations may rise accordingly.

### Case Study 6. Reindeer and Arctic char in northern Scandinavia

Atmospheric deposition is the dominant source of Hg to northern Scandinavia. Early Hg deposition measurements were made at irregular intervals in Jergul and Överbygd in 1986 and 1987 (Iverfeldt, 1991). Between 1991 and 1996, Hg bulk deposition measurements were performed close to Kiruna on a monthly basis (Berg et al., 2002). Deposition measurements have been ongoing at the Pallas-Matorova station since 1996 (Wängberg et al., 2007). When comparing the bulk atmospheric deposition of Hg at these four locations, there seems to have been a 30% to 50% decrease within the past 20 years in this region, depending on whether the Överbygd data are included or not (Figure 5.15a). This reduction in Hg deposition is supported to some extent by a moss survey in Sweden. A monitoring program to measure atmospheric heavy metal deposition using mosses was established in 1980 (Harmens et al, 2008). Data collected at five-year intervals between 1985 and 2005 show Hg concentrations in moss from this region to range from < 0.05 to 0.1 µg/g dw for the period 1985 to 1995, but to decrease to < 0.05 µg/g dw after 2000 (www3.ivl.se/miljo/projekt/mossa/hg.asp).

Mercury levels in reindeer (*Rangifer tarandus*) and Arctic char (*Salvelinus alpinus*) from the Abisko National Park, Sweden, have been monitored since the early 1980s. The area is located around 450 to 700 m above sea level and is not affected by local pollution. Reindeer are strict herbivores feeding predominantly on lichen in winter, while the summer diet also includes low growing sedges and willows. Due to this short terrestrial food web, reindeer have been suggested as a useful species for monitoring change in Hg deposition as a result of the direct contaminant pathway air → plant → reindeer (Poissant et al., 2008; Lokken et al., 2009). As part of the Swedish contaminant monitoring program, muscle tissue

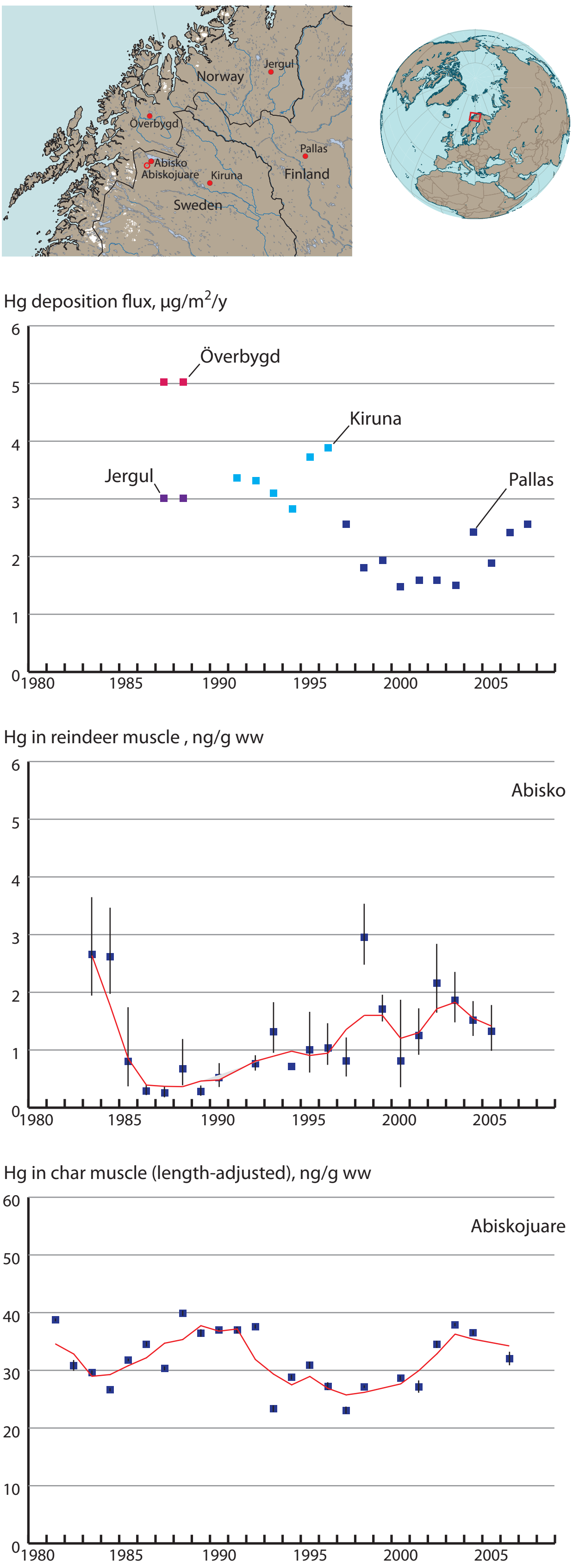

Figure 5.15. (a) Atmospheric Hg deposition at various sites in northern Scandinavia between 1986 and 2007. (b) Total Hg concentrations in muscle of reindeer from Abisko, northern Sweden (geometric mean ± 95% confidence limits). (c) Total Hg concentrations in muscle of Arctic char from Lake Abiskojaure, northern Sweden (length-adjusted geometric means). The red line shows a three-point running mean smoother ($p < 0.05$). Data from Wängberg et al. (2007), Odsjö et al. (2007) and Bignert (2002).

from the front tibia of male reindeer (3 years old) is sampled before the rutting period in September each year. The uptake of Hg in freshwater fish is probably more complex, due to several factors affecting uptake, such as the humic content of the water, acidity and temperature, although recent data suggest a rapid response in fish Hg content to changes in air deposition (Harris et al., 2007). Arctic char of equal size (ca. 30 cm, 220 g, 4 years old) are sampled in August/September each year from Lake Abiskojaure, which is an oligotrophic lake with no vegetation.

Temporal trends show no significant change in THg concentration in the muscle tissue of reindeer (Odsjö et al., 2007) or char (Bignert, 2002) from Abisko over the past 25 years (Figure 5.15b and c). For reindeer, the same is true for THg liver concentrations, which generally follow the same pattern as for muscle concentrations (data not shown). Although not significant for the time period as a whole, the apparent increase in reindeer muscle Hg levels since around 1990 (Figure 5.15b) contradicts the calculated decrease in atmospheric Hg deposition between the late 1980s and 2000s in the same region. It should be noted, however, that the concentrations in reindeer muscle are very low, with a geometric mean of 1.00 ng/g ww (0.73 to 1.37 ng/g ww; 95% confidence limits), and often close to the detection limit. Liver concentrations are about 40 times higher but this tissue showed no trend (Table 5.3). Similarly for char, there is no notable relationship between Hg deposition levels and time trends in fish (Figure 5.15c).

It can be assumed that the Hg deposition in Abisko mimics reasonably well the measured deposition at the various stations in northern Scandinavia. The apparent decrease in Hg deposition and moss concentration in the area is not reflected in the Hg levels in terrestrial herbivore reindeer or in Arctic char over the same time period. This indicates that factors other than atmospheric Hg deposition are more important drivers for Hg concentration in biota in this region. These factors may be process-based and dependent on environmental characteristics, such as changes in food availability, food selection, or food web structure. Climate change may alter food availability and food selection for reindeer, thus affecting dietary exposure to Hg more than changes in deposition. Consequently, even moderate changes in deposition fluxes may not be reflected in these species over short periods.

## Case Study 7. Beluga from the western Canadian Arctic

Mercury concentrations in various tissues of beluga from the western Canadian Arctic have been monitored since 1981, making this the longest temporal dataset for Hg concentrations in Arctic beluga (Lockhart et al., 2005b; Stern and Lockhart, 2009). Since 1981, Hg concentrations in the beluga population at Hendrickson Island have increased significantly (Table 5.3). Although there is a good relationship between beluga age and liver Hg concentration (Figure 5.16), there is no simple relationship between muscle Hg concentration and beluga age. However, larger individuals tend to have higher Hg concentrations in their muscle and this reflects habitat use and diet (Loseto et al., 2008a) (Figure 5.16). This temporal trend and size-dependence cannot be explained by the atmospheric Hg trend, and so there have been extensive studies in recent years on Hg sources other than atmospheric deposition (Leitch et al., 2007), as well as on the habitat and feeding behavior of beluga (Loseto et al., 2006, 2008b, 2009).

Evaluating the relative importance of Hg sources to food webs provided a bottom-up approach to examining drivers of Hg temporal trends in top predators. In addition to atmospheric deposition, Hg is also transported to the Beaufort Sea from riverine discharge, thawing permafrost, coastal erosion, and oceanic circulation (Leitch et al., 2007). The Mackenzie River was found to be a particularly important Hg source, transporting about 2 tonnes of THg per year to the Mackenzie Delta, which is similar to or higher than the atmospheric Hg depositional flux to the Beaufort Sea (Leitch et al., 2007). The Mackenzie River is the largest river emptying into the Beaufort Sea, providing many of the nutrients and much of the particulate organic matter that fuel nearshore and potentially offshore pelagic food webs (Carmack and Macdonald, 2002). The impact of the large Hg flux associated with the Mackenzie River outflow may not be limited to the nearshore food web; the Hg could be further deposited and re-distributed in the biologically active

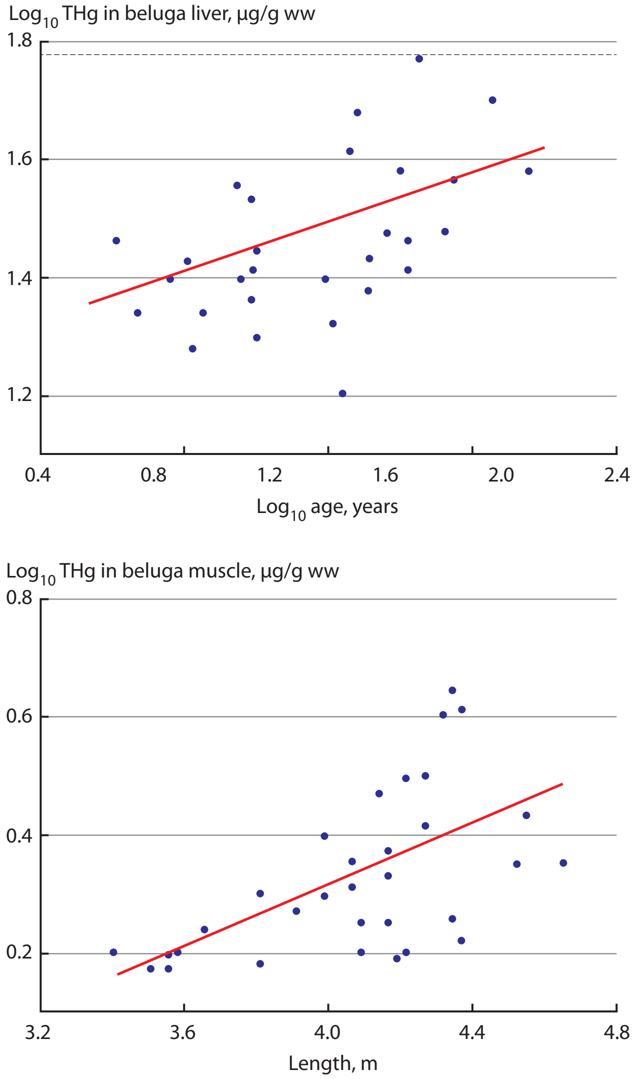

Figure 5.16. The relationship between THg concentrations in beluga liver and age (in years, estimated based on 1 growth layer group) is best described by an exponential relationship (R2 = 0.24; $p$ = 0.006) demonstrating accumulation over time, whereas for THg in beluga muscle it is best described by an exponential relationship with length (R2 = 0.35; $p$ <0.0001) where the biomagnification process dominates. The dashed line indicates the observed effects level in marine mammals of 60 µg/g ww (see Section 6.3.2). Modified from Loseto et al. (2008a).

shelf break area where Hg may be resuspended and/or made bioavailable to the offshore food web (Loseto et al., 2008b).

In contrast to evaluating sources to food webs that biomagnify to levels measured in top predators, a top-down approach was considered to evaluate food web processes (guild and trophic transfer of Hg) and predator behavior (habitat use, diet preferences) to understand Hg concentrations in the Beaufort Sea beluga population. First, beluga behavior was examined to gain insight into diet preferences and dietary exposure to Hg. Combining beluga movement patterns (with use of satellite telemetry) and features of the physical environment (sea ice, bathymetry), the Beaufort Sea beluga population was found to sexually segregate during their summer habitat use (Loseto et al., 2006). This provided a basis for considering food webs and dietary Hg sources associated with the different habitats to which individuals of the population were potentially exposed (see Chapter 3, Figure 3.6). Food webs were then characterized according to the three habitats the Beaufort Sea beluga population appeared to feed in (Loseto et al., 2008b). Hypothetical feeding groups and food webs provided a framework to begin merging the predator behavior, food web dynamics and dietary sources of Hg. Results demonstrated the role and importance both of Hg sources to food webs and the processes within food webs that may differ from benthic to pelagic systems (i.e., bioaccumulation and biodilution) and finally the importance of food web length toward describing sources to predators (i.e., beluga) (Loseto et al., 2008b).

A detailed fatty acid biomarker approach was also used to define diet (Loseto et al., 2009). Data revealed Arctic cod to be the dominant prey item for the Beaufort Sea beluga population. However, size-related dietary differences were evident, whereby larger-sized beluga preferred offshore Arctic cod, and smaller-sized beluga appeared to feed on prey in nearshore habitats that included nearshore Arctic cod. If these size trends can be explained by energetics then the large males need to maintain body mass by adjusting foraging behavior to feed either on energy-rich prey or to feed more often (Boyd et al., 1997), suggesting a greater abundance or availability of Arctic cod in the deep offshore Arctic Ocean.

Therefore, evaluating beluga Hg levels required that both a top-down and bottom-up perspective be considered. That is, the top-down factors influencing beluga habitat use, such as predation, resource selection, and nursing also defined feeding behavior and associated dietary Hg exposure among size and sex classes in the population. From the bottom-up perspective, different food webs, for example the nearshore estuarine food web, had lower Hg levels relative to the offshore pelagic food web that biomagnified to top predators (see Chapter 3). When integrating the sources of Hg, the food web processes and structure, and predator feeding ecology, they revealed the size-dependence of Hg concentration in beluga muscle. A concerted effort to merge the two approaches is needed to further clarify the dominance of source or process in driving Hg trends in the Beaufort Sea beluga and other higher trophic level species (Chapter 7).

### Case Study 8. Greenland polar bears

Recent time series of Hg concentrations in polar bear hair from northwestern Greenland, East Greenland and Svalbard have been reported by Dietz et al. (2006a) and are updated in Figure 5.17. There appears to be an overall upward trend in the annual median Hg concentration in polar bear hair from Greenland and no overall trend for Svalbard. Further analysis was carried out to evaluate whether the medians as well as the residuals from the trend line calculated from the annual medians could

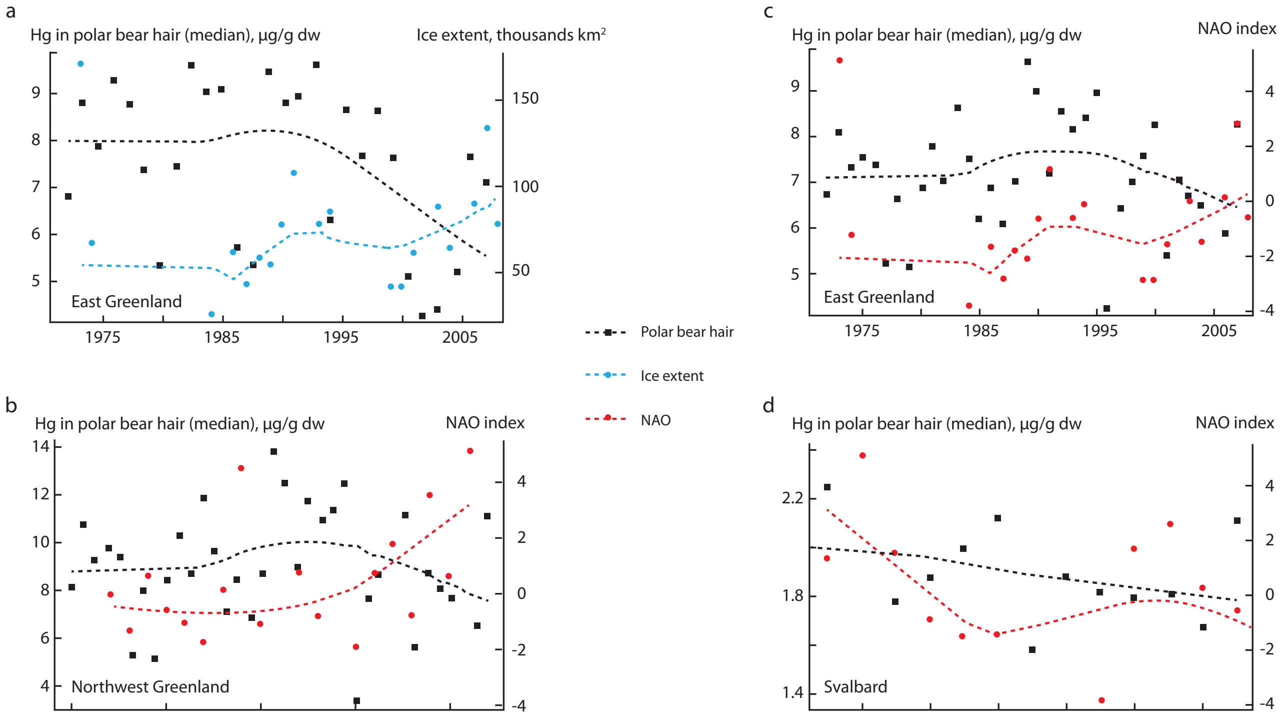

Figure 5.17. Temporal trends and Loess smoother estimates of (a) median Hg concentrations in polar bear hair and ice extent in East Greenland; and polar bear hair and the North Atlantic Oscillation Index for (b) northwestern Greenland, (c) East Greenland and (c) Svalbard. Source: Dietz et al. (2008a,b, 2009b).

Table 5.6. Correlation coefficients and significance levels (in brackets) between the Loess smoother estimate (see Figure 5.17) based on median mercury concentrations in polar bear hair and ice extent and the North Atlantic Oscillation Index for northwestern Greenland, East Greenland and Svalbard. Source: Dietz et al. (2006a, 2008a,b, 2009b).

| Hg concentration vs | Ice extent | North Atlantic Oscillation Index |
|---|---|---|
| Region | Loess smoother estimate based on median values | Loess smoother estimate based on median values |
| Northwestern Greenland | | -0.97 (0.001) |
| East Greenland | -0.59 (0.02) | -0.48 (0.04) |
| Svalbard | | 0.67 (0.02) |

be linked to climate variables such as polar sea-ice coverage and the North Atlantic Oscillation (NAO) Index (Dietz et al., 2008a,b, 2009b). Using median Hg values, significant correlations were found with ice extent (average for September) in East Greenland and for the NAO Index in all three regions (Table 5.6, Figure 5.17). For the residuals deviating from the median, a significant negative correlation was detected between the NAO Index and Hg concentration in East Greenland polar bear hair, whereas a weak positive correlation was detected for bears from the Svalbard area. Significant negative correlations were also found between Hg concentration in East Greenland polar bear hair and the sea-ice extent in the same year. Overall the decreasing sea-ice extent and the decline in the NAO Index in East Greenland were correlated with increases in Hg concentration in polar bears, whereas the opposite was observed at Svalbard. Ongoing calculations on the effect on stable isotopes will be used to resolve whether changes in the food chain can explain part of the change in Hg concentration. It remains unresolved why such differences appear in these two regions and to what extent these are linked to changes in transport routes or the food chain. However, East Greenland polar bears have easier access to the harp and hooded seals breeding areas as the ice edge gets closer to the coast (R. Dietz, National Environmental Research Institute, Denmark, and E.W. Born, Greenland Institute of Natural Resources, unpublished data). On the other hand, reduced sea ice at Svalbard may result in longer fasting periods on land resulting in lower Hg exposure. Clearly, the relationships found indicate that climate parameters should be taken into consideration when predicting trends in biotic Hg concentration.

## 5.5. Conclusions and recommendations

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

### How much higher are current mercury levels in Arctic biota than in the pre-industrial period, and thus what is the anthropogenic contribution to mercury in modern biota?

1. Long-term trend studies using archeological and museum collections suggest that on average over 90% (median 92%, range 74% to 94%) of the present-day Hg in upper trophic level marine biota (beluga, ringed seal, polar bear, birds of prey) is of anthropogenic origin.
2. This roughly ten-fold increase in Hg concentration in upper trophic level marine biota over the past few centuries is much greater than the increase in ambient environmental Hg levels (~25% in global upper oceans, see Chapter 2), probably because of a non-linear relationship between increases in environmental Hg levels and biotic Hg levels due to biomagnification.
3. The late 19th to 20th century showed a steep increase in biotic Hg levels compared to relatively constant values over the previous four to six centuries. The average rate of Hg increase over the past 150 years was usually within the range of 1% to 4% per year.

*In terms of long-term trends, available information is limited to fewer than ten wildlife species in the Canadian and Greenlandic regions of the Arctic; coverage of low trophic level species and invertebrates is particularly limited. Historical time series from the Alaskan and Russian Arctic would be a valuable addition to knowledge of anthropogenic impacts on modern Hg levels.*

### In which areas and species have mercury levels recently increased or decreased?

4. Of the 83 recent time series (i.e., covering the past few decades) which met the specified requirement of at least six years of data, 13 (16%) showed a statistically significant increasing trend (including two from different tissues in the same animals), four (5%) showed a statistically significant downward trend, 21 (25%) showed a statistically significant non-linear trend (non-linear trend component is significant), with the rest (54%) showing no statistically significant trend.
5. Most of the time series showing significantly increasing trends involved marine species, followed by freshwater fish species. No significant increases in Hg were found for terrestrial animals in recent decades.
6. A greater number of significantly increasing trends occurred in Canada and Greenland compared with northern Europe, suggesting that Hg concentrations are increasing to a greater extent in the western Arctic (west of 40° W) compared with the eastern Arctic (east of 40° W).
7. The statistical 'adequacy' of recent time series to detect pre-determined annual changes in Hg concentration has increased from 10% to 19% of total datasets over the past five years, owing to continued monitoring and the resulting growth in the statistical power of available time series.

*For recent biotic time series, there is a regional imbalance in data availability. Few or no tissue monitoring data which met* *the specified data requirements were available from the Alaskan, Russian or Finnish areas of the Arctic. Continued support for ongoing time series, and initiation of biotic Hg monitoring in regions presently lacking coverage, will further add to the accuracy of the picture of recent trends in biotic Hg concentrations.*

### Why are mercury levels in Arctic biota increasing or decreasing?

8. The significant increase in Hg concentration in present-day Arctic animals compared to their pre-industrial counterparts is probably explained primarily by the increase in anthropogenic Hg in Arctic ecosystems.

9. The temporal variations in Hg concentration in Arctic animals over recent decades, however, cannot be solely explained by changes in anthropogenic atmospheric Hg emissions. Recent biotic Hg trends that are increasing in the Canadian and Greenlandic Arctic do not match regional atmospheric Hg records which show stable or declining trends over recent decades.

10. The extent to which regional shifts in Hg emissions from Europe and North America to Asia are currently affecting Hg concentrations in Arctic biota remains unknown. Environmental and ecological processes appear to play an increasingly important role in determining Hg trends in Arctic animals, particularly those at higher trophic levels.

*Uncertainties concerning the net deposition rate of Hg from AMDEs and other wet and dry atmospheric deposition processes in the Arctic (see Chapter 3) limit the ability to evaluate competing theories about the important drivers of recent trends in biotic Hg levels. Little is known about how changes in the Arctic cryosphere (snow, lake and sea ice, brine, permafrost) are affecting Hg bioaccumulation in Arctic ecosystems. Also lacking is systematic information on habitat and feeding behavior for many Arctic species, which can affect Hg concentrations in biota through alterations in MeHg assimilation and biomagnification.*

# Chapter 6

# What are the Toxicological Effects of Mercury in Arctic Biota?

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## 6.1. Introduction

Previous AMAP assessments reported, as for other ecosystems, that the highest biological mercury (Hg) concentrations in the marine environment were found within the upper trophic levels (Dietz et al., 1998a,b; AMAP, 2005). Therefore, Hg effects assessments relating to those species considered at risk (i.e., with the highest presumed exposure) have been almost entirely carried out on species inhabiting this ecological niche both in the Arctic and at lower latitudes. For these reasons, this assessment focuses on addressing possible toxicological effects in marine animals with elevated Hg concentrations, as well as other higher trophic level species in the Arctic, rather than addressing the entire Arctic ecosystem. A recent review reported that Hg concentrations have increased over the past 150 years, resulting in more than 92% of the Hg body burden in higher trophic level species being of man-made origin (see Section 5.2; Dietz et al., 2009a). This means that many Arctic species are exposed to much higher Hg levels today than in historic times.

Biological effects can be considered at different temporal and spatial scales and at varying levels of organization, from the molecular to the global level. Biomarkers measurable at the molecular level may respond early or at lower exposure concentrations than those at higher levels of organization but are not readily interpreted ecologically and may not easily be anchored with a phenotypic response (especially one that is clearly adverse). Bio-indicator measures with established ecological relevance, such as population declines or reduced reproductive rates, respond late or at higher concentrations in this cascade and usually involve multi-factorial scenarios that complicate diagnosis and thus implementation of preventive measures. Thus, these population level impacts are hard to detect and subtle, yet potentially significant for populations (especially those declining or targeted for recovery) and provide a difficult dilemma for scientists and managers.

In the previous AMAP assessments (Dietz et al., 1998a,b; AMAP, 2005), there was limited information on the biological effects of heavy metals and persistent organic pollutants (POPs) in Arctic species, but concern was raised that the concentrations in some species put them at risk of adverse effects on reproduction, endocrine disruption, the immune system, and on subtle neurobehavioral functions. More recent studies of biomarkers linked to Hg and POPs exposure are beginning to show evidence that chemical contaminants may be present in sufficient quantities in some species to elicit biologically significant responses, that warrant further investigation into toxicopathology and other measures of negative impacts (AMAP, 2004).

Two approaches have generally been taken in identifying and estimating the risk of possible effects of Hg or other contaminants in Arctic species. The first involves a comparison of concentrations in Arctic species against known detrimental levels or toxicity thresholds. In most cases, the detrimental levels are derived from laboratory studies, semi-field studies or observations of affected animals in the wild, with varying levels of study design rigor and certainty with respect to the actual cause or causes. Extrapolation is routinely used in toxicology but difficulties in extrapolation relate generally to differences in sensitivity, where the same types of effects are seen but at different doses, or to differences in structure and function. These scenarios are also complicated by dose (exposure) reconstruction and range from high certainty of daily intake to very gross estimates. Comparison and extrapolation have some inherent weaknesses and lack of relevance, however. Laboratory animals are most often exposed to a single contaminant at high doses for short periods of time, and it is difficult to extrapolate the toxic effects seen at high acute doses to possible adverse effects at lower but chronic exposures. Wild animals are generally exposed to lower concentrations of Hg or other contaminants than laboratory animals, but they are exposed to mixtures of contaminants and other stressors, and they are exposed over their entire lifetime. In addition, captive animals tend to be housed under optimal conditions while free-ranging animals are experiencing a variety of stressors that may lower their resilience to toxicants. Differences in species sensitivities to the effects of contaminants make it difficult to know which of the tested species best represents those in the Arctic (e.g., Ross, 2000; O'Hara and Becker, 2003).

The focus here has been on recent (i.e. post-2000) biotic concentration data from species and regions for which sufficient data are available. Only in cases where no post-2000 data were available or when clearly rising Hg trends were emerging were earlier data used to compare against toxicity threshold values. For some species and regions (stocks), the lack of raw data prevents an estimation of the percentage of the investigated populations exceeding reported threshold levels.

The second approach involves the study of subtle indicators of biological responses (biomarkers) to contaminants. Examination of animals for responses known to be associated with the contaminants found in their tissues is possibly the only way to make a convincing case either for or against the hypothesis that potentially toxic substances are acting biologically on the animals. Biomarkers, typically, are measures of normal processes that take on abnormal values as a result of exposure to the chemicals of interest. Another design, less commonly encountered, is the comparison of individuals within a group, to search for linkages between biomarker values and exposure as indicated by chemical residues. This is a valuable approach for those contaminants stable enough to remain identifiable as residues for long periods of time. There are limitations with such studies, however. It is not possible to determine causality, only that a statistical association has been found between a biomarker and the contaminant in question.

Mercury bioaccumulates and biomagnifies in Arctic marine species; the focus to date has been on marine mammals. Ringed seals (*Phoca hispida)*, bowhead whales (*Balaena mysticetus*) and beluga (*Delphinapterus leucas*) have been included as monitoring species due to their importance for indigenous peoples and because they reflect various levels of the marine food web. Pilot whales (*Globicephala melas*) from the Faroe Islands have been included in the AMAP monitoring program due to their high contaminant loads and their role as a human food source, and to supplement the monitoring various 'effect studies' have been undertaken since the late 1990s. Among the first Arctic initiatives was the investigation of ringed seal kidneys with high cadmium (Cd) concentrations from northwestern Greenland (Dietz et al., 1998c). Meanwhile in Alaska, a large multi-species program was initiated and many results have been reported in the international scientific literature including the histopathological reports (e.g., Woshner, 2000; Woshner et al., 2002; Rosa et al., 2008) discussed in Section 6.3.2. Polar bears (*Ursus maritimus*) have been included in research programs in Alaska and Greenland, among others, over the past 25 years or so in order to assess spatial distributions and temporal trends in Hg concentration (Dietz et al., 2006a; Cardona-Marek et al., 2009). The reason for including polar bears as a sentinel species is their ability to integrate concentrations within the majority of the marine ecosystem and their comparable trophic position to indigenous people. In previous investigations, the main focus of Hg studies has been on concentrations in tissues such as muscle, not least because of human exposure via intake and liver and kidney because they are target organs. In recent years, hair and blood have also been analyzed to harmonize and expand time series as well as to study the hair excretion pathway, these studies are conducted especially during live capture operations. Later studies have included whole blood or plasma as this can be obtained from live animals and represents circulating concentrations that would be very closely related to the exposure of key target organs, and studies on the brain and the central nervous system have lately attracted more attention as an important target organ worthy of assessment.

## 6.2. Combined effects

A number of biological effects are not contaminant-specific and so the presence of a lesion or a particular finding of concern does not automatically lead to a particular chemical or chemical class. In addition, many contaminants and other variables such as age and infection frequency may co-vary, which would raise the question as to whether the contaminant was definitely involved in generating the effect. Contaminants may either work as antagonists (see also Section 6.2.1) or in a synergistic manner (Section 6.2.2), with one another and with nutrients (e.g., Hg and selenium; Se). Although quite different in nature, heavy metals and POPs are likely to interact; it is the significance of these interactions about which there is still much uncertainty. In some cases, determining the cause is not important and assessing the lesions or poor health indicator and potential impact on population health and dynamics should be the priority. Concern for contaminants must parallel the development of, and an appreciation for, measures of adverse health effects and condition indices (measures of robustness or resilience).

### 6.2.1. What is known about the combined effects of contaminants, and other types of environmental stressors?

In many cases, heavy metals and POPs positively co-vary (i.e., increase in parallel), and so it is difficult to establish causality between concentrations and effects for specific chemicals. This is also complicated by the form of the metal and the profile of the POPs present (i.e., the dominant congeners). Plus, there may be significant contaminants that are not analyzed for or that have an impact but which are then eliminated and so do not leave a detectable residue, that may be just as important, or the response may be the result of synergistic, additive or antagonistic effects of contaminant and nutrient mixtures. Biological variables such as age, sex, reproductive status, life stage, body condition, nutritional status, genetic predisposition, and the presence of disease or other stressors may act as confounding factors, in that they can cause similar biological effects to those due to the presence of heavy metals and POPs. For many of the biological effects reported in wildlife, confounding factors may have resulted in evidence for causal links with a specific chemical contaminant that may not actually be valid due to the correlative nature of the investigation. This is mainly due to the complex mixtures of contaminants present, a lack of chemical exposure data, a lack of data on the sensitivity of the species concerned, and a lack of knowledge about the mechanisms of action for the substances of concern. Understanding of the links between contaminants and health effects (e.g., brain effects, tissue damage, reproduction or immuno-suppression) is most likely to have come from studies on laboratory animals where mechanisms can be rigorously assessed. To establish causal evidence for chemical-induced effects on wildlife it is essential to undertake field operations based on hunter-killed animals, live capture and release, temporary or permanent captivity, and strandings, etc., or controlled laboratory studies using the wildlife species of concern. A major advantage with such studies is that it should be possible to have a control group with minimal exposure. However, differences in the exposed natural food sources versus control group food sources may, in addition to their contaminant load, contain differences (e.g., the presence of other contaminants, fatty acids, vitamins or micronutrients) that may confound the contaminant being investigated.

## 6.2.2. What role does mercury speciation play in uptake and toxic effects?

### 6.2.2.1. Mercury uptake and demethylation

More than 95% of the methylmercury (MeHg) in food items is taken up by mammals, whereas the corresponding proportion for inorganic Hg is only 15% (Berlin, 1986). Once the MeHg has been transported through the intestinal mucosa, lymph and blood vascular portal systems transport it into the organ in which it is being demethylated, stored or from which it is being excreted. The main organ where Hg occurs in the highest concentrations, as well as being demethylated, is the liver for marine mammals and birds. For terrestrial mammals, including polar bears, kidney has the highest Hg concentrations and hence may be the main target organ (see Section 6.2.2.2). Animals that show either less ability to demethylate MeHg or to increase Se uptake, may have a greater sensitivity to the toxic effects of MeHg. Indeed, some high trophic level predators, such as polar bears and pinnipeds, may use other strategies as well as demethylation in the liver, such as excreting MeHg into growing hair and excretion through urine and feces (e.g., Dietz et al., 2006a; Brookens et al., 2007, 2008; Cardona-Marek et al., 2009). Birds utilize a similar excretion strategy via feathers (e.g., Dietz et al., 2006b). Hair and feathers may represent a means to limit the bioavailability of MeHg to the central nervous system (Basu et al., 2009). Additional studies are needed to better explain interspecies differences in sensitivity to MeHg exposure, including the demethylation process and the role of Se.

### 6.2.2.2. Mercury-selenium relationships and interactions

For nearly four decades, scientists have documented strong positive correlations between the concentrations of Hg and Se in tissues (e.g., liver, kidney) of many fish-eating wildlife species, especially predatory marine mammals (Koeman et al., 1973; Koeman and van de Ven, 1975; Smith and Armstrong, 1978; and others). The Hg–Se relationship is a toxicant–nutrient interaction that has relevance for both basic biology and environmental risk assessment; however, important physiological details of the relationship are still unclear. For further details regarding the different chemical forms of Se and their biological functions, see Shibata et al. (1992).

High trophic level mammals and birds, especially those linked to marine or other aquatic food webs, may be partially protected against MeHg toxicity by a range of mechanisms including demethylation and subsequent binding of inorganic Hg with Se in an approximate 1:1 molar ratio (Figure 6.1), thereby sequestering Hg in a stable non-toxic complex. This complex probably represents a direct covalent (or other strong) interaction of Hg and Se. In some wild aquatic predatory bird and mammal species, it has been shown that MeHg predominates in the liver at low total Hg (THg) concentrations whereas at higher concentrations an increasingly large percentage of THg is present as inorganic Hg associated with Se, and some studies have identified this complex as HgSe (tiemanite) (Koeman and van deVen, 1975; Dietz et al., 1990, 1998a,b, 2000b,c; O'Shea, 1999; Scheuhammer et al., 1998, 2008; Wang et al., 2001; Woshner et al., 2001a,b, 2008; O'Hara et al., 2003; Arai et al., 2004; Ikemoto et al., 2004; Dehn et al., 2005, 2006; Eagles-Smith et al., 2009; Moses et al., 2009).

The Figure 6.1 inflection point below which the majority of hepatic Hg is organic and above which the proportion of hepatic inorganic Hg increases, was reported to be about 2.2 µg/g ww based on 20 Greenland marine animal species (Dietz et al., 1990). This finding fits well with later studies on North American aquatic bird species (Scheuhammer et al., 2008; Eagles-Smith et al., 2009). These results are also consistent with the amount of organic Hg present in liver as well as the generally lower exposed kidney (except for polar bears). In muscle tissue, Se is present in a large molar surplus to Hg, and the Hg is entirely organic (Dietz et al., 1990, 2000c).

Interspecies differences in MeHg demethylation have been reported. Eagles-Smith et al. (2009) observed that avocets (*Recurvirostra* sp.) and stilts (*Himantopus* sp.) had higher hepatic demethylation rates than terns (*Sterna paradisaea*). Scheuhammer et al. (2008) reported significant differences between common loons (*Gavia immer*) and bald eagles (*Haliaeetus leucocephalus*) with respect to Hg and Se

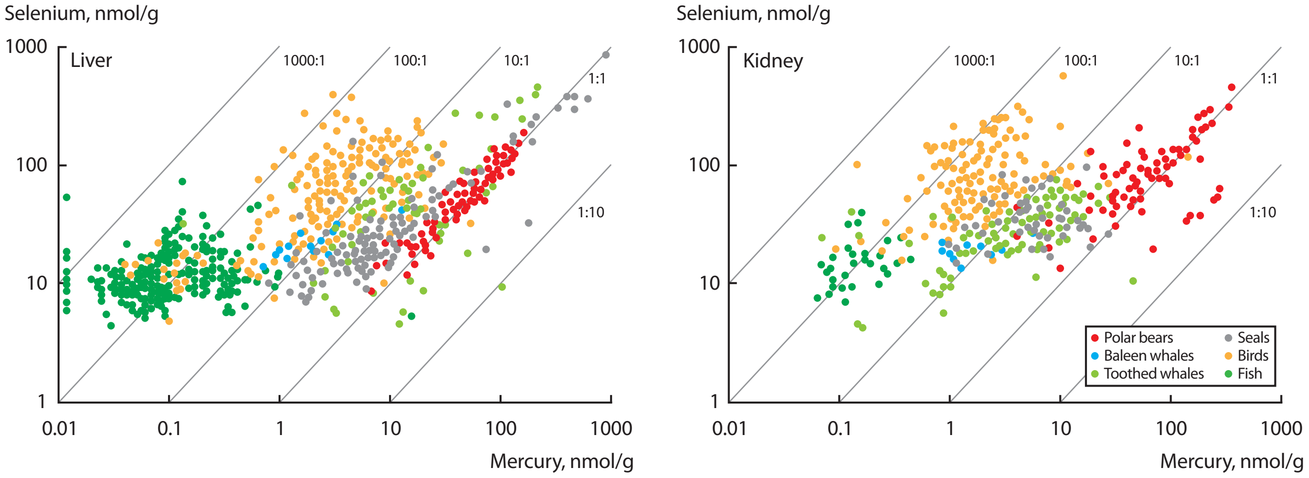

Figure 6.1. The mercury-selenium relationship in liver (left) and kidney (right) tissue in various animal groups from Greenland. The lines represent different decadal molar ratios. Source: after Dietz et al. (2000c) and Dietz (2008).

accumulation in brain tissue, with eagles showing a highly significant co-accumulation of Se with Hg, and efficient demethylation of MeHg in brain, relative to loons. For loons, but not eagles, the molar ratio of Hg:Se in brain often exceeded 1 (Scheuhammer et al., 2008). Ralston et al. (2007) suggested that a molar excess of Hg over Se in target organs may be a major determinant of MeHg toxicity. Certain seleno-enzymes (e.g., thioredoxin reductase) are highly sensitive to inhibition by low nanomolar concentrations of Hg, and may be important early targets of MeHg toxicity at the molecular level (Carvalho et al., 2008). For some pinniped species, hepatic MeHg (as a percentage of THg) decreases rapidly with age, and reaches an asymptote (from 30-60%, to 5% or less) even as levels of THg continue to increase (Dehn et al., 2005; Brookens et al., 2007). For dolphins, detoxification has been proposed to involve demethylation of MeHg by reactive oxygen species.

Measuring the amount of Hg present in the environment or food sources may not provide an adequate reflection of the potential for health risks if the protective effects of Se are not also considered. The involvement of Se is apparent throughout the Hg cycle, influencing its transport, biogeochemical exposure, bioavailability, toxicological consequences, and remediation. Likewise, many animal studies indicate that Se, present in many foods (including fish), protects against Hg toxicity. Studies have also shown that Hg exposure reduces the activity of Se-dependent enzymes. While seemingly separate, these concepts may actually be complementary perspectives of the Hg–Se binding interaction. Owing to the extremely high affinity between Hg and Se, Se sequesters Hg and reduces its biological availability. It is clear that the converse is also true; as a result of the high affinity complexes formed, Hg sequesters Se. This is important because Se is required for the normal activity of many Se-dependent enzymes.

#### 6.2.2.3. Selenium as an antioxidant

Selenium can act directly or as a cofactor with other antioxidants to protect cells from oxidative stress due to exposure to Hg and/or other stressors. As an essential element and component of the amino acid seleno-cysteine, Se is physiologically regulated. Selenium is a constituent of many proteins, including the Se-dependent glutathione peroxidases, which have antioxidant properties (Brigelius-Flohé, 1999). Other seleno-enzymes include type I iodothyronine deiodinase, which converts thyroxine (T4) to the more active 5-tri-iodothyronine (T3), and impacts on metabolic rate can be linked to Se (Hawkes and Keim, 2003). Thus, the role of Se in the mechanism for Hg detoxification may not be completely due to covalent binding of Hg with Se, but may also involve seleno-proteins and/or other biomolecules (Woshner et al., 2001a, 2008).

According to Raymond and Ralston (2004), if a toxicant can enter the brain and disrupt seleno-protein synthesis, detrimental effects would be expected. Methylmercury has the ability to cross the blood-brain barrier, and its exceptionally high affinity for Se may enable it to specifically sequester the Se in the central nervous system and diminish seleno-protein synthesis. The free selenides that form during each cycle of seleno-cysteine synthesis have a high affinity for Hg, and the low solubility mercury selenide precipitates that result are metabolically inert. It is reasonable then to assume that not only does Se have an effect on Hg bioavailability, but that Hg may also have an effect on Se bioavailability. Therefore, the 'protective effect' of Se against Hg exposure may actually be in the opposite direction as well. Mercury propensity for Se sequestration in brain and endocrine tissues may inhibit formation of essential Se-dependent proteins (seleno-proteins). Hence, the 'protective effect' of Se against Hg toxicity may simply reflect the importance of maintaining sufficient free Se to support normal Se-dependent enzyme synthesis and activity.

The role of compounds containing sulfhydryl groups (such as metallothionein and keratinized tissues), especially for binding of inorganic Hg (Satoh et al., 1997) might also be important, and other nutrients such as fatty acids may be involved (Woshner et al., 2001a, 2008). It is important to remember that the Hg–Se complex represents the end product of a process and that other factors may be important in producing this final interaction. The Hg-centric view of this interaction should also be considered, in that, in some instances, it might be proposed that the toxicity of Se is being prevented by the Hg, or that the formation of Hg–Se complexes promotes Se deficiency (Tinggi, 2003). Other metals, such as silver, have also been found in association with Se in tissues of some marine mammals (Becker et al., 1995), thus the elemental interactions may be more complicated for species such as beluga.

## 6.3. Is there any evidence that tissue mercury concentrations at present are harmful to Arctic biota?

### 6.3.1. Cerebral exposure and potential neurological effects of mercury on Arctic marine mammals

Characterizing Hg exposure and possible neurological outcomes is a critical component in assessing the health impacts of Hg. Much of the work on the central nervous system is new relative to previous assessments and the recently developed methods provide much needed effect information.

Mercury has the potential to cause neurotoxicity in Arctic biota and human residents and this is of major concern; especially for women of childbearing age and the developing fetus. The neurotoxic potential of Hg was exemplified during well-documented, human poisoning events in Japan and Iraq (reviewed by U.S. EPA, 1997; ATSDR, 1999; Clarkson and Magos, 2006), and more recently from studies involving human populations in the Faroe Islands and Brazilian Amazon (Mergler et al., 2007). Besides humans, Hg is also neurotoxic to wildlife and Hg-associated poisoning events have been documented in some fish-eating species, such as mink (*Mustela vison*) and common loons (Scheuhammer et al., 2007).

While all chemical forms of Hg have intrinsic neurotoxic properties, environmental public health is most concerned with organic Hg and in particular MeHg. Methylmercury biomagnifies through aquatic and marine ecosystems, including food chains in the Arctic (Atwell et al., 1998). Once ingested, MeHg is readily absorbed into the circulatory system and transported to all tissues mainly through the blood (see Section 6.3.3). Methylmercury can cross the blood-brain barrier (Aschner and Aschner, 1990), and the brain is considered the primary target organ of MeHg toxicity in higher organisms. At sufficient concentrations, MeHg may disrupt a range of neurological processes within the brain owing to its high affinity for protein thiols (Clarkson and Magos, 2006). Characteristic outcomes of MeHg poisoning in both humans and mammalian wildlife include structural degeneration of the occipital cortex and the cerebellum which leads to paresthesia (numbness, tingling), ataxia (incoordination), sensory impairment, and memory loss (ATSDR, 1999; Clarkson and Magos, 2006; Basu et al., 2007a; Basu and Head, 2010). There is some concern that Hg levels in Arctic wildlife and humans may be approaching concentrations that can cause impacts on behavior and health. For example, an associative study on 43 Inuit children (Qaanaaq, Greenland) reported that Hg exposure may be related to subtle neurological deficits in a few cases examined (Weihe et al., 2002). Balancing the risks/benefits of Hg exposure via dietary pathways is an immense challenge as fish and marine mammals are the primary means by which Hg is transferred to humans and high trophic level wildlife but are also an excellent and critical source of nutrients for Arctic consumers.

Substantial levels of Hg (both THg and MeHg) have been documented in various tissues of polar bears (Norstrom et al., 1986; Dietz et al., 1990, 2000b,c; Braune et al., 1991; Atwell et al., 1998; Woshner et al., 2001b; Rush et al., 2008) and ringed seals (Dietz et al., 1998b, 2000c; Woshner et al., 2001b; Dehn et al., 2005). However, little is known about the uptake of Hg into the brain tissue of Arctic marine mammals. The lack of understanding of brain Hg levels in Arctic wildlife limits the ability to accurately assess its health effects. In a recent study, THg and MeHg levels were evaluated in the lower medulla oblongata (brain stem) brain region of 82 polar bears collected by subsistence hunters in Greenland (Basu et al., 2009). In that study, concentrations of THg of less than 1 µg/g were found (mean = 0.36 ± 0.12 µg/g dw; range 0.11 to 0.87 µg/g). In this same brain region, MeHg comprised 82.8% of the THg present. In a previous study of eight ringed seals from northern Quebec, the mean THg level in the cerebral cortex was 0.09 ± 0.05 µg/g ww (N. Basu, unpublished results based on animals from Basu et al., 2006a). Similar THg levels (0.13 ± 0.03 µg/g ww) were found in the brain tissue of six harp seal (*Phoca groenlandica*) pups collected from the Grise Fjord and Pangnirtung region of Nunavut (Ronald et al., 1984). A number of studies are underway to characterize the distribution of Hg in specific brain regions as this may enable a greater understanding of possible effects on animal behavior and health (Figure 6.2). Of particular note are recent findings from Canadian beluga showing brain mercury levels to be an order of magnitude greater than those in polar bears and seals (Ostertag et al., 2009).

At a neurochemical level, MeHg may cause a range of sub-clinical effects and so neurochemical biomarkers have recently been used to assess the early risks of Hg to several fish-eating wildlife species that accumulate high levels of Hg. For example, changes in the levels of muscarinic cholinergic receptors (increased) and N-methyl-D-aspartate (NMDA) glutamate receptors (decreased) were related to concentrations of brain Hg in wild mink (Basu et al., 2005, 2007b), common eagles, and bald eagles (Scheuhammer et al., 2008). Several of these neurochemical effects have been substantiated in laboratory studies involving captive mink experimentally fed environmentally realistic MeHg doses (Basu et al., 2006b, 2007b). These results suggest that Hg at ecologically relevant levels may be exerting subtle, sub-clinical neurological changes in the 3 to 5 µg/g dw range (dry weight concentration in

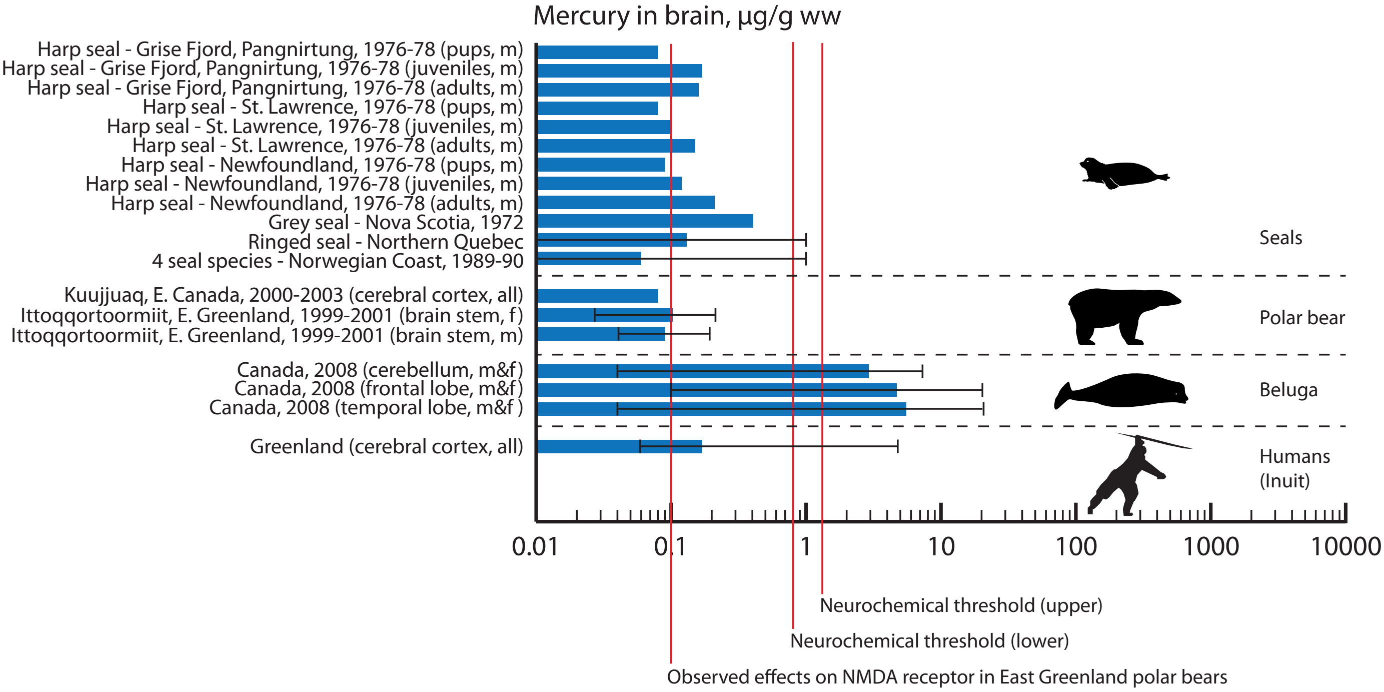

Figure 6.2. Overview of mean mercury concentrations in brain from Arctic biota and humans. Red lines indicate the mean mercury concentrations in East Greenland polar bear brain stem that were associated with lower N-methyl-D-aspartate (NMDA) receptor levels and the mercury-associated neurochemical effect threshold in the 3 to 5 µg/g dw range based on previous studies on fish-eating mammals (Basu et al., 2006b, 2007b) and birds (Scheuhammer et al., 2008). For detailed data see Appendix Table A6.1.

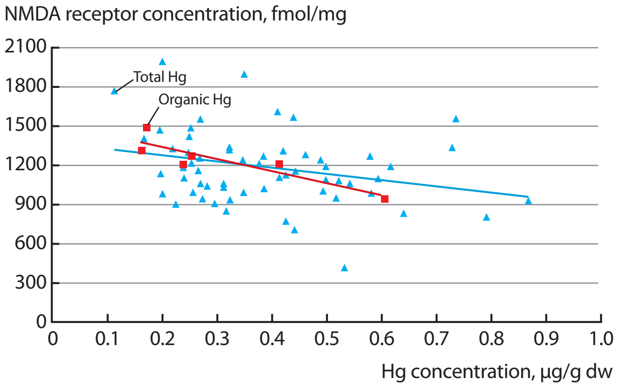

Figure 6.3. Correlation between glutamate N-methyl-D-aspartate (NMDA) receptor levels and total mercury (n = 60; r = -0.34, $p < 0.01$) and methylmercury (n = 6; r = -0.89; $p < 0.05$) in the medulla oblongata brain region of free-ranging East Greenland polar bears. Source: adapted from Basu et al. (2009).

brain tissue) in several fish-eating wildlife species. It should be emphasized that these results are limited as they do not necessarily indicate toxic damage, and are correlative in nature, although additional field- and laboratory-based studies are underway to address the physiological significance of these findings.

Neurochemical biomarkers have recently been applied to studies on Arctic biota (Basu et al., 2009). Despite finding relatively low levels of Hg in the lower brain stem of polar bears, a negative association between brain Hg levels and NMDA receptors was observed similarly to other organisms (Figure 6.3). In these polar bear tissues, several chlorinated and brominated organic chemicals were measured and did not associate with Hg levels or neurochemical biomarkers (Basu et al., 2009). In a captive mink study, ingestion of food containing MeHg levels as low as 0.1 ppm (corresponding to brain Hg concentration of 1 to 2.2 µg/g ww) was linked to decreased NMDA receptors levels (Basu et al., 2007b). A decreased level of brain glutamate NMDA receptors is potentially of ecological and physiological concern because glutamate is the main excitatory neurotransmitter, and glutamate receptors have essential roles in multiple facets of animal health, behavior, reproduction, and survival (Siegel et al., 2006). Changes to these receptors may represent one of the earliest and most sensitive biochemical indicators of MeHg exposure and effect. To substantiate the importance of these neurochemical findings in the polar bear, future efforts need to explore Hg-associated neurochemical changes in other high trophic level Arctic species, in other brain regions shown to accumulate more Hg than the brain stem, and to examine linkages (via modeling or carefully designed laboratory experiments) between neurochemical effects and possible changes in animal neurobehavior.

## 6.3.2. Mercury-related histopathology of Arctic marine mammals

Few studies have investigated the histopathology of Hg in Arctic wildlife. It is important to understand that all Arctic marine mammals are contaminated with a range of toxic substances. Histopathological investigations have largely focused on Hg- and Cd-related lesions. Histopathological effects in relation to Hg exposure are the focus of the following section, but references to Cd are also included. It should also be emphasized that in addition to these heavy metals, POPs (organochlorines, brominated flame retardants and perfluorinated compounds) bioaccumulate in kidney and liver tissue and that these compounds may interact with heavy metals to cause tissue lesions in an additive or synergistic manner. In the following sections, threshold Hg levels for harmful and lethal impacts in terrestrial mammals (30 µg/g ww; Thompson, 1996) and marine mammals (60 µg/g ww; Law, 1996) have been used.

### 6.3.2.1. Liver lesions

The functions of the liver are to serve as lymphatic and intestine drainage, to support metabolic processes and to synthesize plasma proteins and coagulation factors, as well as being an endocrine / immunological modulator and storage site of energy (glycogen) (Janeway et al., 2001; Ganong, 2005; Klaassen et al., 2007). In addition, the liver is the key site where xenobiotic compounds are biotransformed (Janeway et al., 2001; Ganong, 2005; Klaassen et al., 2007). Studies of Hg hepatotoxicity have been conducted both in the laboratory and in the field in recent decades (Kelly, 1993; MacLachlan and Cullen, 1995; Law, 1996; Thompson, 1996; AMAP, 1998, 2005; Klaassen et al., 2007). In the Arctic, investigations of histopathological lesions in hepatic tissue from Arctic wildlife have focused on polar bears, pilot whales, bowhead whales, beluga and ringed seals (e.g., Woshner, 2000; Woshner et al., 2002; Sonne et al., 2007, 2010). Various liver lesions have been found in these five species in relation to Hg (and Cd) concentrations, and the nature of these associations is similar across species. Briefly, measured lesions are of parenchymal (zonary hepatocytic lipid accumulation) and of non-parenchymal (lipid-filled Ito cells, bile duct proliferation, focal lipid granulomas, cell infiltrations and necrosis) origin (Kelly, 1993; MacLachlan and Cullen, 1995; Thompson, 1996). Most of these lesions are due to age, exposure to toxic substances such as contaminants and to infection/inflammatory reactions. In the case of Ito cell lipid accumulation this is ascribed to vitamin A deposition (Leighton et al., 1988). However, the significance of these lesions to the overall health of the organ and the organism requires further investigation within the context of other health measures (e.g., clinical chemistries, biochemical measures and others).

Hepatocytes react to exposure to POPs/Hg in a biochemical manner that includes three major pathways: induction of the sER (smooth endoplasmic reticulum, including CYP-450); disruption of the ADP→ATP pathway; and free radical oxidative stress of the cell membrane resulting in hypoxia and hepatomegaly (enlarged liver) as a first sign of liver toxicosis (Kelly, 1993; MacLachlan and Cullen, 1995; Klaassen et al., 2007). Therefore, liver weight may be a preliminary indicator (invasive biomarker) for POPs/Hg exposure and effects in Arctic marine mammals, while non-specific histopathological changes such as intracellular hepatocytic steatosis (foamy cytoplasm), inflammation (lymphocytic and multinuclear cells) and necrosis also occur but cannot be used as specific contaminant biomarkers (Kelly, 1993, MacLachlan and Cullen, 1995; Klaassen et al., 2007).

In the wild, only a few studies have associated metal exposure to pathological changes in the liver. For example, Hg in Atlantic

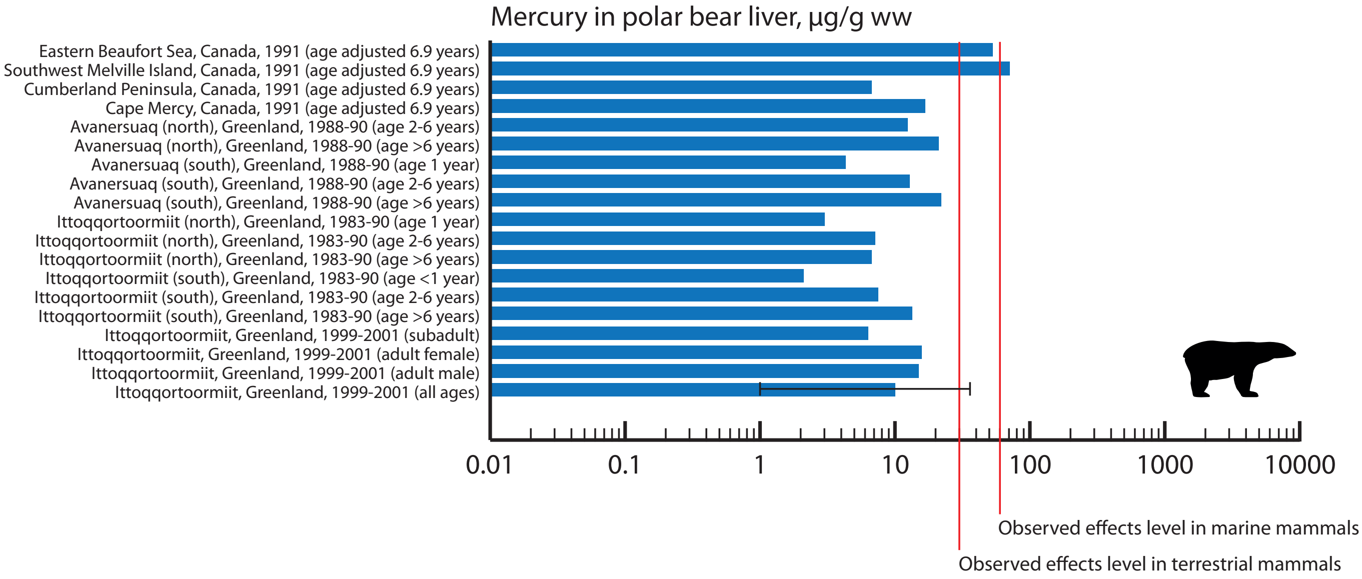

Figure 6.4. Mercury concentrations in polar bear liver for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.2.). The lethal/harmful effects level for terrestrial free-ranging wildlife (30 µg/g ww; Thompson, 1996) and the observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) are also shown.

bottlenose dolphins (*Tursiops truncatus*) showed that liver abnormalities and lysosomal Hg granula were associated with high Hg concentrations (Rawson et al., 1993). The histopathological changes found in the liver of Arctic marine mammals (i.e., Arctic beluga, polar bear, bowhead whale, pilot whale and ringed seal) are similar to those observed in other Hg-exposed marine and laboratory mammals (Woshner, 2000; Woshner et al., 2002; Sonne et al., 2007, 2010). In these studies, however, histopathological changes are also ascribed to age and dietary composition (lipid content), creating some difficulty in ascribing the lesions specifically to Hg.

Figure 6.4 shows the mean liver Hg concentrations in polar bears of several age classes from various Arctic locations. By plotting these mean values against an estimated toxic threshold value for marine mammals of 60 µg/g ww it is evident that the only polar bears that exceeded this threshold were from Southwest Melville Island in 1991 (Law, 1996). Comparing the results to the terrestrial toxic threshold value of 30 µg/g ww, indicates that eastern Beaufort Sea polar bear means are above this level, which may indicate a risk of Hg-induced adverse health effects (Thompson, 1996). Lacking access to the raw data precluded an estimate of the percentage of bears from different regions that exceeded the threshold concentrations, however, it is likely that different pre-1990 populations may have exceeded the terrestrial threshold. The recent increases observed in hair Hg concentrations indicate that liver concentrations may also have increased in some populations (Dietz et al., 2006a). The prediction of the northeastern Canadian bears as being at risk of Hg toxicity fits well with the hair data in Section 6.3.4.

Figure 6.5 shows the mean liver Hg concentration in different seal species. The only population where the mean value exceeded the threshold value for toxic effects in marine mammals (60 µg/g ww) was for hooded seals (*Cystophora cristata*) from Davis Strait sampled in 1984 (mean 78 µg/g ww; no later data available from this region). Several other species and populations, such as ringed seals (>5 years) from Grise Fiord (in 1998) and hooded seals from the Greenland Sea (in 1999) had means that approached the terrestrial mammal toxic threshold value of 30 µg/g ww. Again, the paucity of raw data prevents an estimate of the percentage of seals from all populations exceeding the threshold. It is unclear to what extent Arctic seals have shown any increase in concentration over recent years (see Chapter 5). The prediction of the northeastern Canadian seals as being at risk of Hg toxicity fits well with the polar bear liver, kidney and hair data described elsewhere in this section and in Section 6.3.4.

Figure 6.6 shows the mean Hg concentrations in liver tissue from baleen and toothed whales. All baleen whale populations had liver Hg concentrations far below the toxic threshold levels. However, pilot whales from the Faroe Islands had liver concentrations above the 60 µg/g ww toxic threshold value (Hoydal and Damm, 2009; Sonne et al., 2010) for marine mammals provided by Law (1996). Beluga from the St Lawrence River and Point Lay had mean liver concentrations close to the 30 µg/g ww toxic threshold value for terrestrial mammals provided by Thompson (1996).

### 6.3.2.2. Renal lesions

Renal lesions can be divided into those of the parenchyma (tubular and glomerular) and the interstitium (Maxie, 1993; Churg et al., 1995; Cotran et al., 1999). Briefly, the pathogenesis underlying inorganic Hg (and Cd) tubular toxicity is a co-enzyme inhibition via high affinity to various microsome and mitochondria SH-group enzymes, while glomerular changes are due to immune complex interactions with the capillary basement membrane (Maxie, 1993; Churg et al., 1995; Cotran et al., 1999). Lesions to the kidney are of health concern since this organ has endocrine functions, acts as a blood filter that clears metabolic waste products such as urea, and maintains calcium and phosphorus homeostasis, blood pressure, water and electrolyte levels as well as activating vitamin D (Ganong, 2005).

Several studies of Arctic marine mammals have shown measurable and species-dependent prevalence of tubular and

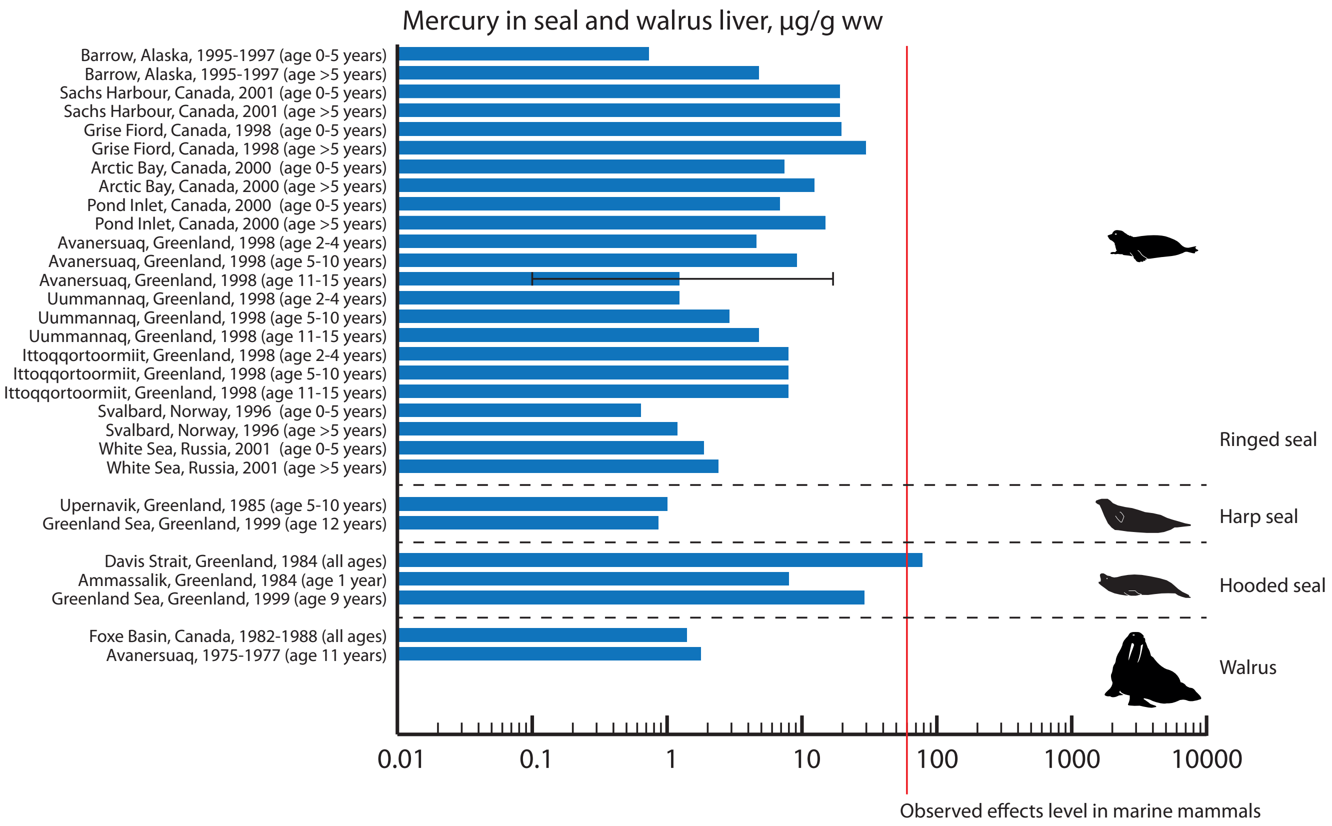

Figure 6.5. Mercury concentrations in seal and walrus liver for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.3.). The observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) is also shown.

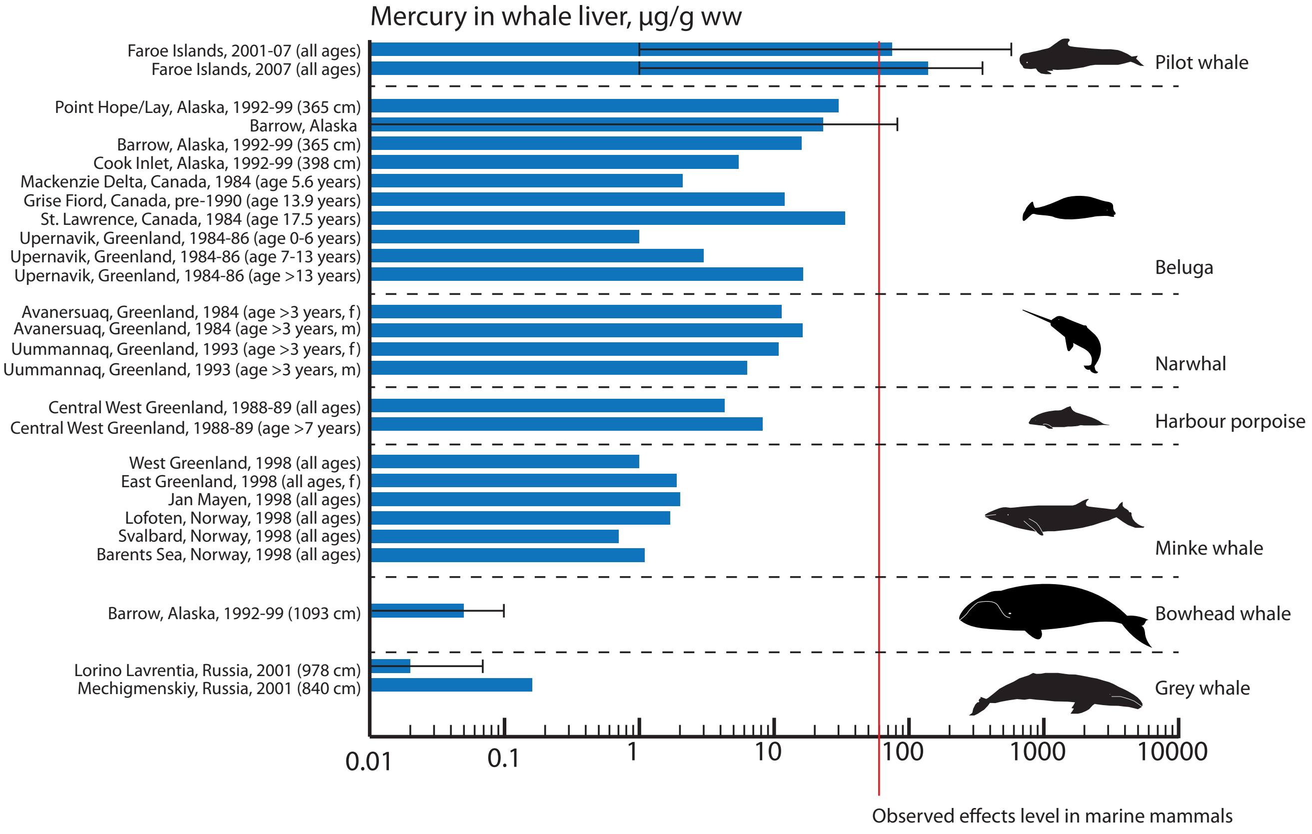

Figure 6.6. Mercury concentrations in whale liver for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.4.). The observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) is also shown.

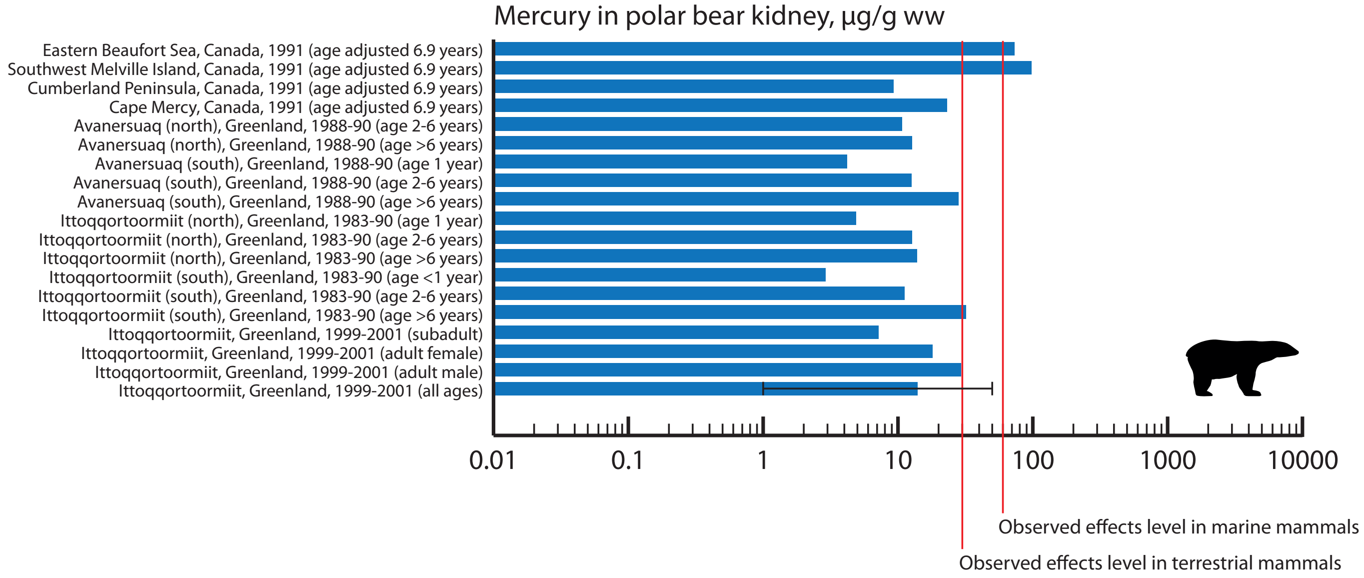

Figure 6.7. Mercury concentrations in polar bear kidney for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.2.). The lethal/harmful effects level for terrestrial free-ranging wildlife (30 µg/g ww; Thompson, 1996) and the observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) are also shown.

glomerular lesions. The lesions found include glomerular sclerosis and obliteration, immune complex-like glomerulonephritis, tubular hyalinization and tubular necrosis, as well as interstitial fibrosis and multifocal lymphohistiocytic and/or mononuclear cell infiltrations (Woshner, 2000; Woshner et al., 2002; Sonne et al., 2007, 2010; Rosa et al., 2008). The glomerular lesions reported resemble those of heavy metal and organohalogen polluted Baltic grey seals (*Halichoerus grypus*) and ringed seals and bottlenose dolphins (Lavery et al., 1999; Bergman et al., 2001). Studies have shown that age and micro-pathogens (e.g., bacteria and parasites) are important co-factors in the development of renal lesions in Arctic marine mammals which must be considered when evaluating metal toxicosis (Woshner, 2000; Woshner et al., 2002; Sonne et al., 2007, 2010; Rosa et al., 2008). Furthermore, the concentrations of many metals co-vary with age (increase), as do histological lesions, which makes it difficult to establish cause-effect relationships between Hg exposure and renal endpoints (Maxie, 1993; Banerjee et al., 1994; Churg et al., 1995; Cotran et al., 1999; Rumbeiha et al., 2000; Afonne et al., 2002; Sonne, 2010).

According to Dietz et al. (1996, 2000b,c), Hg:Se molar ratios in the renal tissues of several East Greenland polar bears exceeded 1, which indicates that a large amount of the THg was in the ionic form, suggesting a toxic potential. In Alaskan beluga, bowhead whales and ringed seals, Woshner (2000) showed that the Hg:Se ratio was <1 in renal tissue indicating that Se was in molar surplus. Metallothionein also binds and thereby detoxifies Hg (Klaassen et al., 2007, 2009), but in the Arctic only a single study (in Greenland and Barents Sea ringed, hooded and harp seals) has been conducted on its relationship to Hg (Sonne et al., 2010). Based on metallothionein concentrations, the metallothionein metal-binding capacity was higher in kidney than liver for all three species and increased in the order ringed seals < hooded seals < harp seals. It was suggested that species differences exist in the sub-cellular handling of heavy metals which implies differences in Hg sensitivity.

Figure 6.7 shows Hg concentrations in renal tissue from polar bears. It is clear that two populations where kidney mean concentrations exceeded the toxic threshold value for marine mammals (60 µg/g ww) were from Southwest Melville Island and the eastern Beaufort Sea (sampled prior to 1991). These values were, however, calculated from tissue ratios from Greenland bears as no kidney data were available from these regions. If, on the other hand, the terrestrial toxic threshold value of 30 µg/g ww is used then polar bears from East Greenland also exceeded the threshold level. Lacking access to raw data precluded an estimate of the percentage of bears exceeding the threshold levels but it is likely that a substantial proportion of the pre-1990 bears older than six years from northwestern Greenland exceeded the terrestrial threshold level. The increases observed in Hg concentration in polar bear hair in recent years indicate that kidney concentrations have increased in some of the northern populations (Dietz et al., 2006a, and Section 6.3.4). The prediction of the northeastern Canadian bears as being at risk of Hg toxicity fits well with the liver and hair data described above and in Section 6.3.4.

Figure 6.8 shows mean Hg concentrations in renal tissue for various seal species. None of the seal populations have renal Hg concentrations that reach the 60 µg/g ww toxic threshold value for marine mammals or the 30 µg/g ww toxic threshold value for terrestrial mammals.

Figure 6.9 shows mean Hg concentrations in renal tissue from baleen and toothed whales. All baleen whale populations had lower kidney Hg concentrations than the toothed whales. No whale population had kidney concentrations that reach the 60 µg/g ww toxic threshold value for marine mammals or the 30 µg/g ww toxic threshold value for terrestrial mammals.

### 6.3.2.3. Other tissues

Multiple tissue histological examinations have been conducted on polar bears, ringed seals, bowhead whales and beluga by Woshner (2000) and others. These comprehensive examinations and reports have not shown any particular relationships with

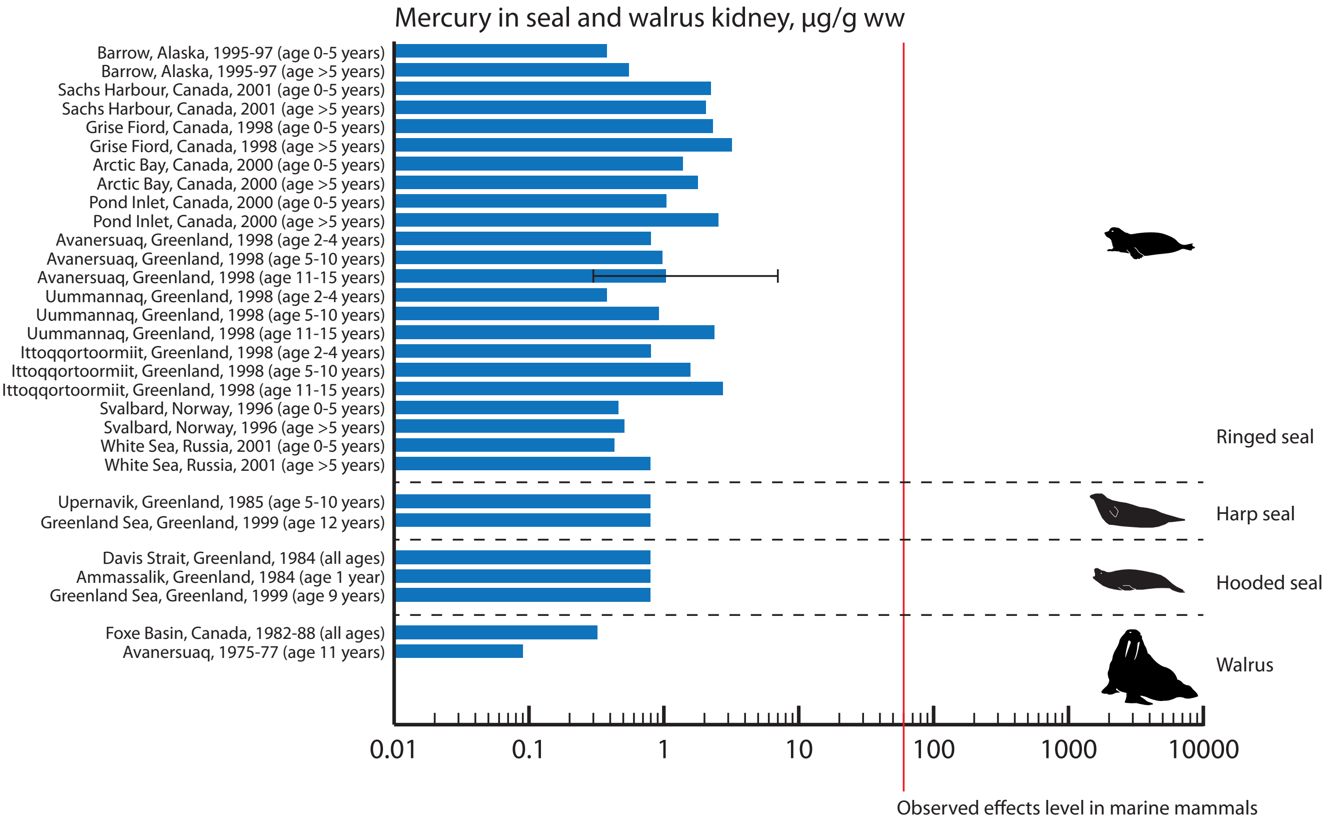

Figure 6.8. Mercury concentrations in seal and walrus kidney for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.3.). The observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) is also shown.

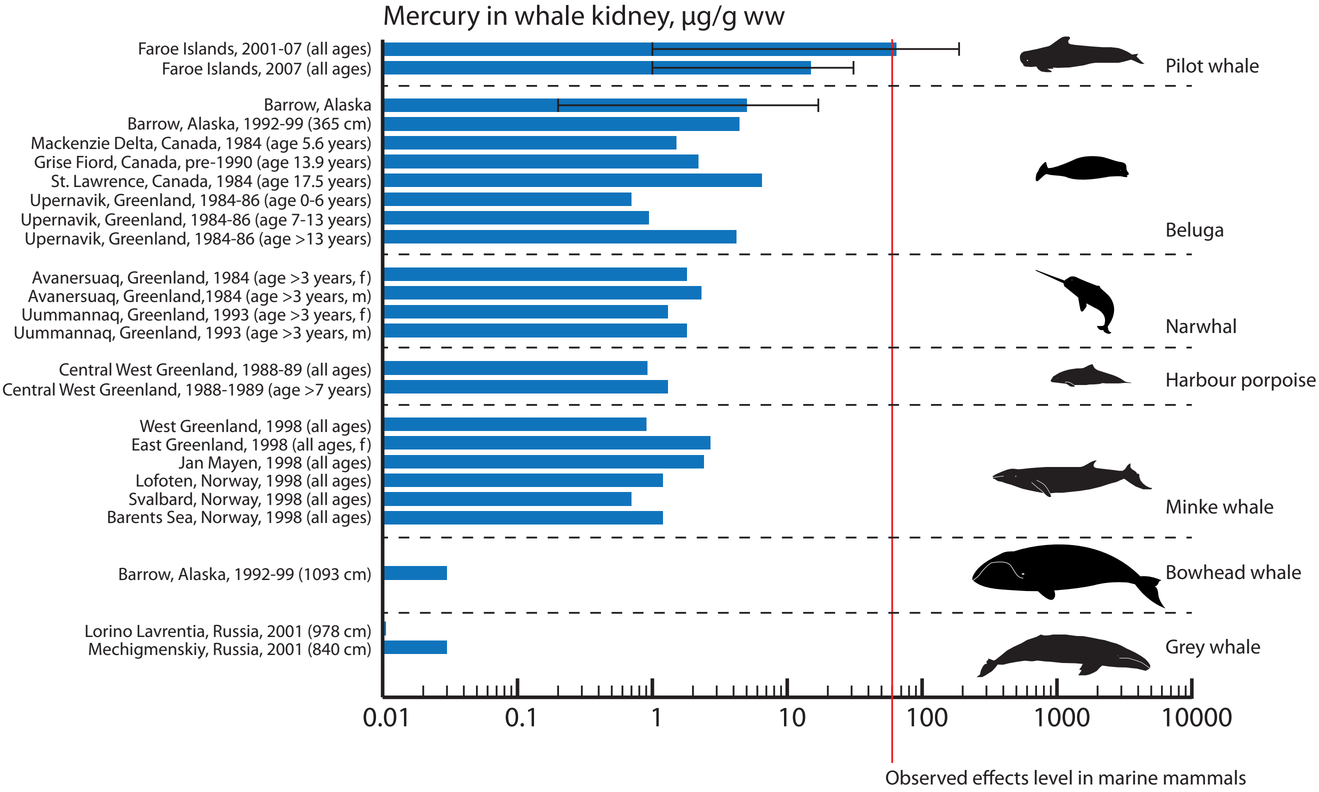

Figure 6.9. Mercury concentrations in baleen and toothed whale kidney for selected regions of the Arctic and selected periods (for full datasets see Appendix Table A6.4.). The observed effects level for marine mammals associated with liver lesions in bottle-nosed dolphins (60 µg/g ww; Law, 1996) is also shown.

Hg or other heavy metals. However, an examination by Rosa et al. (2008) linked pulmonary fibromuscular hyperplasia to Cd in bowhead whales and also to age. Again, this shows that metals and histopathology co-vary with age and that it is difficult to isolate the possible impact of Hg from co-variables.

### 6.3.2.4. Ecological significance and interpretations

The relationships between Hg concentration, histopathology and health impacts could not be confidently evaluated as the studies were not conducted under controlled circumstances. However, despite the possible detoxification mechanisms via Se binding and metallothionein regulation, Hg may in the future represent a stressor to the animals. This is possible because of the rising trends in Hg concentration in the western Arctic and because climate change may induce shifts in pathogen organisms, food access, and contaminant transfer and bioaccumulation in the marine food webs which, ultimately, may have additive health impacts at least on the most susceptible individuals.

### 6.3.3. Blood mercury in high trophic level Arctic species in comparison with human health guidelines

Because blood represents one of the few minimally invasive monitoring matrices for live vertebrates and because multiple organs are being exposed through blood, this matrix is widely used in toxicology studies. Mercury concentrations in blood are mainly in the methylated form (MeHg) and represent post-absorptive processing (diet), and release (mobilized) of stored sources (e.g., MeHg in muscle, liver). Guideline values for Hg in blood have also been established in conjunction with hair Hg concentrations (a less invasive procedure). Many studies have used these tissue types – this assessment focuses on recent studies in polar bears; because of a lack of recent blood data from other Arctic mammals some pre-2000 data from harp seals are included for comparative purposes (Figure 6.10).

The blood Hg concentrations for polar bears were in the same range as for harp seals from St. Lawrence, northeastern Canada and West Greenland, but greater than levels in the Labrador harp seals. Only blood Hg concentrations in Inuit women from Qaanaaq, northwestern Greenland, were similar to levels in polar bear. The geographical pattern has previously been monitored in liver and polar bear hair (e.g., Eaton and Farant, 1982; Renzoni and Norstrom, 1990; Born et al., 1991; Braune et al., 1991; Dietz et al., 1995, 1996, 1998a, 2000a; Cardona-Marek et al., 2009). Previous data and the more recent data presented here, show that the highest Hg concentrations in liver and hair are found in the northern Canadian Arctic, with polar bears from Hudson Bay, Svalbard and the Russian regions having the lowest concentrations. Blood does not have a similarly high resolution in the spatial coverage, but does show a similar pattern with the lowest concentrations in western Hudson Bay and comparable concentrations between Alaska and the somewhat seasonally variable concentrations in East Greenland (Cardona-Marek et al., 2009; Dietz et al., unpubl.). Total Hg concentrations in blood of southern Beaufort Sea polar bears did not differ much by year (2005, 2007), age, or sex. Cardona-Marek et al. (2009) assessed sub-adults (3 to 5 years) and dependent young (1 to 2 years) and found a considerable amount of Hg in both blood

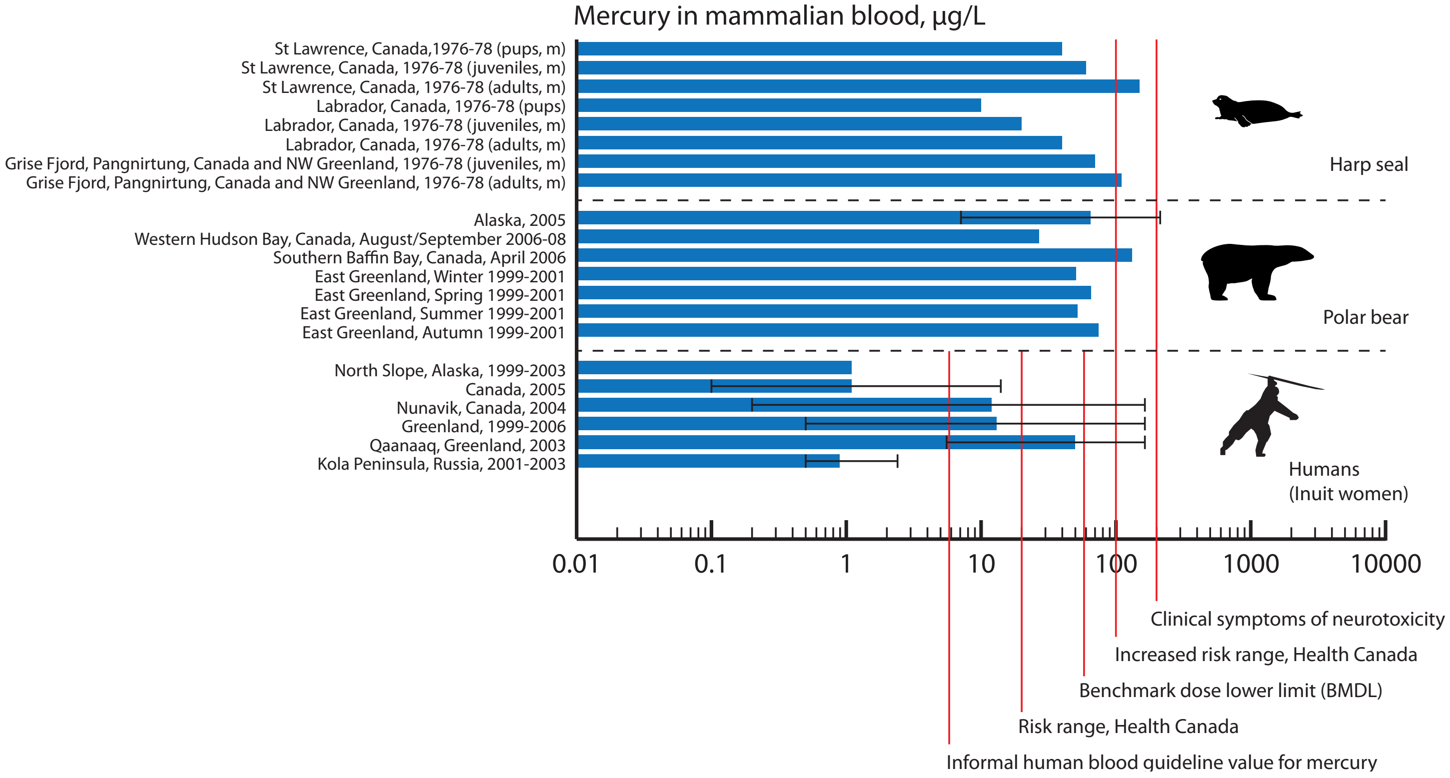

Figure 6.10. Mean blood mercury concentrations in Arctic marine mammals, Arctic Inuit populations and guideline levels for wildlife and humans. For sources and raw data see Appendix Table A6.5.

and hair. Mercury in dependent young was suggested to be via maternal sources of Hg (i.e., during gestation and/or lactation). This is an important exposure route for Hg in young animals, and indicates an important elimination route for reproductive females. Concentrations of THg in adult polar bears ranged from 7 to 210 µg/L for blood, with adult females having a greater concentration of THg in hair than adult males, again indicating a cohort of concern exposed to higher Hg (i.e., the fetus and neonate) as reported by Cardona-Marek et al. (2009). The explanation for this difference may be due to a higher dietary exposure of pregnant or lactating female polar bears as they may eat more high protein and high Hg-exposed tissues than males, who tend preferentially to eat blubber which is low in Hg. Also, Alaskan female bears may target species higher in Hg (smaller pinnipeds), while males may target larger species with less Hg (bowhead whales, bearded seals and walrus) simply based on larger males taking larger prey. The implication of maternal transfer of Hg to polar bear offspring is unknown and further research should examine the potential of Hg accumulation (and resulting effects) on the developing organism.

The data from Appendix Table A6.5. also indicate a seasonal difference linked to the seasonality of polar bear feeding in East Greenland (Dietz et al., unpubl.). Hence the spring and autumn Hg concentrations in polar bear blood are higher than during summer, when limited sea ice is available on which to hunt, and during winter when females hibernate and seals are harder to access.

In the absence of ursid-specific guidelines for Hg in blood, Hg blood concentrations in polar bears are compared to those derived for humans. The caveats for such an approach are fully respected and comparisons with human guidelines are made for illustrative purposes only. The blood guideline established by Health Canada for Hg considers concentrations below 20 µg/L in human blood to be within an acceptable range (Health Canada, 1984). Individuals with Hg concentrations between 20 and 100 µg/L have been determined to be at 'increasing risk', whereas individuals with blood Hg concentrations that exceed 100 µg/L are considered to be 'at risk'. Following the observations at Minamata Bay, Japan where thousands of people suffered from MeHg poisoning, it was concluded that 200 µg Hg/L whole blood may be considered a value associated with clinical symptoms of neurotoxicity (Clarkson and Magos, 2006). Based on a review of human epidemiological data from studies from the Faroe Islands and New Zealand, the NAS/NRC (U.S. National Academy of Sciences / U.S. National Research Council) derived a benchmark dose lower limit (BMDL) of 58 µg/L Hg in cord blood. The U.S. National Research Council re-evaluated the Hg risk assessment (NRC, 2000). The NRC report suggested that a ten-fold uncertainty factor should be applied in the development of a Tolerable Daily Intake (NRC, 2000). Based on this evaluation an informal blood guideline value for Hg of 5.8 µg/L in blood has been developed (see AMAP, 2003, section 9.3.1 for further details about Hg guidelines).When this guideline value is applied to the polar bear, it is clear that most bears possess blood Hg levels that would be of health concern in humans. It should be emphasized that variable sensitivity to Hg exists across species and that the human 5.8 µg/L guideline is highly conservative and may not apply to mammals in general. For example, primates with blood Hg levels exceeding 1000 µg/L did not show any signs of clinical toxicity (Clarkson and Magos, 2006).

As in humans (fellow omnivores) the feeding ecology of bears complicates this assessment. Mercury was measured in whole blood of 64 southern Beaufort Sea polar bears and the variability observed was likely to be due to intraspecific variation in prey selection (including tissue-specific consumption) and movement patterns rather than strictly trophic level interactions (Cardona-Marek et al., 2009). Thus, as in humans, feeding is not simply 'bear eats seal' because the concentrations of Hg vary greatly within a seal and among seal species. Cardona-Marek et al. (2009) indicated that circulating concentrations of blood Hg during spring were similar between sexes for Hg, but that feeding ecology may drive cohort differences (e.g., sex and age interactions). This is currently being evaluated. Thus, the changes in prey abundance and distribution patterns predicted with future reductions in sea ice in the southern Beaufort Sea may alter dietary exposure and subsequent tissue distribution based on bear condition.

Because many bears are above the human 'increasing risk' (20 and 100 µg/L) and the 'at risk' (over 100 µg/L) criteria levels, this raises questions about possible implications for polar bear health. In addition, Cardona-Marek et al. (2009) reported that the highest Hg concentration in blood (213 µg/L) was from a 16-year old female captured near Barrow. The maximum concentrations observed in the East Greenland, southern Baffin Bay and western Hudson Bay populations were 287, 739 and 56 µg/L, respectively (Dietz et al., unpubl.) Thus, the study of blood Hg concentrations in polar bears from the Chukchi Sea, East Greenland, and southern Baffin Bay is warranted in order to examine the trends and effects of Hg concentrations. The northern Arctic Canada and northwestern Greenland populations are likely to have even higher levels of blood Hg, as indicated in the geographical Hg exposure pattern for polar bear liver and hair (Dietz et al., 1998a, 2000a).

### 6.3.4. Comparison of polar bear hair concentrations with effect guidelines

As polar bear hair has been analyzed extensively over time and across regions, and as the Hg levels relate to effects thresholds, this matrix was used to evaluate circumpolar temporal trends in Hg exposure. Hair represents a good biomarker of Hg exposure since it accumulates organic Hg from blood and can be collected through minimally invasive sampling methods. Hair is a well established research matrix for Hg among humans, from which effect guidelines have been set. As for blood, it is not known to what extent these effect levels are applicable to wildlife or polar bears in particular.

Dietz et al. (2006a; 2011) reported that Hg concentrations in polar bear hair have increased more than 14-fold since pre-industrial times in Greenland, indicating a trend that is likely to involve anthropogenic sources. These increases are in accordance with increases in other hard tissue from high trophic level Arctic species (see Section 5.2; Dietz et al., 2009a). Such increases require an assessment of the recent temporal trends in Hg in a harmonized substrate that has been analyzed over time for a number of different regions. Polar bear hair represents such a substrate and is one for which effect levels exist, and from which therefore a risk assessment can be developed.

Table 6.1. Suggested thresholds for mercury in wildlife and polar bear and effects guidelines in human hair.

| Group | Hg µg/g dw | Symptoms | Source |
|---|---|---|---|
| Fish-eating wildlife | > 20 | Neurological effect levels | Thompson, 1996 |
| | > 30 | Neurological effect levels | Evers et al., 2007 |
| | > 30 | Neurological effect levels | Basu et al., 2007a |
| Polar bear | 5.4 | Reduction in NMDA receptor levels | Basu et al., 2009 |
| | 5.4 | Reduction in genomic DNA methylation | Pilsner et al., 2010 |
| Human | 12 | NOEL and BMDL for the Faroese population | FAO/WHO, 2003 |
| | 6 | Revised NOEL and BMDL for the Faroese population | Grandjean and Budtz-Jørgensen, 2007 |
| | 1 | U.S. EPA guideline values | U.S. EPA cited in FAO/WHO, 2003 |

For mammalian wildlife, such as mink and river otters, fur Hg levels exceeding 30 µg/g dw may be considered a threshold for clinical effects (i.e., sublethal and clinical health responses) according to Basu et al. (2007a) and Evers et al. (2007). A somewhat lower threshold of 20 µg/g dw was set by Thompson (1996) for terrestrial mammals (Table 6.1). Recent studies on polar bears from the East Greenland coast have documented Hg-associated reduction of the NMDA receptor levels and of genomic DNA methylation status in the brain stem (Table 6.1; Basu et al., 2009; Pilsner et al., 2010). These sub-clinical, biochemical alterations have been reported for populations with hair Hg means of about 5.4 µg/g dw. These means are 4- to 6-fold lower than the wildlife clinical effect thresholds, but comparable to the revised NOEL (No Observed Effect Level) for Hg in human hair (6.0 µg/g dw) from the Faroe Islands as suggested by Grandjean and Budtz-Jørgensen (2007). The revised NOEL from the Faroe Island human population is half the previous NOEL (12.0 µg/g dw) set for the region (FAO/WHO, 2003). The U.S. EPA Hg guideline value of 1.0 µg/g dw for human hair is among the lowest guideline values and is based on a NOEL of 12.0 µg/g dw with a safety factor of about 10 (U.S. EPA, cited in FAO/WHO, 2003).

As seen from Figure 6.11 (and Table 6.2) some populations of polar bears like those in Svalbard and western Hudson Bay have among the lowest hair Hg median concentrations. These levels are below the neurochemical effect level of 5.4 µg/g dw observed in East Greenland (Basu et al., 2009) and the NOEL of 6.0 µg/g dw in humans on the Faroe Islands (Grandjean and Budtz-Jørgensen, 2007). No bears from Svalbard exceeded the brain stem effect level or any of the higher effect levels (Table 6.2), but 6.8% and 1.7% of the western Hudson Bay bears exceeded the brain stem effect level and the Faroe Islands NOEL, respectively (Table 6.2).

None of the bears from western Hudson Bay exceeded any of the higher Hg threshold levels – from 12 to 30 µg/g dw. Among East Greenland bears, those sampled between 1973 and 2000 and between 2001 and 2008 exceeded the brain stem effect limit in 46.3% and 60.5% of cases, respectively. Conversely, among the bear fur samples from 1892 to 1950 sampled by Dietz et al. (2006a), none exceeded this effect level. The 12 µg/g dw NOEL level was exceeded in 4.0% to 5.1% of the bears sampled between 1973 and 2000 and between 2001 and 2008 (Table 6.2). In northwestern Greenland the exceeding percentages were greater than for East Greenland, but still none of the

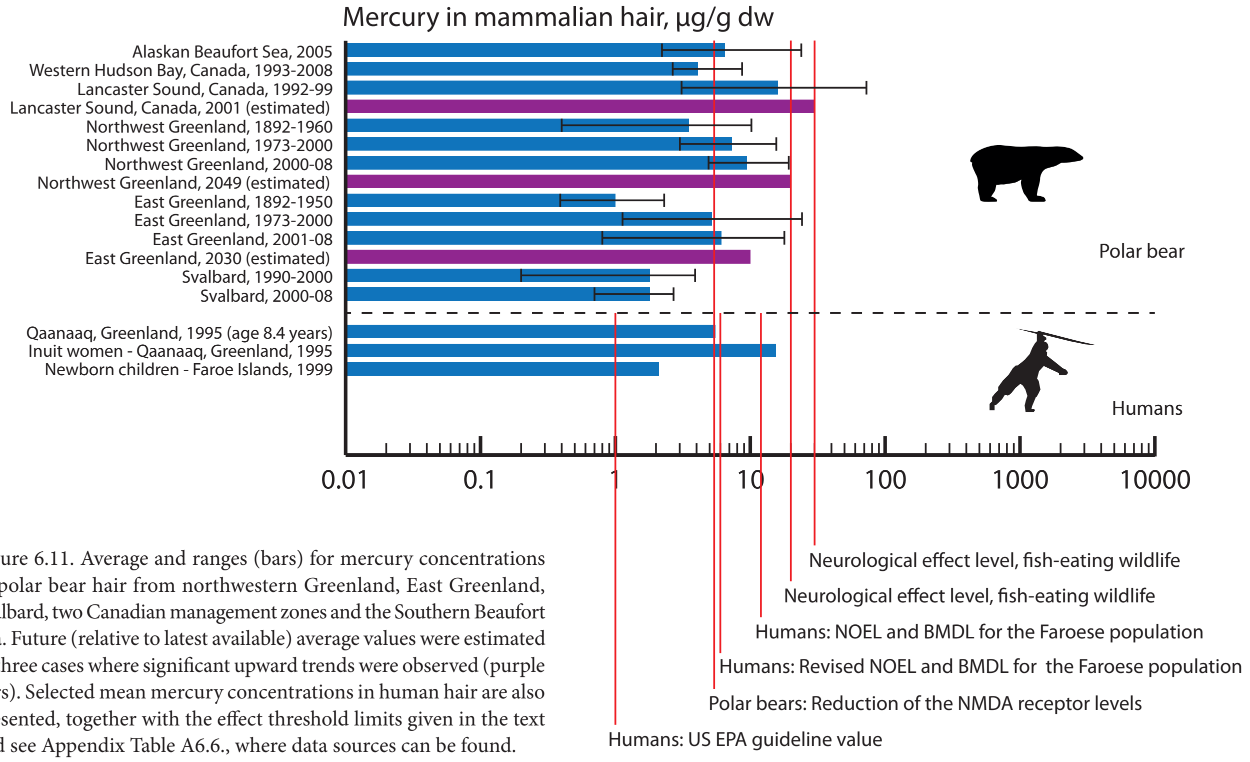

Figure 6.11. Average and ranges (bars) for mercury concentrations in polar bear hair from northwestern Greenland, East Greenland, Svalbard, two Canadian management zones and the Southern Beaufort Sea. Future (relative to latest available) average values were estimated in three cases where significant upward trends were observed (purple bars). Selected mean mercury concentrations in human hair are also presented, together with the effect threshold limits given in the text and see Appendix Table A6.6., where data sources can be found.

Table 6.2. Polar bear populations and periods exceeding the selected effect levels given in Table 6.1.

| | | | | Percentage exceeding the hair effect levels listed in Table 6.1. The effects levels below are expressed in µg/g dw | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Population | Period | Median Hg, µg/g dw | N | 1 | 5.4 | 6 | 12 | 20 | 30 | Data source |
| Alaskan Beaufort Sea | 2005 | 6.5 | 52 | 96.2 | 65.4 | 59.6 | 9.6 | 1.9 | 0 | Cardona-Marek et al., 2009 |
| Western Hudson Bay | 1993 – 2008 | 4.1 | 59 | 100.0 | 6.8 | 1.7 | 0 | 0 | 0 | Dietz et al., unpubl. |
| Lancaster Sound | 1992 – 1999 | 16.0 | 54 | 100.0 | 98.1 | 98.1 | 75.9 | 27.8 | 13.0 | Dietz et al., unpubl. |
| Northwestern Greenland | 1892 – 1960 | 3.5 | 10 | 90.0 | 10.0 | 10.0 | 0 | 0 | 0 | Dietz et al., 2006a, 2011 |
| | 1973 – 2000 | 7.3 | 76 | 100.0 | 84.2 | 73.7 | 6.6 | 0 | 0 | Dietz et al., 2006a, 2011 |
| | 2000 – 2008 | 9.4 | 31 | 100.0 | 93.5 | 93.5 | 25.8 | 0 | 0 | Dietz et al., 2006a, 2009b, 2011 |
| East Greenland | 1892 – 1950 | 1.0 | 9 | 55.6 | 0 | 0 | 0 | 0 | 0 | Dietz et al., 2006a |
| | 1973 – 2000 | 5.2 | 296 | 100.0 | 46.3 | 38.9 | 5.1 | 0.3 | 0 | Dietz et al., 2006a |
| | 2001 – 2008 | 6.1 | 124 | 99.2 | 60.5 | 50.8 | 4.0 | 0 | 0 | Dietz et al., 2006a, 2009b |
| Svalbard | 1990 – 2000 | 1.8 | 203 | 93.1 | 0 | 0 | 0 | 0 | 0 | Dietz et al., 2009b |
| | 2000 – 2008 | 1.8 | 28 | 93.8 | 0 | 0 | 0 | 0 | 0 | Dietz et al., 2009b |

🟦 0% Not occurring 🟧 0% – 10% Seldom occurring 🟪 10% – 90% Occurring 🟥 90% – 100% Very common

bears exceeded the 20 and 30 µg/g dw threshold limits. The population with the highest Hg concentrations and hence the population of greatest concern was the Lancaster Sound bears sampled between 1992 and 1999. Here the three lowest effect levels were exceeded by 98.1% to 100% of the bears and even the 20 and 30 µg/g dw effect thresholds limits were exceeded in 27.8% and 13.0% of bears, respectively. Whether hair Hg levels in this population have continued to increase as they have in the Greenland bears sampled after 2000 is uncertain, but the high concentrations certainly call for updated hair analysis and accompanying effect studies in the brain and other relevant target organs.

The steep increases observed in the Lancaster Sound (1992 to 1999) polar bears were predicted to have reached the 30 µg/g dw level by around 2001. If the increases observed in Greenland continue, then the median concentrations will have reached the 20 µg/g dw level by around 2049 in northwestern Greenland and 10 to 12 µg/g dw by around 2030 in East Greenland (Figure 6.11).

Polar bears sampled in East Greenland around 2000 exhibiting neurochemical effects in the brain stem had mean hair Hg concentrations of 5.4 µg/g dw. The finding of Hg concentrations continuing to increase in some regions since then, and the higher Hg levels in the northwestern Greenland and northern Canadian High Arctic populations, gives rise to concern for these populations. Finally there are parts of the polar bear brain that contain even higher Hg concentrations (such as the pituitary gland, which has about 6-fold higher concentrations) than the brain stem, where more severe effects may be expected (see Section 6.3.1).

The hair Hg future scenarios draw attention to quite high Hg levels in polar bear fur, which have increased dramatically compared to the pre-industrial average concentration and which, in several regions, continue to increase. However, high Hg concentration in hair is also an effective way of excreting Hg from the body. Other species have less fur, such as seals and walruses, and in toothed whales (beluga, narwhal, pilot whale) this excretion route is non-existent. Toothed whales are thus more at risk from Hg, and this is also reflected in their higher concentrations in brain, liver and muscle (Olsen et al., 2003; Hoydal and Dam, 2005, 2009; Ostertag et al., 2009; Sonne et al., 2010).

### 6.3.5. Comparison of safe guidelines in bird eggs with Arctic seabirds

Dietary Hg is rapidly transferred to avian eggs on a dose-dependent basis, making reproduction one of the most sensitive endpoints of Hg toxicity in birds (Wolfe et al., 1998). Nearly all of the Hg transferred to eggs is in the form of MeHg, with the majority (about 85% to 95%) deposited in the albumen (Wiener et al., 2003). Mercury concentrations in the egg are a good indicator of Hg risk to avian reproduction (Wolfe et al., 1998). Some of the documented effects of Hg on avian reproduction include reduced hatchability due to increases in early mortality of embryos, reduced clutch size, and embryonic deformity (Thompson, 1996; Wolfe et al., 1998).

A strong positive relationship between female blood Hg and egg Hg concentration has been used to demonstrate adverse reproductive effects in the common loon (Evers et al., 2003). By using this relationship and integrating a number of other endpoints related to MeHg exposure into a population matrix model, Evers et al. (2008) were able to characterize certain North American loon breeding populations which were experiencing reduced fledging success as 'population sinks', that is, as having negative population-level impacts. Overall, reproductive success in birds can decrease by 35-50% from a level of dietary MeHg exposure that is insufficient to cause obvious signs of toxicity in adults (Wolfe et al., 1998).

The currently accepted lowest observed adverse effect level (LOAEL) for Hg in avian eggs is 0.5 µg/g ww (range 0.5 to 1.0 µg/g ww) as determined from multi-generational feeding studies in ring-necked pheasants (*Phasianus colchicus*) and mallards (*Anas platyrhynchos*) (Fimreite, 1971; Heinz, 1976). Based on a review of the literature, Thompson (1996) concluded that, overall, Hg concentrations in excess of 2.0 µg/g ww in eggs appear to have some detrimental effect, leading to the suggestion that Hg concentrations of 0.5 to 2.0 µg/g ww in eggs are sufficient to induce impaired reproductive success in a range of bird species. However, a recent study, in which eggs of

26 species of birds were dosed with MeHg, demonstrated that the sensitivity of avian embryos to MeHg can vary dramatically among species with median lethal concentrations ($LC_{50}$) ranging from 1 µg/g ww or more in eggs of the low sensitivity group (e.g., hooded merganser, *Lophodytes cucullatus*; lesser scaup, *Aythya affinis*; double-crested cormorant, *Phalocrocorax auritus*; laughing gull, *Larus atricilla*) to less than 0.25 µg/g ww in eggs of those species exhibiting high sensitivity (e.g., osprey, *Pandion haliaetus*; white ibis, *Eudocimus albus*; snowy egret, *Egretta thula*) (Heinz et al., 2009).

A survey of recently published concentrations of Hg in eggs of Arctic birds (Figure 6.12) shows that none of the mean Hg concentrations reported for eggs of a wide range of aquatic birds exceeded 2.0 µg/g ww and that only mean values for glaucous gull (*Larus hyperboreus*) and ivory gull (*Pagophila eburnea*) eggs from the Canadian Arctic, and black guillemot (*Cepphus grylle*) eggs from the Canadian Arctic and the Faroe Islands approached or exceeded 0.50 µg/g ww. Braune et al. (2006) noted that two of the six ivory gull (*Pagophila eburnea*) eggs sampled in the Canadian Arctic exceeded Hg concentrations of 2.0 µg/g ww and five out of six eggs exceeded 0.50 µg/g ww, compared with the maximum concentrations for ivory gull eggs from the Russian Arctic which ranged from 0.24 to 0.48 µg/g ww (Miljeteig et al., 2009). Although mean Hg concentrations were similar in black guillemot eggs from the Canadian Arctic and the Faroe Islands, maximum Hg concentrations were higher in eggs from the Faroe Islands, ranging from 0.898 µg/g ww in 2002 to 1.31 µg/g ww in 2006, compared with maximum values of 0.60 to 0.84 µg/g ww at three colonies in the Canadian Arctic in 2004 (see Figure 6.12, Braune et al., 2006; Hoydal and Dam, 2005, 2009). Knudsen et al. (2005) reported a maximum Hg concentration of 0.4 µg/g ww in glaucous gull eggs from northern Norway which is similar to the mean Hg concentrations found in thick-billed murre (*Uria lomvia*) eggs from Prince Leopold Island and northern fulmar (*Fulmarus glacialis*) eggs from two locations

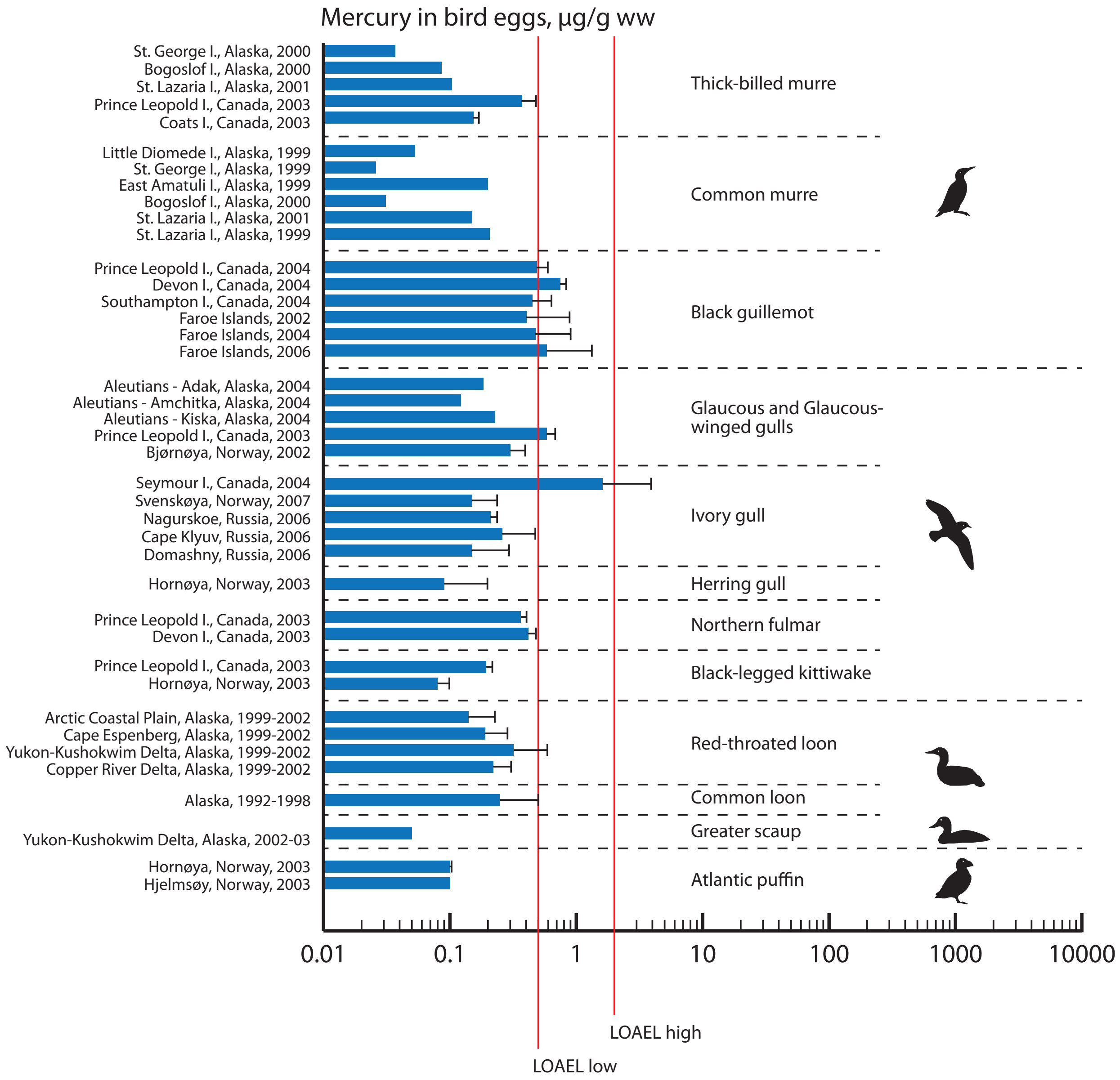

Figure 6.12. Mean total mercury concentrations in eggs from a range of Arctic bird species as summarized from the literature, in comparison with effect levels for potential reproductive impairment from Thompson (1996). The bars indicate maximum range values, where available. For sources and raw data see Appendix Table A6.7.

in the Canadian Arctic (see Figure 6.12, Braune et al., 2006; Braune, 2007). Schmultz et al. (2009) reported a maximum Hg concentration of 0.60 µg/g ww in eggs of red-throated loons (*Gavia stellata*) from Alaska compared with a maximum of 0.50 µg/g ww in eggs of common loons from Alaska (Evers et al., 2003). Burger et al. (2009) suggested that the Hg concentrations found in the eggs of glaucous-winged gulls (*Larus glaucescens*) from the Aleutian Islands off Alaska were within the range known to affect avian predators although these latter authors also noted that seabirds seem to be less vulnerable to Hg than other birds. Thompson (1996) suggested that pelagic seabirds have yet to be exposed to sufficiently high burdens of Hg to induce measurable effects on reproduction or survival. This could well be due to the ability of some seabirds to demethylate MeHg in the liver (Kim et al., 1996) although the capacity for demethylation appears to vary among species (Kim et al., 1996; Eagles-Smith et al., 2009). Nevertheless, Hg concentrations in eggs, which approach or exceed published threshold values for reproductive impairment, have been reported recently for a number of aquatic birds breeding in the Arctic. Furthermore, although there is no conclusive evidence to date, that the Hg exposure levels found in the Arctic aquatic environment are resulting in adverse biological effects in the birds studied, it is generally acknowledged that it is difficult to attribute population-level impacts to a specific factor.

### 6.3.6. Comparison of fish effect levels with mercury concentrations in Arctic fish species

Mercury toxicology in fish was not extensively studied before the late 1990s. Indeed, it was commonly believed that fish were important mainly as vectors of MeHg transfer to humans and fish-eating wildlife. This view was partially supported by the observation that direct mortality due to MeHg exposure in fish was observed only at very high tissue Hg concentrations (over 5 µg/g ww in muscle) that were characteristic solely of highly contaminated local environments (Wiener and Spry, 1996). However, more recent studies have reported a range of toxic effects in fish at much lower Hg concentrations. It is now believed that current levels of exposure to environmental MeHg are sufficiently high to be chronically toxic to a number of predatory freshwater fish in many environments (Scheuhammer et al., 2007). For example, in some independent field studies, body condition in fish of various species was reported to be inversely correlated with tissue Hg over a range of about 0.1 to 1.0 µg/g ww in liver or axial muscle (Munn and Short, 1997; Cizdziel et al., 2003; Drevnick et al., 2008). In a controlled feeding study, Webber and Haines (2003) reported that golden shiners (*Notemigonus crysoleucas*) with whole-body Hg concentrations averaging 0.52 µg/g ww were hyperactive and had altered shoaling behavior relative to fish with lower Hg concentrations. However, the most important negative effects of Hg exposure reported in fish may be on reproductive parameters, such as impaired spawning behavior, mediated through a disruption of normal neuroendocrine function (Hammerschmidt et al., 2002; Drevnick and Sandheinrich, 2003; Klaper et al., 2006; Sandheinrich and Miller, 2006; Crump and Trudeau, 2009). In a critical review of the recent literature, Sandheinrich and Wiener (2010) concluded that changes in biochemical processes, damage to cells and tissues, and reduced reproduction in fish occur at MeHg concentrations of about 0.5 to 1.2 µg Hg/g ww in axial muscle. The lower values of this range are common in some larger freshwater piscivorous fish throughout eastern North America (Kamman et al., 2005) and elsewhere. The principal effects of MeHg on fish populations at existing exposure levels in North American freshwaters are most likely to be mediated through sublethal damage to tissues and depressed reproduction (Sandheinrich and Wiener, 2010).

As shown in Figure 6.13, the minimum Hg toxicity threshold in fish muscle of 0.5 µg/g ww, based on the review by Sandheinrich and Wiener (2010), is seldom exceeded in Arctic marine fish species. Similarly, a survey of Hg in muscle of fish species from the Barents Sea reported that mean Hg concentrations did not exceed 0.25 µg/g ww in any species (Zauke et al., 1999). Arctic freshwater species tended to have higher Hg concentrations than marine species (Figure 6.13), but most species from most locations sampled between 1990 and 2008 had mean Hg concentrations in muscle of less than 0.5 µg/g ww. However, the putative toxicity threshold was approached or exceeded for some freshwater predatory species such as lake trout (*Salvelinus namaycush*), northern pike (*Esox lucius*), and landlocked Arctic char (*Salvelinus alpinus*) from some sampling sites (Figure 6.13; Evans et al., 2005a; Lockhart et al., 2005a). The highest mean Hg value (1.78 µg/g ww; Figure 6.13) was for landlocked Arctic char sampled from Amituk Lake, Cornwallis Island, Canada; however, as discussed by Lockhart et al. (2005a), this value is an adjusted (not a measured) value based on a length regression, and may be erroneously high. Nevertheless, landlocked char in general have higher Hg concentrations than sea run char (Rigét et al., 2004; Lockhart et al., 2005a).

The range of fish Hg toxicity thresholds (0.5 to 1.2 µg/g ww in muscle) suggested by Sandheinrich and Wiener (2010) was based on a review of the fish toxicology literature which deals almost exclusively with freshwater species. Although Arctic marine fish species tended to have relatively low muscle Hg concentrations, it is uncertain how well toxicity thresholds based on freshwater fish may be applied to marine species. There is far less information on the effects of MeHg on saltwater fish, and the issue of the interaction between Se and Hg in marine species adds potential complexity to the issue. In addition, there do not appear to be any Hg data for large predatory marine fish such as sharks in Arctic waters, for which Hg levels would be expected to be considerably higher than for the species shown in Figure 6.13. Nonetheless, currently available data on Hg in Arctic fish does not indicate a significant risk of toxicity for most species analyzed to date, with the possible exception of some larger freshwater predatory species. As the vast majority of fish Hg data concern muscle concentrations, the above assessment was based on muscle levels alone. To what extent additional information could be obtained by analyzing Hg in other fish tissues such liver, kidney and brain remains unanswered in the present assessment.

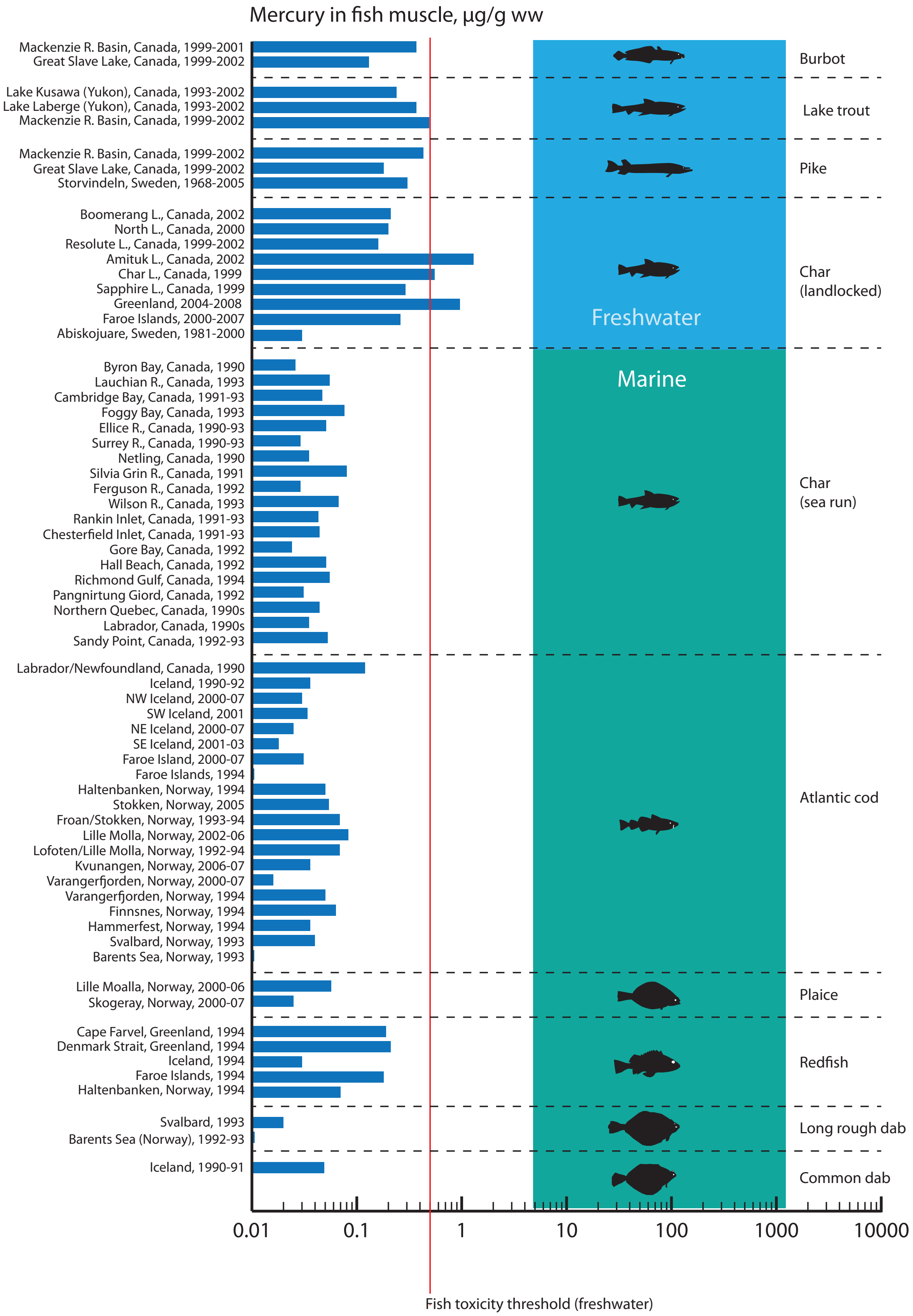

Figure 6.13. Mean total mercury concentrations in muscle summarized from data for selected Arctic fish species sampled from locations in Arctic Canada, Norway, Iceland, Greenland, the Faroe Islands and Sweden. Plotted values are means for five or more individuals per location sampled between 1990 and 2009. The solid red line indicates the lowest suggested threshold in dorsal muscle for mercury toxicity in fish (0.5 µg/g; Sandheinrich and Wiener, 2010). The fish mercury data are from a range of sources (Hellou et al., 1992; Maage et al., 1996; Stange et al., 1996; Rigét et al., 1997; Larsen and Dam, 2003; Evans et al., 2005a; Lockhart et al., 2005a; OSPAR, unpubl. data; A. Bignert, Swedish Museum of Natural History, Sweden, unpubl. data; F. Rigét, National Environmental Research Institute, Denmark, 2009 unpubl. data; G. Stern, Fisheries and Oceans Canada, 2009 unpubl. data). See Appendix Table A6.8. for further details.

## 6.4. Conclusions and recommendations

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

### What is known about the combined effects of contaminants, and other types of environmental stressors?

1. Interactions between Hg and other chemical stressors (e.g., Cd, POPs), nutritional factors (e.g., Se, food availability, vitamin status), and environmental changes (e.g., climate change and its impacts on sea-ice habitat loss, prey availability) are relevant to health concerns about Arctic biota, and are complicated.

*Investigations that explore combined effects under a multiple stressor framework should be initiated to improve understanding of how chemical and non-chemical stressors interact to affect the health of Arctic biota and the broader Arctic ecosystem.*

### What role does mercury speciation play in uptake and toxic effects?

2. Many high trophic level predators associated with marine and other aquatic ecosystems are exposed to Hg primarily as MeHg in their diet (via muscle, epidermis); however, a variable proportion of absorbed MeHg is demethylated, and some tissues (such as liver and kidney) can accumulate high inorganic Hg concentrations bound to Se reaching an approximate 1:1 molar ratio. This process of demethylation and sequestration with Se is speculated to be a protective mechanism by which some animals can detoxify MeHg.

*The possible interspecies differences in the effectiveness of demethylation, selenium biochemistry, and sensitivity to MeHg exposure would be highly relevant to future studies on Arctic species. The antioxidant role of Se directly and indirectly (e.g., as cofactor for glutathione peroxidase) should also be investigated. Future studies should also consider sequestration of Se by Hg, which may result in Se deficiency.*

### Is there any evidence that tissue mercury concentrations at present are harmful to Arctic biota?

*Summary on mercury and effects in brains*

3. The overall results show that the highest concentrations in brain tissue are found in toothed whales and that these are in the range of Hg-associated neurochemical effects. Despite relatively high levels of Hg in liver and kidney, Hg levels are surprisingly low in the polar bear brain stem. Despite these lower-than-expected Hg levels, significant correlations were found between brain Hg levels and changes in neurochemical biomarkers in a manner consistent with other fish-eating wildlife. These results indicate that excretion through fur may substantially reduce the brain exposure in fur-bearing species compared to species without such excretion possibilities, for example whales.

*Owing to the importance of brain neurochemistry in multiple aspects of animal health, the ecological and physiological significance of prolonged disruption to brain neurochemistry needs to be addressed. Future studies should also evaluate Hg exposure and effects in other high trophic level Arctic wildlife and in other brain regions that may accumulate more Hg than the brain stem. Other toothed whales, such as pilot whales and narwhal, should be investigated to see if Hg concentrations as high as those in beluga can be detected.*

*Histopathology of Arctic marine mammals*

4. Histopathological changes in liver and kidney tissues have been observed in polar bears from East Greenland, beluga, bowhead whales and ringed seals from Alaska, and pilot whales from the Faroe Islands. Some of these changes have been related to tissue Hg levels, although links with other key parameters such as age, disease and other contaminants have also been found. The significance of these tissue lesions on the individual and at population level is uncertain.
5. Mean liver Hg concentrations and probably also kidney concentrations in polar bears from southwestern Melville Island and the eastern Beaufort Sea exceeded the general toxic threshold Hg values for terrestrial and marine mammals. These regional patterns and findings fit well with the areas of concern based on hair Hg measurement. Few recent data are available to evaluate the recent loads in the most exposed seals, such as hooded seals.
6. Pilot whales from the Faroe Island and in some cases beluga populations from St. Lawrence and Point Lay have mean Hg liver concentrations exceeding the threshold values for liver damage.

*The populations having tissue concentrations of concern should be investigated for Hg-induced health effects. Future histopathological work should include other physiologically important tissues such as the brain, reproductive organs, and the developing organism.*

7. Although the developing fetus is known to be sensitive to MeHg, no investigations have been carried out on Hg-related impairments to reproduction and neurodevelopment in Arctic marine mammals.

### Comparison of observed blood mercury levels in high trophic level species with effect concentrations and safe guidelines

8. Blood Hg concentrations are useful in assessing ongoing target organ exposure and mostly represent recent dietary exposures, thus this minimally invasive sampled matrix has utility in combination with hair Hg data to offer insight into toxicity if carefully compared to human guidelines, while considering the numerous caveats (e.g., cross species extrapolation, highly conservative nature of human derived guidelines).

*Continued sampling of blood should include measures of Se and Se-associated enzymes to better assess the Hg-Se interaction in the blood and to assess Se as a nutrient (not just in countering Hg toxicity), along with measures of carbon-, nitrogen- and sulfur-stable isotopes and fatty acids to better assess pathways of exposure (diet).*

### Comparison of polar bear hair mercury concentrations with effect thresholds and guidelines

9. High Hg concentrations in polar bear hair indicative of high concentrations in other tissues such as brain and liver raise concern about Hg exposure and possible health effects in some regions of the Arctic (northern Canada and Greenland) especially taking the observed temporal increases into account.

*Effect studies that correlate Hg exposure with biological responses should be carried out on polar bears in northern Canada and northwestern Greenland (as well as reference areas) showing upward Hg trends and hair and (other tissue) concentrations of concern.*

### Comparison of bird safe guidelines in eggs with Arctic seabirds

10. Some bird species (ivory gull, black guillemot) have Hg levels in their eggs sufficiently high to raise concern about negative effects on reproductive success.

*A MeHg egg-injection study was recently conducted on thick-billed murres to develop toxicity thresholds, and this should be extended to include other relevant Arctic species.*

### Comparison of fish effect levels with Arctic fish species concentrations

11. Arctic fish species (especially marine species) generally have Hg concentrations below suggested toxicity thresholds, and only for a few species (e.g., landlocked Arctic char) are the guideline limits exceeded.

*Additional studies should be undertaken to determine Hg levels and possible effects in a wider range of marine species, especially including top predatory species such as sharks.*

### Overall conclusion and recommendation

12. Compared to the amount of contaminant data available for the Arctic region, knowledge of the effects of these contaminant loads are very limited.

*Additional studies to determine levels and possible effects in species at risk should be conducted, especially studies on top predators from areas with the highest contaminant loads.*

## Chapter 6 Appendix

Table A6.1. Mercury concentrations in brain tissue from Arctic biota and humans. Concentrations expressed in µg/g ww. See also Figure 6.2.

| Species | Location | Tissue | Year | Age/size | Sex | N | Mean | SD | Min | Max | Source |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Harp seal | Newfoundland | Brain | 1976-1978 | Pups | M | 4 | 0.09 | 0.04 | | | Ronald et al., 1984 |
| | Newfoundland | Brain | 1976-1978 | Juveniles | M | 2-18 | 0.12 | 0.04 | | | Ronald et al., 1984 |
| | Newfoundland | Brain | 1976-1978 | Adults | M | 1-2 | 0.21 | 0.08 | | | Ronald et al., 1984 |
| | St. Lawrence | Brain | 1976-1978 | Pups | M | 10-28 | 0.08 | 0.04 | | | Ronald et al., 1984 |
| | St. Lawrence | Brain | 1976-1978 | Juveniles | M | 10 | 0.1 | 0.05 | | | Ronald et al., 1984 |
| | St. Lawrence | Brain | 1976-1978 | Adults | M | 2 | 0.15 | 0.02 | | | Ronald et al., 1984 |
| | Grise Fjord, Pangnirtung and NW Greenland | Brain | 1976-1978 | Pups | M | 1 | 0.08 | | | | Ronald et al., 1984 |
| | Grise Fjord, Pangnirtung and NW Greenland | Brain | 1976-1978 | Juveniles | M | 1-8 | 0.17 | 0.05 | | | Ronald et al., 1984 |
| | Grise Fjord, Pangnirtung and NW Greenland | Brain | 1976-1978 | Adults | M | 1-4 | 0.16 | 0.03 | | | Ronald et al., 1984 |
| Grey seal | Nova Scotia | Brain | 1972 | | | | 0.40 | 0.06 | | | Freeman and Horne, 1973 |
| 4 seal species | Norwegian Coast | Brain | 1989-1990 | | | | 0.06 | 0.06 | 0.01 | 0.1 | Skaare et al., 1994 |
| Ringed seal | Northern Quebec | Cerebral cortex | | | | | 0.13 | 0.19 | 0.01 | 0.15 | Basu unpubl. based on Basu et al., 2006a |
| Polar bear | Ittoqqortoormiit, East Greenland | Brain stem | 1999-2001 | All ages | F | 37 | 0.104 | | 0.028 | 0.217 | Basu et al., 2009 |
| | Ittoqqortoormiit, East Greenland | Brain stem | 1999-2001 | All ages | M | 45 | 0.092 | | 0.042 | 0.197 | Basu et al., 2009 |
| | Kuujjuaq, Eastern Canada | Cerebral cortex | 2000-2003 | All ages | M&F | 21 | 0.08 | | | | Krey et al., 2008, Poster Setac |
| Beluga | Canada | Cerebellum | 2008 | Adults | M&F | 21 | 2.9 | 2.0 | 0.04 | 7.3 | Ostertag et al., 2009 |
| | Canada | Frontal lobe | 2008 | Adults | M&F | 18 | 4.7 | 4.7 | 0.1 | 20.3 | Ostertag et al., 2009 |
| | Canada | Temporal lobe | 2008 | Adults | M&F | 20 | 5.5 | 4.8 | 0.04 | 20.7 | Ostertag et al., 2009 |
| Inuit | Greenland | Cerebral cortex | | All ages | M&F | 17 | 0.17 | | 0.059 | 4.782 | Pedersen et al., 1999 |

Table A6.2. Mercury concentrations in polar bear liver and kidney. Concentrations expressed in µg/g ww. See also Figures 6.4 and 6.7.

| | | | | | Liver | | | Kidney | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Species | Location | Year | Age/sex | N | Mean | Min | Max | Mean | Min | Max | Source |
| Polar bear | Ittoqqortoormiit, Greenland | 1983-1990 | <1 | | 2.1 | | | 2.9 | | | Dietz et al., 2000a[a] |
| | Ittoqqortoormiit, Greenland | 1983-1990 | 2-6 | | 7.5 | | | 11.2 | | | Dietz et al., 2000a[a] |
| | Ittoqqortoormiit, Greenland | 1983-1990 | >6 | | 13.4 | | | 32 | | | Dietz et al., 2000a[a] |
| | Ittoqqortoormiit, Greenland | 1999-2001 | Subadult | | 6.3 | | | 7.2 | | | Sonne et al., 2007 |
| | Ittoqqortoormiit, Greenland | 1999-2001 | Adult females | | 15.8 | | | 18 | | | Sonne et al., 2007 |
| | Ittoqqortoormiit, Greenland | 1999-2001 | Adult males | | 15.0 | | | 29.4 | | | Sonne et al., 2007 |
| | Ittoqqortoormiit, Greenland | 1999-2001 | All | 59 | 10.0 | 1 | 36 | 14 | 1 | 50 | Sonne et al., 2007 |
| | Avanersuaq North, Greenland | 1988-1990 | 2-6 | | 12.4 | | | 10.7 | | | Dietz et al., 2000a[a] |
| | Avanersuaq North, Greenland | 1988-1990 | >6 | | 21.0 | | | 12.7 | | | Dietz et al., 2000a[a] |
| | Avanersuaq South, Greenland | 1988-1990 | 1 | | 4.3 | | | 4.2 | | | Dietz et al., 2000a[a] |
| | Avanersuaq South, Greenland | 1988-1990 | 2-6 | | 12.9 | | | 12.6 | | | Dietz et al., 2000a[a] |
| | Avanersuaq South, Greenland | 1988-1990 | >6 | | 22.0 | | | 28.1 | | | Dietz et al., 2000a[a] |
| | Cumberland Peninsula, Canada | 1991 | 6.9 | | 6.7 | | | | | | Braune et al., 1991b[b] |
| | Cape Mercy, Canada | 1991 | 6.9 | | 16.7 | | | | | | Braune et al., 1991b[b] |
| | Eastern Beaufort Sea, Canada | 1991 | 6.9 | | 53.0 | | | | | | Braune et al., 1991b[b] |
| | Southwest Melville Island, Canada | 1991 | 6.9 | | 71.1 | | | | | | Braune et al., 1991b[b] |

[a] Geometric mean; [b] age normalized data.

Table A6.3. Mercury concentrations in seal and walrus liver and kidney. Concentrations expressed in µg/g ww. See also Figures 6.5 and 6.8.

| | | | | Liver | | | | | | Kidney | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Species | Location | Year | Age | Mean | Min | Max | SD | 95 % CL lower | 95 % CL higher | Mean | Min | Max | N | SD | 95 % CL lower | 95 % CL higher | Source |
| Walrus | Bering Strait | 1981-1984 | All | 1.23 | | | | | | | | | 120 | | 1.230 | 1.230 | Wagemann and Stewart, 1994 |
| | Foxe Basin, Canada | 1982-1988 | All | 1.4 | | | | | | 0.32 | | | 120 | | 1.400 | 1.400 | Wagemann and Stewart, 1994 |
| | Hudson Bay, Canada | 1990 | 11 | 2 | | | | | | | | | 13 | | 2.000 | 2.000 | Kingsley, 1994 |
| | Avanersuaq | 1975-1977 | 11 | 1.78 | | | | | | 0.09 | | | 46 | | 1.780 | 1.780 | Born et al., 1981 |
| Ringed seal | Barrow, Alaska | 1995-1997 | 0-5 | 0.734 | | | 0.653 | -0.54588 | 2.01388 | 0.379 | | | | 0.285 | 0.175 | 1.293 | Rigét et al., 2005 |
| | Barrow, Alaska | 1995-1997 | >5 | 4.78 | | | 5.72 | -6.4312 | 15.9912 | 0.551 | | | | 0.271 | 4.249 | 5.311 | Rigét et al., 2005 |
| | Sachs Harbour, Canada | 2001 | 0-5 | 19.2 | | | 23.6 | -27.056 | 65.456 | 2.23 | | | | 1.24 | 16.770 | 21.630 | Rigét et al., 2005 |
| | Sachs Harbour, Canada | 2001 | >5 | 19.1 | | | 9.6 | 0.284 | 37.916 | 2.04 | | | | 0.81 | 17.512 | 20.688 | Rigét et al., 2005 |
| | Holman, Canada | 2001 | 0-5 | 19.6 | | | 10 | 0 | 39.2 | | | | | | 19.600 | 19.600 | Rigét et al., 2005 |
| | Holman, Canada | 2001 | >5 | 29.9 | | | 26.5 | -22.04 | 81.84 | | | | | | 29.900 | 29.900 | Rigét et al., 2005 |
| | Arctic Bay Canada | 2000 | 0-5 | 7.42 | | | 7.11 | -6.5156 | 21.3556 | 1.38 | | | | 0.89 | 5.676 | 9.164 | Rigét et al., 2005 |
| | Arctic Bay Canada | 2000 | >5 | 12.4 | | | 14.4 | -15.824 | 40.624 | 1.78 | | | | 0.95 | 10.538 | 14.262 | Rigét et al., 2005 |
| | Grise Fiord, Canada | 1998 | 0-5 | 19.6 | | | 10 | 0 | 39.2 | 2.31 | | | | 0.87 | 17.895 | 21.305 | Rigét et al., 2005 |
| | Grise Fiord, Canada | 1998 | >5 | 29.9 | | | 26.5 | -22.04 | 81.84 | 3.19 | | | | 1.48 | 26.999 | 32.801 | Rigét et al., 2005 |
| | Pond Inlet, Canada | 2000 | 0-5 | 6.84 | | | 16.9 | -26.284 | 39.964 | 1.04 | | | | 0.45 | 5.958 | 7.722 | Rigét et al., 2005 |
| | Pond Inlet, Canada | 2000 | >5 | 14.9 | | | 14.9 | -14.304 | 44.104 | 2.54 | | | | 0.73 | 13.469 | 16.331 | Rigét et al., 2005 |
| | Avanersuaq, Greenland | 1998 | 0-5 | 4.59 | | | 4.2 | -3.642 | 12.822 | | | | | | 4.590 | 4.590 | Rigét et al., 2005 |
| | Avanersuaq, Greenland | 1998 | >5 | 9.15 | | | 6.58 | -3.7468 | 22.0468 | | | | | | 9.150 | 9.150 | Rigét et al., 2005 |
| | Qeqertarssuaq, Greenland | 1999-2000 | 0-5 | 1.23 | | | 2.66 | -3.9836 | 6.4436 | | | | | | 1.230 | 1.230 | Rigét et al., 2005 |
| | Qeqertarssuaq, Greenland | 1999-2000 | >5 | 2.91 | | | 2.03 | -1.0688 | 6.8888 | | | | | | 2.910 | 2.910 | Rigét et al., 2005 |
| | Ittoqqortoormiit, Greenland | 1999-2000 | 0-5 | 4.78 | | | 4.35 | -3.746 | 13.306 | | | | | | 4.780 | 4.780 | Rigét et al., 2005 |
| | Ittoqqortoormiit, Greenland | 1999-2000 | >5 | 7.96 | | | 5.08 | -1.9968 | 17.9168 | | | | | | 7.960 | 7.960 | Rigét et al., 2005 |
| | Svalbard, Norway | 1996 | 0-5 | 0.641 | | | 0.317 | 0.01968 | 1.26232 | 0.46 | | | | 0.114 | 0.418 | 0.864 | Rigét et al., 2005 |
| | Svalbard, Norway | 1996 | >5 | 1.19 | | | 0.74 | -0.2604 | 2.6404 | 0.51 | | | | 0.74 | -0.260 | 2.640 | Rigét et al., 2005 |
| | White Sea, Russia | 2001 | 0-5 | 1.87 | | | 1.44 | -0.9524 | 4.6924 | 0.43 | | | | 0.106 | 1.662 | 2.078 | Rigét et al., 2005 |
| | White Sea, Russia | 2001 | >5 | 2.41 | | | 2.41 | -2.3136 | 7.1336 | 0.79 | | | | 0.404 | 1.618 | 3.202 | Rigét et al., 2005 |
| Harp seal | Greenland Sea, Greenland | 1999 | 12 | 0.19 | 0.13 | 0.28 | 0.04 | 0.1116 | 0.2684 | 0.23 | 0.03 | 0.66 | 25 | 0.04 | 0.112 | 0.268 | Bruunborg et al., 2006 |
| | Upernavik, Greenland | 1985 | 5-10 | 1.01 | | | | 1.01 | 1.01 | 0.79 | | | | | | | Dietz et al., 1998 |
| Hooded seal | Davis Strait, Greenland | 1984 | All | 77.9 | | | 22.2 | 34.388 | 121.412 | 0.79 | | | 3 | | | | Dietz et al., 1996 |
| | Ammassalik, Greenland | 1984 | 1 | 7.85 | | | | | | 0.79 | | | | | | | Dietz et al., 1996 |
| | Greenland Sea, Greenland | 1999 | 9 | 29 | | | | | | 0.79 | | | | | | | Bruunborg et al., 2006 |

Table A6.4. Mercury concentrations in whale liver and kidney. Concentrations expressed in µg/g ww. See also Figures 6.6 and 6.9.

| | | | | | Liver | | | Kidney | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Species | Location | Year | Age/sex | N | Mean | Min | Max | Mean | Min | Max | Source |
| *Baleen whales* | | | | | | | | | | | |
| Grey whale | Lorino Lawrentia, Russia | 2001 | 978 cm | | 0.02 | 0 | 0.07 | 0.01 | 0 | 0.03 | Dehn et al., 2006 |
| | Mechigmenskiy, Russia | 2001 | 840 cm | | 0.16 | | | 0.03 | | | Tilbury et al., 2002 |
| Bowhead whale | Barrow, Alaska | 1992-1999 | 1093 cm | | 0.05 | 0 | 0.1 | 0.03 | 0 | 0.1 | Woshner, 2000 |
| Minke whale | West Greenland | 1998 | All | 45 | 1 | | | 0.9 | | | Born et al., 2003 |
| | East Greenland | 1998 | Females all ages | 4 | 1.9 | | | 2.7 | | | Born et al., 2003 |
| | Jan Mayen | 1998 | All | 24 | 2 | | | 2.4 | | | Born et al., 2003 |
| | Svalbard, Norway | 1998 | All | 16 | 0.7 | | | 0.7 | | | Born et al., 2003 |
| | Barents Sea, Norway | 1998 | All | 33 | 1.1 | | | 1.2 | | | Born et al., 2003 |
| | Lofoten, Norway | 1998 | All | 14 | 1.7 | | | 1.2 | | | Born et al., 2003 |
| *Toothed whales* | | | | | | | | | | | |
| Harbour porpoise | Central West Greenland | 1988-1989 | All | | 4.3 | | | 0.92 | | | Paludan-Müller et al., 1993 |
| | Central West Greenland | 1988-1989 | >7 | | 8.2 | | | 1.3 | | | Paludan-Müller et al., 1993 |
| Beluga | Barrow, Alaska | | | 45 | 23 | 0 | 82 | 5 | 0.2 | 17 | Woshner et al., 2003 |
| | Barrow, Alaska | 1992-1999 | 365 cm | 48 | 16 | | | 4.4 | | | Woshner et al., 2001a |
| | Upernavik, Greenland | 1984-1986 | 0-6 | | 1 | | | 0.7 | | | Hansen et al., 1990 |
| | Upernavik, Greenland | 1984-1986 | 7-13 | | 3 | | | 0.95 | | | Hansen et al., 1990 |
| | Upernavik, Greenland | 1984-1986 | >13 | | 16.4 | | | 4.2 | | | Hansen et al., 1990 |
| | Grise Fiord, Canada | <1990 | 13.9 | 25 | 12 | | | 2.2 | | | Dietz et al., 2004 |
| | Mackenzie Delta, Canada | 1984 | 5.6 | 25 | 2.1 | | | 1.5 | | | Dietz et al., 2004 |
| | St. Lawrence, Canada | 1984 | 17.5 | 25 | 33.5 | | | 6.5 | | | Dietz et al., 2004 |
| Narwhal | Avanersuaq, Greenland | 1984 | Females >3 | 25 | 11.4 | | | 1.8 | | | Dietz et al., 2004 |
| | Avanersuaq, Greenland | 1984 | Males >3 | 11 | 16.3 | | | 2.3 | | | Dietz et al., 2004 |
| | Uummannaq, Greenland | 1993 | Females >3 | 14 | 10.8 | | | 1.3 | | | Dietz et al., 2004 |
| | Uummannaq, Greenland | 1993 | Males >3 | 28 | 6.3 | | | 1.8 | | | Dietz et al., 2004 |
| Pilot whale | Faroe Islands | 2001-2007 | All age groups | 50 | 75 | 54 | 574 | 64.6 | 7 | 188 | Hoydal and Damm, 2009[a] |
| | Faroe Islands | 2007 | All age groups | 14 | 138 | 54 | 351 | 15 | 7 | 31 | Sonne et al., 2009 |

[a] Median values.

Table A6.5. Mercury concentrations in mammalian blood. Concentrations expressed in μg/L. See also Figure 6.10.

| Species | Location | Year | Age/sex | N | Mean | Min | Max | Source |
|---|---|---|---|---|---|---|---|---|
| Harp seal | Labrador | 1976-1978 | pups | 3 | 10 | | | Ronald et al., 1984 |
| | Labrador | 1976-1978 | juvenile males | 19 | 20 | | | Ronald et al., 1984 |
| | Labrador | 1976-1978 | adult males | 3 | 40 | | | Ronald et al., 1984 |
| | St Lawrence | 1976-1978 | male pups | 16 | 40 | | | Ronald et al., 1984 |
| | St Lawrence | 1976-1978 | male juveniles | 7 | 60 | | | Ronald et al., 1984 |
| | St Lawrence | 1976-1978 | male adults | 2 | 150 | | | Ronald et al., 1984 |
| | Grise Fjord, Pangnirtung and NW Greenland | 1976-1978 | male juveniles | 1-3 | 70 | | | Ronald et al., 1984 |
| | Grise Fjord, Pangnirtung and NW Greenland | 1976-1978 | male adults | 6 | 110 | | | Ronald et al., 1984 |
| Polar bear | East Greenland | Winter, 1999-2001 | | 8 | 51 | | | Dietz et al. unpubl. |
| | East Greenland | Spring, 1999-2001 | | 12 | 65 | | | Dietz et al. unpubl. |
| | East Greenland | Summer, 1999-2001 | | 6 | 52 | | | Dietz et al. unpubl. |
| | East Greenland | Autumn, 1999-2001 | | 22 | 74 | | | Dietz et al. unpubl. |
| | Southern Baffin Bay | April 2006 | | 10 | 132 | | | Dietz et al. unpubl. |
| | Western Hudson Bay | August September 2006-2008 | | 27 | 27 | | | Dietz et al. unpubl. |
| | Alaska | 2005 | | 31 | 65 | 7.0 | 213 | Cardona-Marek et al., 2009 |
| Inuit women | North Slope, Alaska | 1999-2003 | | 43 | 1 | | | AMAP, 2009b |
| | Canada | 2005 | | 52 | 1 | 0.1 | 14 | AMAP, 2009b |
| | Nunavik, Canada | 2004 | | 37 | 12 | 0.2 | 164 | AMAP, 2009b |
| | Greenland | 1999-2006 | | 299 | 13 | 0.5 | 164 | AMAP, 2009b |
| | Qaanaaq, Greenland | 2003 | | | 50 | 5.7 | 164 | AMAP, 2009b |
| | Kola Peninsula, Russia | 2001-2003 | | | 1 | 0.5 | 2 | AMAP, 2009b |
| Informal Human blood guideline value for mercury | | | | | 6 | | | |
| Increasing risk range, Health Canada | | | | | 20 | | | |
| Benchmark Dose Lower Limit (BMDL) | | | | | 58 | | | |
| Risk range, Health Canada | | | | | 100 | | | |
| Clinical symptoms of neurotoxicity | | | | | 200 | | | |

Table A6.6. Mercury concentrations in polar bear and human hair. Concentrations expressed in μg/g dw. See also Figure 6.11.

| Species | Location | Year | Age | N | Median | Min | Max | Source |
|---|---|---|---|---|---|---|---|---|
| Polar bear | Svalbard | 1990-2000 | | 203 | 1.8 | 0.2 | 3.9 | Dietz et al., 2009b |
| | Svalbard | 2000-2008 | | 28 | 1.8 | 0.7 | 2.7 | Dietz et al., 2009b |
| | East Greenland | 1892-1950 | | 9 | 1.0 | 0.4 | 2.3 | Dietz et al., 2006a |
| | East Greenland | 1973-2000 | | 296 | 5.2 | 1.1 | 24.2 | Dietz et al., 2006a |
| | East Greenland | 2001-2008 | | 124 | 6.1 | 0.8 | 17.9 | Dietz et al., 2006a, 2009b |
| | East Greenland | 2030 | | 124 | 10.0 | | | Dietz et al., 2006a, 2009b |
| | Northwest Greenland | 1892-1960 | | 10 | 3.5 | 0.4 | 10.2 | Dietz et al., 2006a |
| | Northwest Greenland | 1973-2000 | | 76 | 7.3 | 3.0 | 15.6 | Dietz et al., 2006a |
| | Northwest Greenland | 2000-2008 | | 31 | 9.4 | 4.9 | 19.3 | Dietz et al., 2006a, 2011 |
| | Northwest Greenland | 2049 | | 31 | 20.0 | | | Dietz et al., 2006a, 2011 |
| | Lancaster Sound | 1992-1999 | | 54 | 16.0 | 3.1 | 72.7 | Dietz et al., unpubl. |
| | Lancaster Sound | 2001 | | 54 | 30.0 | | | Dietz et al., unpubl. |
| | Western Hudson Bay | 1993-2008 | | 59 | 4.1 | 2.6 | 8.7 | Dietz et al., unpubl. |
| | Alaskan Beaufort Sea | 2005 | | 52 | 6.5 | 2.2 | 23.9 | Cardona-Marek et al., 2009 |
| Human | Qaanaaq, Greenland | 1995 | 8.4 y | | 5.5 | | | Weihe et al., 2002 |
| | Qaanaaq, Greenland | 1995 | Adult F | 43 | 15.5 | | | Weihe et al., 2002 |
| | Faroe Island | 1999 | Newborn | | 2.1 | | | Weihe et al., 2002 |

Table A6.7. Mercury concentrations in bird eggs. Concentrations expressed in µg/g ww. See also Figure 6.12.

| Species | Location | Year[a] | N | Mean[b] ww | Mean[b] dw | Source |
|---|---|---|---|---|---|---|
| Common murre | Bogoslof I, Alaska | 2000 | 9 | 0.031 | | Day et al., 2006 |
| | St. Lazaria I, Alaska | 1999 | 10 | 0.207 | | Christopher et al., 2002 |
| | St. Lazaria I, Alaska | 2001 | 10 | 0.150 | | Day et al., 2006 |
| | Little Diomede I, Alaska | 1999 | 9 | 0.053 | | Christopher et al., 2002 |
| | St. George I, Alaska | 1999 | 11 | 0.026 | | Christopher et al., 2002 |
| | East Amatuli I, Alaska | 1999 | 11 | 0.200 | | Christopher et al., 2002 |
| Thick-billed murre | St. George I, Alaska | 2000 | 7 | 0.037 | | Day et al., 2006 |
| | Bogoslof I, Alaska | 2000 | 10 | 0.086 | | Day et al., 2006 |
| | St. Lazaria I, Alaska | 2001 | 10 | 0.104 | | Day et al., 2006 |
| Glaucous-winged gull | Aleutians – Adak, Alaska | 2004 | 8 | 0.184[c] | 0.734 | Burger et al., 2009 |
| | Aleutians – Amchitka, Alaska | 2004 | 7 | 0.123[c] | 0.490 | Burger et al., 2009 |
| | Aleutians – Kiska, Alaska | 2004 | 6 | 0.228[c] | 0.910 | Burger et al., 2009 |
| Red-throated loon | Arctic Coastal Plain, Alaska | 1999-2002 | 12 | 0.14 | | Schmutz et al., 2009 |
| | Cape Espenberg, Alaska | 1999-2002 | 10 | 0.19 | | Schmutz et al., 2009 |
| | Yukon-Kushokwim Delta, Alaska | 1999-2002 | 15 | 0.32 | | Schmutz et al., 2009 |
| | Copper River Delta, Alaska | 1999-2002 | 8 | 0.22 | | Schmutz et al., 2009 |
| Common loon | Alaska | 1992-1998 | 10 | 0.25 | | Evers et al., 2003 |
| Greater scaup | Yukon-Kushokwim Delta, Alaska | 2002-2003 | 6 | ≤ 0.05[c] | ≤ 0.2[d] | Badzinski et al., 2009 |
| Thick-billed murre | Prince Leopold I, Canada | 2003 | 15 | 0.37[e] | 1.33 | Braune, 2007 |
| | Coats I, Canada | 2003 | 15 | 0.15[e] | 0.56 | Braune et al., 2006 |
| Northern fulmar | Prince Leopold I, Canada | 2003 | 15 | 0.36[e] | 1.41 | Braune, 2007 |
| | Devon I, Canada | 2003 | 14 | 0.42[e] | 1.57 | Braune et al., 2006 |
| Black-legged kittiwake | Prince Leopold I, Canada | 2003 | 12 | 0.19[e] | 0.82 | Braune, 2007 |
| Glaucous gull | Prince Leopold I, Canada | 2003 | 15 | 0.58[e] | 2.57 | Braune et al., 2006 |
| Black guillemot | Prince Leopold I, Canada | 2004 | 15 | 0.49[e] | 1.92 | Braune et al., 2006 |
| | Devon I, Canada | 2004 | 9 | 0.75[e] | 2.65 | Braune et al., 2006 |
| | Southampton I, Canada | 2004 | 9 | 0.45[e] | 1.71 | Braune et al., 2006 |
| Ivory gull | Seymour I, Canada | 2004 | 6 | 1.61[e] | 6.37 | Braune et al., 2006 |
| Black guillemot | Faroe Islands | 2002 | 17 | 0.404 | | Hoydal and Dam, 2009 |
| | Faroe Islands | 2004 | 17 | 0.479 | | Hoydal and Dam, 2005 |
| | Faroe Islands | 2006 | 20 | 0.583 | | Hoydal and Dam, 2009 |
| Herring gull | Hornøya, Norway | 2003 | 5 | 0.09 | | Helgason et al., 2008 |
| Black-legged kittiwake | Hornøya, Norway | 2003 | 5 | 0.08 | | Helgason et al., 2008 |
| Atlantic puffin | Hornøya, Norway | 2003 | 5 | 0.10 | | Helgason et al., 2008 |
| | Hjelmsøy, Norway | 2003 | 5 | 0.10 | | Helgason et al., 2008 |
| Glaucous gull | Bjørnøya, Norway | 2002 | 4 | 0.3 | | Knudsen et al., 2005 |
| Ivory gull | (Svenskøya, Norway | 2007 | 10 | 0.15 | | Miljeteig et al., 2009 |
| | (Nagurskoe, Russia | 2006 | 6 | 0.21 | | Miljeteig et al., 2009 |
| | Cape Klyuv, Russia | 2006 | 7 | 0.26 | | Miljeteig et al., 2009 |
| | Domashny, Russia | 2006 | 12 | 0.15 | | Miljeteig et al., 2009 |

[a] Collection year(s); [b] arithmetic mean; [c] data reported on a dw basis, ww concentrations estimated assuming a typical egg moisture content of 75%; [d] mean THg concentration for whole egg contents based on authors' estimate using THg concentrations measured in egg yolk and albumen; [e] data reported on a dw basis, ww concentrations calculated using measured moisture content data for samples.

Table A6.8. Mercury concentrations in fish muscle. Concentrations expressed in μg/g ww. See also Figure 6.13.

| Species | Location | Year | Mean | Source |
|---|---|---|---|---|
| Burbot | Mackenzie R. Basin, Canada | 1999-2001 | 0.37 | Evans et al., 2005a |
| | Great Slave Lake, Canada | 1999-2002 | 0.13 | Evans et al., 2005a |
| Lake trout | Kusawa (Yukon), Canada | 1993-2002 | 0.24 | Evans et al., 2005a |
| | Laberge (Yukon), Canada | 1993-2002 | 0.37 | Evans et al., 2005a |
| | Mackenzie R. Basin, Canada | 1999-2002 | 0.49 | Evans et al., 2005a |
| Pike | Mackenzie R. Basin, Canada | 1990-2002 | 0.43 | Evans et al., 2005a |
| | Great Slave Area, Canada | 1999-2002 | 0.18 | Evans et al., 2005a; Lockhart et al., 2005a |
| | Storvindeln, Sweden | 1968-2005 | 0.306 | A. Bignert, unpubl. data |
| Char (landlocked) | Amituk L., Canada | 2002 | 1.3 | Evans et al., 2005a |
| | Boomerang L., Canada | 2002 | 0.21 | Evans et al., 2005a |
| | Char L., Canada | 1999 | 0.55 | Evans et al., 2005a |
| | North L., Canada | 2000 | 0.2 | Evans et al., 2005a |
| | Resolute L., Canada | 1999-2002 | 0.16 | Evans et al., 2005a |
| | Sapphire L.,Canada | 1999 | 0.29 | Evans et al., 2005a |
| | Greenland | 2004-2008 | 0.96 | F. Rigét, unpubl. data |
| | Faroe Islands | 2000-2007 | 0.26 | F. Rigét, unpubl. data |
| | Abiskojuare, Sweden | 1981-2000 | 0.030 | A. Bignert, unpubl. data |
| Char (sea run) | Northern Quebec, Canada | 1990s | 0.044 | Evans et al., 2005a |
| | Labrador, Canada | 1990s | 0.035 | Evans et al., 2005a |
| | Cambridge Bay, Canada | 1991-1993 | 0.047 | Lockhart et al., 2005a |
| | Lauchian R., Canada | 1993 | 0.055 | Lockhart et al., 2005a |
| | Byron Bay, Canada | 1990 | 0.026 | Lockhart et al., 2005a |
| | Hall Beach, Canada | 1992 | 0.051 | Lockhart et al., 2005a |
| | Foggy Bay, Canada | 1993 | 0.076 | Lockhart et al., 2005a |
| | Ellice R., Canada | 1990-1993 | 0.051 | Lockhart et al., 2005a |
| | Surrey R., Canada | 1990-1993 | 0.029 | Lockhart et al., 2005a |
| | Netling, Canada | 1990 | 0.035 | Lockhart et al., 2005a |
| | Gore Bay, Canada | 1992 | 0.024 | Lockhart et al., 2005a |
| | Pangnirtung Giord, Canada | 1990-1992 | 0.031 | Lockhart et al., 2005a |
| | Silvia Grin R., Canada | 1991 | 0.08 | Lockhart et al., 2005a |
| | Chesterfield Inlet, Canada | 1991-1993 | 0.044 | Lockhart et al., 2005a |
| | Rankin Inlet, Canada | 1991-1993 | 0.043 | Lockhart et al., 2005a |
| | Wilson R., Canada | 1993 | 0.067 | Lockhart et al., 2005a |
| | Ferguson R., Canada | 1992 | 0.029 | Lockhart et al., 2005a |
| | Sandy Point, Canada | 1992-1993 | 0.053 | Lockhart et al., 2005a |
| | Richmond Gulf, Canada | 1994 | 0.055 | Lockhart et al., 2005a |
| Atlantic cod | Labrador/Newfoundland, Canada | 1990 | 0.12 | Hellou et al., 1992 |
| | Iceland | 1990-1992 | 0.036 | OSPAR, unpubl.data |
| | northeastern Iceland | 2000-2007 | 0.025 | F. Rigét, unpubl. data |
| | northwestern Iceland | 2000-2007 | 0.03 | F. Rigét, unpubl. data |
| | southeastern Iceland | 2001-2003 | 0.018 | F. Rigét, unpubl. data |
| | southwestern Iceland | 2001 | 0.034 | F. Rigét, unpubl. data |
| | Faroe Islands | 2000-2007 | 0.031 | F. Rigét, unpubl. data |
| | Faroe Islands | 1994 | 0.01 | Stange et al., 1996 |
| | Stokken, Norway | 2005 | 0.054 | F. Rigét, unpubl. data |
| | Froan/Stokken, Norway | 1993-1994 | 0.069 | OSPAR, unpubl.data |
| | Lille Molla, Norway | 2002-2006 | 0.083 | F. Rigét, unpubl. data |
| | Lofoten/Lille Molla, Norway | 1992-1994 | 0.069 | OSPAR, unpubl.data |
| | Kvunangen, Norway | 2006-2007 | 0.036 | F. Rigét, unpubl. data |
| | Varangerfjordan, Norway | 2000-2007 | 0.016 | F. Rigét, unpubl. data |
| | Varangerfjordan, Norway | 1994 | 0.05 | OSPAR, unpubl.data |
| | Finnsnes, Norway | 1994 | 0.063 | OSPAR, unpubl.data |
| | Hammerfest, Norway | 1994 | 0.036 | OSPAR, unpubl.data |
| | Halten Banken, Norway | 1994 | 0.05 | OSPAR, unpubl.data |
| | Svalbard, Norway | 1993 | 0.04 | OSPAR, unpubl.data |
| | Barents Sea, Norway | 1993 | 0.01 | OSPAR, unpubl.data |
| Plaice | Lille Moalla, Norway | 2000-2006 | 0.057 | F. Rigét, unpubl. data |
| | Skogeray, Norway | 2000-2007 | 0.025 | F. Rigét, unpubl. data |
| Redfish | Kap Farvel, Greenland | 1994 | 0.19 | Stange et al., 1996 |
| | Denmark Str., Greenland | 1994 | 0.21 | Stange et al., 1996 |
| | Halten Banken, Norway | 1994 | 0.07 | Stange et al., 1996 |
| | Iceland | 1994 | 0.03 | Stange et al., 1996 |
| | Faroe Islands | 1994 | 0.18 | Stange et al., 1996 |
| Long rough dab | Svalbard, Norway | 1993 | 0.02 | Maage et al., 1996 |
| | Barents Sea, Norway | 1992-1993 | 0.01 | Maage et al., 1996 |
| Common dab | Iceland | 1990-1991 | 0.049 | OSPAR, unpubl.data |

## Chapter 7

# To What Extent will Projected Changes in Global Emissions Affect Mercury Levels in the Arctic Atmosphere and Ocean?

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## 7.1. Introduction

For policy-makers to decide whether and how best to implement strategies to reduce environmental pollutants such as mercury (Hg), information is required on a number of factors, including possible future developments. From an Arctic perspective, projections of future global emissions of Hg and how these may affect levels of Hg in the region's atmosphere and ocean are therefore important questions to address in this assessment. In addition, in order to evaluate the effectiveness of possible reductions in anthropogenic Hg emissions, it is necessary to consider how long it might take for the Arctic atmosphere and ocean to respond to source reduction measures. As long as global economic activities continue to increase, and current patterns, practices and uses are maintained, Hg pollution will undoubtedly increase in the future. There are however, various ways to reduce Hg emissions and their negative impacts on the environment and human health. Often the question is how to allocate limited resources to reducing Hg emissions in the most cost-effective manner possible.

## 7.2. How are anthropogenic mercury emissions likely to change in the future?

The AMAP/UNEP project *Global Atmospheric Mercury Assessment: Sources, Emissions and Transport* (UNEP, 2008; Pacyna et al., 2010a) included a first attempt to construct global emissions inventories for the year 2020 in order to investigate the implications of action to reduce Hg emissions. This section outlines the main results.

Future Hg emissions are dependent upon a number of variables, including the development of national and regional economies, the development and implementation of technologies for reducing Hg emissions, possible regulatory changes, and factors connected to global climate change.

As a first attempt to gain insight into the possible implications for global anthropogenic emissions of Hg to the atmosphere, of taking (additional) actions *vs.* not taking (additional) actions to control emissions, three emissions scenarios were considered for the target year of 2020: the 'Status Quo' (SQ) scenario, the 'Extended Emissions Control' (EXEC) scenario, and the 'Maximum Feasible Technological Reduction' (MFTR) scenario.

- The SQ scenario assumes that current patterns, practices and uses that result in Hg emissions to air will continue. Economic activity is assumed to increase in various regions; however, emission control practices remain unchanged from those currently employed, leading to increased emissions from several sectors.
- The EXEC scenario assumes economic progress at a rate reflecting the future development of industrial technologies and emissions control technologies; that is, Hg-reducing technologies currently generally employed throughout Europe and North America would be implemented elsewhere. It further assumes that emissions control measures currently committed to in Europe to reduce Hg emissions to air or water would be implemented throughout the world. These include certain measures adopted under the Heavy Metals Protocol to the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), EU Directives, and agreements to meet targets set by the Kyoto Protocol to the United Nations Framework Convention on Climate Change on reduction of greenhouse gases causing climate change (which will also result in reductions in Hg emissions).
- The MFTR scenario assumes implementation of all available solutions/measures, leading to the maximum degree of reduction in Hg emissions and Hg discharges to any environment; cost is taken into account but only as a secondary consideration.

Table 7.1 summarizes the assumptions made for Hg emissions in 2020.

Scenario estimates of by-product (and chlor-alkali) sector emissions of Hg in 2020 for the three scenarios (SQ, EXEC, MFTR) are presented for different regions in Figure 7.1. The scenario emissions inventories were based on the 2005 (v5) global inventory of anthropogenic Hg emissions to air produced as part of a joint UNEP project in 2008 (UNEP, 2008; see also Section 2.2). The 2005 (v5) emissions estimates are included in Figure 7.1 for comparison.

If no major changes in the efficiency of emission control are introduced and economic activity continues to increase (the SQ scenario), significant increases in global anthropogenic Hg emissions (equivalent to about one quarter of the 2005 Hg emissions from these sectors) are projected for 2020. The greatest increase is projected for stationary combustion, mainly from combustion of coal. A comparison of the 2020 emissions projected by the EXEC scenario (850 t) and the SQ scenario (1850 t) suggests that a further 1000 t of Hg could be emitted globally in 2020, if Hg continues to be emitted under the control measures and practices that are in operation today against a backdrop of increasing population and economic growth in some regions. In other words, implementation of available measures and practices (the basic assumption of the EXEC scenario), implies a reduction in Hg emissions of up to 1000 t/y in the period to 2020. The difference between the SQ

Table 7.1. Scenario assumptions for mercury emissions in 2020 (UNEP, 2008).

| Sector | SQ 2020 | EXEC 2020 | MFTR 2020 |
|---|---|---|---|
| Large combustion plants | Increase in coal consumption in Africa (20%), South America (50%) and Asia (50%). Application of current technology. | SQ 2020 + De-dusting: fabric filters (FFs) and electrostatic precipitators (ESPs) operated in combination with flue gas desulfurization (FGD). Activated carbon filters. Sulfur-impregnated absorbents. Selenium-impregnated filters. | SQ 2020 + Integrated gasification combined cycle (IGCC). Supercritical polyvalent technologies. 50% participation in electricity generation by thermal method. |
| Iron and steel production | Application of current technology. | In sintering: fine wet scrubbing systems or FFs with addition of lignite coke powder.<br>In blast furnaces (BF): scrubbers or wet ESPs for BF gas treatment.<br>In basic oxygen furnace: dry ESP or scrubbing for primary de-dusting and FFs or ESPs for secondary de-dusting.<br>In electric arc furnaces: FFs and catalytic oxidation. | EXEC 2020 techniques in existing installations plus: Sorting of scrap. New iron-making techniques. Direct reduction and smelting reduction. |
| Cement industry | Increase in global cement production (50%). | SQ 2020 plus: De-dusting: FFs and ESPs. | SQ 2020 and EXEC 2020 plus: All plants with techniques for heavy metals reduction. |
| Chlor-alkali industry | Application of current technology. | Phase-out of mercury-cell plants by 2010 | Phase-out of mercury-cell plants by 2010 |

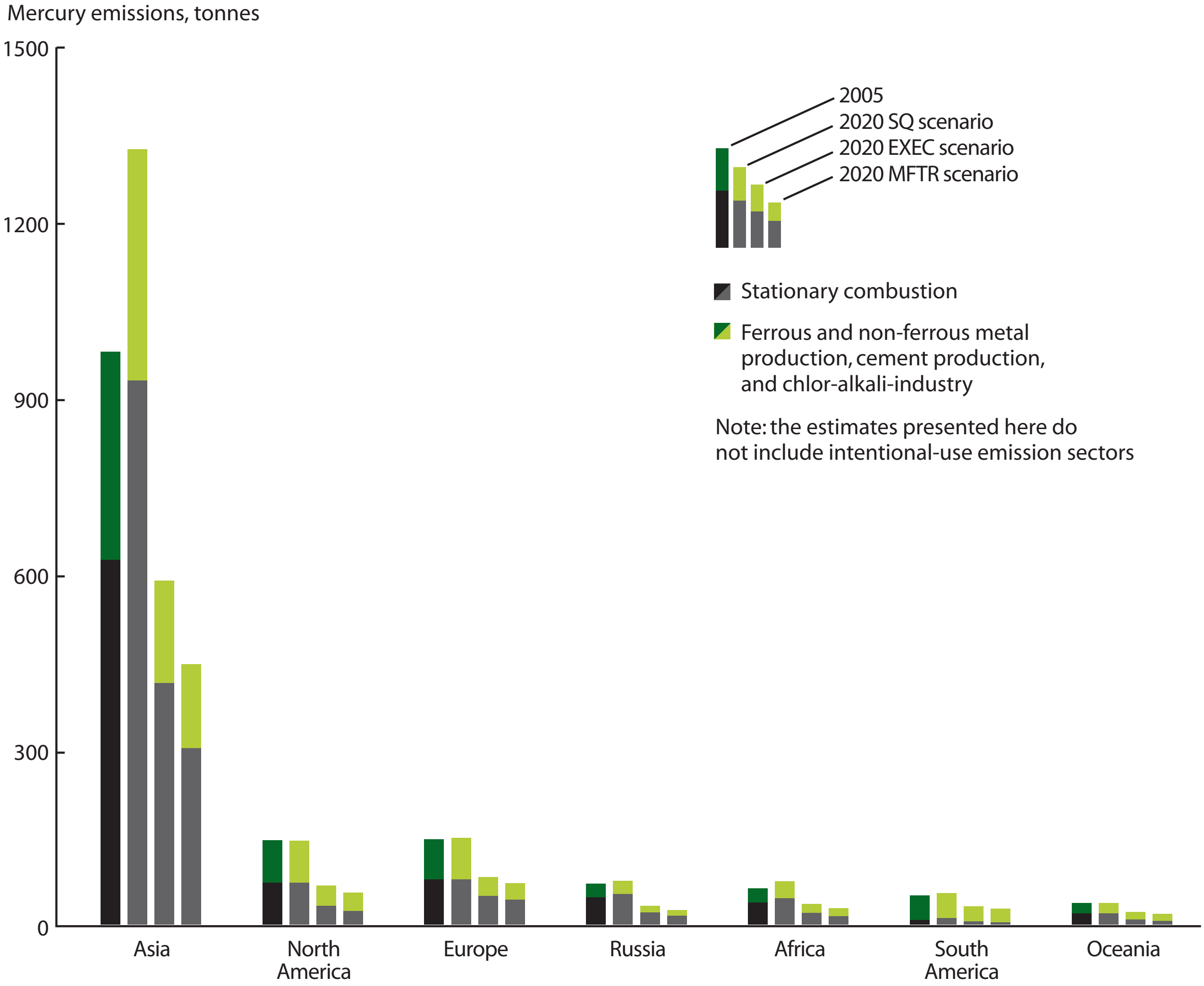

Figure 7.1. Comparison of anthropogenic emissions of mercury from the 'by-product' plus chlor-alkali sectors in 2005 and as projected under the 2020 SQ, EXEC and MFTR scenarios (UNEP, 2008).

scenario and the MFTR scenario is even greater. In this case, Hg emissions from various industrial sectors (e.g., cement production and metal manufacturing) could be 2- to 3-fold higher by 2020 if nothing is done to improve emission control.

Under the EXEC scenario, clear decreases in Hg emissions between 2005 and 2020 are projected for all continents (Figure 7.1), with the greatest Hg emissions in 2020 still projected to occur in Asia. Emissions in China (almost 635 t in 2005) are projected to decrease by 2020 to between 380 t (EXEC scenario; 40% reduction) and 290 t (MFTR scenario; 55% reduction). The projections assume that by 2020 all Chinese power plants will be equipped with improved emission control installations, and that coal consumption and industrial production in China will increase by factors of 2 and 1.5, respectively, between 2005 and 2020. The projections are also based on rigorous implementation of emissions reduction measures, particularly concerning major improvement in the efficiency of emission controls installed. This means that, if the improvement is (for example) 50% lower than assumed under the EXEC and MFTR scenarios, Chinese emissions will increase rather than decrease by 2020 (i.e., reductions due to emission control would not compensate for the projected increase in emissions due to economic development).

Similar assumptions were made in scaling emission factors according to projected improvement in the efficiency of emission controls installed at Indian power stations and industrial plants by 2020.

Projected decreases in Hg emissions in Europe, North America, Australia, Japan and Russia are between 40% and 60%.

An increase of up to 96% in global Hg emissions by 2050 relative to 2006 has been projected by Streets et al. (2009) using a range of assumptions on socio-economic and technological development. Streets and co-workers identified the expansion of coal-fired electricity generation in the developing world, particularly Asia, as the main driving force for this increase. Their projections imply a shift in the speciation of the emissions, with the share of elemental Hg declining relative to divalent Hg species, possibly due to a change from long-range transport to deposition closer to sources.

Since projections of future global emissions of Hg are necessarily based on a range of assumptions concerning national and regional economic development, the development and implementation of emission control technology, and possible regulatory change, they can only be hypothetical in nature. Furthermore, assumptions about the ambition level for emission reductions (especially in developing regions/countries) as well as willingness to invest in emission reduction measures, can result in over-optimistic reduction scenarios. Nevertheless, the scenarios illustrate well the differences between 'action' *vs* 'no action' in terms of reducing Hg emissions.

Scenarios for future intentional use of Hg are highly uncertain due to the lack of consistent international agreements or policies to reduce Hg demand. Although large efforts are being made in many countries to reduce Hg use in products and industrial applications, actual compliance is difficult to estimate.

## 7.3. How will future changes in global emissions and climate affect mercury levels in the Arctic atmosphere?

### 7.3.1. Arctic atmospheric mercury concentrations under different emissions scenarios for 2020

Three global Hg models (GRAHM, Environment Canada; GLEMOS, Meteorological Synthesizing Centre-East; DEHM, Danish National Environmental Research Institute; DMU/NERI) were employed to analyze the impact of the SQ, EXEC and MFTR emissions scenarios on Hg levels in the Arctic atmosphere relative to the baseline scenario for 2005. The models represent the atmospheric components of the global Hg cycle, including emissions from anthropogenic and natural sources and re-emissions of previously deposited Hg (originating both from anthropogenic and natural sources), atmospheric transport, chemical transformations, and deposition to terrestrial and ocean surfaces. Descriptions of the models' parameterizations are given in Section 2.6.1. With respect to uncertainties in the atmospheric models, the relative importance of the various potential atmospheric oxidants of gaseous elemental Hg (GEM) ($O_3$, OH, $H_2O_2$ and reactive halogen species: Br, Cl, I, $Br_2$, $Cl_2$, BrO, ClO, IO, etc.) is currently insufficiently understood and represents one of the largest potential sources of error in model predictions. The size and mechanisms of natural emissions and re-emissions of Hg are also unclear and present an equally significant source of uncertainty in the models. Chapter 2 provides a more detailed discussion of model uncertainties (Section 2.6.1.2) and summarizes the main differences between the GRAHM, DEHM and GLEMOS models (Table 2.5).

Estimates of Hg emissions in 2005 (the baseline year) and emissions scenarios for 2020 in the SQ, EXEC and MFTR schemes were used in similar runs in the three models (GRAHM, GLEMOS, DEHM) to estimate annual average concentrations of GEM for 2005 and 2020. The models used the anthropogenic emissions reported in Section 7.2, but each model used its own estimates of natural and revolatilized emissions. The model estimates were performed keeping the global meteorological conditions the same for all simulations. The meteorology for 2005 was used as a reference and so no account was made for the impact of climate change during the period 2005 to 2020. The impact of change in anthropogenic emissions on re-emissions from terrestrial and oceanic surfaces was included in the GLEMOS model and shown to be negligible.

The overall global Hg emissions are projected to increase by 19% between 2005 and 2020 under the SQ scenario. In contrast, global emissions are projected to decrease by up to 45% under the EXEC scenario and by up to 55% under the MFTR scenario. The models project an increase in air concentrations of GEM between 2005 and 2020 under the SQ scenario, particularly in regions where the highest Hg emissions are expected to occur. These regions include eastern and southern Asia, Europe, and north-western South America. If no major action is taken to reduce current emissions (the SQ scenario) the greatest increase, of up to 20%, is projected for eastern Asia, where most of the emissions occur today. Concentrations of Hg in

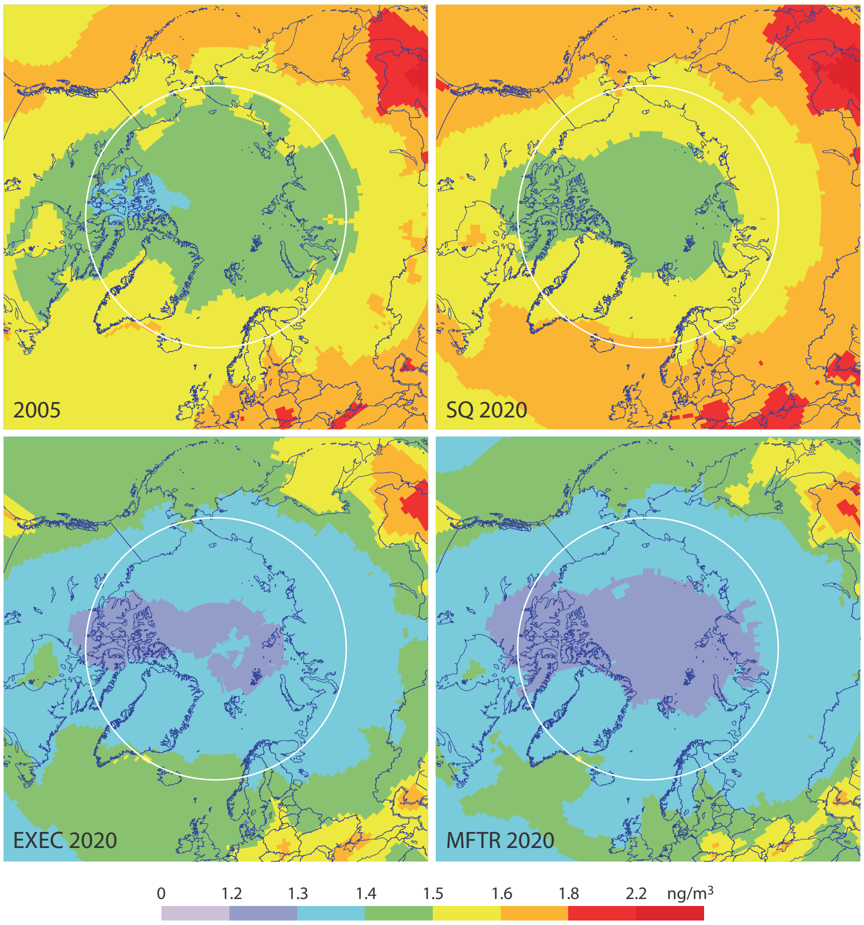

Figure 7.2. Model ensemble average estimate of gaseous elemental mercury concentrations over the Arctic in 2005 and in 2020 under the SQ, EXEC and MFTR emissions scenarios.

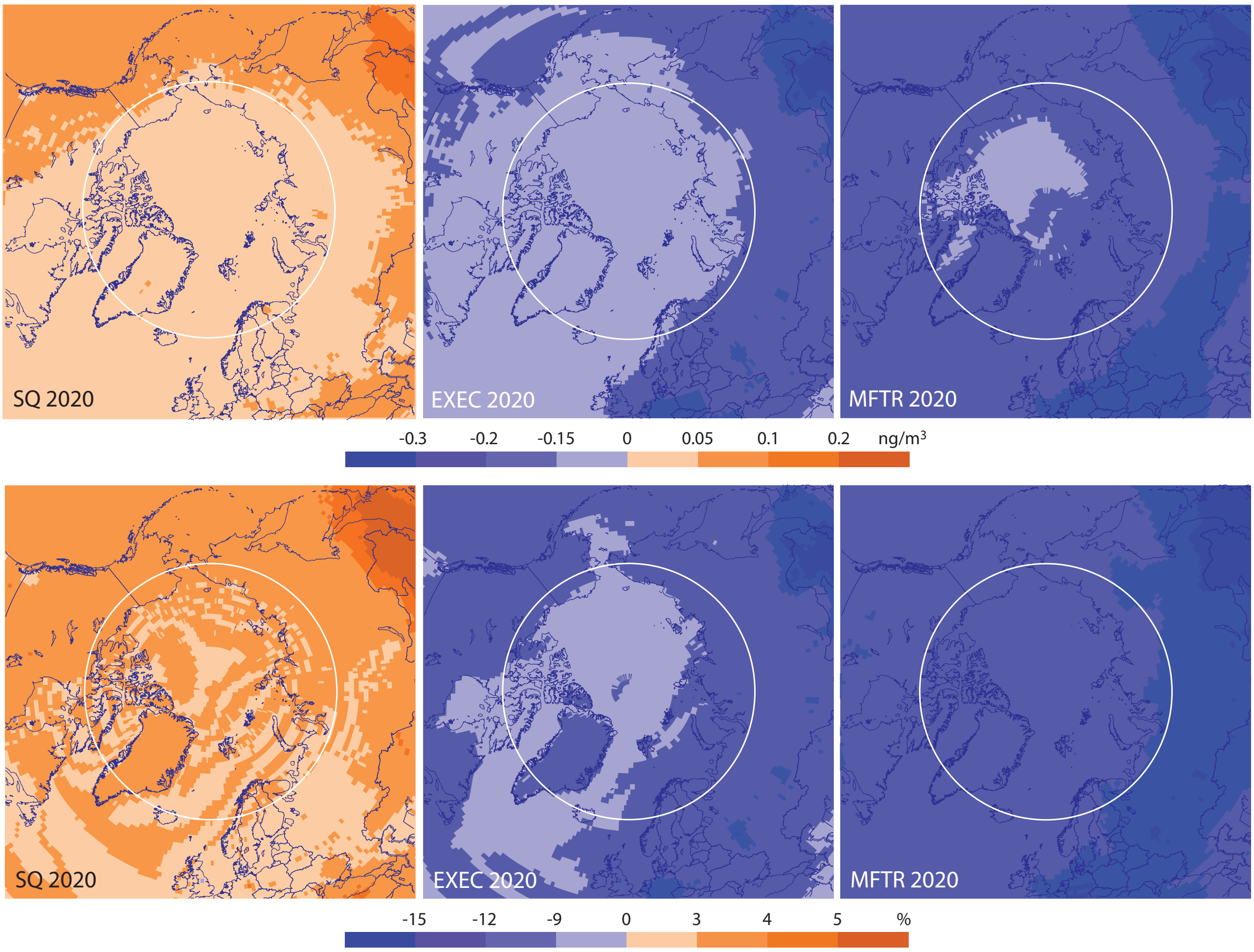

Figure 7.3. Model ensemble average estimate of absolute (above) and relative changes (below) in gaseous elemental mercury concentration over the Arctic between 2005 and 2020 under the SQ, EXEC and MFTR emissions scenarios. Positive values represent an increase.

Table 7.2. Global anthropogenic mercury emissions to air and average atmospheric mercury concentrations for Arctic and sub-Arctic regions in 2005 and as projected for 2020 under the SQ, EXEC and MFTR scenarios.

| | Base 2005 | SQ 2020 | EXEC 2020 | MFTR 2020 |
|---|---|---|---|---|
| Global anthropogenic mercury emissions, t | 1925 | 2295 | 1060 | 862 |
| | Surface air Hg concentration, ng/m$^3$ | | | |
| Arctic 66.5° – 90° N | 1.47 | 1.51 | 1.34 | 1.31 |
| European Arctic 10° W – 60° E | 1.49 | 1.54 | 1.35 | 1.33 |
| Asian Arctic 60° E – 170° W | 1.47 | 1.51 | 1.33 | 1.30 |
| North American Arctic 170° – 10° W | 1.46 | 1.51 | 1.33 | 1.31 |
| Sub-Arctic 60° – 66.5° N | 1.54 | 1.59 | 1.39 | 1.36 |
| Western European sub-Arctic 10° W – 20° E | 1.57 | 1.62 | 1.43 | 1.40 |
| Eastern European sub-Arctic 20° – 60° E | 1.56 | 1.61 | 1.40 | 1.37 |
| Western Asian sub-Arctic 60° – 100° E | 1.52 | 1.57 | 1.36 | 1.33 |
| Eastern Asian sub-Arctic 100° E – 170° W | 1.54 | 1.59 | 1.39 | 1.36 |
| Western North American sub-Arctic 170° – 100° W | 1.52 | 1.58 | 1.38 | 1.35 |
| Eastern North American sub-Arctic 100° – 10° W | 1.53 | 1.57 | 1.39 | 1.37 |

air in 2020 are projected to decrease by up to 20% in the most polluting regions of the world under the EXEC scenario and by slightly more under the MFTR scenario.

The model ensemble mean GEM surface air concentrations in the Arctic for 2005 emissions and according to the three future scenarios are presented in Figure 7.2. The spatial variation of the changes (absolute and relative) within the Arctic and sub-Arctic is shown in Figure 7.3. Average air concentrations and percentage change vary for the different regions (see Tables 7.2 and 7.3). Results show an average increase of 3% for the Arctic and 3.1% for the sub-Arctic under the SQ scenario, and an average decrease of 9.1% and 10.9% in the Arctic and 9.6% and 11.5% for the sub-Arctic, under the EXEC and MFTR scenarios, respectively. Variation in the projected change in Hg concentration between different sectors of the Arctic and sub-Arctic is small (SQ: up to 21%, EXEC: up to 19%, MFTR: up to 19%). The increase is greatest in the western North American sub-Arctic under the SQ scenario and the decrease greatest in the eastern European sub-Arctic and western Asian sub-Arctic. These differences are consistent with air flow patterns and the spatial distribution of changes in emissions reported in Section 2.6.1.1.

### 7.3.2. Projections of atmospheric mercury deposition based on the 2020 emissions scenarios

Estimates of Hg deposition in 2005 and in 2020 according to the SQ, EXEC and MFTR emissions scenarios were modeled using the GRAHM, GLEMOS, and DEHM models. Two types of re-emission terms are considered in the GRAHM model; recent re-emission and legacy re-emission. The re-emission occurring from deposited Hg within the same year is considered as recent and the rest is legacy re-emission from all terrestrial and aquatic surfaces. GLEMOS and DEHM assume no recent re-emission. However, both models are constrained with the measured surface air concentrations and so the deposition could be considered as net deposition. It should be noted that net deposition estimated here is the net Hg being added in a given year to the Arctic environment (gross deposition – quick re-emission of Hg from snow).

The models project an increase in the atmospheric deposition of total Hg by 2020 using the SQ scenario, particularly in eastern and southern Asia, where emissions are projected to increase the most. In the other major source areas most relevant for the Arctic, namely Europe and north-eastern North America, modest rates of increase in emissions are projected. The model

Table 7.3. Change in global anthropogenic mercury emissions to air and mercury concentrations for Arctic and sub-Arctic regions in 2020 under the SQ, EXEC and MFTR scenarios relative to 2005.

| | Change, % | | |
|---|---|---|---|
| | SQ 2020 | EXEC 2020 | MFTR 2020 |
| Global anthropogenic mercury emissions | 19.2 | -44.9 | -55.2 |
| Arctic 66.5° – 90° N | 3.0 | -9.1 | -10.9 |
| European Arctic 10° W – 60° E | 3.0 | -9.3 | -11.1 |
| Asian Arctic 60° E – 170° W | 3.1 | -9.3 | -11.1 |
| North American Arctic 170° – 10° W | 3.1 | -8.8 | -10.6 |
| Sub-Arctic 60° – 66.5° N | 3.1 | -9.6 | -11.5 |
| Western European sub-Arctic 10° W – 20° E | 2.9 | -9.4 | -11.3 |
| Eastern European sub-Arctic 20° – 60° E | 2.8 | -10.5 | -12.6 |
| Western Asian sub-Arctic 60° – 100° E | 3.1 | -10.5 | -12.6 |
| Eastern Asian sub-Arctic 100° E – 170° W | 3.3 | -9.8 | -11.8 |
| Western North American sub-Arctic 170° – 100° W | 3.4 | -9.4 | -11.3 |
| Eastern North American sub-Arctic 100° – 10° W | 3.0 | -8.8 | -10.6 |

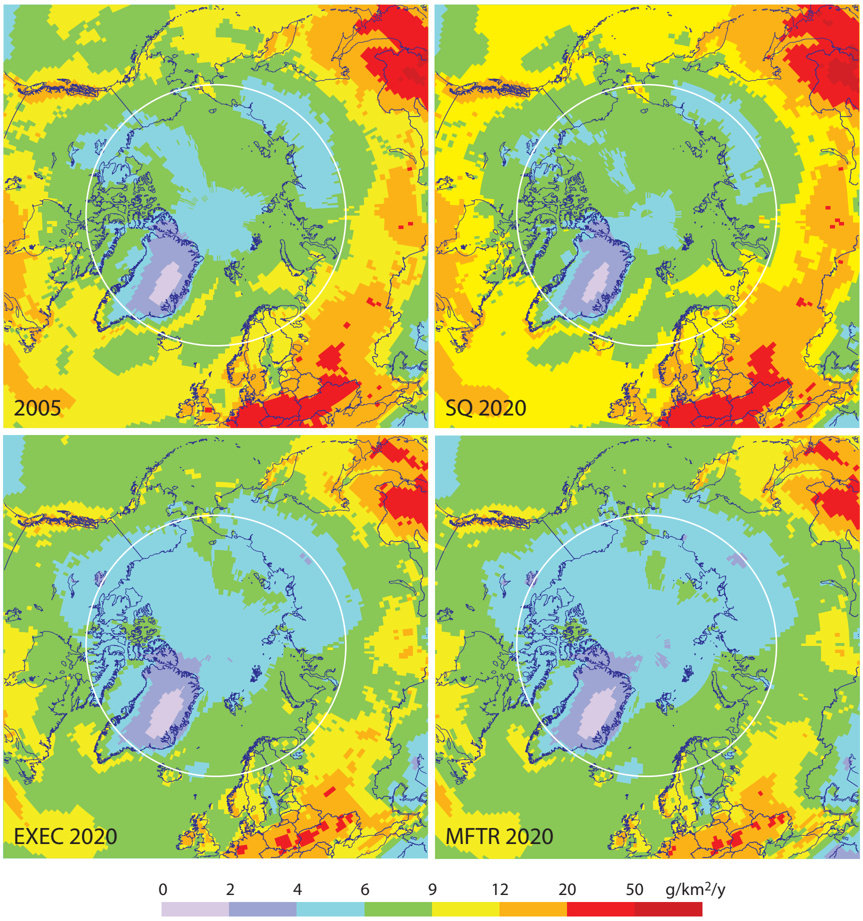

Figure 7.4. Model ensemble average estimate of total mercury deposition over the Arctic in 2005 and in 2020 under the SQ, EXEC and MFTR emissions scenarios.

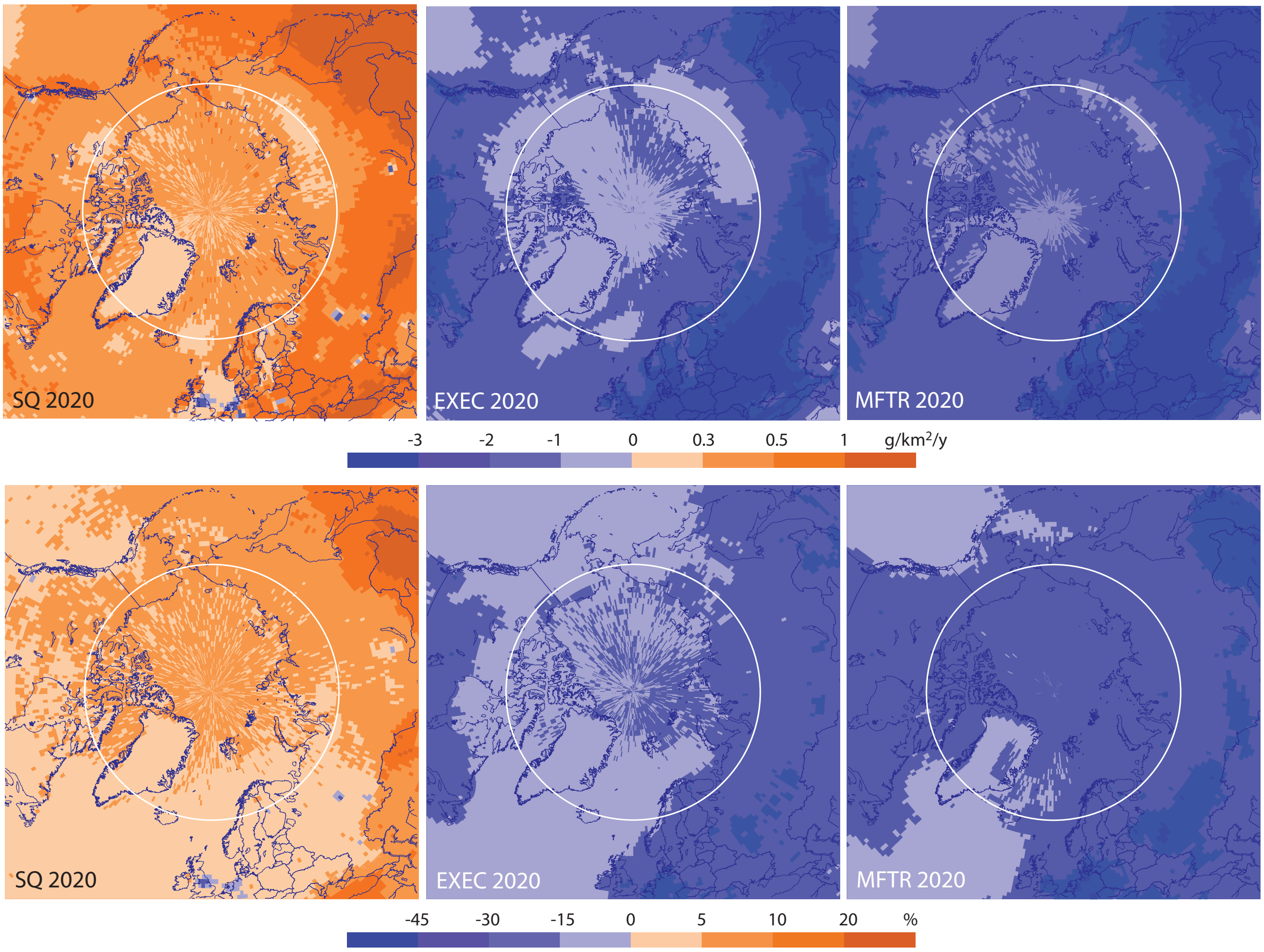

Figure 7.5. Model ensemble average estimate of absolute (above) and relative (below) changes in total mercury deposition over the Arctic between 2005 and 2020 under the SQ, EXEC and MFTR emissions scenarios. Positive values represent an increase.

Table 7.4. Global anthropogenic mercury emissions to air and average total mercury deposition for Arctic and sub-Arctic regions in 2005 and as projected for 2020 under the SQ, EXEC and MFTR emissions scenarios.

| | Base 2005 | SQ 2020 | EXEC 2020 | MFTR 2020 |
|---|---|---|---|---|
| Global anthropogenic mercury emissions, t | 1925 | 2295 | 1060 | 862 |
| | Hg deposition, μg/m²/y | | | |
| Arctic 66.5° – 90° N | 6.53 | 6.87 | 5.56 | 5.36 |
| European Arctic 10° W – 60° E | 8.29 | 8.66 | 7.03 | 6.78 |
| Asian Arctic 60° E – 170° W | 6.67 | 7.03 | 5.62 | 5.40 |
| North American Arctic 170° – 10° W | 5.67 | 5.97 | 4.88 | 4.72 |
| Sub-Arctic 60° – 66.5° N | 8.96 | 9.39 | 7.48 | 7.18 |
| Western European sub-Arctic 10° W – 20° E | 10.60 | 10.99 | 8.81 | 8.47 |
| Eastern European sub-Arctic 20° – 60° E | 12.40 | 12.86 | 9.46 | 8.90 |
| Western Asian sub-Arctic 60° – 100° E | 10.40 | 10.96 | 8.30 | 7.86 |
| Eastern Asian sub-Arctic 100° E – 170° W | 7.61 | 8.06 | 6.43 | 6.17 |
| Western North American sub-Arctic 170° – 100° W | 7.35 | 7.73 | 6.33 | 6.12 |
| Eastern North American sub-Arctic 100° – 10° W | 8.81 | 9.19 | 7.71 | 7.48 |

results indicate that a significant proportion of the projected increased emissions deposit close to source areas. This may be related to shifts in the speciation of emitted Hg from elemental to divalent forms, as discussed by Streets et al. (2009). Changes in the amounts of elemental Hg between the 2005 and 2020 SQ inventories used in this modeling work are, however, only very modest (of the order of a few percent) compared to particulate and divalent forms of Hg.

The model ensemble mean total Hg deposition (dry and wet deposition) in the Arctic for 2005 and in 2020 according to the three future emissions scenarios is presented in Figure 7.4. The spatial variation of changes (absolute and relative) within the Arctic and sub-Arctic is illustrated in Figure 7.5. Average deposition and percentage change vary for the different regions (see Tables 7.4 and 7.5). Results show an average increase of 5.2% for the Arctic and 4.8% for the sub-Arctic under the SQ scenario, and an average decrease of 14.9% and 18% in the Arctic and 16.5% and 19.9% in the sub-Arctic, under the EXEC and MFTR scenarios, respectively.

A comparison of changes in airborne Hg concentration and deposition reveals that the projected percentage change in deposition is greater than the projected change in air concentration. Furthermore, variations in changes in Hg deposition to the Arctic and sub-Arctic between different sectors are also greater for deposition than for air concentration (SQ: up to 64%, EXEC: up to 88%, MFTR: up to 87%). These results suggest that the differences in anthropogenic oxidized Hg between the three scenarios affect deposition in the Arctic and sub-Arctic through the direct transport of these species. The stronger variation in changes in deposition can be explained by the gradient in deposition of the directly transported oxidized Hg, regional differences between meteorological factors influencing dry and wet deposition, and differences in upper air concentrations of Hg since wet deposition scavenges Hg at higher altitudes. The impact of changes in remote emissions, such as in Asia, is greater in the free troposphere than in surface air. The projected increase in deposition is found to be somewhat larger for the Arctic than the sub-Arctic, and this could be due to the occurrence of 'atmospheric mercury depletion events' (AMDEs) in the Arctic. Under the SQ scenario, the largest projected regional increase will be in the Asian Arctic and sub-Arctic, followed by the western North American sub-Arctic. The largest projected regional decrease will be in the eastern European sub-Arctic followed by the western Asian sub-Arctic. These differences are consistent with air flow patterns and regional airborne Hg concentrations.

Table 7.5. Changes in global anthropogenic mercury emissions to air and total mercury deposition for Arctic and sub-Arctic regions in 2020 under the SQ, EXEC and MFTR emissions scenarios and relative to 2005.

| | Change, % | | |
|---|---|---|---|
| | SQ 2020 | EXEC 2020 | MFTR 2020 |
| Global anthropogenic mercury emissions, t | 19.2 | -44.9 | -55.2 |
| Arctic 66.5° – 90° N | 5.2 | -14.9 | -18.0 |
| European Arctic 10° W – 60° E | 4.5 | -15.2 | -18.2 |
| Asian Arctic 60° E – 170° W | 5.5 | -15.8 | -19.1 |
| North American Arctic 170° – 10° W | 5.3 | -13.9 | -16.8 |
| Sub-Arctic 60° – 66.5° N | 4.8 | -16.5 | -19.9 |
| Western European sub-Arctic 10° W – 20° E | 3.6 | -17.0 | -20.1 |
| Eastern European sub-Arctic 20° – 60° E | 3.7 | -23.7 | -28.2 |
| Western Asian sub-Arctic 60° – 100° E | 5.3 | -20.2 | -24.4 |
| Eastern Asian sub-Arctic 100° E – 170° W | 5.9 | -15.5 | -18.9 |
| Western North American sub-Arctic 170° – 100° W | 5.2 | -13.8 | -16.6 |
| Eastern North American sub-Arctic 100° – 10° W | 4.3 | -12.6 | -15.1 |

### 7.3.2.1. Differences in model estimates of changes in net deposition

Figure 7.6 illustrates total net Hg deposition to the Arctic (north of the Arctic Circle) according to the three models (GRAHM, GLEMOS and DEHM). The models estimate total net deposition of Hg to the Arctic to vary within the range ~115 to ~143 t. As discussed in Chapter 2 (Section 2.6.1.2), there are two major sources of uncertainty causing the difference between the model estimates: the halogen chemistry resulting in AMDEs, and global estimates of natural Hg emissions and re-emissions. Under the SQ scenario, deposition is projected to increase by about 10 t in the GRAHM and GLEMOS models while an increase of ~2 t is estimated by DEHM. On the other hand, under the emission reduction scenarios (EXEC and MFTR), the amount of Hg deposited in the Arctic in 2020 is projected to decrease by up to ~40 t (GRAHM), or ~30 t (GLEMOS, DEHM) compared to 2005. The range in projected deposition estimates for the Arctic is presented in Table 7.6. In terms of differences between models, the range is greater for GRAHM than GLEMOS and DEHM, and this can be attributed to higher model resolution in the GRAHM simulations.

Mercury in the Arctic mostly originates from a number of major source areas outside the Arctic (see Figure 7.7). Figure 7.8 illustrates the source attribution of net Hg deposited in the Arctic under the three future emissions scenarios as projected by GRAHM and GLEMOS. Source attribution simulations were not conducted with DEHM. The impact of changing anthropogenic emissions on oceanic and terrestrial re-emissions in the short term was considered in the GLEMOS simulation. Short-term changes in terrestrial and oceanic re-emissions (within a few years) are minimal under the scenarios considered; it is expected that over the long term, changes in anthropogenic emissions will lead to further changes in terrestrial and oceanic re-emissions. Eastern Asia is seen to be a major source region with the greatest potential for emission reduction and thus for reduction of Hg deposition in the Arctic. The GRAHM and GLEMOS models indicate that as much as 22 to 25 t of Hg will be deposited to the Arctic from anthropogenic emission sources in eastern Asia if the SQ scenario is maintained. Alternatively, under EXEC and MFTR the deposited emissions will be reduced by 13 to 17 t from eastern Asia alone. Relative changes in anthropogenic emissions in the source regions lead to corresponding changes in source attribution of net Hg deposition in the Arctic. Figure 7.8 also illustrates that a large proportion of the Hg that ends up in the Arctic is carried in via ocean currents.

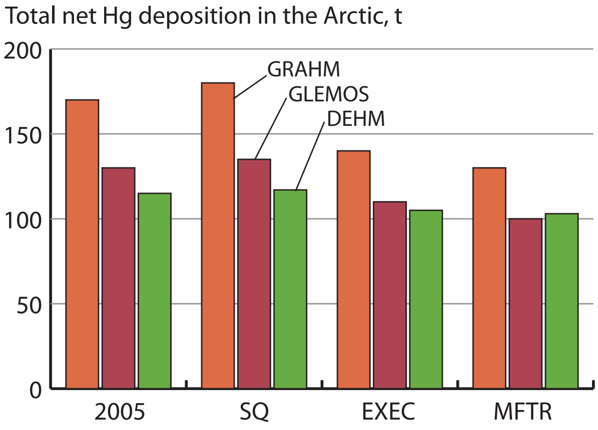

Figure 7.6. Total net mercury deposition in the Arctic (north of the Arctic Circle) according to the GRAHM, GLEMOS and DEHM models, for 2005 and as projected for 2020 under the SQ, EXEC and MFTR emissions scenarios.

The GRAHM and GLEMOS models agree with respect to the contribution to deposition in the Arctic from anthropogenic sources, but differ with respect to the contribution from natural sources and re-emissions in the major source regions (Figure 7.8). Re-emissions in Europe, North America and eastern Asia are significantly higher in GRAHM compared to GLEMOS and this results in a larger overall deposition contribution simulated by GRAHM from these regions to the Arctic.

In summary, the models agree well in terms of their projected changes in net deposition (Figure 7.6), as well as their projected changes in source attribution. Changes in the relative contributions of the source regions to net Hg deposition in the Arctic, increase or decrease consistent with changes in anthropogenic emissions in these regions. Given that a significant proportion of the Hg being deposited in the Arctic is from the re-emission of previously deposited Hg, more studies are required for quantitative and mechanistic understanding of the long-term impact of changes in anthropogenic emissions on re-emissions from soils, water and vegetation.

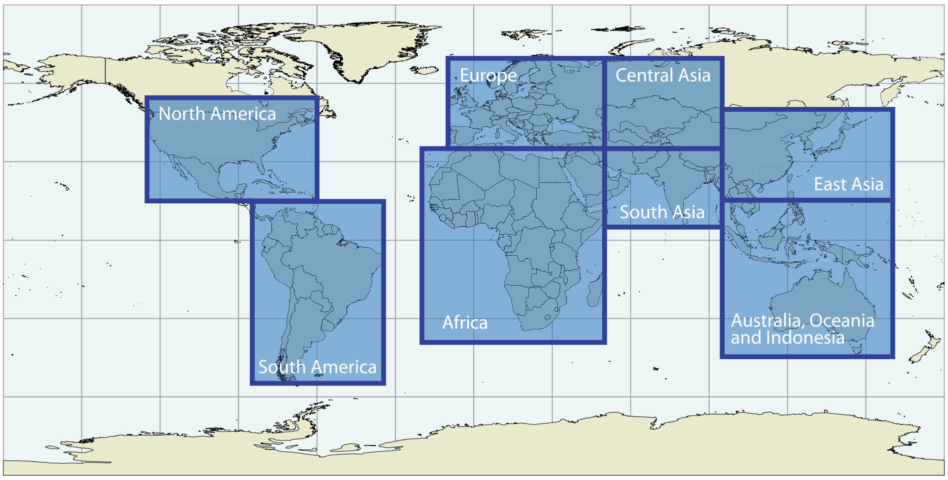

Figure 7.7. Major source regions for atmospheric mercury in the Arctic.

Table 7.6. Range in total net mercury deposition projected for the Arctic.

| | GRAHM | | GLEMOS | | DEHM | |
|---|---|---|---|---|---|---|
| Total net Hg deposition Baseline (2005) | 2 to 12 g/km²/y | | 0 to 9 g/km²/y | | 1 to 12 g/km²/y | |
| Change in net deposition | Absolute, g/km²/y | Relative, % | Absolute, g/km²/y | Relative, % | Absolute, g/km²/y | Relative, % |
| SQ | 0 to 0.5 | 0 to 15 | 0 to 1 | 3 to 5 | 0 to 0.5 | 0 to 5 |
| EXEC | -0.5 to -5 | -5 to -30 | 0 to -2 | -10 to <-30 | 0 to -2 | 0 to -15 |
| MFTR | -0.5 to -5 | -5 to -30 | 0 to -2 | -15 to <-30 | 0 to -2 | 0 to -15 |

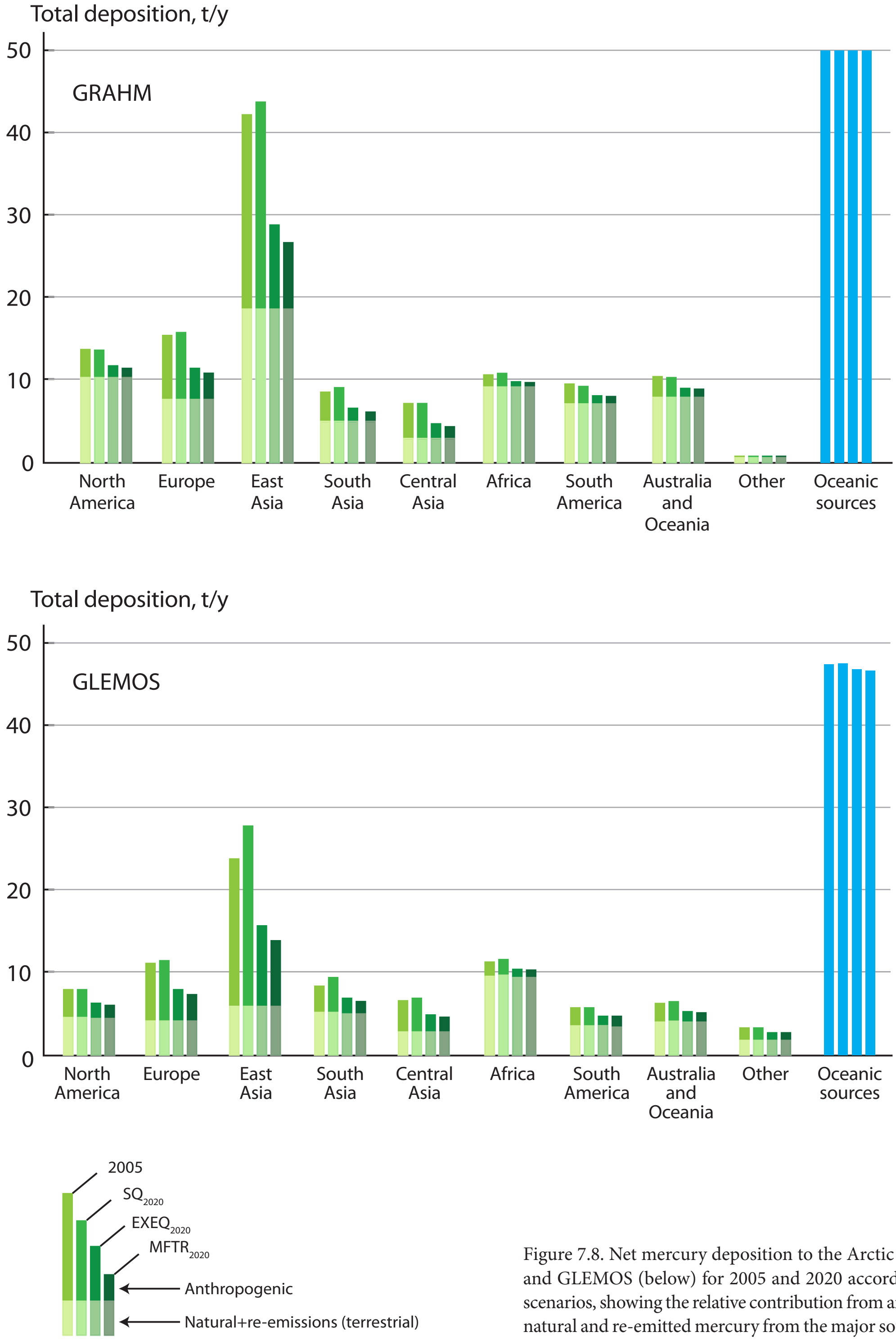

Figure 7.8. Net mercury deposition to the Arctic as modelled by GRAHM (above) and GLEMOS (below) for 2005 and 2020 according to the three future emissions scenarios, showing the relative contribution from anthropogenic emissions, terrestrial natural and re-emitted mercury from the major source regions, and the global ocean.

### 7.3.3. Projections of change in mercury deposition with changing climate

To compare the relative effects of changes in global emissions on airborne Hg deposition in the Arctic against those from future climate changes, two different modeling exercises were undertaken. First, the GRAHM model was used to investigate the effects of meteorological variations on atmospheric Hg deposition in the Arctic. Preliminary results for temporal changes in GEM surface air concentrations at Alert, Canada are shown in Figure 7.9. Concentrations during October to December represent background levels and the model estimates represent average concentrations in the region around the measurement site. Comparison of model output with measured concentration data suggests that interannual variability in meteorology is partly responsible for the year-to-year variation in GEM observed at Alert. The modeling results also suggest that the decrease in surface air GEM concentrations between 1995 and 2000 and the subsequent increase between 2000 and 2005 is primarily due to changes in global anthropogenic emissions. The model has not yet been used to examine temporal trends in air concentration and deposition across the Arctic as a whole. Changes in natural emissions and re-emissions are not considered.

In a second exercise, the DEHM model was used to examine the effects of climate change on future projections of Hg deposition in the Arctic. Emissions were kept at the 2005 level and meteorological data from ECHAM5/MPI-OM were used. Two historic decades were simulated (1890-1899 and 1990-1999) along with two future decades (2090-2099 and 2190-2199) with the meteorology from the same scenario (IPCC A1B scenario) for consistency between simulations. One of the weaknesses of such simulations is that the parameterizations of some processes may not be adequate to represent the changing environmental conditions. Uncertainties in the model projections can be reduced by using an ensemble of models rather than estimates from a single model. However, at present climate impact simulations from other models are not available. By comparing mean values for a decade with variations in the yearly values within the decade, it is possible to establish whether the difference between decades is significant compared to the year-to-year variation. Figure 7.10 compares the differences between total Hg deposition for the area north of the Arctic Circle for each of the four decades. The results show minimal differences between the 1890s and 1990s but a significant decrease from the 1990s to 2190s. Figure 7.11 compares yearly mean deposition of total Hg for the 1990s and 2190s. The results show a significant decrease in Hg deposition over the Arctic Ocean and a significant increase over the continents. The main reason for the decrease over the Arctic Ocean is the change in ice cover, and its influence on AMDEs in the DEHM model. The main reason for the increase in deposition over the continents is a significant increase in ozone concentrations in the troposphere; ozone is the main oxidant of Hg in the DEHM model.

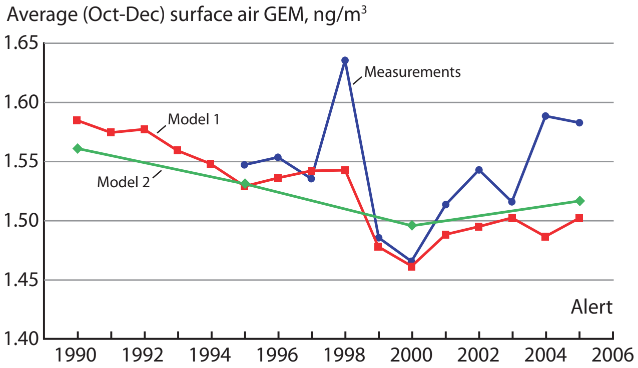

Figure 7.9. Average (October-December) surface air GEM concentrations at Alert, Canada between 1995 and 2005. The graphic compares measured concentrations with two sets of output from the GRAHM model: one which includes changing meteorological conditions and one with conditions kept constant. Source: data from A. Steffen, pers. comm.

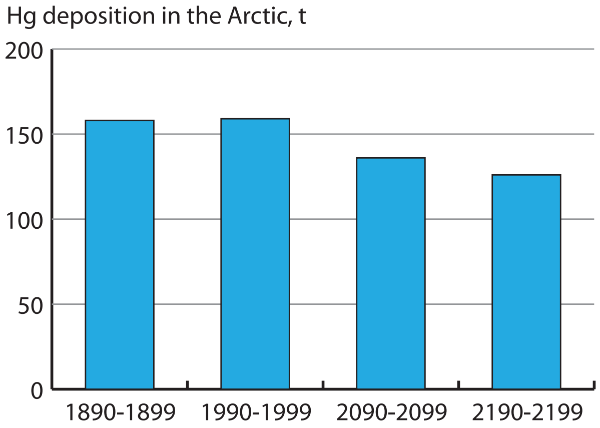

Figure 7.10. Mean mercury deposition in the Arctic for two historic decades (1890-1899 and 1990-1999) and two future decades (2090-2099 and 2190-2199) as modeled by DEHM.

## 7.4. What will be the recovery time for mercury in the Arctic atmosphere and ocean under future scenarios of emissions reductions?

### 7.4.1. Recovery time of the Arctic atmosphere

If the negotiations currently underway to establish a global agreement on Hg under the auspices of UNEP are successful, it can be expected that there will be an increased impetus in the adoption of measures to reduce emissions of Hg in the coming years, beyond those that are already planned in some countries.

In the work presented in Section 7.3, the SQ scenario represents, if not a worst case scenario, then certainly a pessimistic scenario for developments up to 2020, with increased emissions driven by continuing economic growth in the absence of new control measures. Conversely, while the MFTR scenario is unrealistic because it is not constrained by costs associated with implementing control technologies, and it is highly unlikely that some of the more ambitious control technologies assumed could be introduced worldwide within the next ten years, it could be considered a qualified best-case scenario. It should also be remembered that the SQ and MFTR scenarios only consider changes in emissions from 'by-product' source sectors (see Section 2.2), and not emissions associated with intentional-use sectors. The latter are very difficult to project into the future and thus are treated as unchanged

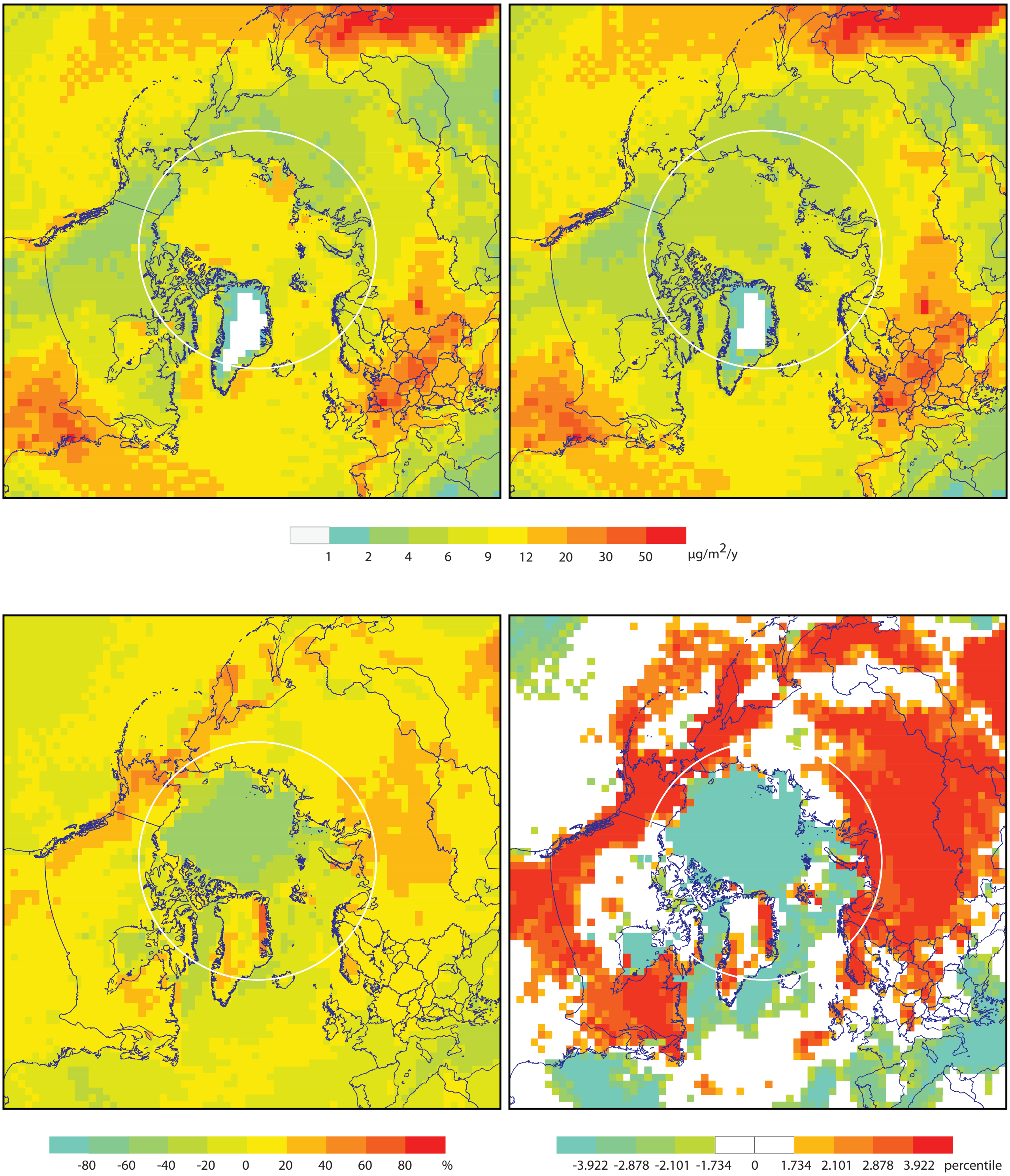

Figure 7.11. Yearly mean deposition of total mercury for 1990-1999 (upper left) and for 2190-2199 (upper right), the percentage difference (lower left) and the t-test (lower right). The t-test legend corresponds to differences that are significant at $p<0.10$, 0.05, 0.01 and 0.001.

relative to 2005 in the modeling applications described in the previous section. There is potential for further reductions in emissions beyond the MFTR scenario if, for example some major (intentional-use) emission sources, such as artisanal and small-scale gold mining (which accounts for some 350 t/y of Hg emissions) could be restrained. Also, emissions from crematoria may decrease (with some time lag) as Hg use in dentistry is phased out. However, there are also potential increases in emissions as, for example, Hg in products currently circulating in society enters the waste stream.

With this in mind, and also considering the uncertainties associated with models, the modeling presented in the previous section using the MFTR scenarios can be used to provide some indication of ecosystem recovery following emissions reductions. Some possible conclusions are as follows:

- Comparing projections for 2020 against 2005, the total (net) Hg deposition within the Arctic is reduced by some 15 to 50 t (DEHM and GRAHM models), compared with the estimates of total net deposition in 2005 of around 120 to 170 t by these models. Both model outputs, it should be noted, are highly dependent upon accurate AMDE characterization.
- The major effect of the emissions reductions under the MFTR (and EXEC) scenarios are projected to occur in the major source regions (in particular south-eastern Asia). This is likely to reflect the effective control of emissions of particulate and Hg(II) forms that tend to deposit closer to the source areas. The relatively modest reduction of deposition projected for the Arctic is due to moderate decreases in the deposition associated with long-range transport (mainly GEM) to the region.
- The direct response of the Arctic atmosphere to changes in Hg emissions, although modest, can be expected to be relatively fast, reflecting the short atmospheric lifetime of in particular particle-associated and reactive Hg(II) species; GEM has a somewhat longer lifetime in air (about 6 to 24 months).
- There will also be an indirect effect on the atmosphere due to Hg re-emissions from surfaces and environmental reservoirs such as soils and oceans. These add considerable inertia in the system, and load up the atmosphere for a considerable period even if future anthropogenic emissions cease or are strongly reduced. Nevertheless, it is important to remember that reduction in atmospheric emissions (and direct discharges of Hg to aquatic environments) are the essential first step in decreasing the environmental pools of Hg in other compartments.
- Extending modeling projections using the MFTR scenario for longer periods into the future (e.g., to 2050 or 2100) might be one way to investigate the response of the atmosphere to re-cycling of Hg following emissions reductions.
- The atmospheric signal from emissions reductions is stronger close to the major source areas than it is in remote areas because the former are also impacted to a greater extent by deposition of Hg emitted in divalent and particulate-associated species. This is likely to be part of the explanation as to why trends in environmental media close to source areas appear to reflect emissions trends better than those in remote areas, where the trend component from changes in anthropogenic emissions/deposition will be smaller and possibly subjugated by other factors that may determine overall trends, such as changes in food-web structures or climate influence on environmental pathways.
- Changes in Hg loadings in other environmental compartments, including biota and food webs – representing chemical and biological recovery under assumed emissions reduction scenarios – will occur at slower rates, with response times determined by processes that affect environmental Hg cycling. The environmental reservoirs of Hg (in particular in soils and oceans) are larger than they were in the pre-industrial period. For this reason, in the absence of other factors (such as climate change) rates of 'recovery' (i.e., decreasing environmental Hg concentrations) following emissions reductions would be expected to be slower than the rates of 'deterioration' (i.e., increasing environmental Hg concentrations) that occurred as Hg emissions increased following the pre-industrial period. Put another way, the associated lag times in environmental response to changes in emissions are likely to be longer on the way down than they were on the way up.
- All the modeling and scenario-based discussion presented above relates only to controls applied to primary anthropogenic emission to the air. Chapter 4 of this assessment clearly illustrates that climate change will have major influences on contaminant transport pathways and environmental recycling, that could easily act to mask any more intuitive changes in atmospheric Hg concentrations and deposition associated with emissions reductions. It is also likely to have major influences on Arctic ecosystems (in particular marine ecosystems) that will influence apparent biological recovery from emissions reductions. Finally, climate change in itself is likely to impact Hg emissions in the future through, for example, changing patterns of fuel use.
- Assessing the impact of climate change on environmental and ecosystem recovery is a major challenge that is only now beginning to be addressed through, for example, modeling investigations. This represents a likely (and much needed) focus for future research and modeling activities, introducing new demands for coupled multi-compartment models.

### 7.4.2. Recovery time of the Arctic Ocean

Atmospheric inputs are just one of a number of significant pathways for Hg to enter the Arctic Ocean and which control Hg dynamics in Arctic seawater (Outridge et al., 2008). Estimation of the ocean's response to changing global emissions therefore requires: (i) an understanding of the extent to which present-day Hg levels in the ocean are controlled by atmospheric inputs, (ii) the assumption that all of the other inputs/outputs in the ocean will not change significantly as a result of either direct human impacts on the Arctic Hg cycle, or from the effects of future climate warming. As Outridge et al. (2008) pointed out, current understanding of the marine Hg cycle, especially in the Arctic, is insufficient to make this estimation with a great deal of confidence.

#### 7.4.2.1. An updated box-model of mercury in the Arctic Ocean

To provide a basis for estimating the impact of future changes in emissions on Hg levels in Arctic Ocean seawater, the box-model for total Hg in the Arctic Ocean recently constructed by Outridge et al. (2008) (see Section 2.4), was adapted. The latter authors developed the model by referring to published literature for estimates of physical exchanges between the Arctic Ocean and the Pacific and Atlantic Oceans, ice export from the Arctic Ocean, river inflow (particulate and dissolved), coastal erosion (particulate), precipitation and sedimentation. To calculate the Hg flux, all media were assigned plausible Hg concentrations based on literature values from the Arctic or elsewhere (see Table 3 in Outridge et al., 2008). Atmospheric net deposition of Hg to the surface of the Arctic Ocean, which is difficult to estimate directly as there are few suitable measurements, was estimated from a modified GRAHM model. Comparing the inventory of Hg in the Arctic Ocean with the fluxes of Hg from the sources or to the sinks, these authors proposed that Hg had a relatively short residence time (about five years) in the top 200 m of the Arctic Ocean, which suggests that surface waters would respond on about that time scale to changes in Hg fluxes into or out of the Arctic. The Outridge et al. model synthesized a great deal of information from many sources, and found that inputs and outputs of Hg are close to being in balance at present. However, from the perspective of understanding how the Arctic Ocean might respond to proposed changes in atmospheric emission/deposition (or any other input/output parameter), the published model has one shortcoming in that it considers the Arctic Ocean to be a single sea (one box for less than 200 m depth, one box for deeper water).

A particularly important feature of the Arctic Ocean is that its surface waters comprise two distinct domains (see Figures 7.12 and 7.13) (Macdonald and Bewers, 1996), and so this ocean could realistically be considered as two oceans. The distinct domains in Arctic Ocean surface waters have important implications for understanding the distributions and trends of contaminants (e.g., see the contrasting distributions for HCH and radionuclides reported by Carmack et al., 1997; their Figure 6). The eastern Arctic surface water, which communicates predominantly with the Atlantic Ocean, is the terminus for European and North American contaminants following either ocean currents (Gobeil et al., 2001a), or storm tracks leading northward approximately along the prime meridian (Macdonald et al., 2005). In contrast, the western Arctic Ocean receives via Bering Strait an inflow of low-density seawater from the Pacific Ocean, which then rides over the denser Atlantic water and provides the dominant source for western Arctic Ocean surface waters (Figure 7.13). Oceanic and atmospheric transport pathways for the western Arctic therefore favor Asian contaminant sources (e.g., Li et al., 2002, 2004). Within the Arctic Ocean, the two domains are distinguished by a large clockwise eddy in the west (the Beaufort Gyre), and a rapid surface transport (the Transpolar Drift) across the center of the Arctic Ocean roughly aligned with the Lomonosov or Alpha-Mendeleev Ridges (McLaughlin et al., 1996).

Given that the Hg emissions and transport pathways to the Arctic are very different for Europe / North America and Asia, it seems certain that western and eastern Arctic surface waters have responded differently to historical contaminant Hg exposures and will respond differently in the future to whatever emission controls are put in place. The perspective of distinct east-west contaminant domains in the Arctic Ocean may provide part of the answer as to why Hg trends and concentrations in top marine predators appear to differ between these two regions (see Chapter 5).

To revise the Outridge et al. (2008) budget, the Arctic Ocean has been divided into two domains using Stein and Macdonald (2004) to apportion areas and water volumes for shelves and basins (see Figure 7.12). The western Arctic domain has been assigned the shelves north of the Archipelago, the Beaufort and Chukchi Shelves and the eastern half of the East Siberian Shelf, which is dominated by Pacific water (e.g., Semiletov et al., 2005). For this budget, only the upper 200 m of the Arctic Ocean is considered, since this is where the consequences of atmospheric deposition are most immediate and important, and where most of the biological activity occurs. The same methods as outlined in Outridge et al. (2008) are followed, with the exception that (i) fluxes and inventories are partitioned into western and eastern Arctic Ocean basins (Figures 7.12 and 7.13); (ii) particulate and dissolved Hg inputs and outputs are distinguished; (iii) a term for upwelling is specifically included; and, (iv) the Hg budget is balanced, although this need not necessarily be true at present. The Hg budget itself rests on

Figure 7.12. A schematic illustration showing the Arctic Ocean to consist of two major domains roughly separated by the Lomonosov or Alpha-Mendeleev Ridges. The western Arctic Ocean, which is dominated by the Beaufort Gyre, receives input from the Pacific Ocean and supports most of the outflow through the Canadian Arctic Archipelago. The eastern Arctic Ocean is strongly connected with the Atlantic Ocean via Fram Strait and the Barents Sea. It is dominated by the Transpolar Drift. Source: Macdonald and Bewers (1996).

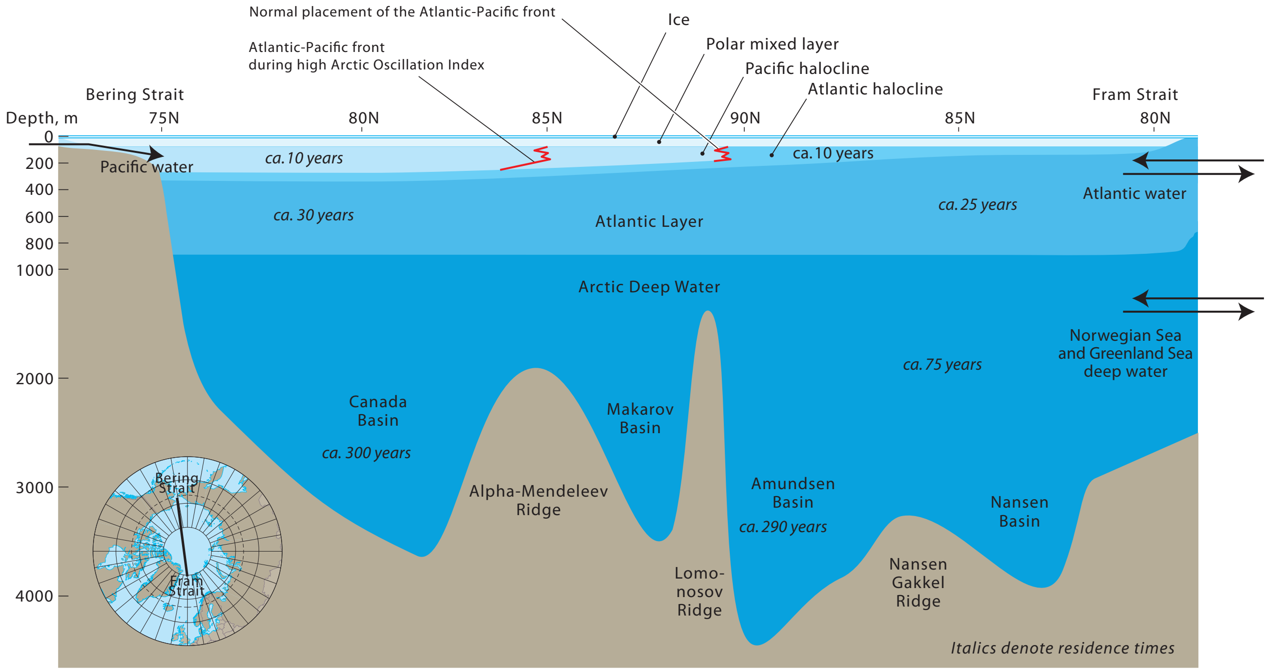

Figure 7.13. A cross section of the Arctic Ocean from Bering Strait, across the North Pole and out through Fram Strait. The upper ocean is shown to consist of two domains, one dominated by water of Pacific origin, the other of Atlantic origin. The surface water is separated from deeper water by pervasive haloclines. Source: Macdonald and Bewers (1996).

balanced budgets for seawater exchange (volumetric flows) and sediments (mass fluxes) within each basin and for the entire Arctic Ocean based on literature compilations (e.g., Rudels and Friedrich, 2000; Stein and Macdonald, 2004; Serreze et al., 2006). Using the balanced water and sediment budgets, the Hg budget is then balanced by minor adjustments of selected Hg concentrations in the various transporting media from those tabulated by Outridge et al. (2008).

In the revised budget (Figure 7.14 and Table 7.7), fluxes involving dissolved aquatic Hg are shown as open arrows while particulate fluxes are in black. In both basins, the atmospheric deposition term is a key term while river contributions of dissolved Hg tend to be relatively small, as is Hg associated with ice export and upwelling. Note that for the purposes of this budget, it is assumed that the net flux of atmospheric Hg is deposited as particulate Hg(II) to the surface but immediately enters the dissolved Hg(II) pool in the ocean. In the western Arctic, Hg entering from atmospheric deposition, and to a minor extent Pacific inflow, are balanced by almost equivalent fluxes of Hg into shelf sediments and out through the Archipelago. The important finding here is that of the 47 t/y of dissolved Hg entering the western Arctic Ocean, almost half becomes scavenged by particles and buried mostly in shelf sediments along with part of the imported particulate Hg, together making up 25 t/y. A small component is exported in the particle flux to the deep ocean. In the eastern Arctic Ocean, atmospheric deposition is also important, but exchange with the Atlantic Ocean clearly cannot be neglected. The flux of Hg associated with the East Greenland Current is partly a consequence of the size of the current and partly due to the Hg concentration assumed for this water. Again, mirroring the western Arctic Ocean, of the 96 t/y of dissolved Hg entering the

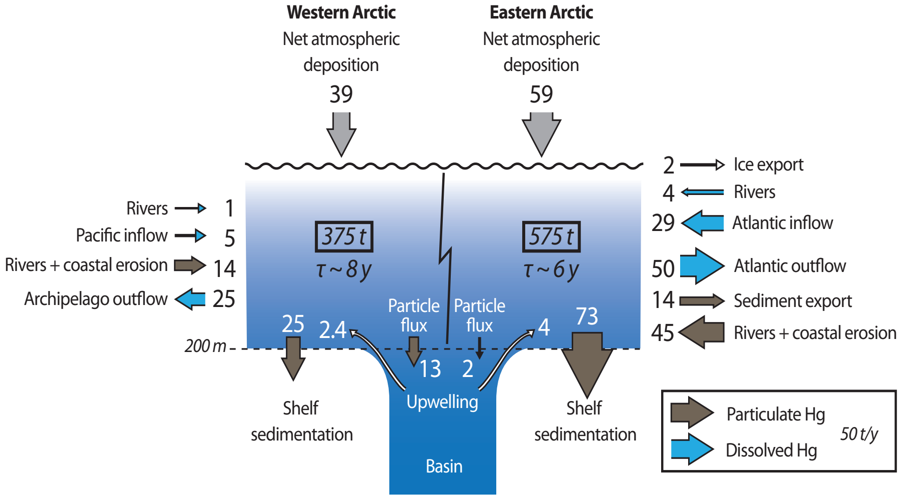

Figure 7.14. A schematic box model showing the mercury budget for the two-domain Arctic Ocean model in circa 2005. The budget is constructed for a Pacific domain (western Arctic) and an Atlantic domain (eastern Arctic) as shown in Figures 7.12 and 7.13.

Atmospheric mercury fluxes include additions to the ocean from wet and dry deposition of reactive gaseous mercury and particulate mercury, and losses through re-emission and evasion of gaseous elemental mercury. A net deposition estimate incorporating the AMDE effect on wet and dry deposition, as well as re-emission from snowpacks and evasion from the ocean, was determined using a modified GRAHM model.

Table 7.7. Elements of the two-domain mercury mass budget for the Arctic Ocean (see Figure 7.14). Source: adapted from Outridge et al. (2008).

| | Western Arctic | | | Eastern Arctic | | Whole Arctic | |
|---|---|---|---|---|---|---|---|
| Inventory, t | 375 | | | 575 | | 950 | |
| | Inputs, t/y | Outputs, t/y | | Inputs, t/y | Outputs, t/y | Inputs, t/y | Outputs, t/y |
| Atmospheric deposition | 38.6 | | Atmospheric deposition | 59.4 | | 98.0 | |
| Pacific inflow | 5.0 | | Atlantic inflow | 29.3 | | 34.4 | |
| River inflow | 0.9 | | River inflow | 3.7 | | 4.6 | |
| Upwelling | 2.4 | | Upwelling | 4.3 | | 6.7 | |
| Sediment influx | 14.0 | | Sediment influx | 45.1 | | 59.2 | |
| Archipelago outflow | | 24.6 | Atlantic outflow | | 50.4 | | 75.0 |
| Shelf sedimentation | | 25.0 | Shelf sedimentation | | 73.0 | | 98.0 |
| Basin sedimentation | | 12.6 | Basin sedimentation | | 2.1 | | 14.7 |
| | | | Sediment export | | 14.4 | | 14.4 |
| | | | Ice export | | 1.8 | | 1.8 |
| Dissolved | 47.0 | 24.6 | Dissolved | 96.7 | 52.1 | 143.7 | 89.7 |
| Particulate | 14.0 | 37.6 | Particulate | 45.1 | 75.1 | 59.2 | 114.1 |
| Total balance | 61.0 | 62.2 | Total balance | 141.8 | 141.6 | 202.9 | 203.8 |
| Residence time, t/y | 8.0 | | Residence time, t/y | 5.9 | | 6.6 | |
| k, 1/y | 0.13 | | k, 1/y | 0.17 | | 0.15 | |

Eastern Arctic Ocean about 44 t/y – or half – is buried in shelf sediments together with Hg on particles from coastal erosion and riverine sources. Particle flux of Hg into basin waters is low and probably occurs predominantly as leakage of terrigenous particles at the shelf edge via resuspension over the slopes (e.g., O'Brien et al., 2006). The interior basins of the Arctic Ocean have low productivity and very low associated particle fluxes (Hargrave et al., 1994; O'Brien et al., 2006), which are estimated to support a Hg flux of < 1 t/y. The balance of the 15 t/y lost to basins is made up from resuspended material advected laterally from continental shelves. An interesting implication of the budget in Figure 7.14 is, therefore, that Hg is scavenged over the shelves by the large supply of terrigenous and marine particles whereas waters in the interior ocean have a very weak particle scavenging and flux potential and so are unable to lose Hg, except by exchange of seawater. The result of this large-scale distribution of scavenging would then lead to generally higher dissolved Hg concentrations in the interior ocean relative to the shelves which might then help to explain biogeographic domains in Hg observed in zooplankton of the western Arctic (Stern and Macdonald, 2005) and higher concentrations of Hg in beluga feeding offshore compared to those feeding in the estuary/shelf region of the Beaufort Sea (Loseto et al., 2008b).

### 7.4.2.2. Response time of mercury in the Arctic Ocean

The time required for the Arctic Ocean to respond to changes in the magnitude of Hg sources can be considered in two ways. First, as a conservative estimate of the Arctic Ocean's ability to adjust to changes in contaminant loading, the natural time scales for replacing the ocean water or ice within the Arctic Ocean are considered. Arctic Ocean surface waters have an estimated flushing time of about 10 years, where flushing time is the inventory of meteoric freshwater in the ocean divided by the inflow of freshwater from land and by precipitation (Östlund, 1982). The shelves themselves have freshwater flushing times of < 1 year for the Beaufort Sea to 3.5 years for the large Siberian shelves (Macdonald, 2000). These residence times correspond to half-lives of up to 2.5 years for shelf waters and about 7 years for Arctic Ocean surface waters. Therefore, change in an input parameter, like deposition from the atmosphere, will take up to 35 years (5 half-lives) to fully manifest the change in water concentrations. Sea ice in the Arctic Ocean comprises first year ice, which melts out every summer, and multi-year ice, which survives at least one summer. For seasonal ice, Hg deposited to the ice surface in winter and spring is lost to the water during summer and only a seasonal build-up is possible. The memory of first-year ice for contaminant deposition is therefore less than a year and first-year ice-associated food webs might be expected to respond to changes in annual deposition. Although multi-year ice survives the summer, it goes through ablation during the warm period and then new ice is formed on the bottom during the subsequent winter such that the ice will lose a proportion of deposited Hg but then accumulate new Hg during the frozen season (e.g., see Macdonald et al., 2005, their Figure 17, and Stern and Macdonald, 2005). Ice drift tracks and speeds within the permanent pack follow the large-scale surface transport patterns set by the Beaufort Gyre and the Transpolar Drift (see Macdonald et al., 2005, their Figures 14 and 15). If multi-year ice is formed in the Beaufort Gyre, it may take up to 7 years before drifting out of the Arctic via Fram Strait, but less than 2 years if it is formed in the Transpolar Drift. Therefore, the memory of contaminant deposition on ice within the Arctic Ocean is less than 1 year for seasonal ice and up to 7 years for multi-year ice. Ice does not survive transport through the Archipelago, although its melt products may and, therefore, ice exiting the Arctic Ocean into the Archipelago will yield its Hg burden to the water during transit.

In the box model (Figure 7.14), the inventories (375 t, 575 t, and 950 t for the eastern, western and whole Arctic Ocean, respectively) divided by respective dissolved Hg input components imply residence times for Hg of 8 years in the west and 6 years in the east. These values are highly plausible when compared to the flushing times: they imply that Hg is not conservative (i.e., there are losses within the two domains) and that replacement of water in the western Arctic is slightly slower than in the eastern Arctic, which is also reasonable given the contrast of storage of water within the Beaufort Gyre versus rapid transport by the Transpolar Drift. The box-model budget now makes it possible to ask specifically how the surface water of the Arctic Ocean (western and eastern) would respond to changes in atmospheric Hg deposition. The simplest approach is to proceed based on the scenarios proposed in Section 7.3 for atmospheric deposition. Specifically, it is assumed that in response to the emissions control scenarios it will take 15 years for atmospheric deposition of Hg in the Arctic to be reduced by 5-20% from the 2005 levels. Using the box model, the atmospheric deposition term in the eastern and western Arctic Ocean boxes is reduced linearly between 2005 and 2020. Starting with the 2005 ocean Hg inventories (375 t western, 575 t eastern), the inventories are recalculated annually by summing the new inputs and outputs reflecting change in atmospheric deposition. In this type of model, the reduction in inventories directly implies a parallel reduction in total Hg concentration in the water. Therefore, it is also assumed that fluxes out of the Arctic, including Archipelago and Atlantic outflows, ice export and shelf/basin sedimentation scale linearly with the inventories/concentrations. It is further assumed that other Hg inputs (river inflow, Atlantic and Pacific inflow) remain constant over the time period in question.

Following this procedure it is apparent that for a 5% reduction in atmospheric deposition between 2005 and 2020, Arctic Ocean surface water inventories are reduced by 2.4% in the west and 2.1% in the east by 2020. Likewise, a 20% reduction between 2005 and 2020 corresponds to reductions of 9.5% in the west and 8.3% in the east. If it is assumed that the atmospheric deposition stabilizes after 2020, by 2050 the reductions resulting from the 5% and 20% scenarios will be 4.2% and 16.4% in the west compared to 8.3% and 12.1% in the east. At first, these results seem surprising, and contrary to the longer residence time for Hg in the western Arctic Ocean. However, in the eastern Arctic Ocean, the atmospheric input is accompanied by large input from the Atlantic Ocean such that a given percentage reduction in deposition becomes a smaller percentage reduction in the total Hg input. If it is assumed that Atlantic inflowing water undergoes a reduction in Hg scaled to the lower atmospheric deposition, the eastern basin response becomes slightly faster than the western basin, as would be expected. However, this brings up an important consideration of how the global upper ocean is likely to respond to reductions in Hg emissions. Sunderland and Mason (2007) proposed that the anthropogenic Hg enrichment of the surface ocean is a mere 25% compared to 300-500% in the atmosphere. If this is applicable to the North Atlantic and Pacific Oceans, then the prospects of altering the input of Hg via Fram Strait, the Barents Sea and the Bering Strait inflows would seem to be minor and take time (the upper global ocean has a Hg residence time estimated at ~70 years). These circumstances are clearly different to those for HCH (Li et al., 2004) and DDT (Stemmler and Lammel, 2009).

The box model also has other implications. The river inflows of dissolved Hg provide only a small part of the budgets, which implies that changes in river inflow or Hg concentration in river waters are likely to have only local (estuarine/shelf) impacts. Likewise, the Hg inflow from the Pacific is estimated to be small, but there are no Hg data for Bering Strait seawater that could provide a confident estimate of present flux. If Hg concentrations at Bering Strait were higher, similar to those in the North Atlantic Ocean (i.e., ~0.3 ng/L), the influx could be as much as 15 t/y, which then becomes a significant component of the western Arctic Ocean budget. Climate variability and change can affect the parameters in this box model. Of all the parameters, the net atmospheric deposition would seem to offer the greatest potential for change given that ice cover has undergone large and rapid change during the past decade, and the Arctic Ocean is projected to be clear of ice seasonally possibly before the mid-century (e.g., see Kerr, 2009). The removal of ice would certainly alter deposition processes for particulate Hg(II) but would also provide a stronger evasion of Hg(0) (e.g., see Andersson et al., 2008). Stronger Hg(0) evasion, together with greater opportunity for photo reduction, would favor a decrease in the net deposition of Hg, with effects on the Hg inventories in the upper ocean similar to those resulting from emissions reductions of up to 20%.

## 7.5. How feasible and costly will be future global mercury emission reductions?

Measures available for reducing Hg emissions differ with regard to emission control efficiency and cost. Costs and benefits associated with Hg emission reductions from major anthropogenic sources were assessed by Pacyna et al. (2010b). They concluded that measures that include the application of technology, such as technology to remove Hg from flue gases in electric power plants, waste incinerators, and smelters, are expensive compared to non-technological measures such as prevention activity and promotion of Hg-containing waste separation. However, some technologies can be relatively inexpensive when used as an incremental approach with other pollutant-reduction measures. Economic benefits from decreasing Hg emissions were estimated by Sundseth et al. (2010). They suggested that the annual global cost would be approximately USD 3.7 billion (2005) based merely on loss of IQ (Intelligent Quotient) from exposure to methylmercury if the present projector for 2020 is maintained. Table 7.8 summarizes the qualitative costs and benefits assessment of the major by-product emission categories as presented by Pacyna et al. (2010b)

At present, it is uncommon to invest in technologies to reduce only Hg from the emissions stream. Instead, a multi-pollutant approach is commonly used, which is much more cost effective. For example, approaches and technologies for controlling conventional air pollutants, including particulate

Table 7.8. A qualitative assessment of the costs and benefits from different mercury by-product reduction options. Source: Pacyna et al. (2010b).

| Reduction option | | Costs | Benefits |
|---|---|---|---|
| 1 | Reduction from coal usage | Medium → Large | Large |
| 2 | Reduction from industrial processes | Medium → Large | Medium → Large |
| 3 | Reduction from waste | Small → Large | Large |
| 4 | Reduction from chlor-alkali industry | Small → Large | Medium → Large |

matter, sulfur dioxide and nitrogen oxides, typically result in some reduction of Hg emissions as a co-benefit. In most cases, Hg controls are contingent upon controls for conventional pollutants, although the degree of the Hg capture by various technologies varies widely. In this context, the incremental cost of adding a Hg reduction effort to a certain strategy is much smaller.

Efficient, non-technological measures and pre-treatment methods are also available for the reduction of Hg releases from various uses of products containing Hg. These measures include bans on use and substitution of products containing Hg and cleaning of raw materials before their use (e.g., coal cleaning). These measures also include energy conservation options, such as energy taxes, consumer information, energy management, and improvement of efficiency of energy production through a co-generation of electricity and heat in coal-fired power plants. Other potential measures affecting Hg emissions also comprise prevention options aimed at reducing Hg in wastes, material separation, labeling of Hg-containing products, and input taxes on the use of Hg in products.

The message from the review of abatement installations for reduction of Hg emissions from various anthropogenic sources from UNEP's second Ad Hoc Open-ended Working Group on Mercury, is that there are a number of technological and non-technological solutions available that could be employed at present in order to reduce Hg emissions by 2020. Of course, it is expected that even more technological measures will be available in the near future, particularly in the field of application of renewable sources of energy production and the improvement of Hg removal using the 'add on' measures in addition to electrostatic precipitators (ESPs) / fabric filters (FFs) combined with various types of flue gas desulfurization (FGDs). There is also a great potential for improvement of non-technological measures such as decrease in the use of Hg in the future and development of incentives for application of measures aiming at reduction of Hg emissions to the environment.

### 7.5.1. Mercury emission reductions from coal combustion

In coal-burning facilities, any viable means to improve the efficiency of the plant should be considered for controlling Hg emissions. Improvement of plant efficiency also provides for reduction of greenhouse gas emissions in addition to reduction of Hg emissions. Some of the most commonly applicable measures at a coal-burning facility include: new burners, improved air preheater, improved economizer, improved combustion measures, minimization of short cycling, minimization of gas-side heat transfer surface deposits, and minimization of air infiltration. In addition, operation and maintenance practices have a significant impact on plant performance, including its efficiency, reliability, and operating cost. Depending on the coal used, a certain decrease in Hg emissions may be obtained by the deployment of coal treatment technologies prior to combustion. Coal treatment technologies considered in the context of plant efficiency and Hg removal, include conventional coal washing, coal beneficiation for Hg content, coal blending, and coal additives. Fuel substitution schemes are also capable of delivering decreased Hg emissions (e.g., substitution of coal with natural gas or renewable energy sources).

Next, secondary measures should be applied, that is, a set of approaches designed to maximize the so-called co-benefit removal, or the amount of Hg removal that is realized as the effect of operation of air pollution control equipment originally designed to limit emissions of criteria pollutants (particulate matter, sulfur dioxide and nitrogen oxides) and already in place at the power plant (Table 7.9). Depending on the available air pollution control equipment, these approaches could include modernization of ESPs, modification of wet desulfurization scrubber chemistry, alteration of selective catalytic reduction (SCR) operation, or a combination of these.

For plants where the amount of Hg capture desired is beyond what can be achieved through co-benefit removal, deployment of dedicated Hg control technologies may be required. To date, use of sorbent injection has shown the most promise as a near-term Hg control technology. In the basic scenario envisioned for sorbent injection, powdered activated carbon is injected between the air heater and the particulate control device.

The incremental cost of Hg reduction (i.e., the cost, in USD per kg Hg removed, to achieve a specific reduction) is influenced largely by the level of baseline Hg capture exhibited by the existing air pollution control device (APCD) configuration and coal Hg content. For example, the incremental cost of Hg control will increase when: (i) baseline Hg capture by existing APCD is high, or (ii) the coal Hg content is low, because a smaller quantity of Hg is removed from the flue gas for a given level of control. The incremental cost of Hg emission reduction varies substantially depending on factors such as type of coal used, type of combustion unit, type of APCD already in place to control other pollutants, facility configuration, and percentage reductions expected from the existing APCD. For example, wet scrubbers installed primarily for Hg have been estimated to cost between USD 76 000 and 174 000 per pound of Hg removed (or USD 168 000 to 384 000 per kg of Hg removed). This result is very close to the cost of USD 234 000 per kg of Hg removed, estimated and used in a study of the effectiveness of the UNECE Heavy Metals Protocol and cost of additional measures.

Early estimates of Hg control costs indicated that it would cost between USD 67 700 and 70 000 per pound (or USD

Table 7.9. Average mercury capture by existing post-combustion control configurations installed on coal-fired units. As presented in Pacyna et al. (2010b).

| Post-combustion control strategy | Post-combustion emission control device configuration | Average mercury capture by control configuration, % | | |
|---|---|---|---|---|
| | | Coal burned in PC-fired boiler unit | | |
| | | Bituminous coal | Subbituminous coal | Lignite |
| PM control only | ESPc | 36 | 9 | 1 |
| | ESPh | 14 | 7 | not tested |
| | FF | 90 | 72 | not tested |
| | PS | not tested | 9 | not tested |
| PM control and spray dryer absorber | SDA + ESP | not tested | 43 | not tested |
| | SDA + FF | 98 | 25 | 2 |
| | SDA + FF + SCR | 98 | not tested | not tested |
| PM control and wet FGD System[a] | PS + FGD | 12 | 10 | not tested |
| | ESPc + FGD | 81 | 29 | 48 |
| | ESPh + FGD | 46 | 20 | not tested |
| | FF + FGD | 98 | not tested | not tested |

[a] Estimated capture across both control devices. ESPc = cold-side electrostatic precipitator; ESPh = hot-side electrostatic precipitator; FF = fabric filter PS = particle scrubber; SDA = spray dryer absorber system.

149 300 to 154 000 per kg) to achieve a 90% control level using sorbent injection. However, following the Research, Development and Demonstration (RD&D) activities sponsored by the US Department of Energy (DOE), the costs of sorbent injection for Hg removal have shown significant advances along with the potential for reductions in overall installation and operational costs. A DOE economic analysis released in 2007 indicated that the cost of Hg control could be drastically lowered compared to original estimates due to a reduction in the injection rate of a sorbent. The analysis indicated that a levelized incremental cost of 90% Hg emission control by means of powdered activated carbon injection ranged from about USD 30 000 to less than USD 10 000 per pound of Hg removed for DOE field testing sites[1]. These DOE test sites used a chemically-treated (brominated) activated carbon. While the capital cost of a Hg control system (i.e., activated carbon injection; ACI) is relatively low, the major expenditure comes from the cost of carbon itself. Generally, brominated carbon affords much lower injection rates (mass sorbent / flue gas flow) than the untreated carbon to accomplish the same level of Hg removal. Thus, despite the fact that chemically treated carbons are more expensive than untreated ones, the use of chemically treated carbons allows a significant reduction in the cost of Hg removal.

### 7.5.2. Mercury emission reductions from industrial processes

Abatement costs for reduction of heavy metals, including Hg, within various industries were assessed for the heavy metal emission reduction Protocol of the UNECE Convention on Long-range Transboundary Air Pollution. The results of this assessment are similar to the data presented in Table 7.10.

Industrial processes contribute about 25% to the total emissions of anthropogenic Hg to the atmosphere (UNEP, 2008). Emissions from the non-ferrous and ferrous metal industries are estimated to contribute about 10% each to the total emissions. With regard to Hg emissions from non-ferrous metal production, amounts depend mainly on: (i) the Hg content of non-ferrous metal ores used mostly in primary processes or scrap used in secondary non-ferrous production, (ii) the type of industrial technology employed in the production of non-ferrous metals, and (iii) the type and efficiency of the emission control installations.

The content of Hg in ores varies widely from one ore field to another (e.g., Pacyna, 1986) as does the Hg content of scrap. Depending on the country, Hg emissions from primary production using ores in non-ferrous smelters are between one and two orders of magnitude higher than the Hg emissions from secondary smelters with scrap metal as the main raw material. Pyro-metallurgical processes in the primary production of non-ferrous metals, employing high temperature roasting and thermal smelting, emit Hg and other raw material impurities, mostly to the atmosphere. Non-ferrous metal production with electrolytic extraction is responsible more for risks of water contamination.

The primary sources of Hg emissions from cement manufacturing contribute about 10% to the total anthropogenic emissions of this element. Mercury emissions are mostly generated during the processing of raw materials in the kiln. Kiln operations consist of pyro-processing (thermal treatment) of raw materials, which are transformed into clinkers. Raw material processing differs for the wet- and dry-kiln processes. Regardless of kiln type, Hg is introduced into the kiln with raw material (limestone) and with fuels (e.g., coal), which are used to provide heat for calcination and sintering of raw materials. Other fuels, such as shredded municipal garbage, chipped rubber, petroleum coke, and waste solvents, are also frequently used and may contribute to Hg emission from cement production.

In addition, fly ash from coal combustion may be added to clinker for concrete production. This added fly ash may contain Hg as a result of the condensation of gaseous Hg on fine fly ash particles in the flue gas before the collection of fly

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[1] Potential loss of revenue for plants that sell fly ash for beneficial reuse (e.g., in concrete manufacture) is not taken into account. An increase of 172–300 % on the Hg removal cost has been indicated if relevant (NESCAUM, 2010).

Table 7.10. Maximum and minimum annual costs for technological reduction of mercury in various source sectors as calculated within the EU ESPREME project (ESPREME, 2007). Capital costs are calculated with the assumption of a 15-year technology lifetime and a 4% discount factor, assumptions on inflation included.

| Sector | Specific activity indicator (SAI) | Minimum percentage Hg reduction | Maximum percentage Hg reduction | Minimum annual costs, USD 2008/ SAI | Maximum annual costs, USD 2008/ SAI |
|---|---|---|---|---|---|
| Coal combustion | MWh | 24 | 98 | 1.4 | 5.7 |
| Sintering | metric ton sinter | 5 | 99 | 0.2 | 3.2 |
| Primary lead | metric ton primary lead | 5 | 90 | 0.1 | 3.8 |
| Primary zinc | metric ton primary zinc | 5 | 10 | 0.2 | 5.6 |
| Primary copper | metric ton primary copper | 5 | 10 | 15.6 | 29.5 |
| Secondary lead | metric ton secondary lead | 5 | 10 | 0.2 | 7.9 |
| Secondary zinc | metric ton secondary zinc | 5 | 10 | 0.2 | 1.5 |
| Secondary copper | metric ton secondary copper | 5 | 10 | 26.8 | 50.6 |
| Cement production | metric ton cement | 5 | 98 | 0.4 | 1.8 |
| Coke production | metric ton coke | 5 | 98 | 0.02 | 3.0 |
| Pig iron production | metric ton cast iron | 5 | 72 | 1.0 | 6.0 |
| Iron and steel foundry | metric ton cast iron | 5 | 98 | 93.6 | 148.8 |
| Electric arc furnace steel | metric ton steel | 98 | 98 | 1.7 | 1.7 |
| Basic oxygen furnace steel | metric ton steel | 5 | 70 | 4.2 | 8.8 |
| Waste incineration | metric ton waste | 20 | 99 | 0.2 | 12.7 |
| Chlorine production[a] | metric ton chlorine | 15 | 100 | 0.04 | 37.0 |

[a] Mercury cell plants.

ash in particulate control devices, such as ESPs or FFs. The US Environmental Protection Agency reported that Hg is retained by fly ash from the use of sorbents for enhanced Hg capture, and is thus unlikely to be leached into the environment (US EPA, 2006). The same was also found to be the case for wet FGD scrubbers (US EPA, 2008).

Large non-ferrous smelters use high efficiency air pollution control devices to control particulate matter and sulfur dioxide emissions from roasters, smelting furnaces, and convertors. Electrostatic precipitators are the most commonly used devices for the control of particulates. Mercury is emitted mostly in a gaseous elemental form from large non-ferrous smelters, and therefore, the ESPs are not very effective in its removal. The elemental Hg does not end up in sulfuric acid plants and is instead emitted to the atmosphere from the smelter stacks. The amount of these emissions depends on the Hg content of the ore. This varies widely from one ore field to another. Because Hg emissions are mostly in the elemental form, ACI or wet scrubbers may be needed to control them. Other options to control Hg emissions from industrial sources include those discussed for the coal combustion sector.

Mercury can be emitted to the atmosphere during the production of metallurgical coke, which is used in the iron and steel industry. Electrostatic precipitators or FFs and, less frequently wet scrubbers, are used in the coke production plants to control emissions, particularly those generated during quenching. Quenching is performed to cool down coke and to prevent complete combustion of coke upon exposure to air. Although no data are available for the performance of ESPs and FFs in coke production plants, it is expected that Hg removal is limited. Thus, ACI would need to be deployed to control Hg emissions from metallurgical coke production facilities.

A major review of information on the costs of abatement for coal combustion and other economic sectors was carried out within the EU ESPREME (*http://espreme.ier.uni-stuttgart.de*) and DROPS (*http://drops.nilu.no*) projects. The annualized investment and operational costs for installations that are used to remove Hg, including ESPs, FFs, FGD, and 'add on' measures just for Hg removal are presented in Table 7.10. The accuracy of cost estimates in Table 7.10 is within ± 50% as calculated within the EU ESPREME project. These costs are given in relation to the production of 1 t of specific production and are indicated in Table 7.10 as a specific activity indicator. The information on efficiency of Hg removal using these installations is also included in Table 7.10.

Industrial sources of Hg emissions often include small industrial boilers. Because of the economy of scale, different control strategies may be needed for these small industrial boilers than for large industrial sources or for coal-burning utility power plants. Major assessment of costs and environmental effectiveness of options for reducing Hg emissions to air from small-scale combustion installations (<50 MWh) was prepared for the European Commission by Pye et al. (2005). Pye and co- workers concluded that preventive options were one of the most cost-effective options (e.g., options prior to combustion to minimize emissions), such as coal washing and fuel switching. Such options require the use of a better quality, cleaner fuel within the same fuel type, or switching to a different type of fuel with a lower Hg content and resultant emissions.

Another preventive option is reduction in energy consumption through energy efficiency, as discussed for the coal combustion sector. Only limited technical abatement options (such as removal of Hg from flue gases after combustion) were identified for small-scale combustion installations.

An assessment of abatement costs for reduction of heavy metals, including Hg, within various industries was undertaken for the heavy metal emission reduction Protocol of the UNECE Convention on Long-range Transboundary Air Pollution (Visschedijk et al., 2006).The results of this assessment are similar to the data presented in Table 7.10.

## 7.6. Conclusions and recommendations

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

### How are anthropogenic mercury emissions likely to change in the future?

1. An increase equivalent to about one quarter of the 2005 global anthropogenic Hg emissions, or about 500 t per year, is expected by 2020 if there are no major changes in economic trends or in the efficiency of emission controls (i.e. the SQ or 'business as usual' option).

2. Alternately, the widespread implementation of available control technologies (the 'EXEC' or the more stringent 'MFTR' options) could reduce global Hg emissions by up to 60% by 2020 compared to current practices.

*More accurate assessment of future scenarios is needed. In particular, there is a need to take into account different energy mixes and changes in terms of the increased use of renewable energy. More complete emission inventories are also needed with regard to intentional use- and by-product emission sources, especially for intentional use of Hg in products.*

*Emissions scenarios for 2050 and 2100 should be estimated to give an idea of long-term future trends under different scenarios, and more accurate information on economic and social variables worldwide should be introduced into the emissions scenarios.*

### How will future changes in global emissions and climate affect mercury levels in the Arctic atmosphere?

3. The average increase in atmospheric gaseous Hg (GEM) concentrations in the Arctic and sub-Arctic between 2005 and 2020 under the 'business as usual' emissions scenario is relatively small (~3%), but increases in deposition (up to ~5%) will be slightly higher because of the predicted greater proportion of oxidized anthropogenic Hg in Arctic air which has a faster deposition rate than GEM.

4. Similarly, the decreases in atmospheric Hg deposition in the Arctic by 2020 achieved under the EXEC and MFTR control scenarios will be greater than those in GEM concentrations, because of proportionately larger reductions in emissions of oxidized Hg species.

*Model parameterization (e.g., emissions data, meteorological conditions, and inclusion of natural emissions and re- emissions in the models) should be improved.*

### What will be the recovery time for mercury in the Arctic atmosphere and ocean under future scenarios of emissions reductions?

5. It may take 15 years for the atmospheric deposition of Hg in the Arctic to be reduced by 20% relative to levels in 2005.

6. For a 5% reduction in atmospheric deposition between 2005 and 2020, Arctic Ocean surface water inventories may be reduced by 2.4% on average in the western Arctic Ocean and 2.1% in the eastern Arctic Ocean. A 20% emissions reduction between 2005 and 2020 is predicted to produce reductions of 9.5% and 8.3% in average seawater Hg concentrations, respectively.

7. Owing to the large mass of Hg involved, and the slow turn-over times of deep-ocean waters, total clearance of anthropogenic Hg from the whole Arctic Ocean is expected to take decades to centuries to achieve following significant emissions reductions. More rapid responses are likely to occur in surface waters down to 200 m depth.

*Extensive use of models is needed for relating changes in Hg emissions to changes in concentration in the Arctic. Research should be adapted to improve the dose-response functions needed for assessing biological recovery; more accurate information on speciation will give more accurate information on dose-response relationships.*

### How feasible and costly will be future global mercury emission reductions?

8. Measures for reducing Hg emissions are available, but some removal technologies are rather expensive. A multi-pollutant approach is commonly used for removing Hg from the emissions stream and is more cost-effective. Non-technological methods and pre-treatment of raw materials can be used in combination with technical measures.

*Further assessment of the benefits in the Arctic resulting from global Hg emissions reductions is needed to improve the basis for cost-bearing decisions that are taken to achieve Hg reductions. Improved information should also be obtained on costs and benefits of multi-pollutant reduction measures.*

### General recommendations

- *Invite research funding agencies to prioritize improvements to Hg emissions scenarios and projections.*
- *Undertake research on Hg emissions, concentrations of Hg, and impacts of Hg in the Arctic environment.*
- *Investigate the socio-economic consequences in the Arctic of global Hg emissions. Address changes in Arctic Hg contamination within the context of climate change.*

# Chapter 8

# What is the Impact of Mercury Contamination on Human Health in the Arctic?

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## 8.1. Introduction

The subject of contaminants (including mercury; Hg) and human health has been addressed in three previous AMAP assessment reports (AMAP, 1998, 2003, 2009b), of which the two most recent comprised stand-alone human health assessment reports. These assessments, and particularly the most recent, have evaluated contaminant related exposure and effects within the broader context of overall human health in Arctic indigenous communities. When examined in this way, assessing the impacts that contaminants in the Arctic environment have on human health goes beyond typical contaminant related risk assessment with a focus on toxicological effects, and considers broader issues of social and cultural well being, and food security. As alluded to in Chapter 1, Arctic indigenous communities are particularly vulnerable to impacts of contaminants in their traditional/local foods for a number of reasons. Some of the most important foods, such as those derived from marine mammals and predatory fish species, often have elevated concentrations of contaminants which can lead to high levels of human dietary exposure and potential adverse health effects (AMAP, 1998, 2003, 2009b). These same foods, however, are often the most important and readily available source of those essential nutrients that are not easily found in generally accessible store-bought foods. The social, cultural, and spiritual health of indigenous communities is also closely tied to the harvesting, consuming, and sharing of traditional/local foods. Reducing these activities could have serious consequences for the continued integrity of some Arctic indigenous communities.

Mercury, along with several persistent organic pollutants (such as PCBs, chlordanes and toxaphenes) that are found at elevated concentrations in some Arctic populations, is a contaminant of major concern to health authorities in the Arctic. Among this group of contaminants, Hg toxicity is considered to be an important contributor to the overall health risk presented by contaminants in the environment. This chapter summarizes information on the impacts of Hg on human health taken primarily from the most recent AMAP human health assessment (AMAP, 2009b), with some additional updates from recent studies. In answering the primary question of this chapter – *What is the impact of mercury contamination on human health in the Arctic?* – the following sections illustrate links between findings presented in the rest of this assessment and their implications for human health.

## 8.2. What are the global influences on mercury exposure in northern peoples?

In this assessment, Chapters 2 through 4 address general and specific questions related to factors controlling Hg levels in the Arctic, including sources, transport, ecosystem processes, and the influence of climate change. As stated in Chapter 5, on average over 90% of the present-day Hg in Arctic wildlife is estimated to be of anthropogenic origin. While environmental characteristics of, and processes in, the Arctic play a large role in governing ecosystem uptake and accumulation of Hg, it is apparent that global anthropogenic factors make a critical contribution to the sources of Hg to the Arctic, as well as changes in climate that influence aspects of the Hg cycle leading to and including human exposure. Important from a human health perspective is that all of these factors influence the concentrations of Hg, particularly methylmercury (MeHg), in the fish and wildlife consumed by Arctic indigenous peoples.

Chapter 4 discusses the impact of climate change on the Hg cycle, including a number of aspects that may change human Hg exposure in the Arctic. For example, rising air temperatures associated with climate change may increase re-emissions of Hg from lower latitudes. At the same time, rising temperatures and incident solar radiation are increasing primary productivity and methylation of Hg within the Arctic. Climate change is therefore likely to have as yet undefined implications for the transfer of Hg through food webs, in particular marine food webs. It has been argued that the effect of climate change on methylation may be the most important effect from the perspective of human and wildlife health (Outridge et al., 2008). A study by Booth and Zeller (2005) modeled climate change impacts on Hg concentration in fish and pilot whales (*Globicephala melas*) in the Faroe Islands marine ecosystem. The results showed that increases in water temperature of 0.4 and 1.0 °C might result in average MeHg increases of between 1.7% and 4.4% respectively. The authors noted that pilot whales displayed a greater nominal change in MeHg concentration compared to cod, and that fishing mortality had a cumulative effect. When exposure levels for Faroe Islanders were calculated based on a dietary intake of whale meat (12 g/person/d) and cod (72 g/person/d), it was found that a large proportion of the general adult population would exceed the World Health Organization (WHO) tolerable weekly intake (TWI) limits of 1.6 µg/ kg body weight (bw) and the U.S. Environmental Protection Agency (EPA) reference dose (RfD) of 0.1 µg/ kg bw/d (equivalent to a TWI of 0.7 µg/ kg bw) under all simulated conditions (Booth and Zeller, 2005). The authors estimated that environmental inflow rates of Hg would need to be reduced by about 50% (under prevailing conditions) to achieve MeHg intake levels that fall below WHO guideline levels. It was further concluded that increasing methylation rates due to higher water temperatures are likely to lead to continuous increases in biota concentrations and therefore higher exposure levels for Faroe Islanders on the basis of the current marine-based diet. However, while the study considered the effects of higher water temperatures and altered fish and whale mortality rates on future marine methylation rates, other possible mechanisms by which climate change may increase methylation rates, such as higher oceanic productivity and organic carbon concentrations (Sunderland et al., 2009; Cossa et al., 2009), and increased MeHg outflows from rivers (see Chapter 4), were not included in the model. The predicted methylation rate increase of 1.7–4.4%, while of potential significance, may not accurately reflect the likely overall impact on methylation rates and the Hg concentration increases in Arctic marine biota that could result from a warming climate. The study by Booth and Zeller (2005) still serves as a good example of how two global issues, Hg emissions and climate change, may influence the exposure scenarios for Arctic people. Many factors have been identified in this assessment that influence Hg levels in different ecosystem components, each of which has the potential to influence human exposure through changes in concentration in traditional/local foods.

Anthropogenic sources of Hg that contribute to human exposure through general contamination of Arctic ecosystems are global in nature and largely located outside the Arctic region. Large industrial centers within the Arctic, particularly those that produce energy from coal also contribute to the global pool of Hg, although their contribution is relatively small (see Chapter 2). Local sources of Hg in the Arctic, can lead to increased Hg concentrations in surrounding ecosystems, which could lead to elevated levels of human Hg exposure. Examples include past Hg mining activities in Alaska (Gray et al., 2000) and tar sands development in northern Alberta, Canada (Timoney and Lee, 2009) which have lead to locally elevated levels of Hg in aquatic ecosystems. Hydroelectric dams that flood large areas of land are also known to cause increased levels of Hg in fish in the reservoirs that are created, which can also have downstream influences (see Section 5.4: Case Study 3).

## 8.3. What are the dietary influences on mercury exposure?

Arctic indigenous peoples are primarily exposed to Hg through their diet, which includes traditional/local food items such as fish, seabirds and marine mammals. Other northern residents may also be exposed to Hg through their diet, however, for the purposes of assessments, there is a focus on Arctic indigenous peoples, in particular those that rely heavily on marine foods as part of their traditional diet as they constitute 'critical groups' for potential Hg exposure and health effects. Food security is becoming an increasingly important issue for Arctic communities, with a number of factors contributing to this. Although some studies (e.g., Furgal et al., 2001; Donaldson et al., 2006) have found that many people continue to eat traditional/local foods despite their knowledge of contaminants, there remains a risk that the consumption of foods that are in other respects a healthy and important part of traditional diets will be reduced as a result of concern about contaminants. For example, studies conducted in a few isolated indigenous communities in Arctic Canada found rates of expressed concern over traditional/local food availability ranging from 40% to 83% of the populations surveyed (AMAP, 2009b). In other circumpolar countries, the Survey of Living Conditions in the Arctic (SLICA) reported that only 14% of people in the circumpolar Arctic (Greenland, Chukotka, Alaska) were satisfied with the amount of fish and game available to them (Poppel et al., 2007). While the satisfaction rate was highest in Alaska at 40%, Greenland and Chukotka had very low rates of 9% and 6%, respectively. Among the many factors that lead to food insecurity, including availability and cost of healthy store-bought foods, some of the most important and regularly cited factors relate to accessibility of traditional/local foods. Accessibility to traditional/local foods is also dictated by a number of factors, including access to a hunter/fisher, cost of hunting/fishing, and the health and abundance of wildlife. The presence of Hg and other contaminants in fish and wildlife, and the related perception of diminished food quality and safety may exacerbate the issue of accessibility to traditional/local foods.

The situation is further complicated by the problem of 'nutrition transition', which has been taking place for indigenous peoples all over the world. A nutrition transition has been described in several studies (Daman et al., 2008) and is commonly associated with industrialization, urbanization, economic development, and globalization of markets. During nutrition transition, the traditional/local food diet is replaced by a more 'western', store-bought diet. The store-bought diet often consists of inexpensive foodstuffs that have high contents of refined carbohydrates and saturated fatty acids, but low contents of nutrients, vitamins and essential unsaturated fatty acids (Johnson-Down and Egeland, 2010 and references therein). Along with a more sedentary lifestyle, this diet can cause obesity and related diseases such as diabetes and coronary heart disease.

Health professionals therefore need to balance the health benefits of traditional diets against the increased health risks associated with the contaminants that they contain when developing advice on food consumption and related risk communication.

The potential importance of Hg levels in Arctic biota to human health becomes apparent when dietary surveys are conducted. For example, dietary surveys in 1999 to 2002 by the Alaskan Department of Fish and Game in northwestern Alaska showed that the average composition of subsistence harvest by rural residents comprised 60% fish, 14% marine mammals, 20% land mammals, and 2% each of plants, birds, and shellfish. When blood values of Hg (a measure of recent exposure) were compared in Alaskan non-fish consumers and fish consumers, it was found that the former had blood Hg values of less than 1 μg/L, while levels in people consuming large amounts of fish could be higher than 4.2 μg/L (AMAP, 2009b).

Arctic biota differ in their levels of Hg, depending on whether the animals are terrestrial or marine based, their level in the food web (i.e., the extent of biomagnification), their age, and feeding location (AMAP, 1998, 2004). There is also general spatial and temporal variation in biota levels across the Arctic. In the following discussion, Hg concentrations in some Arctic biota are summarized in relation to their importance for safe food consumption and possible exceedence of tolerable intake levels. It is also important to recognize that significant variation has been found in Hg concentrations in tissues and organs of the same animal species (in general increasing in the order fat, muscle, kidney and liver). This influences which parts of the animal may exceed guidelines for safe consumption and needs to be taken into account when developing dietary advice to limit, for example, Hg intake (AMAP, 1998, 2009b). It should also be noted that most of the monitoring data discussed are for measurements of total Hg (THg), not MeHg, and that the percentage of THg that is actually MeHg varies from species to species, and tissue to tissue, with muscle generally containing mostly MeHg and organs, such as liver and kidney containing mostly less toxic inorganic forms of Hg.

Mercury analyses were conducted on several types of mature fish in Alaska: northern pike (*Esox lucius*), Arctic grayling (*Thymallus arcticus*), whitefish (*Coregonus* spp.), burbot (*Lota lota*), Atlantic salmon (*Salmo salar*), and chinook (*Oncorhynchus tshawytscha*), chum (*O. keta*), coho (*O. kisutch*), and sockeye (*O. nerka)* salmon among others. Only pike exceeded the U.S. Food and Drug Administration (USFDA) action level for Hg of 1.0 mg/ kg and the critical value for human consumption of 0.3 mg/ kg set by the U.S. EPA (Jewett and Duffy, 2007). The estimated limit for consumption of pike was about one monthly meal for adults but only two meals per year for children. In contrast, MeHg concentrations in the most frequently consumed fish, such as salmon, cod, halibut, pollock, sole, and herring were very low.

Studies in Arctic regions including Canada, Greenland, and Russia reveal relatively high levels of Hg in marine mammals, as well as in some seabirds and predatory fish (see Chapters 5 and 6), although spatial and temporal variability in concentration can exist. Species that have been found to have higher Hg concentrations in some areas of the Arctic include seals and whales (meat and blubber), polar bear (*Ursus maritimus*) and some seabird species, although variation has been found in Hg concentration between the meat, fat, liver, and kidney within the same species, influencing which parts of the animal exceed safety guidelines or levels (AMAP, 1998, 2009b).

In Chukotka, the results of an unpublished study by Dudarev (referenced in AMAP, 2009b: p.45) suggest that seal had higher levels of Hg than terrestrial mammals, birds and fish. Mercury levels in seal meat exceeded the food safety limits in Russia for commercial and wild foods (RFSL) by 3 to 10 times; seal kidney by 10 times; and seal liver by 20 to 100 times. The highest Hg levels were observed in bearded seal (*Erignathus barbatus*), particularly in the liver. Meat of walrus (*Odobenus rosmarus*) and grey whale (*Eschrichtius robustus*) is less contaminated by Hg, with levels lower than the RFSL. However, kidney and liver of walrus had Hg levels two to four times higher than the RFSL. In whales, on the other hand, Hg levels in kidney are below the RFSL and the liver level is similar to the RFSL. The percentage of the population exceeding the RFSL levels was not reported. Mercury levels in subsistence-hunted whales were determined in a study looking at bowhead whale (*Balaena mysticetes*) and beluga (*Delphinapterus leucas*) in Alaska and grey whales in Chukotka (Dehn et al., 2006). While average THg levels were low in bowhead and grey whale meat (0.02 µg/g ww) and safe for consumption, beluga had high levels with an average of 1.12 µg/g ww, which exceeds several consumption guidelines (e.g., the USFDA action level for Hg of 1.0 mg/ kg).

In a summary of Russian data it was concluded that the overall levels of Hg in venison were low in the four main studied regions of Arctic Russia (Kola Peninsula, Nenets Autonomous Okrug, Taymir APO, Chukotka AO). However, in some regions the Hg levels in reindeer (*Rangifer tarandus*) kidney exceeded the food safety limits in Russia for commercial and wild foods (RFSL for kidney is 0.2 mg/ kg; AMAP, 2004) by up to 50%. In waterfowl, Hg levels were two to three times higher than the RFSL. Mercury levels were below Finnish reference values in most terrestrial-based traditional/local food items in Finland, which included reindeer, game, vegetables and berries (AMAP, 2009b). Mercury levels in most fish species were also below Finnish reference values (0.5 mg/ kg), except fish from new water reservoirs where old burbot and pike were found to exceed 1 mg/ kg.

In Greenland, the results of Dietz et al. (1998a, 2000b) suggested that marine mammals had higher levels of Hg than terrestrial mammals, birds and fish. The highest Hg levels were observed in polar bear kidneys and hooded seal (*Cystophora cristata*) liver (Dietz et al., 1998a, 2000a). A comprehensive study of contaminant concentrations in the local diet in Greenland (Johansen et al., 2004) included Hg levels in the major animal species and tissues consumed by Greenlanders. Tissue from about 25 animal species was included in the study and, in general, contaminant levels were very low (less than 0.01 µg/g) in muscle and fat of terrestrial species, marine fish such as capelin (*Malotus villosus*) and Atlantic cod (*Gadus morhua*) liver, as well as seal blubber. Low to medium Hg levels (between 0.01 and 0.09 µg/g) were found in liver and kidney of many terrestrial species (including reindeer), marine fish (including Arctic char (*Salvelinus alpinus*) liver, salmon, Greenland cod (*Gadus ogac*), Atlantic cod muscle) as well as some whales (minke whale (*Balaenoptera acutorostrata*), beluga and narwhal (*Monodon monoceros*) blubber). High Hg levels (0.1 to 1 µg/g) were present in halibut, in seabirds and in seals and whales. Mercury concentrations above 1 µg/g were measured in liver and kidney of seals, beluga and narwhal. Methylmercury intake by consumers of these foods was found to vary with the season. For example, individual MeHg intakes of 66 µg/d were estimated in spring and 42 µg/d in autumn for West Greenlanders. This is a high intake, and one which exceeded the European Food Safety Authority's tolerable daily intake (TDI) of 0.23 µg/ kg bw/d and the U.S. EPA Reference dose of 0.1 µg/ kg bw/d (AMAP, 2009b).

A recent study compared dietary exposure of Hg to levels in the hair of preschool children in three regions in Nunavut: Kitikmeot (northwest), Baffin (northeast) and Kivalliq (south) (Tian et al., 2011). The estimated daily total Hg intake was positively related to hair Hg levels and varied between 0 and 200 µg/d, with a mean of 16.28 µg/d. The authors also noted a regional effect, with the estimated daily intake being significantly higher for children in Baffin (mean: 22.7 µg/d) compared to Kivalliq (mean: 10. 7 µg/d) and Kitikmeot (mean: 11.8 µg/d). Almost 59% of children exceeded the provisional tolerable weekly intake (PTWI) level for children of 1.6 µg/ kg bw/wk for MeHg (WHO, 1998).

In Nunavut children, the top contributors to Hg intake from the most commonly consumed traditional/local food items were beluga *muktuk* (33%), followed by narwhal *muktuk* (26%), and ringed seal (*Phoca hispida*) liver (15%). Together with fish (11%), caribou meat (6%) and ringed seal meat (5%), these food items accounted for over 95% of the total Hg intake. Although caribou meat was the most highly consumed traditional/local food item (30% of total traditional/local foods), it ranked only fifth on the contributors list for Hg intake due to its low Hg concentration (0.03 µg/g ww). Overall, only three traditional/local food items had THg concentrations above the 0.5 µg/g ww action level established by Agriculture Canada: ringed seal liver (10.5 µg/g ww), aged narwhal *muktuk* (0.8 µg/g ww), and caribou kidney (0.5 µg/g ww). It should be noted that although the average concentration of ringed seal liver was very high, 20% to 50% of that Hg was in a less toxic and less bioavailable inorganic form (Tian et al., 2011). In their review of dietary transition and contaminants, Hansen et al. (2008) concluded that marine mammal muscle, particularly ringed seal muscle, is the main source of dietary MeHg for Greenland Inuit. Organs, such as liver and kidney, were considered to be minor sources since most of the Hg in these organs is in an inorganic form.

The example of the total dietary assessment conducted in northern Canada provides valuable information about sources of dietary Hg exposure, which can only be determined with total dietary assessments. Unfortunately this type of assessment, that includes analyses of contaminant levels, has only been carried out in Greenland and Canada. The findings of several assessments conducted over the past 10 to 15 years suggest that some populations in Greenland and some Inuit communities in Canada exceeded the TDI values set for Hg (AMAP, 2009b).

Higher concentrations of Hg in human tissues in some areas have been linked to the higher consumption of marine mammals by indigenous people in those regions as part of their traditional diet. Previous human health assessments have shown a three- to ten-fold increase in Hg concentration in Inuit women of child-bearing age that consume marine mammals, when compared to people in other populations in the Arctic, that consume store-bought foods (AMAP, 1998, 2003). Despite the changes in many Arctic communities towards a more 'western' diet, in the Inuvik region (Canada), dietary studies indicated that the participants increased their traditional/local food consumption between 1998 and 2005/06, although the amount and type varied by community and population (Armstrong et al., 2007). There was a moderate but significant correlation between food intake and Hg concentration measured in the blood of Inuit and Dene-Metis mothers in Inuvik, with the main food sources for exposure to Hg suggested to be fish and marine mammal fat (Armstrong et al., 2007). A relationship between Hg blood levels and dietary nutrients (e.g., n-3 fatty acids) from particular food species is consistent with the connection between intake of marine mammal fat, contained in a variety of tissues (e.g., liver, muscle, skin), and pollutants such as Hg. Among Greenland Inuit, Deutch et al. (2007) found a strong correlation between plasma n-3 fatty acids and blood levels of Hg which were related to the consumption of marine mammal tissues, including fats.

## 8.4. How do human tissue mercury levels compare to guidelines?

Sampling of Hg in human tissue (blood and hair) has taken place in several circumpolar countries since the early 1990s. Pregnant women have been a target population for biomonitoring of contaminants in the Arctic, because Hg can be transferred across the placental barrier and the developing fetus and children are particularly vulnerable to effects of Hg exposure. However, Inuit adults (men and women) have also been monitored in a few Arctic countries, and recently, the 2007-2008 Inuit Health Survey (www.inuithealthsurvey.ca) included a study on Hg exposure of children in Nunavut (as described in Section 8.3).

### 8.4.1. Mothers, pregnant women, and women of child-bearing age

Among mothers, pregnant women, and women of child-bearing age, exposure to Hg appears to be greatest in Inuit from the eastern Arctic regions of Canada (i.e., Nunavut and Nunavik regions) and in Greenland (Figure 8.1; AMAP, 2009b). This spatial pattern is similar to that reported in the 2002 AMAP human health assessment (AMAP, 2003), which showed that elevated blood Hg levels in these regions was associated with high consumption of marine mammals (AMAP, 1998, 2005). The more recent results support the explanation that high human Hg intake is associated with consumption of marine foods, and in particular marine mammals. Yupik maternal blood levels of Hg in the Yukon-Kushokwim River Delta Region of Alaska were only slightly lower than levels in Inuit from the Nunavut and Nunavik regions of Canada. The lowest concentrations of Hg in maternal blood were measured in areas of Russia, Sweden, and the Inuvik region of Canada.

Comparisons of human blood Hg concentrations for different time periods can be made for a number of areas around the Arctic on the basis of a limited number of repeat studies. However, these need to be interpreted with caution due to the differences in populations sampled, number of samples collected, and time periods covered for different countries. Detailed studies of temporal trends, involving frequent sampling, have only been made in the Nunavik region of Arctic Canada, and in the Disko Bay and Nuuk areas of Greenland (Figure 8.2). Studies conducted with different numbers of samples and over different time periods indicate that maternal Hg blood levels have generally decreased in almost all circumpolar regions studied since the 1990s. This includes regions of Alaska (Yukon-Kushokwim River Delta region), Arctic Canada (Inuvik, Nunavut, Nunavik regions), and northern Sweden (Wennberg et al., 2007). Much of this decrease can probably be attributed either to a switch in diet away from more contaminated traditional/local foods (in some cases possibly associated with dietary advice, such as has been given on the Faroe Islands; AMAP, 2009b) or to the nature of traditional/local food items available in a given year. In Nunavik, for example, Hg levels in blood appear to have varied markedly from year to year due to variation in the levels in the biota used as traditional/local food (Dewailly et al., 2001). In contrast, pregnant Inuit women in Greenland (Disko Bay area and Nuuk) have shown no significant decline in THg

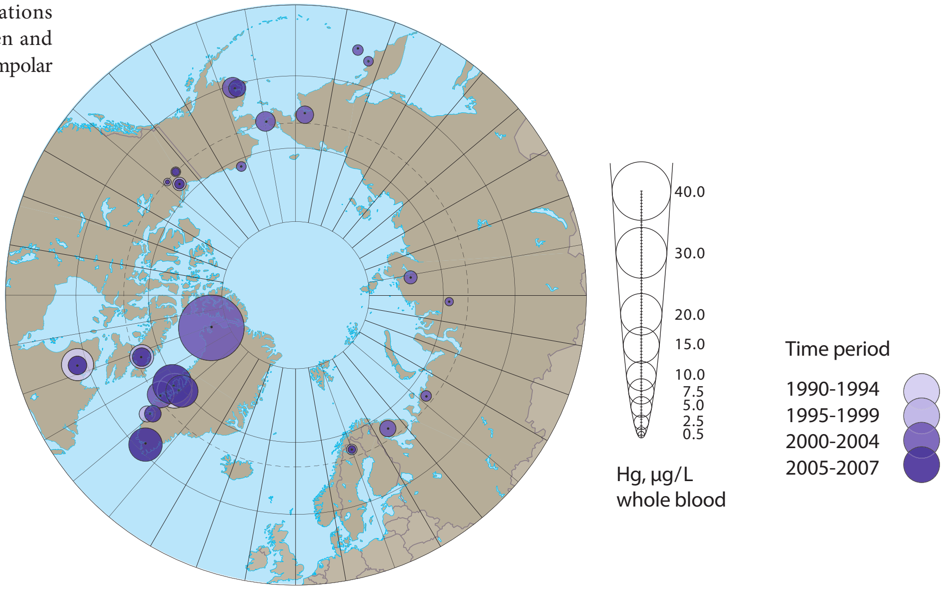

Figure 8.1. Total mercury concentrations in blood of mothers, pregnant women and women of child-bearing age in the circumpolar countries. Source: AMAP (2009b).

concentrations over a time period similar to the above studies (AMAP, 2009b).

Information on changes over time in Hg levels in potential food species is more extensive (Chapter 5) but may not necessarily reflect the trends in humans. Further monitoring and comparisons of biota and human Hg levels, especially for relevant tissues/organs and species used for food, will be useful to strengthen the understanding of the patterns currently observed.

Mercury blood guidelines have been established in Canada (Health Canada, 1984). Mercury concentrations of below 20 µg/L in human blood are considered to be within an acceptable range. Blood Hg concentrations of between 20 and 100 µg/L are classified as at 'increasing risk' and concentrations exceeding 100 µg/L in blood are classified as 'at risk'. The United States, in its re-evaluation of dietary guidelines for MeHg, applied a ten-fold safety factor to a Bench Mark Dose Level of 58 µg/L in the development of a TDI for which a reference dose of 0.1 µg/ kg bw/d was established (NRC, 2000). Consequently, it was suggested that 5.8 µg/L be used to assess risk based on blood concentrations. For comparative purposes, these guidelines and values were used in the AMAP 2009 human health assessment to interpret human contaminant data for all circumpolar countries (AMAP, 2009b).

Figure 8.3 indicates the proportion of mothers and women of child-bearing age that exceed the Canadian blood Hg guideline of 20 µg/L, and the more conservative U.S. guideline of 5.8 µg/L. Regions of Greenland and northern Canada had the highest proportion of mothers and women of child-bearing age exceeding the blood Hg values. Recent biomonitoring studies showed that the proportion of Inuit mothers exceeding both the Health Canada and U.S. guidelines has decreased from earlier studies (Figure 8.3). For example, between 1992 and 1999, 52% to 76% of Inuit mothers and women of child-bearing age from Nunavik, Canada, exceeded the U.S. guideline, compared to 31% to 61% between 2000 and 2007. Similarly, 68% of Inuit mothers from Nunavut, Canada, exceeded the U.S. guideline in 1997, compared to 32% between 2005 and 2007 (AMAP, 2009b).

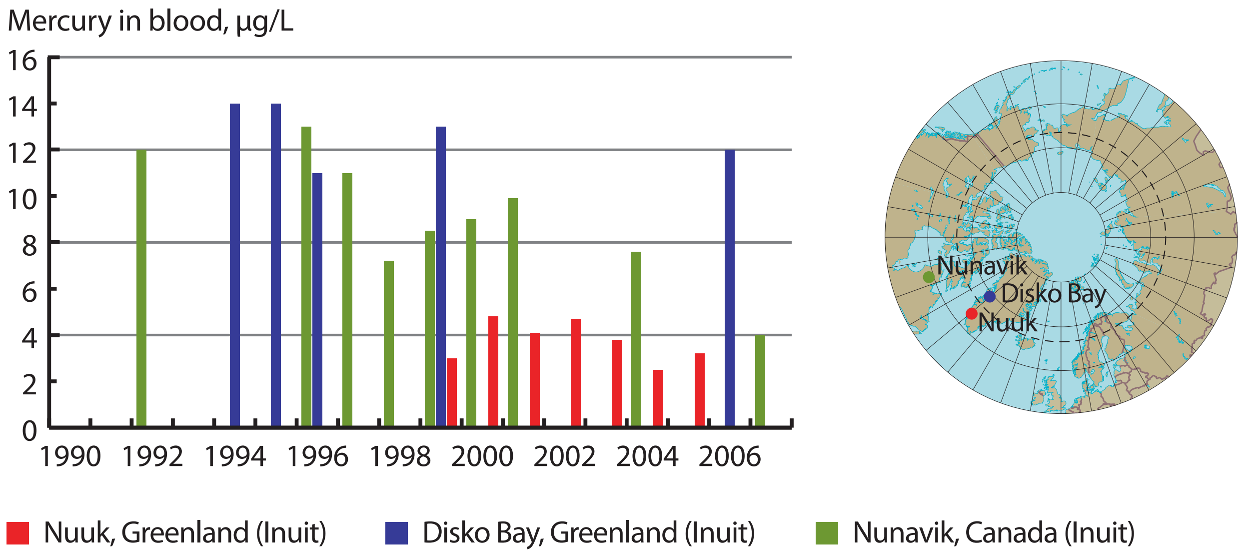

Figure 8.2. Temporal trends of mercury in maternal blood samples from Nunavik, Canada, and Disko Bay and Nuuk, Greenland. Source: AMAP (2009b).

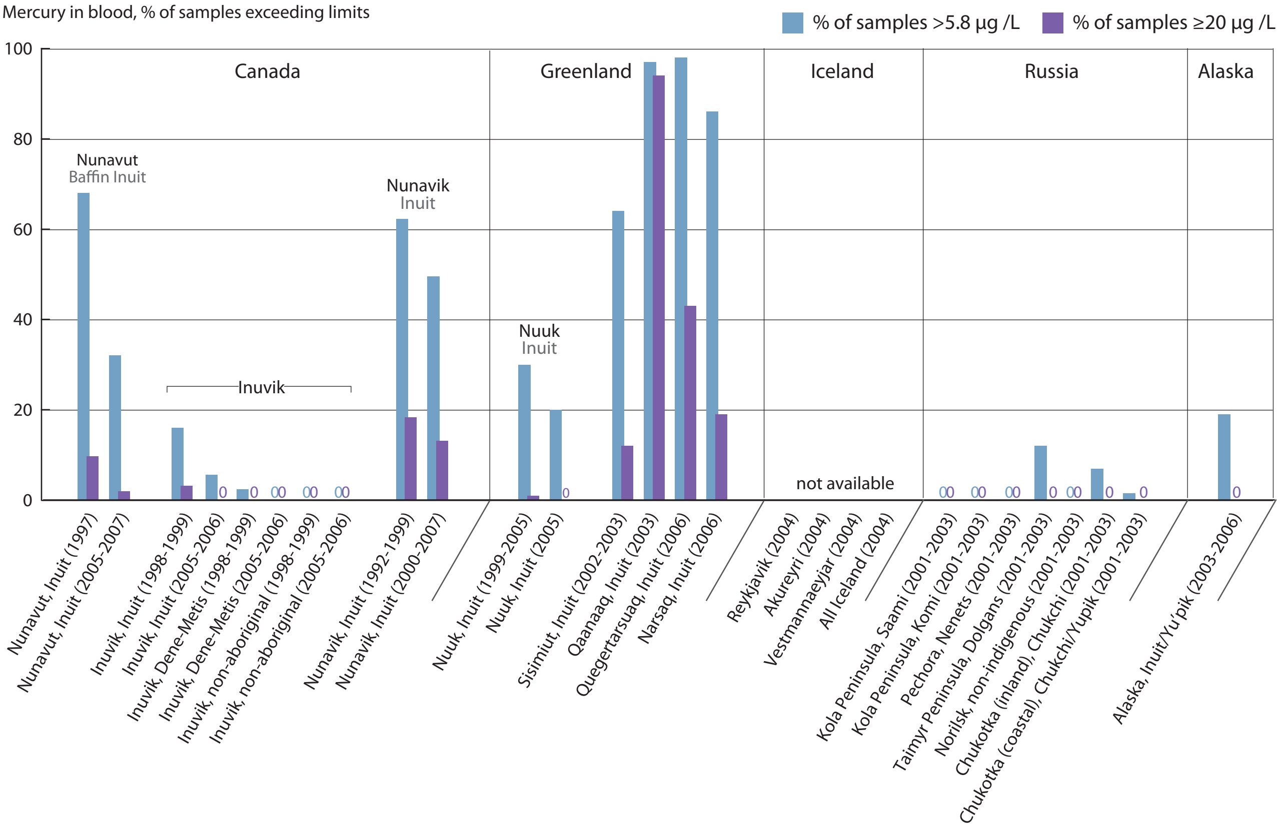

Figure 8.3. Exceedance of blood guideline values for (total) mercury in mothers and women of child-bearing age in different populations around the Arctic (comparable data not available from Norway, Sweden and Finland). Source: AMAP (2009b).

As expected, a smaller proportion of mothers and women of child-bearing age exceeded the higher Canadian guideline.

Following the successful implementation of a dietary intervention in the Faroe Islands that was aimed at reducing consumption of pilot whale meat, in 2007/09 only 0.6% of cord blood samples (n=500) exceeded 20 µg/L of mercury and 12.6% exceeded 5.8 µg/L. This represents a dramatic improvement compared to the 39.2% and 93.3% of samples (n=995) that exceeded the respective guidelines in 1986/87 (Pal Weihe, unpublished data).

Although the results of these analyses suggested declining Hg concentrations in a number of indigenous communities, significant percentages of women in recent years still exceeded guideline values in some parts of the Arctic, particularly in Greenland where some of the highest blood Hg concentrations have been found.

### 8.4.2. Adults (men and women)

Blood Hg levels have been monitored in Inuit adults (men and women) in Nunavik (Canada) and regions of Russia, as well as in Inuit men in regions of Greenland. The 2009 AMAP human health assessment (AMAP, 2009b) considered adult women in Greenland as women of child-bearing age (ages 20 to 50); as a result these were discussed in Section 8.4.1. In general, Hg concentrations are higher among men in Greenland than in men and women in Nunavik and regions of Russia. Blood Hg concentrations significantly decreased in adult Inuit men and women from Nunavik, Canada, between 1992 and 2004 despite several indications of increases in biota (Dewailly et al., 2007a,b; see also Chapter 5).

### 8.4.3. Children

The geometric mean concentration of THg in hair for Inuit children in Nunavut was 0.66 µg/g and no differences were found to exist between different ages or genders (Tian et al., 2011). However, statistically significant differences were observed between the three regions studied. Children in Baffin had higher hair Hg levels (1.14 µg/g) than children in Kivalliq (0.52 µg/g) or Kitikmeot (0.31 µg/g) (Tian et al., 2011). Based on the reference value for Hg in hair established by the World Health Organization of 2 µg/g (WHO, 1990), the study found that 25% of children had Hg levels that exceeded the guideline. When broken down by region, 39% of the children in Baffin exceeded the guideline, which was more than twice the percentage for Kivalliq (19%) and almost fourteen times higher than for Kitikmeot (2.9%).

## 8.5. What are the health effects of mercury in humans?

The presence of Hg and other contaminants in the Arctic environment can have many impacts on human health. As discussed, the perception and knowledge of potential risks associated with contaminants can turn people away from traditional/local foods, even when they represent the most healthy food choice. This can lead, among other things, to a degradation of cultural identity, economic stress arising from the high cost of healthy store-bought foods, and potential nutritional deficits arising from the consumption of poor quality store-bought foods. There are also toxicological risks associated with Hg in country foods. The following section provides a brief synopsis of the potential effects that Hg can have on human health and concludes with a summary of epidemiological studies that have been carried out on populations that are, or have been, chronically exposed to Hg through their diet.

### 8.5.1. Mercury toxicity

The 2002 AMAP human health assessment gave a detailed summary of the potential toxic effects that Hg can have on human biological systems (AMAP, 2003). These include effects on the reproductive, immune, and neurological systems by several modes of action. More recently, the 2009 AMAP human health assessment suggested that Hg can also have adverse effects on the cardiovascular system (AMAP, 2009b). Chapter 6 of this assessment provides a detailed assessment of Hg toxicity and effects in Arctic wildlife. In its review of various Hg toxicity studies, Chapter 6 provides further detail on the modes of toxicity that Hg and MeHg exhibit in Arctic biota (mammals, birds and fish).

The primary Hg exposure pathway for Arctic residents is through consumption of fish and marine mammals. Even though Hg is consumed in both inorganic and organic (methylated) forms, human health risks arising from this exposure are thought to be associated with MeHg only. Inorganic forms of Hg found in fish and mammal tissues are much less bioavailable and therefore do not bioaccumulate in humans. Exposure to inorganic Hg, particularly high doses of elemental Hg, can have adverse health effects, but these are mostly restricted to cases of occupational exposure and are not discussed in this chapter.

High concentrations of dietary MeHg exposure are suspected to have a negative effect on birth weight. In a study of Greenlanders that examined associations between smoking, birth weight and contaminant exposure, only a weak association between lower birth weight and Hg was found in West Greenlanders, while none was identified in East Greenlanders. Smoking on the other hand was strongly associated with low birth weights. The study results suggested that nutritional factors, primarily high levels of n-3 fatty acids, associated with marine mammal consumption may have had a protective effect (AMAP, 2003).

Methylmercury exposure can also have an effect on immune function by altering the relative abundance of TH-lymphocytes, which play a role in determining an individual's immune responsiveness. This is primarily described by the relative abundance of Th1- and Th2-lymphocytes, of which Th1-lymphocytes are typically dominant in individuals with normal immune function. Cases where Th2-lymphocytes are dominant are associated with hyper-immunity which leads to such afflictions as asthma, skin rashes and auto-immunity. Mercury, both in organic and inorganic forms, has also been shown to have cytotoxic activities for cellular components of the immune system in several species of rodent. This type of toxicity can alter non-specific cellular defense mechanisms, decrease activation markers of T-cells, and affect the functions of B-cells, resulting in reduced humoral mediated response. Finally Hg exposure has been shown to impair host resistance to bacterial and viral infections in laboratory animals (AMAP, 2003).

A number of neurological effects of MeHg exposure have been documented in the literature and in epidemiological studies looking at fetal and neonatal development. These findings are discussed along with other epidemiological studies towards the end of this section. Neurological effects of Hg in wildlife are discussed in Section 6.3.1. It is well established that MeHg is a potent neurotoxin that can cause irreparable damage to the central nervous system. While the biological mechanisms responsible for this damage are not well understood, oxidative stress is suspected to be a significant contributor. There are likely to be several mechanisms by which MeHg may cause damage by oxidative stress (AMAP, 2009b). Methylmercury can promote the formation of hydrogen peroxide and enhance subsequent production of lipid peroxides and reactive hydroxyl radicals, which can then alter membrane structure or disrupt mitochondrial function. The increase of reactive oxygen species takes place via deregulation of mitochondrial electron transport as well as through glutathione depletion (AMAP, 2003). Methylmercury also has an inhibitory effect on antioxidant processes by binding to relevant enzymes such as free-radical-quenching enzymes, or it can influence the intracellular oxygen status by binding to glutathione. The notion of Hg-induced oxidative stress is supported by findings that MeHg neurotoxicity can be inhibited by various antioxidants including selenium (Se) and N-acetyl-L-cysteine, a precursor of glutathione. Methylmercury exposure may diminish defense mechanisms against oxidative stress by limiting the availability of glutathione, while Se may afford protection by favoring the destruction of hydrogen peroxide (AMAP, 2003 2009b). Section 6.2.2.2 provides a detailed discussion of Se–Hg interactions in wildlife, including some of the inhibitory effects that Se seems to have on MeHg toxicity.

One of the main recommendations arising from the 2002 AMAP human health assessment was the need to assess the toxicity of Arctic contaminants as a group, and not as single chemical toxicants (AMAP, 2003). In the intervening years, some progress has been made through laboratory studies toward understanding how the contaminant mixture affects biological systems. In doing so, the toxicological study of Arctic contaminants has been better able to reproduce the contaminant exposure experienced by northern populations. In these studies, the effects of MeHg along with other persistent organic pollutants (POPs) and heavy metals have been examined under various exposure scenarios to assess their combined toxicological effects.

The 2009 AMAP human health assessment reports on a study conducted by Health Canada that looked at effects of a specific contaminant mixture (including POPs and MeHg) on reproduction and development in rats (AMAP, 2009b). The mixture was designed to produce, in rat dams, a similar contaminant profile to that found in the maternal blood of Inuit. Rats in the high-dose group experienced several adverse effects including: decreases in maternal weight gain during lactation and in offspring weight gain that persisted into adulthood; increased mortality rates in pups prior to weaning (interestingly, it was noted that overall mortality rates for the offspring in this study were considerably lower than those reported by others using lower doses of only MeHg); changes in organ weight, and biochemical and histopathological changes in liver (see also Section 6.3.2.1), thyroid, and spleen; decrease of pre-weaning neuromuscular development (grip strength) and hyperactivity at post natal day (PND) 16 which did not persist through PND 48; affected learning and memory in adults; and dose-dependent changes in brain dopamine and serotonin levels at PND 35 in high-dose group pups. The only effect seen in all dose groups was an indication of either altered motor performance or decreased reactivity to a novel environment. Preliminary results from the study also indicated that each of the dose groups induced some measured changes in offspring bone development. Blood Hg concentrations measured in the lowest dose group were comparable to blood concentrations measured in humans living in the Canadian Arctic (AMAP, 2009b), whereas the high-dose group had blood concentrations that were 100 times higher.

A second series of mixture studies conducted by Health Canada researchers examined the potential impact of individual components of the chemical mixture (Hg, PCBs and organochlorine pesticides). Comparisons of the toxicity of the full mixture against specific components of the mixture indicated that the increase in pup mortality induced by the full mixture could be attributed to the MeHg component, although the interactions with the POP mixture warrants further investigation owing to the apparent improved survival rates observed with the mixture. The researchers also examined expressions of genes involved in cerebellum nerve cell functions and found that the full mixture produced minimal changes in gene expression, whereas individually, PCB, MeHg and the organochlorine pesticide components all altered the expression of a number of genes, pointing to another area for further research (see also Section 6.3.4). Effects on learning and memory were apparently elicited primarily by MeHg and PCBs and appeared to be additive. The findings of these studies using the rat model supported observations reported in some epidemiological studies of infants and children (AMAP, 2009b).

### 8.5.2. Epidemiological studies

The effects of high level pre-natal exposure to MeHg are fairly well known from publicized cases in Japan and Iraq where children born to accidentally exposed women displayed a range of symptoms including mental retardation, severe sensory impairment, seizures and general paralysis (AMAP, 2003). Since the 1970s, growth and developmental effects of pre-natal MeHg exposure have been studied in nine large birth-cohort and retrospective studies around the world. Additionally, three well designed, prospective, longitudinal studies of children have examined neurobehavioral effects related to Hg exposure in the Faroe Islands, New Zealand and the Seychelles (INAC, 2009). Other cohort studies have been conducted in Michigan, Madeira, Brazil, French Guyana, Philippines, Greenland, and in Cree and Inuit from northern Quebec. In each of these studies the source of MeHg was from the consumption of fish and marine foods (mainly fish, but also marine mammals in the Faroe Islands and Inuit regions such as Greenland and northern Quebec).

Most of these studies looked for associations between Hg exposure and various endpoints assessed at birth. There were no conclusive results indicating a Hg-associated decrease in birth weight; however, in the Faroe Islands, a doubling of cord-blood Hg was associated with lower infant weight at 18 months and persisted to 42 months of age. In the Philippines, where MeHg exposure was two times higher than in the Faroe Islands, there was no association between MeHg and birth weight, but there was an association between MeHg and smaller head circumference at birth. In Michigan, where Hg exposure was half that of the Seychelles cohort, exposure to Hg was related to an increased incidence of pre-term deliveries (less than 35 weeks) (INAC, 2009).

The Faroe Islands study revealed several associations between Hg exposure and neurobehavioral outcomes, including a decreased neurological optimality score in newborns; decreased performance in domains of language, attention, and memory; and decreased auditory and visual brain processing in seven-year olds, which persisted at 14 years of age (INAC, 2009). Similar associations were observed at six to seven years of age in children from New Zealand. In the Seychelles, however, similar endpoints of neurodevelopment revealed no associations with pre-natal MeHg exposure. It was proposed that MeHg toxicity observed in the Faroe Islands cohort might have been potentiated by simultaneous PCB exposure, which was about three to four times higher than in other cohorts. When the results of all the cohorts were looked at in greater detail it was proposed that differences in maternal diet during pregnancy may have an impact on fetal susceptibility to MeHg exposure and that potential neurobehavioral effects of MeHg exposure could be found in the domains of verbal function, visio-motor integration and attention. Another commonly reported effect of pre-natal MeHg exposure has been the latency of brainstem auditory-evoked potentials, a measure of auditory processing. Cohort studies in the Faroe Islands, Spain, and Greenland each reported associations between latencies and MeHg exposure (INAC, 2009).

Some studies summarized by Yokoo et al. (2003) reported neurobehavioral symptoms of low-level MeHg exposure in adults, including vision (chromatic discrimination, contrast sensitivity, peripheral fields) and psychomotor functions (tremor, dexterity, grip strength, complex movement sequences, hand-eye coordination, rapid alternating movement). Among Brazilian adults living in fishing communities of the Pantanal region, they found that hair Hg levels (between 0.56 and 13.6 μg/g) were associated with alterations of fine motor speed, dexterity and concentration. Further effects were related to disruptions of verbal learning and memory. All of the observed effects increased with hair Hg concentration.

One of the more commonly reported effects of chronic low level dietary exposure to MeHg in adults is an increased risk of cardiovascular effects. The 2009 AMAP human health assessment discussed this subject in the context of Arctic populations (AMAP, 2009b), while another review by Mozaffarian (2009) gave further details with a particular focus on risks and benefits of fish consumption for cardiovascular health. Both reviews cover a Finnish study that found the risk of coronary heart disease in men who consumed freshwater fish to be significantly associated with Hg concentrations in hair. Mercury has been found to promote lipid peroxidation resulting in the formation of low-density lipoproteins which have been implicated as initiators of arteriosclerosis.

Previous observations in the same population also associated increased risk of death from coronary heart disease to low serum concentrations of Se, an antioxidant that can block the Hg-induced lipid peroxidation process. Like the Finnish men, Inuit consume high concentrations of MeHg in fish and marine mammals, yet mortality from coronary heart disease is extremely low. It is possible that Inuit are protected by the high levels of Se and polyunsaturated fatty acids that are also contained in the marine foods. The Faroe Islands cohort study examined potential associations between pre-natal Hg exposure and cardiovascular development. The study showed that pre-natal Hg exposure was associated with increased blood pressure and reduced heart rate variability in seven-year old children (AMAP, 2003). A follow-up study at age 14 showed that these effects were still present, although significantly less severe. The interactions between nutrients (mainly Se and n-3 polyunsaturated fatty acids), MeHg and cardiac effects were examined in the Inuit Health Survey of Nunavik, Quebec. The study looked at the activity of Paraoxonase 1 (PON1), an enzyme thought to play a role in cardiovascular disease by metabolizing toxic oxidized lipids associated with low density lipoprotein (LDL) and HDL. Preliminary results suggest that MeHg exposure may have a slight inhibitory effect on PON1 activity which seems to be offset by Se intake. Further investigation is underway to look at other markers of cardiovascular disease, such as relation between PON1 activity, the concentration of oxidized LDL and the thickness of the carotid artery *intima media*, the latter being a biomarker of atherosclerosis (AMAP, 2009b). It is thought that cardiovascular effects associated with low level Hg exposure may be of even greater public health significance compared to some other end points such as neurotoxicity.

## 8.6. What are the risk communication / risk management strategies used to address dietary mercury exposure in the Arctic?

Most risk communication in the Arctic regarding contaminants involves messages about contaminants in general, or groups of contaminants (e.g., POPs). This may be because it is difficult to separate the health effects of isolated contaminants, given differences in contaminant toxicity through mixtures or contaminant-nutrient interactions. That said, risk communication specifically related to Hg is most prominent in the Faroe Islands. Biomonitoring and epidemiological studies have driven efforts to reduce Hg exposure of the Faroese for about three decades. When effects of pre-natal exposure to Hg were observed in children, health authorities focused their attention on reducing exposure to Hg in the meat of pilot whales, the main source of exposure (Weihe et al., 2003). Risk communication focused on the adverse impacts of Hg and POPs and how to avoid these contaminants, while providing information about healthy dietary alternatives. Risk communication in the Faroe Islands has resulted in a marked dietary change, with reduced amounts of pilot whale meat and blubber now present in the diet, particularly among pregnant women (Budtz-Jørgensen et al., 2007). Much of the success has been attributed to the simplicity of communicating about the risks of Hg contamination when it is related to a single species, the pilot whale, as well as easy access to unpolluted fish alternatives from the ocean.

Risk communication in other regions of the Arctic (e.g., Arctic Canada and Russia) provides advice on contaminants in general. This advice is less prescriptive and emphasizes food choices with lower contaminant levels, while emphasizing that the benefits of eating nutritious traditional/local foods outweigh the risks due to contamination. Further understanding of the contaminant levels in indigenous peoples, health effects from contaminants in the diet, and the most effective risk communication schemes will help mitigate the effects of contamination from global and dietary influences, and will reduce the need for indigenous people to have to choose between nutritious traditional/local foods and store-bought foods which bring other health risks.

## 8.7. Conclusions and recommendations

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

### What are the global influences on mercury exposure in northern peoples?

1. The accumulation of anthropogenically emitted Hg from global sources in Arctic ecosystems has resulted in elevated levels of Hg in fish and wildlife that represent an important part of the diet of northern peoples. Global climate change is also resulting in increased levels of Hg in Arctic biota and thereby contributing to higher levels of dietary exposure.

*Monitoring is urgently needed to ensure early detection of climate-induced human health threats related to contaminants. Essential monitoring elements include contaminant levels in humans and wildlife food species, zoonotic diseases in wildlife, and observations of environmental parameters such as water quality, ice, permafrost, and weather.*

*Improved predictive models of contaminant transport and behavior in the Arctic are needed to understand the likely impacts of climate change with respect to contaminants. The models require improved comprehensive circumpolar monitoring of environmental matrices integrated with weather and climate data.*

*A global agreement to control Hg emissions should be pursued to complement national and regional efforts to reduce environmental Hg concentrations and to lower human exposure to Hg in the Arctic.*

### What are the dietary influences on mercury exposure?

2. The dominant sources of dietary Hg exposure are from consumption of marine mammal tissues and fish. The highest levels of dietary exposure occur among Inuit communities that regularly consume the tissues of marine mammals. These same foods that contribute to Hg exposure also represent a valuable source of essential nutrients, like polyunsaturated fatty acids, and also represent immeasurable social and cultural value to communities.

3. Transition to a more commercially-based diet and difficulty in obtaining traditional/local foods, combined with the prevalent condition of food insecurity in some communities all have the potential to lower dietary exposure to Hg, but these changes may come at serious nutritional cost and associated health risk.

*More research about determinants of food choices and availability is needed to provide better dietary advice relevant to local conditions and preferences. This research should focus on differences by age and gender.*

*Because consumption of imported food is likely to continue increasing in most of the Arctic, health authorities should work vigorously with local and national food agencies to promote the availability and consumption of imported food items with high nutritional value.*

*To maximize the benefits of traditional/local food use and reduce the risks associated with the intake of contaminants in some traditional/local foods (e.g., certain marine mammals), health authorities should promote improved access to and consumption of local traditional/local foods such as fish and terrestrial mammals that have lower levels of POPs and metals and high nutrient value.*

*Studies should combine human biomonitoring of contaminants with total diet studies in the Arctic in order to produce better exposure estimates and better dietary advice.*

### How do human tissue mercury levels compare to guidelines?

4. A significant proportion of people from communities in the eastern Canadian Arctic and Greenland still exceed U.S. and Canadian tissue Hg guidelines. In some populations, however, an overall decline has been noted in the proportion of Arctic people that exceed these guidelines. It is tempting to suggest that lower levels of Hg in the environment, brought about through regional action to reduce Hg emissions, is responsible for the decline; however, the temporal trends in biota discussed in Chapter 5 do not support this explanation. It is more plausible that changes in diet through 'nutritional transition' and/or risk management and communication with regard to Hg and other contaminants in the environment are the likely causes.

*Continued monitoring of legacy POPs, Hg, and lead in humans and traditional/local foods is needed to obtain valid exposure trends and to track the effectiveness of national, regional, and international action to reduce releases.*

*Because the exposure level to MeHg continues to be high in some Arctic populations, continued monitoring of temporal trends is warranted.*

### What are the health effects of mercury in humans?

5. It has been shown that exposure to Hg at the current levels in the Arctic can have adverse impacts on human health, particularly for the developing fetus and children, although further research is required to determine if the subtle effects of Hg on human health are persistent.

*Further research is needed on the relationship between Hg and cardiovascular disease in Arctic populations. Contaminant-nutrient interactions should be further investigated in prospective Arctic cohort studies.*

### What are the risk communication / risk management strategies used to address dietary mercury exposure in the Arctic?

6. Risk communication strategies vary between different regions of the Arctic and must be tailored to meet the specific needs of the target population and should contain balanced messages regarding contaminant risks and dietary nutrition. In the case of the Faroe Islands, consumption advisories directed specifically at reducing the consumption of pilot whale have been successful in reducing Hg exposure among pregnant women. In Arctic Canada, dietary advice related to contaminants in general has promoted consumption of a varied traditional diet with further promotion of nutritious species known to be low in contaminants, particularly for women of child-bearing age.

*Regional health authorities should collaborate with communities to develop effective, culturally appropriate communication strategies concerning contaminants and human health. Communication efforts should be evaluated with respect to their impacts on the intended audience.*

*Dietary advice to Arctic residents should include both the benefits of traditional/local food consumption and the results of technical risk assessments concerning contaminants.*

*Risk perception, dietary patterns, and determinants of food choice should be taken into account in the development of communication materials.*

*AMAP should improve the distribution and availability of its reports and information to the general public, health authorities, and scientists in or working in the Arctic. Possible steps include greater prominence on internet search engines and an increased presence at meetings and conferences.*

### Further general recommendations from the 2009 AMAP human health assessment (AMAP, 2009b):

*The human health assessment process initiated through AMAP should be continued with the aim of pursuing a more holistic health impact assessment of the influences of environmental pollution on the health of Arctic peoples and the associated risk factors affecting them. This effort should be coordinated with related public health work initiated through the Sustainable Development Working Group.*

*Considering the importance of general health and the influence of changing diets and contaminants on disease outcomes, more effort needs to be made to systematically collect, analyze, and report on the health status of Arctic populations and especially indigenous peoples.*

*It is very important to maintain and expand current human population cohorts in the Arctic as identified in this assessment, such as those in Canada, Greenland, and the Faroe Islands. Only long-term prospective studies will provide the information needed to track adverse health outcomes associated with contaminants and changing conditions related to climate change, socio-cultural conditions, and diet.*

*Uniform reporting of key health status indicators should occur every three to five years, should include trend information, should* *be broken down by age and gender, and should be provided by all circumpolar jurisdictions at appropriate regional levels.*

*Because genotype may influence responses to contaminants, more knowledge about genetic variability and susceptibility among Arctic peoples is needed. Including genetics in studies that examine lifestyle and contaminant interactions will provide better insight into individual and population vulnerability to contaminants.*

*Public health officials should continue to recommend breast feeding among Arctic populations as a healthy practice which optimizes infant growth and development. However, there is a need to reduce contaminant levels in breast milk through national, regional, and international action to reduce pollution and through relevant food advice to women of child-bearing age.*

# References

Abdalati, W. and K. Steffen, 2001. Greenland ice sheet melt extent: 1979-1999. Journal of Geophysical Research, 106:33983-33988.

ACIA, 2005. Arctic Climate Impact Assessment. 1042 pp. Cambridge University Press.

Adams, J.W., N.S. Holmes and J.N. Crowley, 2002. Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces between 253 and 233 K. Atmospheric Chemistry and Physics, 2:79-91.

AEPS, 1991. Ministerial Declaration on the Protection of the Arctic Environment. First Arctic Ministerial Meeting. 42 pp. Arctic Environmental Protection Strategy, Rovaniemi, Finland.

Afonne, O.J., O.E. Orisakwe, E. Obi, C.E. Dioka and G.I. Ndubuka, 2002. Nephrotoxic actions of low-dose mercury in mice: Protection by zinc. Archives of Environmental Health, 57:98-102.

Allen, E.W., E.E. Prepas, S. Gabos, W.M.J. Strachan and W. Zhang, 2005. Methyl mercury concentrations in macroinvertebrates and fish from burned and undisturbed lakes on the Boreal Plain. Canadian Journal of Fisheries and Aquatic Science, 62:1963-1977.

AMAP, 1997. Arctic Pollution Issues: A State of the Arctic Environment Report. xii+188 pp. Arctic Monitoring and Assessment Programme.

AMAP, 1998. AMAP Assessment Report: Arctic Pollution Issues. xii+859 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2000. Issues of Concern: Updated Information on Human Health, Persistent Organic Pollutants, Radioactivity, and Mercury in the Arctic. 69 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2002. Arctic Pollution 2002: Persistent Organic Pollutants, Heavy Metals, Radioactivity, Human Health, Changing Pathways. 112 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2003. AMAP Assessment 2002: Human Health in the Arctic. xiii+137 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2004. Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian North. Final Report. Arctic Monitoring and Assessment Programme, Oslo, Norway.

AMAP, 2005. AMAP Assessment 2002: Heavy Metals in the Arctic. xvi+265 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2007. Report of the AMAP Workshop on Statistical Analysis of Temporal Trends of Mercury in Biota, Stockholm, 30 October – 2 November 2006. Arctic Monitoring and Assessment Programme.

AMAP, 2009a. The Greenland Ice Sheet in a Changing Climate: Snow, Water, Ice and Permafrost in the Arctic (SWIPA). The Greenland Ice Sheet in a Changing Climate: Snow, Water, Ice and Permafrost in the Arctic (SWIPA). By: Dahl-Jensen, D., J. Bamber, C.E. Bøggild, E. Buch, J.H. Christensen, K. Dethloff, M. Fahnestock, S. Marshall, M. Rosing, K. Steffen, R.Thomas, M. Truffer, M. van den Broeke and C.J. van der Veen. 115 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2009b. AMAP Assessment 2009: Human Health in the Arctic. 254 pp. Arctic Monitoring and Assessment Programme.

AMAP, 2010. Updating Historical Global Inventories of Anthropogenic Mercury Emissions to Air. AMAP Technical Report No. 3. Arctic Monitoring and Assessment Programme.

AMAP/UNEP, 2008. Technical Background Report to the Global Atmospheric Mercury Assessment. 159 pp. Arctic Monitoring and Assessment Programme / UNEP Chemicals Branch.

Amato, P., R. Hennebelle, O. Magand, M. Sancelme, A.-M. Delort, C. Barbante, C. Boutron and C. Ferrari, 2007. Bacterial characterization of the snow cover at Spitzberg, Svalbard. FEMS Microbiological Ecology, 59:255-264.

Amyot, M., D. Lean and G. Mierle, 1997. Photochemical formation of volatile mercury in high Arctic lakes. Environmental Toxicology and Chemistry, 16:2054-2063.

Amyot, M., J.D. Lalonde, P.A. Ariya and A. Dastoor, 2003. Behavior of mercury in snow from different latitudes. Journal de Physique IV, 107:45-48.

Anderson, L.G., K. Olsson, E.P. Jones, M. Chierici and A. Fransson, 1998. Anthropogenic carbon dioxide in the Arctic Ocean: Inventory and sinks. Journal of Geophysical Research, 103:27707-27716.

Andersson, M.E., J. Sommar, K. Gardfeldt and O. Lindqvist, 2008. Enhanced concentrations of dissolved gaseous mercury in the surface waters of the Arctic Ocean. Marine Chemistry, 110:190-194.

Appelquist, H., S. Asbirk and I. Drabaek, 1984. Mercury monitoring – mercury stability in bird feathers. Marine Pollution Bulletin, 15:22-24.

Arai, T., T. Ikemoto, A. Hokura, Y. Terada, T. Kunito, S. Tanabe and I. Nakai, 2004. Chemical forms of mercury and cadmium accumulated in marine mammals and seabirds as determined by XAFS analysis. Environmental Science and Technology, 38:6468-6474.

Arctic Council, 2000. Barrow Declaration, on the occasion of the Second Ministerial Meeting of the Arctic Council. (http://Arctic-council.org/filearchive/barrow%20-%20english.pdf – accessed 24 August 2009).

Arctic Council, 2006. Salkhard Declaration, on the occasion of the tenth Anniversary of the Arctic Council. (http://arctic-council.org/filearchive/SALEKHARD_AC_DECLARATION_2006.pdf – accessed 17 September 2010).

Arctic Council, 2009. Tromsø Declaration, on the occasion of the sixth Ministerial Meeting of the Arctic Council. (http://arctic-council.org/workarea/agenda_tromso_meeting_april_2009/filearchive/final_draft_declaration_28_apr_09_a4.pdf – accessed 17 September 2010).

Ariya, P.A. and K. Peterson, 2005. Chemical transformation of gaseous elemental Hg in the atmosphere. In: Pirrone, N. and K.R. Mahaffey (Eds.). Dynamics of Mercury Pollution on Regional and Global Scales, pp. 261-294, Springer.

Ariya, P.A., A. Khalizov and A. Gidas, 2002. Reactions of gaseous mercury with atomic and molecular halogens: Kinetics, product studies, and atmospheric implications. Journal of Physical Chemistry A, 106:7310-7320.

Ariya, P.A., A.P. Dastoor, M. Amyot, W.H. Schroeder, L.A. Barrie, K. Anlauf, F. Raofie, A. Ryszkov, D. Davignon, J. Lalonde and A. Steffen, 2004. The Arctic: A sink for mercury. Tellus B, 56:397-403.

Ariya, P.A., H. Skov, M.M.L. Grage and M.E. Goodsite, 2008. Gaseous elemental mercury in the ambient atmosphere: Review of the application of theoretical calculations and experimental studies for determination of reaction coefficients and mechanisms with halogens and other reactants. Advances in Quantum Chemistry, 55:43-55.

Armstrong, B., K. Tofflemire, E. Myles, O. Receveur and L. Chan, 2007. Monitoring Temporal Trends of Human Environmental Contaminants in the NWT Study. 94 pp. Department of Health and Social Services, Government of Northwest Territories.

Aschner, M. and J.L. Aschner, 1990. Mercury neurotoxicity – mechanisms of blood-brain barrier transport. Neuroscience and Biobehavioral Reviews, 14:169-176.

Aspmo, K., C. Temme, T. Berg, C. Ferrari, P.A. Gauchard, X. Fain and G. Wibetoe, 2006. Mercury in the atmosphere, snow and melt water ponds in the North Atlantic Ocean during Arctic summer. Environmental Science and Technology, 40:4083-4089.

ATSDR, 1999. Toxicological Profile for Mercury. 617 pp. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services.

Atwell, L., K.A. Hobson and H.E. Welch, 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. Canadian Journal of Fisheries and Aquatic Sciences, 55:1114-1121.

Auel, H. and W. Hagen, 2002. Mesozooplankton community structure, abundance and biomass in the central Arctic Ocean. Marine Biology, 140:1013-1021.

Babaluk, J.A., 1999. Selected chemical analyses of water from lakes in Ellesmere Island national park reserve, Nunavut. Report No. 0706-6465. Department of Fisheries and Oceans, Central and Arctic Region, Winnipeg, Canada.

Babaluk, J.A., N.M. Halden, J.D. Reist, A.H. Kristofferson, J.L. Campbell and W.J. Teesdale, 1997. Evidence for non-anadromous behaviour of arctic charr (*Salvelinus alpinus*) from Lake Hazen, Ellesmere Island, northwest Territories, Canada, based on scanning proton microprobe analysis of otolith strontium distribution. Arctic, 50:224-233.

Babaluk, J.A., N. Gantner, W. Michaud, D.C.G. Muir, M. Power, J.D. Reist, R. Sinnatamby and X. Wang, 2009. Chemical analyses of water from lakes and streams in Quttinirpaaq National Park, Nunavut 2001-2008. Canadian Data Report of Fisheries and Aquatic Sciences, 1217, v + 24 p.

Bada, J.L., R.O. Peterson, A. Schimmelmann and R.E.M. Hedges, 1990. Moose teeth as monitors of environmental isotopic parameters. Oecologia, 82:102-106.

Badzinski, S.S., P.L. Flint, K.B. Gorman and S.A. Petrie, 2009. Relationships between hepatic trace element concentrations, reproductive status, and body condition of female greater scaup. Environmental Pollution, 157:1886-1893.

Baeyens, W., M. Leermakers, T. Papina, A. Saprykin, N. Brion, J. Noyen, M. De Gieter and L. Goeyens, 2003. Bioconcentration and biomagnification of mercury and methylmercury in North Sea and Scheldt Estuary fish. Archives of Environmental Contamination and Toxicology, 45:498-508.

Bahr, D.B., M. Dyurgerov and M.F. Meier, 2009. Sea-level rise from glaciers and ice caps: A lower bound. Geophysical Research Letters, 36:L03501.

Baird, P.H., 1994. Black-legged Kittiwake (*Rissa tridactyla*). In: Poole, A. and F. Gill (Eds.). Birds of North America, No. 92. Academy of Natural Sciences, Philadelphia, and The American Ornithologists' Union, Washington D.C.

Bales, R.C., R.E. Davis and D.A. Stanley, 1989. Ion elution through shallow homogeneous snow. Water Resources Research, 25:1869-1877.

Balogh, S.J., Y.B. Huang, H.J. Offerman, M.L. Meyer and D.K. Johnson, 2002. Episodes of elevated methylmercury concentrations in prairie streams. Environmental Science and Technology, 36:1665-1670.

Balogh, S.J., Y.H. Nollet and E.B. Swain, 2004. Redox chemistry in Minnesota streams during episodes of increased methylmercury discharge. Environmental Science and Technology, 38:4921-4927.

Banerjee, S. and S. Bhattacharya, 1994. Histopathology of kidney of *Channa punctatus* exposed to chronic nonlethal level of Elsan, mercury, and ammonia. Ecotoxicology and Environmental Safety, 29:265-275.

Banic, C.M., S.T. Beauchamp, R.J. Tordon, W.H. Schroder, A. Steffen, K.A. Anlauf and H.K.T. Wong, 2003. Vertical distribution of gaseous elemental mercury in Canada. Journal of Geophysical Research, 108:4264.

Bargagli, R., C. Agnorelli, f. Borghini and F. Monaci, 2005. Enhanced deposition and bioaccumulation of mercury in Antarctic terrestrial ecosystems facing a coastal polynya. Environmental Science and Technology, 39:8150-8155.

Bargagli, R., F. Monaci and C. Bucci, 2007. Environmental biogeochemistry of mercury in Antarctic ecosystems. Soil Biology and Biochemistry, 39:352-360.

Barkay, T. and A.J. Poulain, 2007. Mercury (micro)biogeochemistry in polar environments. Fems Microbiology Ecology, 59:232-241.

Barkay, T., M. Gillman and R.R. Turner, 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. Applied and Environmental Microbiology, 63:4267-4271.

Barkay, T., S.M. Miller and A.O. Summers, 2003. Bacterial mercury resistance from atoms to ecosystems. Fems Microbiology Reviews, 27:355-384.

Barnston, A.G. and R.E. Livezey, 1987. Classification, seasonality and persistence of low-frequency atmospheric circulation patterns. Monthly Weather Review, 115:1083-1126.

Barrie, L.A., J.W. Bottenheim, R.C. Schnell, P.J. Crutzen and R.A. Rasmussen, 1988. Ozone destruction and photochemical-reactions at polar sunrise in the lower arctic atmosphere. Nature, 334:138-141.

Basu, N. and J. Head, 2010. Mammalian wildlife as complementary models in environmental neurotoxicology. Neurotoxicology and Teratology, 32:114-119.

Basu, N., K. Klenavic, M. Gamberg, M. O'Brien, D. Evans, A.M. Scheuhammer and H.M. Chan, 2005. Effects of mercury on neurochemical receptor-binding characteristics in wild mink. Environmental Toxicology and Chemistry, 24:1444-1450.

Basu, N., M. Kwan and H.M. Chan, 2006a. Mercury but not organochlorines inhibit muscarinic cholinergic receptor binding in the cerebrum of ringed seals (*Phoca hispida*). Journal of Toxicology and Environmental Health A, 69:1133-1143.

Basu, N., A.M. Scheuhammer, K. Rouvinen-Watt, N. Grochowina, K. Klenavic, R.D. Evans and H.M. Chan, 2006b. Methylmercury impairs components of the cholinergic system in captive mink (*Mustela vison*). Toxicological Sciences, 91:202-209.

Basu, N., A.M. Scheuhammer, S.J. Bursian, J. Elliott, K. Rouvinen-Watt and H.M. Chan, 2007a. Mink as a sentinel species in environmental health. Environmental Research, 103:130-144.

Basu, N., A.M. Scheuhammer, K. Rouvinen-Watt, N. Grochowina, R.D. Evans, M. O'Brien and H.M. Chan, 2007b. Decreased N-methyl-D-aspartic acid (NMDA) receptor levels are associated with mercury exposure in wild and captive mink. Neurotoxicology, 28:587-593.

Basu, N., A.M. Scheuhammer, C. Sonne, R.J. Letcher, E.W. Born and R. Dietz, 2009. Is dietary mercury of neurotoxicological concern to wild polar bears (*Ursus maritimus*)? Environmental Toxicology and Chemistry, 28:133-140.

Bates, N.R. and J.T. Mathis, 2009. The Arctic Ocean marine carbon cycle: evaluation of air-sea $CO_2$ exchanges, ocean acidification impacts and potential feedbacks. Biogeosciences, 6:2433-2459.

Bauer, D., L. D'Ottone, P. Campuzano-Jost and A.J. Hynes, 2003. Gas phase elemental mercury: a comparison of LIF detection techniques and study of the kinetics of reaction with the hydroxyl radical. Journal of Photochemistry and Photobiology A, 157:247-256.

Baumann, P.Q., W.S. Stirewalt, B.D. O'Rourke, D. Howard and K.S. Nair, 1994. Precursor pools of protein synthesis: a stable isotope study in a swine model. American Journal of Physiology – Endocrinology and Metabolism, 267:203-209.

Bearhop, S., G.D. Ruxton and R.W. Furness, 2000a. Dynamics of mercury in blood and feathers of great skuas. Environmental Toxicology and Chemistry, 19:1638-1643.

Bearhop, S., R.A. Phillips, D.R. Thompson, S. Waldron and R.W. Furness, 2000b. Variability in mercury concentrations of great skuas *Catharacta skua*: the influence of colony, diet and trophic status inferred from stable isotope signatures. Marine Ecology Progress Series, 195:261-268.

Becker, P.R., E.A. Mackey, R. Demiralp, R. Suydam, G. Early, B.J. Koster and S.A. Wise, 1995. Relationship of silver with selenium and mercury in the liver of two species of toothed whales (odontocetes). Marine Pollution Bulletin, 30:262-271.

Becker, P.H., J.M. Cifuentes, B. Behrends and K.R. Schmieder, 2001. Contaminants in bird eggs in the Wadden Sea. Spatial and temporal trends 1991-2000. Wadden Sea Ecosystem No. 11. Common Wadden Sea Secretariat.

Benoit, J.M., C.C. Gilmour, R.P. Mason and A. Heyes, 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environmental Science and Technology, 33:951-957.

Benoit, J.M., C.C. Gilmour, A. Heyes, R.P. Mason and C.L. Miller, 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. In: Biogeochemistry of Environmentally Important Trace Elements, pp. 262-297. ACS Symposium Series No. 835.

Berg, T., C. Dye, J.E. Hanssen, T. Krognes, J. Munthe, A. Reissell, J. Schaug, N. Schmidbauer, A. Semb, K. Tørseth, H.T. Uggerud, A. Aas, K. Aasarød and L. Lisbeth Berntsen, 2002. EMEP Manual for Sampling and Chemical Analysis. Norwegian Institute for Air Research, Kjeller.

Berg, T., S. Sekkesaeter, E. Steinnes, A.K. Valdal and G. Wibetoe, 2003. Springtime depletion of mercury in the European Arctic as observed at Svalbard. Science of the Total Environment, 304:43-51.

Berg, T., R. Kallenborn and S. Manø, 2004. Temporal trends in atmospheric heavy metal and organochlorine concentrations at Zeppelin, Svalbard. Arctic, Antarctic, and Alpine Research, 3:284-291.

Berg, T., W. Aas, J. Pacyna, H.T. Uggerud and M. Vadset, 2008a. Atmospheric trace metal concentrations at Norwegian background sites during 25 years and its relation to European emission. Atmospheric Environment, 42:7494-7501.

Berg, T., K. Aspmo and E. Steinnes, 2008b. Transport of Hg from atmospheric mercury depletion events to the mainland of Norway and its possible influence on Hg deposition. Geophysical Research Letters, 35:L09802.

Bergman, A., A. Bergstrand and A. Bignert, 2001. Renal lesions in Baltic grey seals (*Halichoerus grypus*) and ringed seals (*Phoca hispida botnica*). Ambio, 30:397-409.

Berlin, M., 1986. Mercury. In: Friberg, L., G.F. Nordberg and V.B. Vouk (Eds.). Handbook on the Toxicology of Metals, pp. 187-445, Elsevier Science Publishers.

Bernhard, M. and M.O. Andreae, 1984. Transport of trace metals in marine food chains. In: Nriagu, J.O. (Ed.). Changing Metal Cycles and Human Health, pp. 143-167, Springer-Verlag.

Bertilsson, S., L.A. Hansson, W. Graneli and A. Philibert, 2003. Size-selective predation on pelagic microorganisms in Arctic freshwaters. Journal of Plankton Research, 25:621-631.

Biester, H., R. Bindler, A. Martinez-Cortizas and D.R. Engstrom, 2007. Modeling the past atmospheric deposition of mercury using natural archives. Environmental Science and Technology, 41:4851-4860.

Bignert, A., 2001. Comments concerning the National Swedish Contaminant Monitoring Programme in Marine Biota. Annual report to the Swedish Environmental Protection Agency.

Bignert, A., 2002. Comments Concerning the National Swedish Contaminant Monitoring Programme in Fresh Water Biota. Report to the Swedish Environmental Protection Agency. 66 pp.

Bignert, A., F. Riget, B. Braune, P. Outridge and S. Wilson, 2004. Recent temporal trend monitoring of mercury in Arctic biota – how powerful are the existing data sets? Journal of Environmental Monitoring, 6:351-355.

Bindler, R., I. Renberg, P.G. Appleby, N.J. Anderson and N.L. Rose, 2001a. Mercury accumulation rates and spatial patterns in lake sediments from West Greenland: A coast to ice margin transect. Environmental Science and Technology, 35:1736-1741.

Bindler, R., C. Olofsson, I. Renberg and W. Frech, 2001b. Temporal trends in mercury accumulation in lake sediments in Sweden. Water, Air and Soil Pollution: Focus, 1:343-355.

Bindler, R., A.M. Cortizas and M. Blaauw, 2005. Comment on "Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the High Arctic of Canada recorded by peat hummocks". Environmental Science & Technology, 39:908-909, author reply 910-912.

Biswas, A., J.D. Blum and G.J. Keeler, 2008. Mercury storage in surface soils in a central Washington forest and estimated release during the 2001 Rex Creek Fire. Science of the Total Environment, 404:129-138.

Blais, J.M., D.W. Schindler, D.C.G. Muir, M. Sharp, D. Donald, M. Lafreniere, E. Braekevelt and W.M.J. Strachan, 2001. Melting glaciers: A major source of persistent organochlorines to subalpine Bow Lake in Banff National Park, Canada. Ambio, 30:410-415.

Blais, J.M., L.E. Kimpe, D. McMahon, B.E. Keatley, M.L. Mattory, M.S.V. Douglas and J.P. Smol, 2005. Arctic seabirds transport marine-derived contaminants. Science, 309:445.

Blais, J.M., R.W. Macdonald, D. Mackey, E. Webster, C. Harvey and J.P. Smol, 2007. Biologically mediated transport of contaminants to aquatic systems. Environmental Science and Technology, 41:1075-1084.

Bodaly, R.A., R.E. Hecky and R.J.P. Fudge, 1984. Increases in fish mercury levels in lakes flooded by the Churchill River diversion, northern Manitoba. Canadian Journal of Fisheries and Aquatic Sciences, 41:682-691.

Bodaly, R.A., J.W.M. Rudd, R.J.P. Fudge and C.A. Kelly, 1993. Mercury concentrations in fish related to size of remote canadian shield lakes. Canadian Journal of Fisheries and Aquatic Sciences, 50:980-987.

Bodaly, R.A., V.L. St.Louis, M.J. Paterson, R.J.P. Fudge, B.D. Hall, D.M. Rosenberg and J.W.M. Rudd, 1997. Bioaccumulation of mercury in the aquatic food chain in newly flooded areas. In: Sigel, A. and H. Sigel (Eds.). Mercury and its Effects on Environment and Biology, pp. 257-289, Marcel Dekker.

Bodaly, R.A.D., W.A. Jansen, A.R. Majewski, R.J.P. Fudge, N.E. Strange, A.J. Derksen and D.J. Green, 2007. Postimpoundment time course of increased mercury concentrations in fish in hydroelectric reservoirs of northern Manitoba, Canada. Archives of Environmental Contamination and Toxicology, 53:379-389.

Booth, S. and D. Zeller, 2005. Mercury, food webs, and marine mammals: Implications of diet and climate change for human health. Environmental Health Perspectives, 113:521-526.

Born, E.W., I. Kraul and T. Kristensen, 1981. Mercury, DDT and PCB in the Atlantic walrus (*Odobenus rosmarus rosmarus*) from the Thule District, North Greenland. Arctic, 34:255-260.

Born, E.W., A. Renzoni and R. Dietz, 1991. Total mercury in hair of polar bears (*Ursus maritimus*) from Greenland and Svalbard. Polar Research, 9:113-120.

Born, E.W., P. Outridge, F.F. Riget, K. Hobson, R. Dietz, T. Haug and N. Øien, 2003. Stock structure of North Atlantic minke whales (*Balaenoptera acutorostrata*) inferred from regional variation of elemental and stable isotopic signatures in tissues. Journal of Marine Systems 43:1-17.

Bottenheim, J.W., A.G. Gallant and K.A. Brice, 1986. Measurements of NOy species and $O_3$ at 82° N latitude. Geophysical Research Letters, 13:113-116.

Bottenheim, J.W., S. Netcheva, S. Morin and S.V. Nghiem, 2009. Ozone in the boundary layer air over the Arctic Ocean: measurements during the TARA transpolar drift 2006-2008. Atmospheric Chemistry and Physics, 9:4545-4557.

Boutron, C.F., G.M. Vandal, W.F. Fitzgerald and C.P. Ferrari, 1998. A forty year record of mercury in central Greenland snow. Geophysical Research Letters, 25:3315-3318.

Boyd, I.L., D.J. McCafferty and T.R. Walker, 1997. Variation in foraging effort by lactating Antarctic fur seals: Response to simulated increased foraging costs. Behavioral Ecology and Sociobiology, 40:135-144.

Bradstreet, M.S.W. and W.E. Cross, 1982. Trophic relationships at high arctic ice edges. Arctic, 35:1-12.

Bradstreet, M.S.W., Finley, K.J., Sekerak, A.D., Griffiths, W.B., Evans, C.R., Fabijan, M., Stallard, H.E, 1986. Aspects of the biology of Arctic cod (*Boreogadus saida*) and its importance in Arctic marine food chains. Canadian Technical Report of Fisheries and Aquatic Sciences, No. 1491. 193 pp.

Branfireun, B.A., D.P. Krabbenhoft, H. Hintelmann, R.J. Hunt, J.P. Hurley and J.W.M. Rudd, 2005. Speciation and transport of newly deposited mercury in a boreal forest wetland: A stable mercury isotope approach. Water Resources Research, 41: W06016.

Braune, B.A., 2007. Temporal trends of organochlorines and mercury in seabird eggs from the Canadian Arctic, 1975-2003. Environmental Pollution, 148:599-613.

Braune, B.M., R.J. Norstrom, M.P. Wong, B.T. Collins and J. Lee, 1991. Geographical distribution of metals in livers of polar bears from the northwest-territories, Canada. Science of the Total Environment, 100:283-299.

Braune, B.M., G.M. Donaldson and K.A. Hobson, 2001. Contaminant residues in seabird eggs from the Canadian Arctic. Part I. Temporal trends 1975-1998. Environmental Pollution, 114:39-54.

Braune, B.M., G.M. Donaldson and K.A. Hobson, 2002. Contaminant residues in seabird eggs from the Canadian Arctic. II. Spatial trends and evidence from stable isotopes for intercolony differences. Environmental Pollution, 117:133-145.

Braune, B.M., P.M. Outridge, A.T. Fisk, D.C.G. Muir, P.A. Helm, K. Hobbs, P.F. Hoekstra, Z.A. Kuzyk, M. Kwan, R.J. Letcher, W.L. Lockhart, R.J. Norstrom, G.A. Stern and I. Stirling, 2005. Persistent organic pollutants and mercury in marine biota of the Canadian Arctic: An overview of spatial and temporal trends. Science of the Total Environment, 351:4-56.

Braune, B.M., M.L. Mallory and H.G. Gilchrist, 2006. Elevated mercury levels in a declining population of ivory gulls in the Canadian Arctic. Marine Pollution Bulletin, 52:978-982.

Brigelius-Flohe, R., 1999. Tissue-specific functions of individual glutathione peroxidases. Free Radical Biology and Medicine, 27:951-965.

Brookens, T.J., J.T. Harvey and T.M. O'Hara, 2007. Trace element concentrations in the Pacific harbor seal (*Phoca vitulina richardii*) in central and northern California: influence of age, sex, and trophic level. Science of the Total Environment, 372:676-692.

Brookens, T.J., T.M. O'Hara, R.J. Taylor, G.R. Bratton and J.T. Harvey, 2008. Total mercury body burden in Pacific harbor seal, *Phoca vitulina richardii*, pups from central California. Marine Pollution Bulletin, 56:27-41.

Brooks, S.B., A. Saiz-Lopez, H. Skov, S.E. Lindberg, J.M.C. Plane and M.E. Goodsite, 2006. The mass balance of mercury in the springtime arctic environment. Geophysical Research Letters, 33:L13812.

Brooks, S., S. Lindberg, G. Southworth and R. Arimoto, 2008. Springtime atmospheric mercury speciation in the McMurdo, Antarctica coastal region. Atmospheric Environment, 42:2885-2893.

Brunborg, L.A., I.E. Graff, L. Frøyland and K. Julshamn, 2006. Levels of non-essential elements in muscle from harp seal (*Phagophilus groenlandicus*) and hooded seal (*Cystophora cristata*) caught in the Greenland Sea area. Science of the Total Environment, 366:784-798.

Budtz-Jørgensen, E., P. Grandjean and P. Weihe, 2007. Separation of risks and benefits of seafood intake. Environmental Health Perspectives, 115:323-327.

Bullock Jr., O.R., D. Atkinson, T. Braverman, K. Civerolo, A. Dastoor, D. Davignon, J.-Y. Ku, K. Lohman, T. Myers, R. Park, C. Seigneur, N.E. Selin, G. Sistla and K. Vijayaraghavan, 2008. The North American mercury model intercomparison study (NAMMIS). Study description and model-to-model comparisons. Journal of Geophysical Research-Atmospheres, 113:D17310.

Bullock Jr., O.R., D. Atkinson, T. Braverman, K. Civerolo, A. Dastoor, D. Davignon, J.-Y. Ku, K. Lohman, T.C. Myers, R.J. Park, C. Seigneur, N.E. Selin, G. Sistla and K. Vijayaraghavan, 2009. An analysis of simulated wet deposition of mercury from the North American mercury model intercomparison study (NAMMIS). Journal of Geophysical Research 114:D08301.

Burger, J. and M. Gochfeld, 2004. Metal levels in eggs of common terns (*Sterna hirundo*) in New Jersey: temporal trends from 1971 to 2002. Environmental Research, 94:336-343.

Burger, J., M. Gochfeld, C. Jeitner, S. Burke, C.D. Volz, R. Snigaroff, D. Snigaroff, T. Shukla and S. Shukla, 2009. Mercury and other metals in eggs and feathers of glaucous-winged gulls (*Larus glaucescens*) in the Aleutians. Environmental Monitoring and Assessment, 152:179-194.

Cabana, G. and J.B. Rasmussen, 1994. Modelling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. Nature, 372:255-257.

Calvert, J.G. and S.E. Lindberg, 2005. Mechanisms of mercury removal by O-3 and OH in the atmosphere. Atmospheric Environment, 39:3355-3367.

Campbell, L.M., R.J. Norstrom, K.A. Hobson, D.C.G. Muir, S. Backus and A.T. Fisk, 2005. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). Science of the Total Environment, 351-352:247-263.

Canário, J., V. Branco and C. Vale, 2007. Seasonal variation of monomethylmercury concentrations in surface sediments of the Tagus Estuary (Portugal). Environmental Pollution, 148:380-383.

Cardona-Marek, T., K.K. Knott, B.E. Meyer and T.M. O'Hara, 2009. Mercury concentrations in southern Beaufort Sea polar bears: variation based on stable isotopes of carbon and nitrogen. Environmental Toxicology and Chemistry, 28:1416-1424.

Carmack, E. and D.C. Chapman, 2003. Wind-driven shelf/basin exchange on an Arctic shelf: The joint roles of ice cover extent and shelf-break bathymetry. Geophysical Research Letters, 30:1778.

Carmack, E.C. and R.W. MacDonald, 2002. Oceanography of the Canadian shelf of the Beaufort Sea: A setting for marine life. Arctic, 55:29-45.

Carmack, E.C., K. Aagaard, J.H. Swift, R.W. Macdonald, F.A. McLaughlin, E.P. Jones, R.D. Perkin, J.N. Smith, K. Ellis and K. L, 1997. Changes in temperature and tracer distributions within the Arctic Ocean: results from the 1994 Arctic Ocean section. Deep-Sea Research II, 44:1487-1502.

Carmack, E., D. Barber, J. Christensen, R. Macdonald, B. Rudels and E. Sakshaug, 2006. Climate variability and physical forcing of the food webs and the carbon budget on panarctic shelves. Progress in Oceanography, 71:145-181.

Carrie, J., H. Sanei, F. Goodarzi, G. Stern and F.Y. Wang, 2009. Characterization of organic matter in surface sediments of the Mackenzie River Basin, Canada. International Journal of Coal Geology, 77:416-423.

Carrie, J., G.A. Stern, H. Sanei, R.W. Macdonald, P.M. Outridge and F. Wang, 2010. Increasing contaminant burdens in an Arctic fish, burbot (*Lota lota*), in a warming climate. Environmental Science and Technology, 44:316-322.

Carvalho, C.M.L., E.H. Chew, S.I. Hashemy, J. Lu and A. Holmgren, 2008. Inhibition of the human thioredoxin system – A molecular mechanism of mercury toxicity. Journal of Biological Chemistry, 283:11913-11923.

Chadwick, S.P., C.L. Babiarz, J.P. Hurley and D.E. Armstrong, 2006. Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury. Science of the Total Environment, 368:177-188.

Chen, C.Y. and C.L. Folt, 2005. High plankton densities reduce mercury biomagnification. Environmental Science and Technology, 39:115-121.

Chen, J., S.O. Pehkonen and C.J. Lin, 2003. Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters. Water Research, 37:2496-2504.

Chételat, J. and M. Amyot, 2009. Elevated methylmercury in High Arctic *Daphnia* and the role of productivity in controlling their distribution. Global Change Biology, 15:706-718.

Chételat, J., M. Amyot, L. Cloutier and A. Poulain, 2008. Metamorphosis in chironomids, more than mercury supply, controls methylmercury transfer to fish in High Arctic lakes. Environmental Science and Technology, 42:9110-9115.

Christensen, J.H., J. Brandt, L.M. Frohn and H. Skov, 2004. Modelling of mercury in the Arctic with the Danish Eulerian Hemispheric Model. Atmospheric Chemistry and Physics, 4:2251-2257.

Churg, J., J. Bernstein and R.J. Glassock, 1995. Renal Disease: Classification and Atlas of Glomerular Diseases. Igaku-Shoin, New York.

Cizdziel, J., T. Hinners, C. Cross and J. Pollard, 2003. Distribution of mercury in the tissues of five species of freshwater fish from Lake Mead, USA. Journal of Environmental Monitoring, 5:802-807.

Clarkson, T.W. and L. Magos, 2006. The toxicology of mercury and its chemical compounds. Critical Reviews in Toxicology, 36:609-662.

Cobbett, F.D., A. Steffen, G. Lawson and B.J. Van Heyst, 2007. GEM fluxes and atmospheric mercury concentrations (GEM, RGM and HgP) in the Canadian Arctic at Alert, Nunavut, Canada (February-June 2005). Atmospheric Environment, 41:6527-6543.

Coelho, J.P., M. Nunes, M. Dolbeth, M.E. Pereira, A.C. Duarte and M.A. Pardal, 2008. The role of two sediment-dwelling invertebrates on the mercury transfer from sediments to the estuarine trophic web. Estuarine, Coastal and Shelf Science, 78:505-512.

Cole, A.S. and A. Steffen, 2010. Trends in long-term gaseous mercury observations in the Arctic and effects of temperature and other atmospheric conditions. Atmospheric Chemistry and Physics, 10:4661-4672.

Conaway, C.H., F.J. Black, M. Gault-Ringold, J.T. Pennington, F.P. Chavez and A.R. Flegal, 2009. Dimethylmercury in coastal upwelling waters, Monterey Bay, California. Environmental Science and Technology, 43:1305-1309.

Conlan, K.E., H.S. Lenihan, R.G. Kvitek and J.S. Oliver, 1998. Ice scour disturbance to benthic communities in the Canadian High Arctic. Marine Ecology Progress Series, 166:1-16.

Constant, P., L. Poissant, R. Villemur, E. Yumvihoze and D. Lean, 2007. Fate of inorganic mercury and methyl mercury within the snow cover in the low arctic tundra on the shore of Hudson Bay (Quebec, Canada). Journal of Geophysical Research, 112:D08309.

Coquery, M., D. Cossa and J.M. Martin, 1995. The distribution of dissolved and particulate mercury in three Siberian estuaries and adjacent Arctic coastal waters. Water Air and Soil Pollution, 80:653-664.

Cossa, D., J.-M. Martin, K. Takayanagi and J. Sanjuan, 1997. The distribution and cycling of mercury species in the western Mediterranean. Deep-Sea Research II, 44:721-740.

Cossa, D., B. Averty and N. Pirrone, 2009. The origin of methylmercury in open Mediterranean waters. Limnology and Oceanography, 54:837-844.

Costa, M.F. and P.S. Liss, 1999. Photoreduction of mercury in seawater and its possible implications for Hg0 air–sea fluxes. Marine Chemistry 66:87-95.

Cotran, R.S., V. Kumar and T. Collins, 1999. Robbins Pathologic Basis of Disease. WB Saunders, Philadelphia.

Craig, P.C., W.B. Griffiths, L. Haldorson and H. McElderry, 1982. Ecological studies of Arctic cod (*Boreogadus saida*) in Beaufort Sea coastal waters. Canadian Journal of Fisheries and Aquatic Sciences, 39:395-406.

Cremona, F., D. Planas and M. Lucotte, 2008. Assessing the importance of macroinvertebrate trophic dead ends in the lower transfer of methylmercury in littoral food webs. Canadian Journal of Fisheries and Aquatic Sciences, 65:2043-2052.

Crump, K.L. and V.L. Trudeau, 2009. Mercury-induced reproductive impairment in fish. Environmental Toxicology and Chemistry, 28:895-907.

Cullen, J.T., Y. Rosenthal and P.G. Falkowski, 2001. The effect of anthropogenic $CO_2$ on the carbon isotope composition of marine phytoplankton. Limnology and Oceanography, 46:996-998.

Czimczik, C.I., C.M. Preston, M.W.I. Schmidt and E.D. Schulze, 2003. How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: Stocks, molecular structure, and conversion to black carbon (charcoal). Global Biogeochemical Cycles, 17:1020.

Daman, S., W.B. Eide and H.V. Kuhnlein, 2008. Indigenous peoples' nutrition transition and a right to food perspective. Food Policy, 33:135-155.

Darnis, G., D.G. Barber and L. Fortier, 2008. Sea ice and the onshore-offshore gradient in pre-winter zooplankton assemblages in southeastern Beaufort Sea. Journal of Marine Systems, 74:994-1011.

Dastoor, A.P. and Y. Larocque, 2004. Global circulation of atmospheric mercury: a modelling study. Atmospheric Environment, 38:147-161.

Dastoor, A.P., D. Davignon, N. Theys, M. Van Roozendael, A. Steffen and P.A. Ariya, 2008. Modeling dynamic exchange of gaseous elemental mercury at polar sunrise. Environmental Science and Technology, 42:5183-5188.

Day, R.D., S.S. Vander Pol, S.J. Christopher, W.C. Davis, R.S. Pugh, K.S. Simac, D.G. Roseneau and P.R. Becker, 2006. Murre eggs (*Uria aalge* and *Uria lomvia*) as indicators of mercury contamination in the Alaskan marine environment. Environmental Science and Technology, 40:659-665.

Dehn, L.A., G.G. Sheffield, E.H. Follmann, L.K. Duffy, D.L. Thomas, G.R. Bratton, R.J. Taylor and T.M. O'Hara, 2005. Trace elements in tissues of phocid seals harvested in the Alaskan and Canadian Arctic: influence of age and feeding ecology. Canadian Journal of Zoology, 83:726-746.

Dehn, L.A., E.H. Follmann, C. Rosa, L.K. Duffy, D.L. Thomas, G.R. Bratton, R.J. Taylor and T.M. O'Hara, 2006. Stable isotope and trace element status of subsistence-hunted bowhead and beluga whales in Alaska and gray whales in Chukotka. Marine Pollution Bulletin, 52:301-319.

DeNiro, M.J., 1985. Postmortem preservation and alteration of in vivo bone collagen isotope ratios in relation to palaeodietary reconstruction. Nature, 317:806-809.

Déry, S.J. and E.F. Wood, 2005. Decreasing river discharge in northern Canada. Geophysical Research Letters, 32:L10401.

Deutch, B., H.S. Pedersen, G. Asmund and J.C. Hansen, 2007. Contaminants, diet, plasma fatty acids, and smoking in Greenland 1999-2005. Science of the Total Environment, 372:486-496.

Dewailly, E., P. Ayotte, S. Bruneau, G. Lebel, P. Levallois and P. Weber, 2001. Exposure of the Inuit population of Nunavik (Arctic Quèbec) to lead and mercury. Archives of Environmental Health, 56:350-357.

Dewailly, É., R. Daillaire, D. Pereg, P. Ayotte, J. Fontaine and S. Dery, 2007a. Exposure to environmental contaminants in Nunavik: Persistent organic pollutants and new contaminants of concern. Institute National de Santé Publique du Québec, Nunavik Regional Board of Health and Social Services.

Dewailly, É., P. Ayotte, D. Pereg, S. Dery, R. Dallaire, J. Fontaine and S. Côte, 2007b. Exposure to environmental contaminants in Nunavik: Metals. Institute National de Santé Publique du Québec, Nunavik Regional Board of Health and Social Services.

Dietz, R., 2008. Contaminants in Marine Mammals in Greenland – with linkages to trophic levels, effects, diseases and distribution. 120 pp. National Environmental Research Institute, University of Aarhus, Aarhus.

Dietz, R., C.O. Nielsen, M.M. Hansen and C.T. Hansen, 1990. Organic mercury in Greenland birds and mammals. Science of the Total Environment, 95:41-51.

Dietz, R., E.W. Born, C.T. Agger and C.O. Nielsen, 1995. Zinc, cadmium, mercury and selenium in polar bears (*Ursus maritimus*) from Central East Greenland. Polar Biology, 15:175-185.

Dietz, R., F. Riget and P. Johansen, 1996. Lead, cadmium, mercury and selenium in Greenland marine animals. Science of the Total Environment, 186:67-93.

Dietz, R., J. Pacyna, D.J. Thomas, G. Asmund, V. Gordeev, P. Johansen, V. Kimstach, L. Lockhart, S.L. Pfirman, F.F. Riget, G. Shaw, R. Wagemann and W. M., 1998a. Heavy metals. In: AMAP Assessment Report: Arctic Pollution Issues, pp. 373-524, Arctic Monitoring and Assessment Programme.

Dietz, R., P. Paludan-Müller, C.T. Agger and C. Overgaard Nielsen, 1998b. Cadmium, mercury, zinc and selenium in ringed seals (*Phoca hispida*) from Greenland and Svalbard. NAMMCO Scientific contributions 1:242-273.

Dietz, R., J. Norgaard and J.C. Hansen, 1998c. Have Arctic marine mammals adapted to high cadmium levels? Marine Pollution Bulletin, 36:490-492.

Dietz, R., F. Riget and E.W. Born, 2000a. Geographical differences of zinc, cadmium, mercury and selenium in polar bears (*Ursus maritimus*) from Greenland. Science of the Total Environment, 245:25-47.

Dietz, R., F. Riget, M. Cleemann, A. Aarkrog, P. Johansen and J.C. Hansen, 2000b. Comparison of contaminants from different trophic levels and ecosystems. Science of the Total Environment, 331:107-124.

Dietz, R., F. Riget and E.W. Born, 2000c. An assessment of selenium to mercury in Greenland marine animals. Science of the Total Environment, 245:15-24.

Dietz, R., F. Riget, K. Hobson, M.P. Heide-Jørgensen, P. Møller, M. Cleemann, J. de Boer and M. Glacius, 2004. Regional and interannual patterns of heavy metals, organochlorines and stable isotopes in narwhals (*Monodon monoceros*) from West Greenland. Science of the Total Environment, 331:83-105.

Dietz, R., F. Riget, E.W. Born, C. Sonne, P. Grandjean, M. Kirkegaard, M.T. Olsen, G. Asmund, A. Renzoni, H. Baagoe and C. Andreasen, 2006a. Trends in mercury in hair of Greenlandic polar bears (*Ursus maritimus*) during 1892-2001. Environmental Science and Technology, 40:1120-1125.

Dietz, R., F. Riget, D. Boertmann, C. Sonne, M.T. Olsen, J. Fjeldsa, K. Falk, M. Kirkegaard, C. Egevang, G. Asmund, F. Wille and S. Moller, 2006b. Time trends of mercury in feathers of West Greenland birds of prey during 1851-2003. Environmental Science and Technology, 40:5911-5916.

Dietz, R., F.F. Riget, C. Sonne, R. Letcher, M. McKinney, D. Muir, R. Bossi, K. Vorkamp and E. Born, 2008a. Temporal trends and bioaccumulation of selected contaminants in East Greenland ringed seals and polar bears. Paper presented at SETAC World Congress of the Society of Environmental Toxicology and Chemistry. 3-7 August 2008, Sydney, Australia.

Dietz, R., F.F. Riget, C. Sonne, R. Letcher, M. McKinney, D. Muir, R. Bossi, K. Vorkamp and E. Born, 2008b. Contaminant linkages to climate parameters in polar bears (*Ursus maritimus*) from Greenland and Svalbard. Paper presented at Arctic Change 2008, 9-12 December 2008, Quebec City, Canada.

Dietz, R., P.M. Outridge and K.A. Hobson, 2009a. Anthropogenic contributions to mercury levels in present-day Arctic animals – A review. Science of the Total Environment, 407:6120-6131.

Dietz, R., F. Rigét, M. Forchammer, C. Sonne, A. Aubail, E.W. Born, J. Aars, M. Andersen, Ø. Wiig, J.U. Skaare, N. Basu and P. Grandjean, 2009b. Temporal and geographical trends of Hg in polar bears (*Ursus maritimus*) hair linked to health effect levels and climate change parameters. Paper presented at 9th International Conference on Mercury as a Global Pollutant, 7-12 June 2009, Guiyang, China.

Dietz, R., E.W. Born, F. Riget, A. Aubail, C. Sonne, R.C. Drimmei and N. Basu, 2011. Temporal trends and future predictions of mercury concentrations in Northwest Greenland polar bear (*Ursus maritimus*) hair. Environmental Science and Technology, 45:1458-1465.

Dominé, F. and P.B. Shepson, 2002. Air-snow interactions and atmospheric chemistry. Science, 297:1506-1510.

Dommergue, A., C.P. Ferrari, L. Poissant, P.A. Gauchard and C.F. Boutron, 2003a. Diurnal cycles of gaseous mercury within the snowpack at Kuujjuarapik/Whapmagoostui, Quebec, Canada. Environmental Science & Technology, 37:3289-3297.

Dommergue, A., C.P. Ferrari, P.-A. Gauchard, L. Poissant, M. Pilote, P. Jitaru and F.C. Adams, 2003b. The fate of mercury species in a sub-arctic snowpack during snowmelt. Geophysical Research Letters, 30:1621.

Dommergue, A., C.P. Ferrari, P.A. Gauchard, L. Poissant and C.F. Boutron, 2003c. Diurnal cycles of interstitial gaseous mercury inside a sub-arctic snow-pack prior to and during snowmelt events. Journal de Physique IV, 107:389-392.

Dommergue, A., C. Larose, X. Fain, O. Clarisse, D. Foucher, H. Hintelmann, D. Schneider and C.P. Ferrari, 2010. Deposition of mercury species in the Ny-Ålesund area (79° N) and their transfer during snowmelt. Environmental Science and Technology, 44:901-907.

Donaldson, G.M., A.J. Gaston, J.W. Chardine, K. Kampp, D.N. Nettleship and R.D. Elliot, 1997. Winter distributions of thick-billed murres from the eastern Canadian Arctic and western Greenland in relation to age and time of year. Occasional Paper No. 96. Canadian Wildlife Service, Environment Canada, Ottawa, Canada.

Donaldson, S.G., N.C. Doubleday and J.V. Oostdam, 2006. Factors influencing food choices among women and men living in Cape Dorset, Nunavut, Canada. In: Smith, S. and J. Stow (Eds.). Synopsis of Research Conducted under the Northern Contaminants Program. Department of Indian and Northern Affairs, Ottawa, Canada.

Doney, S.C., V.J. Fabry, R.A. Feely and J.A. Kleypas, 2009. Ocean acidification: The other $CO_2$ problem. Annual Reviews of Marine Science, 1:169-192.

Dong, W., L. Liang, S. Brooks, G. Southworth and B. Gu, 2010. Roles of dissolved organic matter in the speciation of mercury and methylmercury in a contaminated ecosystem in Oak Ridge, Tennessee. Environmental Chemistry 7:94-102.

Donohoue, D.L., D. Bauer and A.J. Hynes, 2005. Temperature and pressure dependent rate coefficients for the reaction of Hg with Cl and the reaction of Cl with Cl: A pulsed laser photolysis-pulsed laser induced fluorescence study. Journal of Physical Chemistry A, 109:7732-7741.

Donohoue, D.L., D. Bauer, B. Cossairt and A.J. Hynes, 2006. Temperature and pressure dependent rate coefficients for the reaction of Hg with Br and the reaction of Br with Br: A pulsed laser photolysis-pulsed laser induced fluorescence study. Journal of Physical Chemistry A, 110:6623-6632.

Douglas, T.A. and M. Sturm, 2004. Arctic haze, mercury and the chemical composition of snow across northwestern Alaska. Atmospheric Environment, 38:805-820.

Douglas, T.A., M. Sturm, W.R. Simpson, S. Brooks, S.E. Lindberg and D.K. Perovich, 2005. Elevated mercury measured in snow and frost flowers near Arctic sea ice leads. Geophysical Research Letters, 32:L04502.

Douglas, T.A., M. Sturm, W.R. Simpson, J.D. Blum, L. Alvarez-Aviles, G.J. Keeler, D.K. Perovich, A. Biswas and K. Johnson, 2008. Influence of snow and ice crystal formation and accumulation on mercury deposition to the Arctic. Environmental Science and Technology, 42:1542-1551.

Drevnick, P.E. and M.B. Sandheinrich, 2003. Effects of dietary methylmercury on reproductive endocrinology of fathead minnows. Environmental Science and Technology, 37:4390-4396.

Drevnick, P.E., A.P. Roberts, R.R. Otter, C.R. Hammerschmidt, R. Klaper and J.T. Oris, 2008. Mercury toxicity in livers of northern pike (*Esox lucius*) from Isle Royale, USA. Comparative Biochemistry and Physiology C, 147:331-338.

Drexel, R.T., M. Haitzer, J.N. Ryan, G.R. Aiken and K.L. Nagy, 2002. Mercury(II) sorption to two Florida Everglades peats: Evidence for strong and weak binding and competition by dissolved organic matter released from the peat. Environmental Science and Technology, 36:4058-4064.

Driscoll, C.T., V. Blette, C. Yan, C.L. Schofield, R. Munson and J. Holsapple, 1995. The role of dissolved organic-carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. Water, Air and Soil Pollution, 80:499-508.

Driscoll, C.T., J. Holsapple, C.L. Schofield and R. Munson, 1998. The chemistry and transport of mercury in a small wetland in the Adirondack region of New York, USA. Biogeochemistry, 40:137-146.

Durnford, D., A. Dastoor, D. Figueras-Nieto and A. Ryjkov, 2010. Long range transport of mercury to the Arctic and across Canada. Atmospheric Chemistry and Physics, 10:6063-6086.

Dyurgerov, M.B. and M.F. Meier, 2005. Glaciers and the changing Earth system: A 2004 snapshot. 117 pp. Institute of Arctic and Alpine Research, University of Colorado.

Eagles-Smith, C.A., J.T. Ackerman, J. Yee and T.L. Adelsbach, 2009. Mercury demethylation in waterbird livers: dose-response thresholds and differences among species. Environmental Toxicology and Chemistry, 28:568-577.

Eaton, R.D.P. and J.P. Farant, 1982. The polar bear as a biological indicator of the environmental mercury burden. Arctic, 35:422-425.

Ebinghaus, R., 2008. Mercury cycling in the Arctic – does enhanced deposition flux mean net-input? Environmental Chemistry, 5:87-88.

Ebinghaus, R., H.H. Kock, C. Temme, J.W. Einax, A.G. Lowe, A. Richter, J.P. Burrows and W.H. Schroeder, 2002. Antarctic springtime depletion of atmospheric mercury. Environmental Science and Technology, 36:1238-1244.

Edwards, M. and A.J. Richardson, 2004. Impact of climate change on marine pelagic phenology and trophic mismatch. Nature, 430:881-884.

Eide, R. and G.R. Wesenberg, 1993. Mercury contents of indicators and target organs in rats after long-term, low-level, mercury-vapor exposure. Environmental Research, 61:212-222.

Eide, R., G.R. Wesenberg and G. Fosse, 1993. Mercury in primary teeth in preindustrial Norway. Scandinavian Journal of Dental Research, 101:1-4.

Eide, R., J.D. Schionning, R. Bjugn, G.R. Wesenberg and G. Fosse, 1994. Autometallographic demonstration of mercury in rat molars. Scandinavian Journal of Dental Research, 102:76-80.

Eide, R., J.D. Schionning, E. Ernst, I.M. Hansen and G.R. Wesenberg, 1995. Mercury content in rat teeth after administration of organic and inorganic mercury. Acta Odontologica Scandinavica, 53:12-16.

Ekstrom, E.B., F.M.M. Morel and J.M. Benoit, 2003. Mercury methylation independent of the acetyl-coenzyme: A pathway in sulfate-reducing bacteria. Applied Environmental Microbiology, 69:5414-5422.

England, J.H., T.R. Lakeman, D.S. Lemmen, J.M. Bednarski, T.G. Stewart and D.J.A. Evans, 2008. A millennial-scale record of Arctic Ocean sea ice variability and the demise of the Ellesmere Island ice shelves. Geophysical Research Letters, 35:L19502.

ESPREME, 2007. ESPREME. Estimation of wiliness-to-pay to reduce risks of exposure to heavy metals and cost- benefit analysis for reducing heavy metals occurrence in Europe. Publishable final activity report. Project coordinator Reiner Friedrich, University of Stuttgart.

Ethier, A.L.M., A.M. Scheuhammer and D.E. Bond, 2008. Correlates of mercury in fish from lakes near Clyde Forks, Ontario, Canada. Environmental Pollution, 154:89-97.

Evans, M.S., D. Muir, W.L. Lockhart, G. Stern, M. Ryan and P. Roach, 2005a. Persistent organic pollutants and metals in the freshwater biota of the Canadian Subarctic and Arctic: An overview. Science of the Total Environment, 351:94-147.

Evans, M.S., W.L. Lockhart, L. Doetzel, G. Low, D. Muir, K. Kidd, G. Stephens and J. Delaronde, 2005b. Elevated mercury concentrations in fish in lakes in the Mackenzie River Basin: The role of physical, chemical, and biological factors. Science of the Total Environment, 351-352:479-500.

Evers, D.C., K.M. Taylor, A. Major, R.J. Taylor, R.H. Poppenga and A.M. Scheuhammer, 2003. Common loon eggs as indicators of methylmercury availability in North America. Ecotoxicology, 12:69-81.

Evers, D.C., Y.J. Han, C.T. Driscoll, N.C. Kamman, M.W. Goodale, K.F. Lambert, T.M. Holsen, C.Y. Chen, T.A. Clair and T. Butler, 2007. Biological mercury hotspots in the northeastern United States and southeastern Canada. Bioscience, 57:29-43.

Evers, D.C., L.J. Savoy, C.R. DeSorbo, D.E. Yates, W. Hanson, K.M. Taylor, L.S. Siegel, J.H. Cooley Jr, M.S. Bank, A. Major, K. Munney, B.F. Mower, H.S. Vogel, H. Schoch, M. Pokras, M.W. Goodale and J. Fair, 2008. Adverse effects from environmental mercury loads on breeding common loons. Ecotoxicology, 17:69-81.

Faïn, X., C.P. Ferrari, P.A. Gauchard, O. Magand and C. Boutron, 2006a. Fast depletion of gaseous elemental mercury in the Kongsvegen Glacier snowpack in Svalbard. Geophysical Research Letters, 33:L06826.

Faïn, X., C.P. Ferrari, P. Gauchard, O. Magand and C. Boutron, 2006b. Correction to "Fast depletion of gaseous elemental mercury in the Kongsvegen Glacier snowpack in Svalbard". Geophysical Research Letters, 33:L20807.

Faïn, X., S. Grangeon, E. Bahlmann, J. Fritsche, D. Obrist, A. Dommergue, C.P. Ferrari, W. Cairns, R. Ebinghaus, C. Barbante, P. Cescon and C. Boutron, 2007. Diurnal production of gaseous mercury in the alpine snowpack before snowmelt. Journal of Geophysical Research-Atmospheres, 112:D21311.

Faïn, X., C.P. Ferrari, A. Dommergue, M. Albert, M. Battle, L. Arnaud, J.M. Barnola, W. Cairns, C. Barbante and C. Boutron, 2008. Mercury in the snow and firn at Summit Station, Central Greenland, and implications for the study of past atmospheric mercury levels. Atmospheric Chemistry and Physics, 8:3441-3457.

Faïn, X., D. Obrist, A.G. Hallar, I. McCubbin and T. Rahn, 2009a. High levels of reactive gaseous mercury observed at a high elevation research laboratory in the Rocky Mountains. Atmospheric Chemistry and Physics, 9:8049-8060.

Faïn, X., C.P. Ferrari, A. Dommergue, M.R. Albert, M. Battle, J. Severinghaus, L. Arnaud, J.M. Barnola, W. Cairns, C. Barbante and C. Boutron, 2009b. Polar firn air reveals large-scale impact of anthropogenic mercury emissions during the 1970s. Proceedings of the National Academy of Sciences of the United States of America, 106:16114-16119.

Fan, S.-M. and D.J. Jacob, 1992. Surface ozone depletion in Arctic spring sustained by bromine reactions on aerosols. Nature, 359:522-524.

FAO/WHO, 2003. Summary and Conclusions, Annex 4, Joint FAO/WHO Expert Committee on Food Additives, 61st Meeting, U.N. Food and Agriculture Organization / World Health Organization.

Farmer, J.G., P. Anderson, J.M. Cloy, M.C. Graham, A.B. MacKenzie and G.T. Cook, 2009. Historical accumulation rates of mercury in four Scottish ombrotrophic peat bogs over the past 2000 years. Science of the Total Environment, 407:5578-5588.

Farris, F.F., R.L. Dedrick, P.V. Allen and J.C. Smith, 1993. Physiological model for the pharmacokinetics of methyl mercury in the growing rat. Toxicology and Applied Pharmacology, 119:74-90.

Fechhelm, R.G., L.R. Martin, B.J. Gallaway, W.J. Wilson and W.B. Griffiths, 1999. Prudhoe Bay causeways and the summer coastal movements of arctic cisco and least cisco. Arctic, 52:139-151.

Feely, R.A., C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson and B. Hales, 2008. Evidence for upwelling of corrosive "acidified" water onto the continental shelf. Science, 320:1490-1492.

Ferrari, C.P., A. Dommergue and C.F. Boutron, 2004. Profiles of mercury in the snow pack at Station Nord, Greenland shortly after polar sunrise. Geophysical Research Letters, 31:L03401.

Ferrari, C.P., 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 and C.F. Boutron, 2005. Snow-to-air exchanges of mercury in an Arctic seasonal snow pack in Ny-Ålesund, Svalbard. Atmospheric Environment, 39:7633-7645.

Ferrari, C.P., C. Padova, X. Fain, P.A. Gauchard, A. Dommergue, K. Aspmo, T. Berg, W. Cairns, C. Barbante, P. Cescon, L. Kaleschke, A. Richter, F. Wittrock and C. Boutron, 2008. Atmospheric mercury depletion event study in Ny-Alesund (Svalbard) in spring 2005. Deposition and transformation of Hg in surface snow during springtime. Science of the Total Environment, 397:167-177.

Fimreite, N., 1971. Effects of dietary methylmercury on ring-necked pheasants with special reference to reproduction. 39 pp. Canadian Wildlife Service, Occasional paper No. 9. 39 pp.

Fitzgerald, W.F. and C.H. Lamborg, 2004. Geochemistry of mercury in the environment. In: Lollar, B.S. (Ed.). Environmental Geochemistry, Vol. 9, Treatise on Geochemistry, pp. 1-47, Elsevier Ltd.

Fitzgerald, W.F., D.R. Engstrom, C.H. Lamborg, C.M. Tseng, P.H. Balcom and C.R. Hammerschmidt, 2005. Modern and historic atmospheric mercury fluxes in northern Alaska: Global sources and Arctic depletion. Environmental Science and Technology, 39:557-568.

Fitzgerald, W.F., C.H. Lamborg and C.R. Hammerschmidt, 2007. Marine biogeochemical cycling of mercury. Chemical Reviews, 107:641-662.

Fleming, E.J., E.E. Mack, P.G. Green and D.C. Nelson, 2006. Mercury methylation from unexpected sources: Molybdate-inhibited freshwater sediments and an iron-reducing bacterium. Applied and Environmental Microbiology, 72:457-464.

Fontaine, J., E. Dewailly, J.-L. Benedetti, D. Pereg, P. Ayotte and S. Dery, 2008. Re-evaluation of blood mercury, lead and cadmium concentrations in the Inuit population of Nunavik (Quebec): a cross-sectional study. Environmental Health, 7:25.

Forest, A., M. Sampei, H. Hattori, R. Makabe, H. Sasaki, M. Fukuchi, P. Wassmann and L. Fortier, 2007. Particulate organic carbon fluxes on the slope of the Mackenzie Shelf (Beaufort Sea): Physical and biological forcing of shelf-basin exchanges. Journal of Marine Systems, 68:39-54.

Francis, J.A., W.H. Chan, D.J. Leathers, J.R. Miller and D.E. Veron, 2009. Winter Northern Hemisphere weather patterns remember summer Arctic sea-ice extent. Geophysical Research Letters, 36:L07503.

Freeman, H.C. and D.A. Horne, 1973. Mercury in Canadian seals. Bulletin of Environmental Contamination and Toxicology, 10:172-180.

Frey, K.E. and L.C. Smith, 2007. 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 Biogeochemical Cycles, 21: GB1016.

Friedli, H., A.F. Arellano, N. Pirrone and S. Cinnirella, 2009a. Mercury emissions from global biomass burning: Spatial and temporal distribution. In: Pirrone, N. and R. Mason (Eds.). Mercury Fate and Transport in the Global Atmosphere. Springer Science + Business Media.

Friedli, H.R., A.F. Arellano, S. Cinnirella and N. Pirrone, 2009b. Initial estimates of mercury emissions to the atmosphere from global biomass burning. Environmental Science and Technology, 43:3507-3513.

Frost, K.J. and L.F. Lowry, 1981. Trophic importance of some marine gadids in Northern Alaska and their body-otolith size relationships. Fishery Bulletin, 79:187-192.

Fu, P., K. Kawamura, J. Chen and L.A. Barrie, 2009. Isoprene, monoterpene, and sesquiterpene oxidation products in the High Arctic aerosols during late winter to early summer. Environmental Science and Technology, 43:4022-4028.

Furgal, C., S. Bernier, G. Godin, S. Gingras, J. Grodin and E. Dewailly, 2001. Decision-making and diet in the North: Balancing the physical, economic and social components. In: Kalhok, S. (Ed.). Synopsis of Research Conducted under the Northern Contaminants Program. Department of Indian and Northern Affairs, Ottawa, Canada.

Gaden, A., S.H. Ferguson, L. Harwood, H. Melling and G.A. Stern, 2009. Mercury trends in ringed seals (*Phoca hispida*) from the Western Canadian Arctic since 1973: Associations with length of ice-free season. Environmental Science and Technology, 43:3646-3651.

Gagné, F., L. Poissant and C. Blaise, 2009. Ecotoxicity of snowpack collected from selected sites in Quebec, Canada. Water Air and Soil Pollution, 201:121-133.

Gajewski, K., P.B. Hamilton and R. McNeely, 1997. A high resolution proxy-climate record from an arctic lake with annually-laminated sediments on Devon Island, Nunavut, Canada. Journal of Paleolimnology, 17:215-225.

Gallaway, B.J., W.B. Griffiths, P.C. Craig, W.T. Gazey and J.W. Helmericks, 1983. An assessment of the Colville River delta stock of Arctic cisco: Migrants from Canada. Biological Papers, University of Alaska 21:4-23

Galloway, M.E. and B.A. Branfireun, 2004. Mercury dynamics of a temperate forested wetland. Science of the Total Environment, 325:239-254.

Gälman, V., J. Rydberg, S.S. de-Luna, R. Bindler and I. Renberg, 2008. Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. Limnology and Oceanography, 53:1076-1082.

Gamberg, M., B. Braune, E. Davey, B. Elkin, P.F. Hoekstra, D. Kennedy, C. Macdonald, D. Muir, A. Nirwal, M. Wayland and B. Zeeb, 2005. Spatial and temporal trends of contaminants in terrestrial biota from the Canadian Arctic. Science of the Total Environment, 351:148-164.

Gandhi, N., S.P. Bhavsar, M.L. Diamond and J.S. Kuwabara, 2007. Development of a mercury speciation, fate, and biotic uptake (BIOTRANSPEC) model: Application to Lahontan reservoir (Nevada, USA). Environmental Toxicology and Chemistry, 26:2260-2273.

Ganong, W., 2005. Review of Medical Physiology, 22nd Edn. 928 pp. Appleton and Lange, USA.

Gantner, N., M. Power, J.A. Babaluk, J.D. Reist, G. Kock, L.W. Lockhart, K.R. Solomon and D.C.G. Muir, 2009. 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. Environmental Toxicology and Chemistry, 28:254-263.

Gantner, N., M. Power, D. Iqaluk, M. Meili, H. Borg, M. Sundbom, K.R. Solomon, G. Lawson and D.C.G. Muir, 2010a. Mercury concentrations in landlocked Arctic char (*Salvelinus alpinus*) from the Canadian High Arctic: Part I – Insights from trophic relationships in 18 lakes. Environmental Toxicology and Chemistry, 29:621-632.

Gantner, N., D.C. Muir, M. Power, D. Iqaluk, J.D. Reist, M. Meili, H. Borg, J. Hammar, W. Michaud, J.B. Dempson and K.R. Solomon, 2010b. Mercury concentrations in landlocked Arctic char (*Salvelinus alpinus*) from the Canadian High Arctic: Part II – Influence of lake biotic and abiotic characteristics on geographic trends in 27 populations. Environmental Toxicology and Chemistry, 29:633-643.

Gårdfeldt, K., J. Sommar, D. Stromberg and X.B. Feng, 2001. Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase. Atmospheric Environment A, 35:3039-3047.

Gårdfeldt, K., J. Munthe, D. Stromberg and O. Lindqvist, 2003. A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase. Science of the Total Environment 304:127-136.

Garneau, M.-È., W.F. Vincent, L. Alonso-Sàez, Y. Gratton and C. Lovejoy, 2006. Prokaryotic community structure and heterotrophic production in a river-influenced coastal arctic ecosystem. Aquatic Microbial Ecology, 42:27-40.

Gauchard, P.A., K. Aspmo, C. Temme, A. Steffen, C. Ferrari, T. Berg, J. Strom, L. Kaleschke, A. Dommergue, E. Bahlmann, O. Magand, F. Planchon, R. Ebinghaus, C. Banic, S. Nagorski, P. Baussand and C. Boutron, 2005. Study of the origin of atmospheric mercury depletion events recorded in Ny-Alesund, Svalbard, spring 2003. Atmospheric Environment, 39:7620-7632.

George, J.C.C., J. Zeh, R. Suydam and C. Clark, 2004. Abundance and population trend (1978-2001) of western Arctic bowhead whales surveyed near Barrow, Alaska. Marine Mammal Science, 20:755-773.

Geynrikh, A., 1986. Mass species of oceanic phytophagous copepods and their ecology. Oceanology, 26:213-217.

Giles, K.A., S.W. Laxon and A.L. Ridout, 2008. Circumpolar thinning of Arctic sea ice following the 2007 record ice extent minimum. Geophysical Research Letters, 35:L22502.

Gilmour, C.C. and E.A. Henry, 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution, 71:131-169.

Gilmour, C.C., E.A. Henry and R. Mitchell, 1992. Sulfate stimulation of mercury methylation in fresh-water sediments. Environmental Science and Technology, 26:2281-2287.

Givelet, N., G. Le Roux, A. Cheburkin, B. Chen, J. Frank, M.E. Goodsite, H. Kempter, M. Krachler, T. Noernberg, N. Rausch, S. Rheinberger, F. Roos-Barraclough, A. Sapkota, C. Scholz and W. Shotyk, 2004a. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. Journal of Environmental Monitoring, 6:481-492.

Givelet, N., F. Roos-Barraclough, M.E. Goodsite, A.K. Cheburkin and W. Shotyk, 2004b. Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the high Arctic of Canada recorded by peat hummocks. Environmental Science and Technology, 38:4964-4972.

Gobeil, C., R.W. Macdonald and B. Sundby, 1997. Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. Geochimica et Cosmochimica Acta, 61:4647-4654.

Gobeil, C., R.W. Macdonald and J.N. Smith, 1999. Mercury profiles in sediments of the Arctic Ocean basins. Environmental Science and Technology, 33:4194-4198.

Gobeil, C., R.W. Macdonald, J.N. Smith and L. Beaudin, 2001a. Lead contamination in Arctic basin sediments tracks Atlantic water flow pathways. Science, 293:1301-1304.

Gobeil, C., B. Sundby, R.W. Macdonald and J.N. Smith, 2001b. Recent change in organic carbon flux to Arctic Ocean deep basins: Evidence from acid volatile sulfide, manganese and rhenium discord in sediments. Geophysical Research Letters, 28:1743-1746.

Goetz, S.J., A.G. Bunn, G.J. Fiske and R.A. Houghton, 2005. Satellite-observed photosynthetic trends across boreal North America associated with climate and fire disturbance. Proceedings of the National Academy of Sciences of the United States of America, 102:13521-13525.

Golding, G.R., C.A. Kelly, R. Sparling, P.C. Loewen, J.W.M. Rudd and T. Barkay, 2002. Evidence for facilitated uptake of Hg(II) by *Vibrio anguillarum* and *Escherichia coli* under anaerobic and aerobic conditions. Limnology and Oceanography, 47:967-975.

Goñi, M.A., M.B. Yunker, R.W. Macdonald and T.I. Eglinton, 2005. The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean. Marine Chemistry, 93:53-73.

Goodsite, M.E., J.M.C. Plane and H. Skov, 2004. A theoretical study of the oxidation of Hg-0 to HgBr$_2$ in the troposphere. Environmental Science and Technology, 38:1772-1776.

Gorham, E., 1991. Northern peatlands – role in the carbon-cycle and probable responses to climatic warming. Ecological Applications, 1:182-195.

Gorski, P.R., L.B. Cleckner, J.P. Hurley, M.E. Sierszen and D.E. Armstrong, 2003. Factors affecting enhanced mercury bioaccumulation in inland lakes of Isle Royale National Park, USA. Science of the Total Environment, 304:327-348.

Gorski, P.R., D.E. Armstrong, J.P. Hurley and D.P. Krabbenhoft, 2008. Influence of natural dissolved organic carbon on the bioavailability of mercury to a freshwater alga. Environmental Pollution 154:116-123.

Gosselin, G., M. Levasseur, P.A. Wheeler, R.A. Horner and B.C. Booth, 1997. New measurements of phytoplankton and ice algal production in the Arctic Ocean. Deep-Sea Research II, 44:1623-1644.

Grandjean, P. and E. Budtz-Jørgensen, 2007. Total imprecision of exposure biomarkers: Implications for calculating exposure limits. American Journal of Industrial Medicine, 50:712-719.

Granskog, M.A., R.W. Macdonald, C.J. Mundy and D.G. Barber, 2007. Distribution, characteristics and potential impacts of chromophoric dissolved organic matter (CDOM) in the Hudson Strait and the Hudson Bay. Continental Shelf Research, 27:2032-2050.

Gray, J.E., P.M. Theodorakos, E.A. Bailey and R.R. Turner, 2000. Distribution, speciation, and transport of mercury in stream sediment, stream water, and fish collected near abandoned mercury mines in southwestern Alaska, U.S.A. Science of the Total Environment, 260:21-33.

Graydon, J.A., C.A. Emmerton, L.F.W. Lesack and E.N. Kelly, 2009. Mercury in the Mackenzie River delta and estuary: Concentrations and fluxes during open-water conditions. Science of the Total Environment, 407:2980-2988.

Grieg, G., H.E. Gunning and O.P. Strausz, 1970. Reactions of metal atoms. II. The combination of mercury and bromine atoms and the dimerization of HgBr. Journal of Chemical Physics, 52:3684-3690.

Grigal, D.F., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environmental Reviews, 10:1-39.

Grigal, D.F., 2003. Mercury sequestration in forests and peatlands: A review. Journal of Environmental Quality, 32:393-405.

Gubala, C.P., D.R. Engstrom and J.R. White, 1990. Effects of iron cycling on $^{210}$Pb dating of sediments in an Adirondack lake, U.S.A. Canadian Journal of Fisheries and Aquatic Sciences, 47:1821-1829.

Guentzel, J.L., R.T. Powell, W.M. Landing and R.P. Mason, 1996. Mercury associated with colloidal material in an estuarine and an open-ocean environment. Marine Chemistry, 55:177-188.

Guiguer, K., J.D. Reist, M. Power and J.A. Babaluk, 2002. Using stable isotopes to confirm the trophic ecology of Arctic charr morphotypes from Lake Hazen, Nunavut, Canada. Journal of Fish Biology, 60:348-362.

Guo, L.D. and R.W. Macdonald, 2006. 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 Biogeochemical Cycles, 20:GB2011.

Guo, L.D., C.L. Ping and R.W. Macdonald, 2007. Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. Geophysical Research Letters, 34: L13603.

Gyrd-Hansen, N., 1981. Toxicokinetics of methyl mercury in pigs. Archives of Toxicology, 48:173-181.

Hall, B., 1995. The gas-phase oxidation of elemental mercury by ozone. Water Air and Soil Pollution, 80:301-315.

Hall, B.D., R.A. Bodaly, R.J.P. Fudge, J.W.M. Rudd and D.M. Rosenberg, 1997. Food as the dominant pathway of methylmercury uptake by fish. Water Air and Soil Pollution, 100:13-24.

Hall, B.D., G.R. Aiken, D.P. Krabbenhoft, M. Marvin-DiPasquale and C.M. Swarzenski, 2008. Wetlands as principal zones of methylmercury production in southern Louisiana and the Gulf of Mexico region. Environmental Pollution, 154:124-134.

Hamel, D., A. de Vernal, M. Gosselin and C. Hillaire-Marcel, 2002. 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 Research II, 49:5277-5295.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. Environmental Science and Technology, 38:1487-1495.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2005. Methylmercury in mosquitoes related to atmospheric deposition and contamination. Environmental Science and Technology, 39:3034-3039.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2006a. Photodecomposition of methylmercury in an Arctic Alaskan lake. Environmental Science and Technology, 40:1212-1216.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2006b. Methylmercury in freshwater fish linked to atmospheric mercury deposition. Environmental Science and Technology, 40:7764-7770.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2006. Methylmercury cycling in sediments on the continental shelf of southern New England. Geochimica et Cosmochimica Acta, 70:918-930.

Hammerschmidt, C.R. and W.F. Fitzgerald, 2008. Methylmercury in arctic Alaskan mosquitoes: implications for impact of atmospheric mercury depletion events. Environmental Chemistry, 5:127-130.

Hammerschmidt, C.R., M.B. Sandheinrich, J.G. Wiener and R.G. Rada, 2002. Effects of dietary methylmercury on reproduction of fathead minnows. Environmental Science and Technology, 36:877-883.

Hammerschmidt, C.R., W.F. Fitzgerald, C.H. Lamborg, P.H. Balcom and C.M. Tseng, 2006. Biogeochemical cycling of methylmercury in lakes and tundra watersheds of Arctic Alaska. Environmental Science and Technology, 40:1204-1211.

Hammerschmidt, C.R., C.H. Lamborg and W.F. Fitzgerald, 2007. Aqueous phase methylation as a potential source of methylmercury in wet deposition. Atmospheric Environment, 41:1663-1668.

Hansen, J.C., T.Y. Toribara and A.G. Muhs, 1989. Trace metals in humans and animal hair from the 15th century graves in Qilakitsoq, compared with recent samples. In: Hansen, J.P. and H. Gulløv (Eds.). The Mummies from Qilakitsoq, pp. 161-167, Meddelelser om Grønland, Man and Society.

Hansen, C.R.T., C.O. Nielsen, R. Dietz and M.M. Hansen, 1990. Zinc, cadmium, mercury and selenium in minke whales, belugas and narwhals from West Greenland. Polar Biology, 10:529-539.

Hansen, J., B. Deutch and J. Odland, 2008. Dietary transitions and contaminants in the Arctic: Emphasis on Greenland. Circumpolar Health Supplements 2.

Hansson, L.A., 1992. Factors regulating periphytic algal biomass. Limnology and Oceanography, 37:322-328.

Hare, A., G.A. Stern, R.W. Macdonald, Z.Z. Kuzyk and F.Y. Wang, 2008. Contemporary and preindustrial mass budgets of mercury in the Hudson Bay marine system: The role of sediment recycling. Science of the Total Environment, 406:190-204.

Hargrave, B.T., B. von Bodungen, P. Stoffyn-Egli and P.J. Mudie, 1994. Seasonal variability in particle sedimentation under permanent ice cover in the Arctic Ocean. Continental Shelf Research, 14:279-293.

Harmens, H., D.A. Norris, G.R. Koerber, A. Buse, E. Steinnes and Å. Rühling, 2008. Temporal trends (1990-2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environmental Pollution, 151:368-376.

Harrington, R. and R.C. Bales, 1998. Interannual, seasonal, and spatial patterns of meltwater and solute fluxes in a seasonal snowpack. Water Resources Research, 34:823-831.

Harris, R.C., J.W.M. Rudd, M. Almyot and 21 others, 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proceedings of the National Academy of Sciences of the United States of America, 104:16586-16591.

Hatch, S.A. and D.N. Nettleship, 1998. Northern fulmar (*Fulmaris glacialis*). In: Poole, A. and F. Gill (Eds.). The Birds of North America, No. 361.

Hawkes, W.C. and N.C. Keim, 2003. Dietary selenium intake modulates thyroid hormone and energy metabolism in men. Journal of Nutrition, 133:3443-3448.

Headon, C.M., R.J. Hall and G. Mierle, 1996. Dynamics of radiolabelled methylmercury in crayfish (*Orconectes virilis*). Canadian Journal of Fisheries and Aquatic Sciences, 53:2862-2869.

Health Canada, 1984. Methylmercury in Canada Vol. II. Ministry of National Health and Welfare, Ottawa, Canada.

Hecky, R.E. and R.H. Hesslein, 1995. Contributions of benthic algae to lake food webs as revealed by stable isotope analysis. Journal of the North American Benthological Society, 14:631-653.

Heinz, G.H., 1976. Methylmercury: second-year feeding effects on mallard reproduction and duckling behavior. Journal of Wildlife Management, 540:82-90.

Heinz, G.H., D.J. Hoffman, J.D. Klimstra, K.R. Stebbins, S.L. Kondrad and C.A. Erwin, 2009. Species differences in the sensitivity of avian embryos to methylmercury. Archives of Environmental Contamination and Toxicology, 56:129-138.

Helgason, L.B., R. Barrett, E. Lie, A. Polder, J.U. Skaare and G.W. Gabrielsen, 2008. Levels and temporal trends (1983-2003) of persistent organic pollutants (POPs) and mercury (Hg) in seabird eggs from Northern Norway. Environmental Pollution, 155:190-198.

Hellou, J., W.G. Warren, J.F. Payne, S. Belkhode and P. Lobel, 1992. Heavy metals and other elements in three tissues of cod *Gadus morhua* from the northwest Atlantic. Marine Pollution Bulletin, 24:452-458.

Hermanson, M.H., 1998. Anthropogenic mercury deposition to arctic lake sediments. Water Air and Soil Pollution, 101:309-321.

Hill, W.R. and I.L. Larsen, 2005. Growth dilution of metals in microalgal biofilms. Environmental Science and Technology, 39:1513-1518.

Hilton, G.M., D.R. Thompson, P.M. Sagar, R.J. Cuthbert, Y. Cherel and S.J. Bury, 2006. A stable isotopic investigation into the causes of decline in a sub-Antarctic predator, the rockhopper penguin *Eudyptes chrysocome*. Global Change Biology, 12:611-625.

Hinzman, L.D., N.D. Bettez, W.R. Bolton and 32 others, 2005. Evidence and implications of recent climate change in northern Alaska and other arctic regions. Climatic Change, 72:251-298.

Hirdman, D., K. Aspmo, J.F. Burkhart, S. Eckhardt, H. Sodemann and A. Stohl, 2009. Transport of mercury in the Arctic atmosphere: Evidence for a springtime net sink and summer-time source. Geophysical Research Letters, 36:L12814.

Hobbie, J.E., B.J. Peterson, N. Bettez, L. Deegan, W.J. O'Brien, G.W. Kling, G.W. Kipphut, W.B. Bowden and A.E. Hershey, 1999. Impact of global change on the biogeochemistry and ecology of an Arctic freshwater system. Polar Research, 18:207-214.

Hobson, K.A. and H.E. Welch, 1995. Cannibalism and trophic structure in a high Arctic lake: insights from stable-isotope analysis. Canadian Journal of Fisheries and Aquatic Sciences, 52:1195-1201.

Hobson, K.A., R.T. Alisauskas and R.G. Clark, 1993. Stable-nitrogen isotope enrichment in avian-tissues due to fasting and nutritional stress – implications for isotopic analyses of diet. Condor, 95:388-394.

Hobson, K.A., A. Fisk, N. Karnovsky, M. Holst, J.M. Gagnon and M. Fortier, 2002. A stable isotope ($\delta^{13}C$, $\delta^{15}N$) model for the North Water food web: implications for evaluating trophodynamics and the flow of energy and contaminants. Deep-Sea Research II, 49:5131-5150.

Hodson, A., A.M. Anesio, M. Tranter, M. Fountain, M. Osborn, J. Priscu, J. Laybourn-Parry and B. Sattler, 2008. Glacial ecosystems. Ecological Monographs, 78:41-67.

Hollweg, T.A., C.C. Gilmour and R.P. Mason, 2009. Methylmercury production in sediments of Chesapeake Bay and the mid-Atlantic continental margin. Marine Chemistry, 114:86-101.

Holmes, C.D., D.J. Jacob, E.S. Corbitt, J. Mao, X. Yang, R. Talbot and F. Slemr, 2010. Global atmospheric model for mercury including oxidation by bromine atoms. Chemistry and Physics Discussions, 10:19845-19900.

Honda, M., J. Inoue and S. Yamane, 2009. Influence of low Arctic sea-ice minima on anomalously cold Eurasian winters. Geophysical Research Letters, 36:L08707.

Hood, E., J. Fellman, R.G.M. Spencer, P.J. Hernes, R. Edwards, D. D'Amorre and D. Scott, 2009. Glaciers as a source of ancient and labile organic matter to the marine environment. Nature, 462:1044-1048.

Horner, R.A., 1985. Sea Ice Biota. CRC Press.

Horner, R. and G.C. Schrader, 1982. Relative contributions of ice algae, phytoplankton, and benthic microalgae to primary production in nearshore regions of the Beaufort Sea. Arctic, 35:485-503.

Horton, T.W., J.D. Blum, Z. Xie, M. Hren and P. Chamberlain, 2010. Stable isotope food-web analysis and mercury biomagnification in polar bears (*Ursus maritimus*). Polar Research, 28:443-454.

Hoydal, K. and M. Dam, 2005. AMAP Faroe Islands Heavy metals and POPs Core programme 2004. Report No. 2005:2. 76 pp. Food-Veterinary and Environmental Agency, Faroe Islands.

Hoydal, K. and M. Dam, 2009. AMAP Faroe Islands Heavy Metals and POPs Core Programme 2005-2008. Report No. 2009:1. 101 pp. Environment Agency, Faroe Islands.

Hylander, L.D. and M.E. Goodsite, 2006. Environmental costs of mercury pollution. Science of the Total Environment, 368:352-370.

Hylander, L.D., J. Grohn, M. Tropp, A. Vikstrom, H. Wolpher, E.D.E. Silva, M. Meili and L.J. Oliveira, 2006. Fish mercury increase in Lago Manso, a new hydroelectric reservoir in tropical Brazil. Journal of Environmental Management, 81:155-166.

Ikemoto, T., T. Kunito, H. Tanaka, N. Baba, N. Miyazaki and S. Tanabe, 2004. Detoxification mechanism of heavy metals in marine mammals and seabirds: Interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Archives of Environmental Contamination and Toxicology, 47:402-413.

INAC, 2009. Canadian Arctic Contaminants and Health Assessment Report. Northern Contaminants Program. Indian and Northern Affairs Canada,

IPCC, 2007. Climate Change 2007 – The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC. Solomon, S., D. Qin, M. Manning, M. Marquis, K. Averyt, M. Tignor, H. Miller and Z. Chen (Eds.). 996 pp. Intergovernmental Panel on Climate Change. Cambridge University Press.

Iverfeldt, A., 1991. Occurrence and turnover of atmospheric mercury over the Nordic countries. Water Air and Soil Pollution, 56:251-265.

Jackson, J.A., 1997. Glossary of Geology. 4th edition. 769 pp. American Geophysical Institute.

Jaeger, I., H. Hop and G.W. Gabrielsen, 2009. Biomagnification of mercury in selected species from an Arctic marine food web in Svalbard. Science of the Total Environment, 407:4744-4751.

Jaffe, D., E. Prestbo, P. Swartzendruber, P. Weiss-Penzias, S. Kato, A. Takami, S. Hatakeyama and Y. Kajii, 2005. Export of atmospheric mercury from Asia. Atmospheric Environment, 39:3029-3038.

Janeway, C.A., P. Travers, M. Walport and M. Shlomchik, 2001. Immune Biology – The Immune System in Health and Disease. 5 edition.732 pp. Garland Publishing.

JECFA, 2003. Sixty-First Meeting, Summary and Conclusions. Available: ftp://ftp. fao.org/es/esn/jecfa/jecfa61sc.pdf. Joint Expert Committee on Food Additives.

Jewett, S.C. and L.K. Duffy, 2007. Mercury in fishes of Alaska, with emphasis on subsistence species. Science of the Total Environment, 387:3-27.

Jia, G.S.J., H.E. Epstein and D.A. Walker, 2003. Greening of arctic Alaska, 1981-2001. Geophysical Research Letters, 30:2067.

Johansen, P., D. Muir, G. Asmund and F. Riget, 2004. Human exposure to contaminants in the traditional Greenland diet. Science of the Total Environment, 331:189-206.

Johnson, K.P., J.D. Blum, G.J. Keeler and T.A. Douglas, 2008. Investigation of the deposition and emission of mercury in arctic snow during an atmospheric mercury depletion event. Journal of Geophysical Research-Atmospheres, 113:D17304.

Johnson-Down, L. and G.M. Egeland, 2010. Adequate nutrient intakes are associated with traditional food consumption in Nunavut Inuit children aged 3-5 years. Journal of Nutrition, 140:1311-1316.

Jones, A.E., P.S. Anderson, E.W. Wolff, H.K. Roscoe, G.J. Marshall, A. Richter, N. Brough and S.R. Colwell, 2010. Vertical structure of Antarctic tropospheric ozone depletion events: characteristics and broader implications. Atmospheric Chemical and Physical Discussions, 10:8189-8246.

Junge, K., H. Eicken, B.D. Swanson and J.W. Deming, 2006. Bacterial incorporation of leucine into protein down to -20 degrees C with evidence for potential activity in sub-eutectic saline ice formations. Cryobiology, 52:417-429.

Kahl, J.D.W., J.A. Galbraith and D.A. Martinez, 1999. Decadal-scale variability in long-range atmospheric transport to the Summit of the Greenland Ice Sheet. Geophysical Research Letters, 26:481-484.

Kaleschke, L., A. Richter, J. Burrows, O. Afe, G. Heygster, J. Notholt, A.M. Rankin, H.K. Roscoe, J. Hollwedel, T. Wagner and H.W. Jacobi, 2004. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. Geophysical Research Letters, 31:L16114.

Kamman, N.C., N.M. Burgess, C.T. Driscoll, H.A. Simonin, W. Goodale, J. Linehan, R. Estabrook, M. Hutcheson, A. Major, A.M. Scheuhammer and D.A. Scruton, 2005. Mercury in freshwater fish of northeast North America – A geographic perspective based on fish tissue monitoring databases. Ecotoxicology, 14:163-180.

Kannan, K., T. Agusa, T.J. Evans and S. Tanabe, 2007. Trace element concentrations in livers of polar bears from two populations in Northern and Western Alaska. Archives of Environmental Contamination and Toxicology, 53:473-482.

Karimi, R., C.Y. Chen, P.C. Pickhardt, N.S. Fisher and C.L. Folt, 2007. Stoichiometric controls of mercury dilution by growth. Proceedings of the National Academy of Sciences of the United States of America, 104:7477-7482.

Karlsson, J. and P. Byström, 2005. Littoral energy mobilization dominates energy supply for top consumers in subarctic lakes. Limnology and Oceanography, 50:538-543.

Karlsson, J., A. Jonsson and M. Jansson, 2005. Productivity of high-latitude lakes: climate effect inferred from altitude gradient. Global Change Biology, 11:710-715.

Keller, W., A.M. Paterson, K.M. Somers, P.J. Dillon, J. Heneberry and A. Ford, 2008. Relationships between dissolved organic carbon concentrations, weather, and acidification in small Boreal Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences, 65:786-795.

Kelly, W.R., 1993. The liver and biliary system. In: Jubb, K.V.F., P.C. Kennedy and N. Palmer (Eds.). Pathology of Domestic Animals, pp. 319-406, Academic Press.

Kerin, E.J., C.C. Gilmour, E. Roden, M.T. Suzuki, J.D. Coates and R.P. Mason, 2006. Mercury methylation by dissimilatory iron-reducing bacteria. Applied and Environmental Microbiology, 72:7919-7921.

Kerr, R.A., 2009. Arctic summer sea ice could vanish soon but not suddenly. Science, 323:1655.

Khalizov, A.F., B. Viswanathan, P. Larregaray and P.A. Ariya, 2003. A theoretical study on the reactions of Hg with halogens: Atmospheric implications. Journal of Physical Chemistry A, 107:6360-6365.

Kidd, K.A., M.J. Paterson, R.H. Hesslein, D.C.G. Muir and R.E. Hecky, 1999. Effects of northern pike (*Esox lucius*) additions on pollutant accumulation and food web structure, as determined by $\delta^{13}C$ and $\delta^{15}N$, in a eutrophic and an oligotrophic lake. Canadian Journal of Fisheries and Aquatic Sciences, 56:2193-2202.

Kim, E.Y., T. Murakami, K. Saeki and R. Tatsukawa, 1996. Mercury levels and its chemical form in tissues and organs of seabirds. Archives of Environmental Contamination and Toxicology, 30:259-266.

King, M.D. and W.R. Simpson, 2001. Extinction of UV radiation in Arctic snow at Alert, Canada (82 degrees N). Journal of Geophysical Research-Atmospheres, 106:12499-12507.

Kinghorn, A., M. Humphries, P. Outridge and H.M. Chan, 2006. Reconstructing historical mercury exposure from beluga whale consumption among Inuit in the Mackenzie Delta. Journal of Ethnobiology, 26:310-326.

Kingsley, M., 1994. Mercury and other inorganic contaminants in country foods in eastern Hudson Bay. In: Murray, J.L. and R.G. Shearer (Eds.). Synopsis of research conducted under the 1993/94 Northern Contaminants Program. Environmental Studies No. 73. Department of Indian Affairs and Northern Development, Ottawa, Canada.

Kirk, J.L., V.L.S. Louis and M.J. Sharp, 2006. Rapid reduction and reemission of mercury deposited into snowpacks during atmospheric mercury depletion events at Churchill, Manitoba, Canada. Environmental Science and Technology, 40:7590-7596.

Kirk, J.L., V.L. St. Louis, H. Hintelmann, I. Lehnherr, B. Else and L. Poissant, 2008. Methylated mercury species in marine waters of the Canadian High and sub-Arctic. Environmental Science and Technology, 42:8367-8373.

Klaassen, C.D., Amdur, M.O., Doull, J., 2006. Casarett and Doulls Toxicology. The Basic Science of Poisons. 6th Edn. McGraw-Hill, 1280 pp.

Klaassen, C.D., J. Liu and B.A. Diwan, 2009. Metallothionein protection of cadmium toxicity. Toxicology and Applied Pharmacology, 238:215-220.

Klaminder, J., K. Yoo, J. Rydberg and R. Giesler, 2008. An explorative study of mercury export from a thawing palsa mire. Journal of Geophysical Research, 113:G04034.

Klaper, R., C.B. Rees, P. Drevnick, D. Weber, M. Sandheinrich and M.J. Carvan, 2006. Gene expression changes related to endocrine function and decline in reproduction in fathead minnow (*Pimephales promelas*) after dietary methylmercury exposure. Environmental Health Perspectives, 114:1337-1343.

Knightes, C.D., E.M. Sunderland, M.C. Barber, J.M. Johnston and R.B. Ambrose, 2009. Application of ecosystem-scale fate and bioaccumulation models to predict fish mercury response times to changes in atmospheric deposition. Environmental Toxicology and Chemistry, 28:881-893.

Knudsen, L.B., G.W. Gabrielsen, J. Verreault, R. Barrett, J.U. Skaare, A. Polder and E. Lie, 2005. Temporal trends of brominated flame retardants, cyclododeca-1,5,9-triene and mercury in eggs of four seabird species from Northern Norway and Svalbard. SPFO-Report 942/2005. 942/2005, 42 pp. Norwegian Polar Institute.

Kochtubajda, B., M.D. Flannigan, J.R. Gyakum, R.E. Stewart, K.A. Logan and T.-V. Nguyen, 2006. Lightening and fires in the Northwest Territories and responses to future climate change. Arctic, 59:211-221.

Koeman, J. and W. van deVen, 1975. Mercury and selenium in marine mammals and birds. Science of the Total Environment, 3:279-287.

Koeman, J., W. Peeters, C. Koudstaal-Hol, P. Tijoe, J. De Goeij, 1973. Mercury-selenium correlations in marine mammals. Nature, 245:385-386.

Koop, T., A. Kapilashrami, L.T. Molina and M.J. Molina, 2000. Phase transitions of sea-salt/water mixtures at low temperatures: Implications for ozone chemistry in the polar marine boundary layer. Journal of Geophysical Research, 105:26393-26402.

Korhola, A., S. Sorvari, M. Rautio, P.G. Appleby, J.A. Dearing, Y. Hu, N. Rose, A. Lami and N.G. Cameron, 2002. A multi-proxy analysis of climate impacts on the recent development of subarctic Lake Saanajarvi in Finnish Lapland. Journal of Paleolimnology, 28:59-77.

Koster, M.D., D.P. Ryckman, D.V.C. Weseloh and J. Struger, 1996. Mercury levels in Great Lakes herring gull (*Larus argentatus*) eggs, 1972-1992. Environmental Pollution, 93:261-270.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley and A.W. Andren, 1995. Mercury cycling in the allequash creek watershed, Northern Wisconsin. Water Air and Soil Pollution, 80:425-433.

Kraepiel, A.M.L., K. Keller, H.B. Chin, E.G. Malcolm and F.M.M. Morel, 2003. Sources and variations of mercury in tuna. Environmental Science and Technology, 37:5551-5558.

Krey, A., M. Kwan and L.H.M. Chan, 2008. Neurochemical changes associated with mercury exposure in polar bears (*Ursus maritimus*). Poster Session: Environmental Toxicology. Ecotoxicology of Emerging And Persistent Pollutants. 5th SETAC World Congress Sydney, Australia 3-7 August 2008.

Krupnik, I. and J. Dyanna (Eds.), 2002. The Earth Is Faster Now: Indigenous Observations of Arctic Environmental Change. 383 pp. Frontiers in Polar Science. Arctic Research Consortium of the United States.

Kuzyk, Z.Z.A., M.A. Goni, G.A. Stern and R.W. Macdonald, 2008. Sources, pathways and sinks of particulate organic matter in Hudson Bay: Evidence from lignin distributions. Marine Chemistry, 112:215-229.

Kuzyk, Z.A., R.W. Macdonald, S.C. Johannessen, C. Gobeil and G.A. Stern, 2009. Towards a sediment and organic carbon budget for Hudson Bay. Marine Geology, 264:190-208.

Kvitek, R.G., K.E. Conlan and O.J. Iampietro, 1998. Black pools of death: hypoxic, brine-filled ice gouge depressions become lethal traps for benthic organisms in a shallow Arctic embayment. Marine Ecology Progress Series, 162:1-10.

Kwok, R. and D.A. Rothrock, 2009. Decline in Arctic sea ice thickness from submarine and ICESat records: 1958-2008. Geophysical Research Letters, 36:L15501.

Lahoutifard, N., M. Sparling and D. Lean, 2005. Total and methyl mercury patterns in Arctic snow during springtime at Resolute, Nunavut, Canada. Atmospheric Environment, 39:7597-7606.

Lahoutifard, N., L. Poissant and S.L. Scott, 2006. Scavenging of gaseous mercury by acidic snow at Kuujjuarapik, Northern Quebec. Science of the Total Environment, 355:118-126.

Laidre, K.L., I. Stirling, L.F. Lowry, O. Wiig, M.P. Heide-Jorgensen and S.H. Ferguson, 2008. Quantifying the sensitivity of arctic marine mammals to climate-induced habitat change. Ecological Applications, 18:S97-S125.

Lalonde, J., M. Amyot, A.M.L. Kraepiel and F.M.M. Morel, 2001. Photo-oxidation of Hg(0) in artificial and natural waters. Environmental Science and Technology, 35:1367-1372.

Lalonde, J.D., A.J. Poulain and M. Amyot, 2002. The role of mercury redox reactions in snow on snow-to-air mercury transfer. Environmental Science and Technology, 36:174-178.

Lalonde, J.D., Amyot, M., Doyon, M.-R., Auclair, J.-C., 2003. Photoinduced Hg(II) reduction in snow from the remote and temperate Experimental Lakes Area (Ontario, Canada). Journal of Geophysical Research, 108:4211.

Lambertsson, L. and M. Nilsson, 2006. Organic material: The primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. Environmental Science and Technology, 40:1822-1829.

Lamborg, C.H., W.F. Fitzgerald, J. O'Donnell and T. Torgersen, 2002a. A non-steady-state compartment model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients. Geochimica et Cosmochimica Acta, 66:1105-1118.

Lamborg, C.H., W.F. Fitzgerald, A.W.H. Damman, J.M. Benoit, P.H. Balcom and D.R. Engstrom, 2002b. Modern and historic atmospheric mercury fluxes in both hemispheres: global and regional mercury cycling implications. Global Biogeochemical Cycles, 16:1104.

Landers, D.H., J. Ford, C. Gubala, M. Monetti, B.K. Lasorsa and J. Martinson, 1995. Mercury in vegetation and lake-sediments from the US Arctic. Water Air and Soil Pollution, 80:591-601.

Landers, D.H., C. Gubala, M. Verta, M. Lucotte, K. Johansson, T. Vlasova and W.L. Lockhart, 1998. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. Atmospheric Environment, 32:919-928.

Landers, D.H., S.L. Simonich, D.A. Jaffe, L.H. Geiser, D.H. Campbell, A.R. Schwindt, C.B. Schreck, M.L. Kent, W.D. Hafner, H.E. Taylor, K.J. Hageman, S. Usenko, L.K. Ackerman, J.E. Schrlau, N.L. Rose, T.F. Blett and M.M. Erway, 2008. The Fate, Transport, and Ecological Impacts of Airborne Contaminants in Western National Parks (USA). EPA/600/R-07/138. U.S. Environmental Protection Agency.

Landis, M.S., R.K. Stevens, F. Schaedlich and E.M. Prestbo, 2002. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. Environmental Science and Technology, 36:3000-3009.

Larsen, R.B. and M. Dam, 2003. AMAP Faroe Islands 1997-1998. In: Hoydal, K. and M. Dam (Eds.). AMAP Greenland and the Faroe Islands 1997- 2001. Vol 3: The environment of the Faroe Islands. Danish Ministry of Environment, Copenhagen. 265 pp.

Larsson, P., N. Holmqvist, P. Stenroth, O. Berglund, P. Nystrom and W. Graneli, 2007. Heavy metals and stable isotopes in a benthic omnivore in a trophic gradient of lakes. Environmental Science & Technology, 41:5973-5979.

Laurier, F.J.G., R.P. Mason, G.A. Gill and L. Whalin, 2004. Mercury distributions in the North Pacific Ocean – 20 years of observations. Marine Chemistry, 90:3-19.

Lavery, T.J., C.M. Kemper, K. Sanderson, C.G. Schultz, P. Coyle, J.G. Mitchell and L. Seuront, 2009. Heavy metal toxicity of kidney and bone tissues in South Australian adult bottlenose dolphins (*Tursiops aduncus*). Marine Environmental Research, 67:1-7.

Lavoie, D., R.W. Macdonald and K.L. Denman, 2009. Primary productivity and export fluxes on the Canadian shelf of the Beaufort Sea: A modelling study. Journal of Marine Systems, 75:17-32.

Lavoie, D., K.L. Denman and R.W. Macdonald, 2010. Effects of future climate change on primary productivity and export fluxes in the Beaufort Sea. Journal of Geophysical Research, 115:C04018.

Law, R.J., 1996. Cadmium in small mammals. In: Nelson Beyer, W., G.H. Heinz and A.W. Redmon-Norwood (Eds.). Environmental Contaminants in Wildlife. Interpreting Tissue Concentrations, pp. 357-376, CRC Press.

Lawrence, D.M., A.G. Slater, R.A. Tomas, M.M. Holland and C. Deser, 2008. Accelerated Arctic land warming and permafrost degradation during rapid sea ice loss. Geophysical Research Letters, 35:L11506.

Laws, E.A., B.N. Popp, R.R. Bidigare, M.C. Kennicutt and S.A. Macko, 1995. Dependence of phytoplankton carbon isotopic composition on growth-rate and $CO_{2aq}$: Theoretical considerations and experimental results. Geochimica et Cosmochimica Acta, 59:1131-1138.

Lawson, N.M. and R.P. Mason, 1998. Accumulation of mercury in estuarine food chains. Biogeochemistry, 40:235-247.

Legendre, L., S.F. Ackley, G.S. Dieckmann, B. Gulliksen, R. Horner, T. Hoshiai, I.A. Melnikov, W.S. Reeburgh, M. Spindler and C.W. Sullivan, 1992. Ecology of sea ice biota. 2. Global significance. Polar Biology, 12:429-444.

Lehnherr, I. and V.L.S. Louis, 2009. The importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. Environmental Science and Technology, 43:5692-5698.

Leighton, F.A., M. Cattet, R. Norstrom and S. Trudeau, 1988. A cellular basis for high levels of vitamin-A in livers of polar bears (*Ursus maritimus*) – the Ito cell. Canadian Journal of Zoology, 66:480-482.

Leitch, D.R., 2006. Mercury distribution in water and permafrost of the lower Mackenzie Basin, their contribution to the mercury contamination in the Beaufort Sea marine ecosystem, and potential effects of climate variation. Department of Environment and Geography. 118 pp. University of Manitoba.

Leitch, D.R., J. Carrie, D. Lean, R.W. Macdonald, G.A. Stern and F.Y. Wang, 2007. The delivery of mercury to the Beaufort Sea of the Arctic Ocean by the Mackenzie River. Science of the Total Environment, 373:178-195.

Letcher, R.J., J. Bustnes, R. Dietz, B.M. Jenssen, E.H. Jørgensen, C. Sonne, J. Verreault, M.M. Vijayan and G.W. Gabrielsen, 2010. Exposure and effects assessment of persistent organohalogen contaminants in arctic wildlife and fish. Science of the Total Environment, 408 2995-3043.

Li, Y.-F., R.W. Macdonald, L.M.M. Jantunen, T. Harner, T.F. Bidleman and W.M.J. Strachan, 2002. The transport of ß-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. Science of the Total Environment, 291:229-246.

Li, Y.-F., R.W. Macdonald, J.M. Ma, H. Hung and S. Venkatesh, 2004. Historical α-HCH budget in the Arctic Ocean: The Arctic mass balance box model (AMBBM). Science of the Total Environment, 324:115-139.

Li, C.S., J. Cornett, S. Willie and J. Lam, 2009. Mercury in Arctic air: The long-term trend. Science of the Total Environment, 407:2756-2759.

Lindberg, S.E., A.B. Brooks, C.J. Lin, K. Scott, T. Meyers, L. Chambers, M. Landis and R.K. Stevens, 2001. Formation of reactive gaseous mercury in the Arctic: evidence of oxidation of Hg0 to gas-phase Hg-II compounds after arctic sunrise. Water Air and Soil Pollution, 1:295-302.

Lindberg, S.E., S. Brooks, C.J. Lin, K.J. Scott, M.S. Landis, R.K. Stevens, M. Goodsite and A. Richter, 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. Environmental Science and Technology, 36:1245-1256.

Lindberg, S., R. Bullock, R. Ebinghaus, D. Engstrom, X. Feng, W. Fitzgerald, N. Pirrone, E. Prestbo and C. Seigneur, 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. Ambio, 36:19-32.

Lindeberg, C., R. Bindler, I. Renberg, O. Emteryd, E. Karlsson and N.J. Anderson, 2006. Natural fluctuations of mercury and lead in Greenland Lake sediments. Environmental Science and Technology, 40:90-95.

Lindeberg, C., R. Bindler, C. Bigler, P. Rosen and I. Renberg, 2007. Mercury pollution trends in subarctic lakes in the northern Swedish mountains. Ambio, 36:401-405.

Lindqvist, O., K. Johansson, M. Aastrup, A. Andersson, L. Bringmark, G. Hovsenius, L. Hakanson, A. Iverfeldt, M. Meili and B. Timm, 1991. Mercury in the Swedish environment – recent research on causes, consequences and corrective methods. Water Air and Soil Pollution, 55:xi-261.

Lindsay, R.W. and J. Zhang, 2005. The thinning of Arctic sea ice, 1988-2003: Have we passed a tipping point? Journal of Climate, 18:4879-4894.

Lockhart, W.L. and M. Evans, 2000. Mercury in fish from stock surveys of lakes in the western Northwest Territories: Investigations into the factors affecting mercury levels. In: Kalhok, S. (Ed.). Synopsis of Research Conducted Under the 1999/2000 Northern Contaminants Program, pp. 181-190, Indian and Northern Affairs Canada, Ottawa.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, R.A. Danell, R.V. Hunt, G.J. Brunskill, J. Delaronde and V. St. Louis, 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. Biogeochemistry, 40:163-173.

Lockhart, W.L., 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.C.G. Muir, M. Stoddart, G. Stephens, S. Stephenson, S. Harbicht, N. Snowshoe, B. Grey, S. Thompson and N. DeGraff, 2005a. A history of total mercury in edible muscle of fish from lakes in northern Canada. Science of the Total Environment, 351-352:427-463.

Lockhart, W.L., G.A. Stern, R. Wagemann, R.V. Hunt, D.A. Metner, J. DeLaronde, B. Dunn, R.E.A. Stewart, C.K. Hyatt, L. Harwood and K. Mount, 2005b. Concentrations of mercury in tissues of beluga whales (*Delphinapterus leucas*) from several communities in the Canadian Arctic from 1981 to 2002. Science of the Total Environment, 351:391-412.

Lodenius, M., A. Seppanen and M. Herranen, 1983. Accumulation of mercury in fish and man from reservoirs in northern Finland. Water Air and Soil Pollution, 19:237-246.

Lokken, J.A., G.L. Finstad, K.L. Dunlap and L.K. Duffy, 2009. Mercury in lichens and reindeer hair from Alaska: 2005-2007 pilot survey. Polar Record, 45:368-374.

Lonne, O.J. and G.W. Gabrielsen, 1992. Summer diet of seabirds feeding in sea-ice-covered waters near Svalbard. Polar Biology, 12:685-692.

Lonne, O.J. and B. Gulliksen, 1989. Size, age and diet of polar cod, *Boreogadus saida* (Lepechin 1773), in ice covered waters. Polar Biology, 9:187-191.

Loseto, L.L., 2007. Beaufort Sea beluga whales: an ecological approach to examining diet and dietary sources of mercury. Ph.D. Thesis. Dept of Zoology. 155 pp. University of Manitoba, Winnipeg.

Loseto, L.L., D.R.S. Lean and S.D. Siciliano, 2004a. Snowmelt sources of methylmercury to High Arctic ecosystems. Environmental Science and Technology, 38:3004-3010.

Loseto, L.L., S.D. Siciliano and D.R.S. Lean, 2004b. Methylmercury production in High Arctic wetlands. Environmental Toxicology and Chemistry, 23:17-23.

Loseto, L.L., P. Richard, G.A. Stern, J. Orr and S.H. Ferguson, 2006. Segregation of Beaufort Sea beluga whales during the open-water season. Canadian Journal of Zoology, 84:1743-1751.

Loseto, L.L., G.A. Stern and S.H. Ferguson, 2008a. Size and biomagnification: How habitat selection explains beluga mercury levels. Environmental Science and Technology, 42:3982-3988.

Loseto, L.L., G.A. Stern, D. Deibel, T.L. Connelly, A. Prokopowicz, D.R.S. Lean, L. Fortier and S.H. Ferguson, 2008b. Linking mercury exposure to habitat and feeding behaviour in Beaufort Sea beluga whales. Journal of Marine Systems, 74:1012-1024.

Loseto, L.L., G.A. Stern, T.L. Connelly, D. Deibel, B. Gemmill, A. Prokopowicz, L. Fortier and S.H. Ferguson, 2009. Summer diet of beluga whales inferred by fatty acid analysis of the eastern Beaufort Sea food web. Journal of Experimental Marine Biology and Ecology, 374:12-18.

Lu, J.Y., W.H. Schroeder, L.A. Barrie, A. Steffen, H.E. Welch, K. Martin, L. Lockhart, R.V. Hunt, G. Boila and A. Richter, 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. Geophysical Research Letters, 28:3219-3222.

Lucotte, M., R. Schetagne, N. Thérien, C. Langlois and A. Trembley (Eds.), 1999. Mercury in the Biogeochemical Cycle: Natural Environments and Hydroelectric Reservoirs in Northern Québec. Springer-Verlag.

Luengen, A.C. and A.R. Flegal, 2009. Role of phytoplankton in mercury cycling in the San Francisco Bay estuary. Limnology and Oceanography, 54:23-40.

Maage, A., K. Stange and J. Klungsoyr, 1996. Trace elements in fish and sediments from the Barents Sea. Draft report. Norwegian Institute for Marine Research.

Macdonald, R.W., 1996. Awakenings in the Arctic. Nature, 380:286-287.

Macdonald, R.W., 2000. Arctic estuaries and ice: a positive-negative estuarine couple In: Lewis, E.L. (Ed.). The Freshwater Budget of the Arctic Ocean, pp. 383-407.

Macdonald, R.W., 2005. Climate change, risks and contaminants: A perspective from studying the Arctic. Human and Ecological Risk Assessment, 11:1099-1104.

Macdonald, R.W. and J.M. Bewers, 1996. Contaminants in the arctic marine environment: priorities for protection. ICES Journal of Marine Science, 53:537-563.

Macdonald, R.W. and L.L. Loseto, 2010. Are Arctic Ocean ecosystems exceptionally vulnerable to global emissions of mercury? A call for emphasized research on methylation and the consequences of climate change. Environmental Chemistry, 7:133-138.

Macdonald, R.W., E.C. Carmack and D.W.R. Wallace, 1993. Tritium and radiocarbon dating of Canada Basin deep waters. Science, 259:103-104.

Macdonald, R.W., T. Harner and J. Fyfe, 2005. Recent climate change in the Canadian Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Science of the Total Environment, 342:5-86.

MacLachlan, N.J. and J.M. Cullen, 1995. Liver, biliary system and exocrine pancreas. In: Carlton, W.W. and M. Donald McGavin (Eds.). Thomsons Special Veterinary Pathology, pp. 81-115, Mosby Year Book, St. Louis.

Mailman, M., L. Stepnuk, N. Cicek and R.A. Bodaly, 2006. Strategies to lower methyl mercury concentrations in hydroelectric reservoirs and lakes: A review. Science of the Total Environment, 368:224-235.

Mallory, M.L., 2005. At the gate to Hell: studying fulmars in northern Nunavut. BirdWatch Canada 32:8-11.

Mann, J.L., S.E. Long, C.A. Shuman and W.R. Kelly, 2005. Determination of mercury content in a shallow firn core from Greenland by isotope dilution inductively coupled plasma mass spectrometry. Water Air and Soil Pollution, 163:19-32.

Markager, S., W.F. Vincent and E.P.Y. Tang, 1999. Carbon fixation by phytoplankton in high Arctic lakes: Implications of low temperature for photosynthesis. Limnology and Oceanography, 44:597-607.

Maslanik, J.A., C. Fowler, J. Stroeve, S. Drobot, J. Zwally, D. Yi and W. Emery, 2007. A younger, thinner Arctic ice cover: Increased potential for rapid, extensive sea-ice loss. Geophysical Research Letters, 34:L24501.

Mason, R., 2009. Mercury emissions from natural sources and their importance in the global mercury cycle. In: Pirrone, N. and R. Mason (Eds.). Mercury Fate and Transport in the Global Atmosphere. Springer Science + Business Media.

Mason, R.P. and W.F. Fitzgerald, 1993. The distribution and biogeochemical cycling of mercury in the Equatorial Pacific Ocean. Deep-Sea Research, 40:1897-1924.

Mason, R.P. and G.R. Sheu, 2002. Role of the ocean in the global mercury cycle. Global Biogeochemical Cycles, 16:1093.

Mason, R.P. and K.A. Sullivan, 1999. The distribution and speciation of mercury in the South and equatorial Atlantic. Deep-Sea Research II, 46:937-956.

Mason, R.P., W.F. Fitzgerald and F.M.M. Morel, 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. Geochimica et Cosmochimica Acta, 58:3191-3198.

Mason, R.P., K.R. Rolfus and W.F. Fitzgerald, 1995. Methylated and elemental mercury cycling in surface and deep ocean waters of the North Atlantic. Water, Air, and Soil Pollution, 80:665-677.

Mason, R.P., J.R. Reinfelder and F.M.M. Morel, 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. Environmental Science and Technology, 30:1835-1845.

Mason, R.P., K.R. Rolfhus and W.F. Fitzgerald, 1998. Mercury in the North Atlantic. Marine Chemistry, 61:37-53.

Mason, R.P., N.M. Lawson and G.-R. Sheu, 2001. Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters. Deep-Sea Research II, 48:2829-2853.

Maxie, M.G., 1993. Pathology of Domestic Animals. Academic Press.

McClelland, J.W., S.J. Dery, B.J. Peterson, R.M. Holmes and E.F. Wood, 2006. A pan-arctic evaluation of changes in river discharge during the latter half of the 20th century. Geophysical Research Letters, 33:L06715.

McDonald, M.E., A.E. Hershey and M.C. Miller, 1996. Global warming impacts on lake trout in arctic lakes. Limnology and Oceanography, 41:1102-1108.

McGuire, A.D., L.G. Anderson, T.R. Christensen, S. Dallimore, L. Guo, D.J. Hayes, M. Heimann, T.D. Lorenson, R.W. Macdonald and N. Roulet, 2009. Sensitivity of the carbon cycle in the Arctic to climate change. Ecological Monographs, 79:523-555.

McIntyre, J.K. and D.A. Beauchamp, 2007. Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. Science of the Total Environment, 372:571-584.

McLaughlin, F.A., E.C. Carmack, R.W. Macdonald and J.K.B. Bishop, 1996. Physical and geochemical properties across the Atlantic/Pacific water mass boundary in the southern Canadian Basin. Journal of Geophysical Research, 101:1183-1197.

McNamara, J.P., D.L. Kane and L.D. Hinzman, 1998. An analysis of streamflow hydrology in the Kuparuk River basin, Arctic Alaska: A nested watershed approach. Journal of Hydrology, 206:39-57.

McPhail, J., Lindsey, CC, 1970. Freshwater Fishes of North Western Canada and Alaska. Fisheries Research Board of Canada Bulletin 173. 381 pp.

McPhee, M.G., A. Proshutinsky, J.H. Morison, M. Steele and M.B. Alkire, 2009. Rapid change in freshwater content of the Arctic Ocean. Geophysical Research Letters, 36:L10602.

Meili, M., K. Bishop, L. Bringmark, K. Johansson, J. Munthe, H. Sverdrup and W. Vries, 2003. Critical levels of atmospheric pollution: criteria and concepts for operational modelling of mercury in forest and lake ecosystems. Science of the Total Environment, 304:83-106.

Melnick, J.G. and G. Parkin, 2007. Cleaving mercury-alkyl bonds: A functional model for mercury detoxifictaion by merB. Science, 317:225.

Melnikov, S.A., S.V. Vlasov and A.N. Gorshkov, 2005. Final report on the Raipon/AMAP/GEF project Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian North. Activity 4. Study of biomagnification in Arctic food-chains. (Results tabulated in AMAP Assessment 2002: Heavy Metals in the Arctic, pp. 146-147).

Mergler, D., H.A. Anderson, H.M. Chan, K.R. Mahaffey, M. Murray, M. Sakamoto and A.H. Stern, 2007. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio, 36:3-11.

Methe, B.A., K.E. Nelson, J.W. Deming and 23 others, 2005. The psychrophilic lifestyle as revealed by the genome sequence of *Colwellia psychrerythraea* 34H through genomic and proteomic analyses. Proceedings of the National Academy of Sciences of the United States of America, 102:10913-10918.

Michaud, J., L. Fortier, P. Rowe and R. Ramseier, 1996. Feeding success and survivorship of Arctic cod larvae, *Boreogadus saida*, in the northeast water polynya (Greenland Sea). Fisheries Oceanography, 5:120-135.

Michelutti, N., A. Wolfe, R. Vinebrooke and B. Rivard, 2005. Recent primary production increases in arctic lakes. Geophysical Research Letters, 32:L19715.

Miljeteig, C., H. Strom, M.V. Gavrilo, A. Volkov, B.M. Jenssen and G.W. Gabrielsen, 2009. High levels of contaminants in ivory gull *Pagophila eburnea* eggs from the Russian and Norwegian Arctic. Environmental Science and Technology, 43:5521-5528.

Moline, M.A., N.J. Karnovsky, Z. Brown, G.J. Divoky, T.K. Frazer, C.A. Jacoby, J.J. Torrese and W.R. Fraser, 2008. High latitude changes in ice dynamics and their impact on polar marine ecosystems. Annals of the New York Academy of Sciences, 1134:267-319.

Montgomery, S., M. Lucotte and I. Rheault, 2000. Temporal and spatial influences of flooding on dissolved mercury in boreal reservoirs. Science of the Total Environment, 260:147-157.

Moore, S.E. and H.P. Huntington, 2008. Arctic marine mammals and climate change: Impacts and resilience. Ecological Applications, 18:S157-S165.

Moore, S.E. and K.L. Laidre, 2006. Trends in sea ice cover within habitats used by bowhead whales in the western Arctic. Ecological Applications, 16:932-944.

Morel, F.M.M., A.M.L. Kraepiel and M. Amyot, 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics, 29:543-566.

Morin, S., G.M. Marion, R. von Glasow, D. Voisin, J. Bouchez and J. Savarino, 2008. Precipitation of salts in freezing seawater and ozone depletion events: A status report. Atmospheric Chemistry and Physics, 8:7317-7324.

Moses, S.K., A.V. Whiting, G.R. Bratton, R.J. Taylor and T.M. O'Hara, 2009. Inorganic nutrients and contaminants in subsistence species of Alaska: linking wildlife and human health. International Journal of Circumpolar Health, 68:53-74.

Mozaffarian, D., 2009. Fish, mercury, selenium and cardiovascular risk: current evidence and unanswered questions. International Journal of Environmental Research and Public Health, 6:1894-1916.

Mueller, D.R., L. Copland, A. Hamilton and D. Stern, 2008. Examining Arctic ice shelves prior to the 2008 breakup. EOS, Transactions, American Geophysical Union, 89:502-503.

Muir, D., X.W. Wang, D. Bright, L. Lockhart and G. Kock, 2005. Spatial and temporal trends of mercury and other metals in landlocked char from lakes in the Canadian Arctic archipelago. Science of the Total Environment, 351:464-478.

Muir, D.C.G., X. Wang, F. Yang, N. Nguyen, T.A. Jackson, M.S. Evans, M. Douglas, G. Kock, S. Lamoureux, R. Pienitz, J.P. Smol, W.F. Vincent and A. Dastoor, 2009. Spatial trends and historical deposition of mercury in eastern and northern Canada inferred from lake sediment cores. Environmental Science and Technology, 43:4802-4809.

Mumm, N., H. Auel, H. Hanssen, W. Hagen, C. Richter and H.J. Hirche, 1998. Breaking the ice: large-scale distribution of mesozooplankton after a decade of Arctic and transpolar cruises. Polar Biology, 20:189-197.

Munn, M.D. and T.M. Short, 1997. Spatial heterogeneity of mercury bioaccumulation by walleye in Franklin D. Roosevelt Lake and the upper Columbia River, Washington. Transactions of the American Fisheries Society, 126:477-487.

Munthe, J., I. Wangberg, A. Iverfeldt, O. Lindqvist, D. Stromberg, J. Sommar, K. Gardfeldt, G. Petersen, R. Ebinghaus, E. Prestbo, K. Larjava and V. Siemens, 2003. Distribution of atmospheric mercury species in Northern Europe: final results from the MOE project. Atmospheric Environment, 37:S9-S20.

NESCAUM, 2010. Technologies for Control and Measurement of Mercury Emissions from Coal- Fired Power Plants in the United States: A 2010 Status Report. Northeast States for Coordinated Air Use Management (NESCAUM),

Newman, J., E. Zillioux, E. Rich, L. Liang and C. Newman, 2005. Historical and other patterns of monomethyl and inorganic mercury in the Florida panther (*Puma concolor coryi*). Archives of Environmental Contamination and Toxicology, 48:75-80.

Newsome, S.D., M.A. Etnier, C.M. Kurle, J.R. Waldbauer, C.P. Chamberlain and P.L. Koch, 2007. Historic decline in primary productivity in western Gulf of Alaska and eastern Bering Sea: isotopic analysis of northern fur seal teeth. Marine Ecology Progress Series, 332:211-224.

Nicholson, M.D., R.J. Fryer and R.J. Larsen, 1998. Temporal trend monitoring: Robust method for analysing contaminant trend monitoring data. ICES Techniques in Marine Environmental Sciences No. 20. 22 pp. International Council for the Exploration of the Sea.

Niki, H., P.D. Maker, C.M. Savage and L.P. Breitenbach, 1983a. A long-path fourier-transform infrared study of the kinetics and mechanism for the ho-radical initiated oxidation of dimethylmercury. Journal of Physical Chemistry, 87:4978-4981.

Niki, H., P.S. Maker, C.M. Savage and L.P. Breitenbach, 1983b. A Fourier-transform infrared study of the kinetics and mechanism of the reaction of atomic chlorine with dimethylmercury. Journal of Physical Chemistry, 87:3722-3724.

Norstrom, R.J., R.E. Schweinsberg and B.T. Collins, 1986. Heavy metals and essential elements in livers of the polar bear (*Ursus maritimus*) in the Canadian Arctic Science of the Total Environment, 48:195-212.

Nozaki, K., 2002. Characteristics of primary production in the littoral zone of lake. Japanese Journal of Limnology, 63:225-231.

NRC, 2000. Toxicological Effects of Methylmercury. National Research Council. 368 pp. National Academy Press.

Nriagu, J.O. and J.M. Pacyna, 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. Nature, 333:134-139.

O'Brien, M.C., R.W. Macdonald, H. Melling and K. Iseki, 2006. Geochemistry and physical forcing of sediment transport and deposition in the Canadian Beaufort Sea. Continental Shelf Research, 26:41-81.

O'Driscoll, N.J., S.D. Siciliano, D.R.S. Lean and M. Amyot, 2006. Gross photo-reduction kinetics of mercury in temperate freshwater lakes and rivers: Application to a general model for DGM dynamics. Environmental Science and Technology, 40:873-843.

O'Hara, T.M. and P.R. Becker, 2003. Persistent organic contaminants in arctic marine mammals. In: Vos, J.G., G.D. Bossart, M. Fournier and T.J. O'Shea (Eds.). Toxicology of Marine Mammals. Taylor & Francis Publishers.

O'Hara, T.M., V. Woshner and G. Bratton, 2003. Inorganic pollutants in Arctic marine mammals. In: Vos, J.G., G.D. Bossart, M. Fournier and T.J. O'Shea (Eds.). Toxicology of Marine Mammals, pp. 206-246, Taylor & Francis.

O'Shea, T.J., 1999. Environmental contaminants and marine mammals. In: Reynolds, J.E. and S.A. Rommel (Eds.). Biology of Marine Mammals, pp. 485-536, Smithsonian Institution Press.

Oberman, N.G., 2008. Contemporary permafrost degradation of Northern European Russia. Paper presented at The Ninth International Conference on Permafrost, pp. 1305-1310, Fairbanks, Alaska.

Obrist, D., A.G. Hallar, I. McCubbin, B.B. Stephens and T. Rahn, 2008. Atmospheric mercury concentrations at Storm Peak Laboratory in the Rocky Mountains: Evidence for long-range transport from Asia, boundary layer contributions, and plant mercury uptake. Atmospheric Environment, 42:7579-7589.

Odsjö, T., J. Räikkönen and A. Bignert, 2007. Time trends of metals in liver and muscle of reindeer (*Rangifer tarandus*) from northern and central Lapland, Sweden, 1983-2005. 33 pp. Rapport till Naturvårdsverket.

Oiffer, L. and S.D. Siciliano, 2009. Methyl mercury production and loss in Arctic soil. Science of the Total Environment, 407:1691-1700.

Olsen, G.H., M. Mauritzen, A.E. Derocher, E.G. Sørmo, S. J.U, Ø. Wiig and B.M. Jenssen, 2003. Space-use strategy determines PCB burdens in female polar bears. Environmental Science and Technology, 37:4919-4924.

Oltmans, S.J. and W.D. Komhyr, 1986. Surface ozone distributions and variations from 1973-1984 measurements at the NOAA geophysical monitoring for climatic change baseline observatories. Journal of Geophysical Research, 91:5229-5236.

Oremland, R.S., C.W. Culbertson and M.R. Winfrey, 1991. Methylmercury decomposition in sediments and bacterial cultures – involvement of methanogens and sulfate reducers in oxidative demethylation. Applied and Environmental Microbiology, 57:130-137.

Oremland, R.S., L.G. Miller, P. Dowdle, T. Connell and T. Barkay, 1995. Methylmercury oxidative-degradation potentials in contaminated and pristine sediments of the Carson River, Nevada. Applied and Environmental Microbiology, 61:2745-2753.

Orihel, D.M., M.J. Paterson, P.J. Blanchfield, R.A. Bodaly and H. Hintelmann, 2007. Experimental evidence of a linear relationship between inorganic mercury loading and methylmercury accumulation by aquatic biota. Environmental Science and Technology, 41:4952-4958.

Osterkamp, T.E., 2008. Themal state of permafrost in Alaska during the fourth quarter of the Twentieth Century. Paper presented at TheNinth International Conference on Permafrost, pp. 1333-1338, Fairbanks, Alaska.

Ostertag, S.K., G. Stern and H.M. Chan, 2009. Mercury concentration and distribution in brains from belugas (*Delphinapterus leucas*) harvested in the western Canadian Arctic. Oral presentation. Paper presented at TheInternational Conference on Mercury as a Global Pollutant. 8-12 June 2009, Guiyang, China.

Östlund, H.G., 1982. The residence time of the freshwater component in the Arctic Ocean. Journal of Geophysical Research, 87:2035-2043.

Outridge, P.M., 2005. Using biological archives to discriminate natural and anthropogenic mercury in animals: a methodological review. In: Parsons, M.B. and J.B. Percival (Eds.). Mercury – Sources, Measurements, Cycles and Effects, pp. 217 – 234, Mineralogical Association of Canada Short Course Halifax, Novia Scotia.

Outridge, P.M., R. Wagemann and R. McNeely, 2000. Teeth as biomonitors of soft tissue mercury concentrations in beluga, Delphinapterus leucas. Environmental Toxicology and Chemistry, 19:1517-1522.

Outridge, P.M., K.A. Hobson, R. McNeely and A. Dyke, 2002. A comparison of modern and preindustrial levels of mercury in the teeth of beluga in the Mackenzie Delta, Northwest Territories, and walrus at Igloolik, Nunavut, Canada. Arctic, 55:123-132.

Outridge, P.M., K.A. Hobson and J.M. Savelle, 2005a. Changes in mercury and cadmium concentrations and the feeding behaviour of beluga (*Delphinapterus leucas*) near Somerset Island, Canada, during the 20th century. Science of the Total Environment, 350:106-118.

Outridge, P.M., G.A. Stern, P.B. Hamilton, J.B. Percival, R. McNeely and W.L. Lockhart, 2005b. Trace metal profiles in the varved sediments of an Arctic lake. Geochimica et Cosmochimica Acta, 69:4881-4894.

Outridge, P.M., H. Sanei, G.A. Stern, P.B. Hamilton and F. Goodarzi, 2007. Evidence for control of mercury accumulation rates in Canadian High Arctic lake sediments by variations of aquatic primary productivity. Environmental Science and Technology, 41:5259-5265.

Outridge, P.M., R.W. Macdonald, F. Wang, G.A. Stern and A.P. Dastoor, 2008. A mass balance inventory of mercury in the Arctic Ocean. Environmental Chemistry, 5:89-111.

Outridge, P.M., K.A. Hobson and J. Savelle, 2009. Long-term changes of mercury levels in ringed seal (*Phoca hispida*) from Amundsen Gulf, and beluga (*Delphinapterus leucas*) from the Beaufort Sea, western Canadian Arctic. Science of the Total Environment, 407:6044-6051.

Overland, J.E., M. Wang and S. Salo, 2008. The recent Arctic warm period. Tellus A, 60:589-597.

Pacyna, J.M., 1986. Emission factors of atmospheric elements. In: Nriagu, J.O. and C.I. Davidson (Eds.). Toxic Metals in the Atmosphere. Advances in Environmental Science and Technology. John Wiley and Sons.

Pacyna, E.G. and J.M. Pacyna, 2002. Global emission of mercury from anthropogenic sources in 1995. Water Air and Soil Pollution, 137:149-165.

Pacyna, J.M. and E.G. Pacyna, 2005. Anthropogenic sources and global inventory of mercury emissions. In: Parsons, M.B. and J.B. Percival (Eds.). Mercury: Sources, Measurements, Cycles and Effects. Mineralogical Association of Canada, Short Course Series Volume No. 32.

Pacyna, J.M., E.G. Pacyna, F. Steenhuisen and S. Wilson, 2003. Mapping 1995 global anthropogenic emissions of mercury. Atmospheric Environment, 37:109-117.

Pacyna, E.G., J.M. Pacyna, F. Steenhuisen and S. Wilson, 2006. Global anthropogenic mercury emission inventory for 2000. Atmospheric Environment, 40:4048-4063.

Pacyna, E.G., J.M. Pacyna, K. Sundseth, J. Munthe, K. Kindbom, S. Wilson, F. Steenhuisen and P. Maxson, 2010a. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. Atmospheric Environment, 40:2487-2499.

Pacyna, J.M., K. Sundseth, E.G. Pacyna, W. Jozewicz, J. Munthe, M. Belhaj and S. Astrom, 2010b. An assessment of costs and benefits associated with mercury emission reductions from major anthropogenic sources. Journal of Air and Waste Management Association, 60:302-315.

Pal, B. and P.A. Ariya, 2004a. Kinetics and mechanism of O3-initiated reaction of Hg0: atmospheric implication. Journal of Physical Chemistry-Chemical Physics, 6:752.

Pal, B. and P.A. Ariya, 2004b. Gas-phase HO center dot-Initiated reactions of elemental mercury: Kinetics, product studies, and atmospheric implications. Environmental Science and Technology, 38:5555-5566.

Paludan-Müller, P., C. Thyge Agger, R. Dietz and C.C. Kinze, 1993. Cadmium, mercury, selenium, copper and zinc in harbour porpoise (*Phocoena phocoena*) from West Greenland. Polar Biology, 13:311-320.

Parker, H.H. and L. Johnson, 1991. Population structure, ecological segregation and reproduction in non-anadromous Arctic charr, *Salvelinus alpinus* (L), in four unexploited lakes in the Canadian high Arctic. Journal of Fish Biology, 38:123-147.

Perry, E., S.A. Norton, N.C. Kamman, P.M. Lorey and C.T. Driscoll, 2005. Deconstruction of historic mercury accumulation in lake sediments, northeastern United States. Ecotoxicology, 14:85-99.

Peterson, B.J., R.M. Holmes, J.W. McClelland, C.J. Vörösmarty, R.B. Lammers, A.I. Shiklomanov, I.A. Shiklomanov and S. Rahmstor, 2002. Increasing river discharge to the Arctic Ocean. Science, 298:2171-2173.

Peterson, C., M. Gustin and S. Lyman, 2009a. Atmospheric mercury concentrations and speciated measured from 2004 to 2007 in Reno, Nevada, USA. Atmospheric Environment, 43:4646-4654.

Peterson, T.C., M.O. Baringer, H.J. Diamond, R.L. Fogt, J.M. Levy, J. Richter-Menge, P.W. Thorne, L.A. Vincent and A.B. Watkins, 2009b. State of the climate in 2008. Bulletin of the American Meteorological Society, 90:S1-S196.

Pickhardt, P.C. and N.S. Fisher, 2007. Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. Environmental Science and Technology, 41:125-131.

Pickhardt, P.C., C.L. Folt, C.Y. Chen, B. Klaue and J.D. Blum, 2002. Algal blooms reduce the uptake of toxic methylmercury in freshwater food webs. Proceedings of the National Academy of Sciences of the United States of America, 99:4419-4423.

Pilsner, J.R., A.L. Lazarus, D. Nam, R.J. Letcher, C. Sonne, R. Dietz and N. Basu, 2010. Mercury-associated DNA hypomethylation in polar bear brains via the LUminometric Methylation Assay: a sensitive method to study epigenetics in wildlife. Molecular Ecology, 19:307-314.

Piot, M. and R. von Glasow, 2008. The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events. Atmospheric Chemistry and Physics, 8:2437-2467.

Poissant, L. and M. Pilote, 2003. Time series analysis of atmospheric mercury in Kuujjuarapik / Whapmagoostui (Quebec). Journal de Physique IV, 107:1079-1082.

Poissant, L., H.H. Zhang, J. Canario and P. Constant, 2008. Critical review of mercury fates and contamination in the arctic tundra ecosystem. Science of the Total Environment, 400:173-211.

Poltermann, M., 2001. Arctic sea ice as feeding ground for amphipods – food sources and strategies. Polar Biology, 24:89-96.

Pongratz, R. and K.G. Heumann, 1998. Production of methylated mercury and lead by polar macroalgae – A significant natural source for atmospheric heavy metals in clean room compartments. Chemosphere, 36:1935-1946.

Pongratz, R. and K.G. Heumann, 1999. Production of methylated mercury, lead, and cadmium by marine bacteria as a significant natural source for atmospheric heavy metals in polar regions. Chemosphere, 39:89-102.

Poppel, B., J. Kruse, G. Duhaime and L. Abryutina, 2007. Survey of living conditions in the Arctic: The Results. Institute of Social and Economic Research, University of Alaska Anchorage.

Porvari, P., 1998. Development of fish mercury concentrations in Finnish reservoirs from 1979 to 1994. Science of the Total Environment, 213:279-290.

Porvari, P. and M. Verta, 2003. Total and methyl mercury concentrations and fluxes from small boreal forest catchments in Finland. Environmental Pollution, 123:181-191.

Post, D.M., M.L. Pace and N.G. Hairston, 2000. Ecosystem size determines food-chain length in lakes. Nature, 405:1047-1049.

Post, E., M.C. Forchhammer, M.S. Bret-Harte and 22 others, 2009. Ecological dynamics across the Arctic associated with recent climate change. Science, 325:1355-1358.

Poulain, A.J., J.D. Lalonde, M. Amyot, J.A. Shead, F. Raofie and P.A. Ariya, 2004. Redox transformations of mercury in an Arctic snowpack at springtime. Atmospheric Environment, 38:6763-6774.

Poulain, A.J., E. Garcia, M. Amyot, P.G.C. Campbell and P.A. Arlya, 2007a. Mercury distribution, partitioning and speciation in coastal vs. inland High Arctic snow. Geochimica et Cosmochimica Acta, 71:3419-3431.

Poulain, A.J., E. Garcia, M. Amyot, P.G.C. Campbell, F. Raofie and P.A. Ariya, 2007b. Biological and chemical redox transformations of mercury in fresh and salt waters of the High Arctic during spring and summer. Environmental Science and Technology, 41:1883-1888.

Poulain, A.J., S.M. Ni Chadhain, P.A. Ariya, M. Amyot, E. Garcia, P.G.C. Campbell, G.J. Zylstra and T. Barkay, 2007c. Potential for mercury reduction by microbes in the High Arctic. Applied and Environmental Microbiology, 73:2230-2238.

Poulain, A.J., V. Roy and M. Amyot, 2007d. Influence of temperate mixed and deciduous tree covers on Hg concentrations and photoredox transformations in snow. Geochimica et Cosmochimica Acta, 71:2448-2462.

Power, M., G.M. Klein, K. Guiguer and M.K.H. Kwan, 2002. Mercury accumulation in the fish community of a sub-Arctic lake in relation to trophic position and carbon sources. Journal of Applied Ecology, 39:819-830.

Proshutinsky, A., R. Krishfield, M.L. Timmermans, J. Toole, E. Carmack, F. McLaughlin, W.J. Williams, S. Zimmermann, M. Itoh and K. Shimada, 2009. Beaufort Gyre freshwater reservoir: State and variability from observations. Journal of Geophysical Research-Oceans, 114:C00A10.

Prowse, T.D. and C. Furgal, 2009. Northern Canada in a Changing Climate: Major Findings and Conclusions. Ambio, 38:290-292.

Prowse, T.D., F.J. Wrona, J.D. Reist, J.J. Gibson, J.E. Hobbie, L.M.J. Levesque and W.F. Vincent, 2006. Climate change effects on hydroecology of Arctic freshwater ecosystems. Ambio, 35:347-358.

Pye, S., G. Jones, R. Tewart, M. Woodfield, K. Kubica, R. Kubica and J.M. Pacyna, 2005. Costs and Environmental Effectiveness of Options for Reducing Mercury Emissions to Air from Small-Scale Combustion Installations. Report AEAT/ED48706. AEA Technology/NILU Polska, Harwell, U.K.

Quay, P.D., B. Tillbrook and C.S. Wong, 1992. Oceanic uptake of fossil fuel $CO_2$; carbon-13 evidence. Science 256:44-79.

Raatz, W.E., 1984. Tropospheric circulation patterns during the Arctic gas and aerosol sampling program (AGASP), March/April 1983. Geophysical Research Letters, 11:449-452.

Ralston, N.V.C., J.L. Blackwell and L.J. Raymond, 2007. Importance of molar ratios in selenium-dependent protection against methylmercury toxicity. Biological Trace Element Research, 119:255-268.

Rankin, A.M., V. Auld and E.W. Wolff, 2000. Frost flowers as a source of fractionated sea salt aerosol in the polar regions. Geophysical Research Letters, 27:3469-3472.

Raofie, F. and P.A. Ariya, 2003. Reactions of BrO with mercury: kinetic studies. Journal de Physique IV, 107:1119-1121.

Rask, M., M. Verta, M. Korhonen, S. Salo, M. Forsius, L. Arvola, R. Jones and M. Kiljunen, 2010. Does thermocline change affect methyl mercury concentrations in fish? Biogeochemistry, 101:311-322.

Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter – a review Chemosphere, 55:319-331.

Rawson, A.J., G.W. Patton, S. Hofmann, G.G. Pietra and L. Johns, 1993. Liver abnormalities associated with chronic mercury accumulation in stranded Atlantic bottle-nosed dolphins. Ecotoxicology and Environmental Safety, 25:41-47.

Raymond, L.J. and N.V. Ralston, 2004. Mercury: selenium interactions and health implications. Seychelles Medical and Dental Journal, 7(1): Special issue.

Regnell, O. and T. Hammar, 2004. Coupling of methyl and total mercury in a minerotrophic peat bog in southeastern Sweden. Canadian Journal of Fisheries and Aquatic Sciences, 61:2014-2023.

Reist, J.D., E.C. Gyselman, J.A. Babaluk, D.J. Johnson and R.H. Wissink, 1995. Evidence for two morphotypes of Arctic char (Salvelinus alpinus) from Lake Hazen, Ellesmere Island, Northwest Territories, Canada. Nordic Journal of Freshwater Research, 71:396-410.

Reist, J.D., F.J. Wrona, T.D. Prowse, M. Power, J.B. Dempson, R.J. Beamish, J.R. King, T.J. Carmichael and C.D. Sawatzky, 2006a. General effects of climate change on Arctic fishes and fish populations. Ambio, 35:370-380.

Reist, J.D., F.J. Wrona, T.D. Prowse, J.B. Dempson, M. Power, G. Kock, T.J. Carmichael, C.D. Sawatzky, H. Lehtonen and R.F. Tallman, 2006b. Effects of climate change and UV radiation on fisheries for Arctic freshwater and anadromous species. Ambio, 35:402-410.

Renberg, I., C. Bigler, R. Bindler, M. Norberg, J. Rydberg and U. Segerstrom, 2009. Environmental history: A piece in the puzzle for establishing plans for environmental management. Journal of Environmental Management, 90:2794-2800.

Renzoni, A. and R.J. Norstrom, 1990. Mercury in the hairs of polar bears *Ursus maritimus*. Polar Record, 26:326-328.

Riget, F.F., K.H. Nygaard and B. Christensen, 1986. Population structure, ecological segregation, and reproduction in a population of arctic char (*Salvelinus alpinus*) from Lake Tasersuaq, Greenland. Canadian Journal of Fisheries and Aquatic Sciences, 43:985-992.

Riget, F., R. Dietz and P. Johansen, 1997. Zinc, cadmium, mercury and selenium in Greenland fish. Meddelser om Gronland, Bioscience, 48:5-29.

Riget, F., G. Asmund and P. Aastrup, 2000. Mercury in Arctic char (*Salvelinus alpinus*) populations from Greenland. Science of the Total Environment, 245:161-172.

Riget, F., R. Dietz, K. Vorkamp, P. Johansen and D. Muir, 2004. Levels and spatial and temporal trends of contaminants in Greenland biota: an updated review. Science of the Total Environment, 331:29-52.

Riget, F., D. Muir, Kwan, T. Savinova, M. Nyman, V. Woshner and T. O'Hara, 2005. Circumpolar pattern of mercury and cadmium in ringed seals. Science of the Total Environment, 351-352:312-322.

Riget, F., R. Dietz, E.W. Born, C. Sonne and K.A. Hobson, 2007. Temporal trends of mercury in marine biota of west and northwest Greenland. Marine Pollution Bulletin, 54:72-80.

Riordan, B., D. Verbyla and A.D. McGuire, 2006. Shrinking ponds in subarctic Alaska based on 1950-2002 remotely sensed images. Journal of Geophysical Research, 111:G04002.

Roehm, C.L., R. Giesler and J. Karlsson, 2009. Bioavailability of terrestrial organic carbon to lake bacteria: The case of a degrading subarctic permafrost mire complex. Journal of Geophysical Research, 114:G03006.

Rognerud, S., J.O. Grimalt, B.O. Rosseland, P. Fernandez, R. Hofer, R. Lackner, B. Lauritzen, L. Lien, J.C. Massabuau and A. Ribes, 2002. 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 and Soil Pollution: Focus, 2:209-232.

Rolfhus, K.R., H.E. Sakamoto, L.B. Cleckner, R.W. Stoor, C.L. Babiarz, R.C. Back, H. Manolopoulos and J.P. Hurley, 2003. Distribution and fluxes of total and methylmercury in Lake Superior. Environmental Science and Technology, 37:865-872.

Ronald, K., R.J. Frank, J. Dougan, R. Frank and H.E. Braun, 1984. Pollutants in harp seals (*Phoca groenlandica*). II. Heavy metals and selenium. Science of the Total Environment, 38:153-166.

Rosa, C., J.E. Blake, G.R. Bratton, L.A. Dehn, M.J. Gray and T.M. O'Hara, 2008. Heavy metal and mineral concentrations and their relationship to histopathological findings in the bowhead whale (*Balaena mysticetus*). Science of the Total Environment, 399:165-178.

Ross, P.S., 2000. Marine mammals as sentinels in ecological risk assessment. Human and Ecological Risk Assessment, 6:29-46.

Rothrock, D.A., D.B. Percival and M. Wensnahan, 2008. The decline in arctic sea ice thickness: Separating the spatial, annual, and interannual variability in a quarter century of submarine data. Journal of Geophysical Research, 113:C05003.

Rudd, J.W.M., 1995. Sources of methyl mercury to freshwater ecosystems – a review. Water Air and Soil Pollution, 80:697-713.

Rudels, B. and H.J. Friedrich, 2000. The transformations of Atlantic water in the Arctic Ocean and their significance for the freshwater budget. In: Lewis, E.L., E.P. Jones, P. Lemke, T.D. Prowse and P.Wadhams (Eds.). The Freshwater Budget of the Arctic Ocean, pp. 503-532, Kluwer Academic.

Rumbeiha, W.K., S.D. Fitzgerald, W.E. Braselton, R.A. Roth, J.J. Pestka and J.B. Kaneene, 2000. Augmentation of mercury-induced nephrotoxicity by endotoxin in the mouse. Toxicology, 151:103-116.

Rush, S.A., K. Borga, R. Dietz, E.W. Born, C. Sonne, T. Evans, D.C.G. Muir, R.J. Letcher, R.J. Norstrom and A.T. Fisk, 2008. Geographic distribution of selected elements in the livers of polar bears from Greenland, Canada and the United States. Environmental Pollution, 153:618-626.

Rydberg, J., J. Klaminder, P. Rosen and R. Bindler, 2010. Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes. Science of the Total Environment, 408:4778-4783.

Saiz-Lopez, A., J.M.C. Plane, A.S. Mahajan, P.S. Anderson, S.J.B. Bauguitte, A.E. Jones, H.K. Roscoe, R.A. Salmon, W.J. Bloss, J.D. Lee and D.E. Heard, 2008. On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for $O_3$, HOx, NOx and the Hg lifetime. Atmospheric Chemistry and Physics Discussions, 2007:9385-9417.

Sakshaug, E., 2004. Primary and secondary production in the Arctic Seas. In: Stein, R. and R.W. Macdonald (Eds.). The Organic Carbon Cycle in the Arctic Ocean. Springer, Berlin.

Sander, R., J. Burrows and L. Kaleschke, 2006. Carbonate precipitation in brine – a potential trigger for tropospheric ozone depletion events. Atmospheric Chemistry and Physics, 6:4653-4658.

Sandheinrich, M.B. and K.M. Miller, 2006. Effects of dietary methylmercury on reproductive behavior of fathead minnows (*Pimephales promelas*). Environmental Toxicology and Chemistry, 25:3053-3057.

Sandheinrich, M.B. and J.G. Wiener, 2010. Methylmercury in freshwater fish: Recent advances in assessing toxicity of environmentally relevant exposures. In: Beyer, N. and J. Meador (Eds.). Environmental Contaminants in Biota: Interpreting Tissue Concentrations. Taylor and Francis.

Sanei, H. and F. Goodarzi, 2006. Relationship between organic matter and mercury in recent lake sediment: The physical-geochemical aspects. Applied Geochemistry, 21:1900-1912.

Sanei, H., P.M. Outridge, F. Goodarzi, F. Wang, D. Armstrong, K. Warren and L. Fishback, 2010. Wet deposition mercury fluxes in the Canadian sub-Arctic and southern Alberta, measured using an automated precipitation collector adapted to cold regions. Atmospheric Environment, 44:1672-1681.

Satoh, M., N. Nishimura, Y. Kanayama, A. Naganuma, T. Suzuki and C. Tohyama, 1997. Enhanced renal toxicity by inorganic mercury in metallothionein-null mice. Journal of Pharmacology and Experimental Therapeutics, 283:1529-1533.

Schaefer, J.K. and F.M.M. Morel, 2009. High methylation rates of mercury bound to cysteine by *Geobacter sulfurreducens*. Nature Geoscience, 2:123-126.

Schell, D.M., 1983. Carbon-13 and carbon-14 abundances in Alaskan aquatic organisms: Delayed production from peat in Arctic food webs. Science, 219:1068-1071.

Schell, D.M., 2000. Declining carrying capacity in the Bering Sea: Isotopic evidence from whale baleen. Limnology and Oceanography, 45:459-462.

Schetagne, R., J.F. Doyon and J.J. Fournier, 2000. Export of mercury downstream from reservoirs. Science of the Total Environment, 260:135-145.

Scheuhammer, A.M., A.H.K. Wong and D. Bond, 1998. Mercury and selenium accumulation in common loons (*Gavia immer*) and common mergansers (*Mergus merganser*) from eastern Canada. Environmental Toxicology and Chemistry, 17:197-201.

Scheuhammer, A.M., M.W. Meyer, M.B. Sandheinrich and M.W. Murray, 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio, 36:12-18.

Scheuhammer, A.M., N. Basu, N.M. Burgess, J.E. Elliott, G.D. Campbell, M. Wayland, L. Champoux and J. Rodrigue, 2008. Relationships among mercury, selenium, and neurochemical parameters in common loons (*Gavia immer*) and bald eagles (*Haliaeetus leucocephalus*). Ecotoxicology, 17:93-101.

Schindler, D.W. and J.P. Smol, 2006. Cumulative effects of climate warming and other human activities on freshwaters of Arctic and subarctic North America. Ambio, 35:160-168.

Schlosser, P., B. Kromer, G. Östlund, B. Ekwurzel, G. Bönisch, H.H. Loosli and R. Furtschert, 1994. On the $^{14}$C and $^{39}$Ar distribution in the central Arctic Ocean: implications for deep water formation. Radiocarbon, 36:327-345.

Schmutz, J.A., K.A. Trust and A.C. Matz, 2009. Red-throated loons (*Gavia stellata*) breeding in Alaska, USA, are exposed to PCBs while on their Asian wintering grounds. Environmental Pollution, 157:2386-2393.

Schroeder, W.H. and J. Munthe, 1998. Atmospheric mercury – An overview. Atmospheric Environment, 32:809-822.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger and T. Berg, 1998. Arctic springtime depletion of mercury. Nature, 394:331-332.

Schroeder, W.H., A. Steffen, K. Scott, T. Bender, E. Prestbo, R. Ebinghaus, J.Y. Lu and S.E. Lindberg, 2003. Summary report: first international Arctic atmospheric mercury research workshop. Atmospheric Environment, 37:2551-2555.

Schuster, P.F., J.B. Shanley, M. Marvin-Dipasquale, M.M. Reddy, G.R. Aiken, D.A. Roth, H.E. Taylor, D.P. Krabbenhoft and J.F. DeWild, 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. Water Air and Soil Pollution, 187:89-108.

Schuur, E.A.G., J.G. Vogel, K.G. Crummer, H. Lee, J.O. Sickman and T.E. Osterkamp, 2009. The effect of permafrost thaw on old carbon release and net carbon exchange from tundra. Nature, 459:556-559.

Scott, K.J., 2001. Bioavailable mercury in arctic snow determined by light-emitting mer-lux bioreporter. Arctic, 54:92-95.

Scott, W.B. and E.J. Crossman, 1973. Freshwater Fishes of Canada. Fisheries Research board of Canada Bulletin No. 184. 966 pp.

Seigneur, C., P. Karamchandani, K. Lohman and K. Vijayaraghavan, 2001. Multiscale modeling of the atmospheric fate and transport of mercury. Journal of Geophysical Research, 106:27,795-727,809.

Seigneur, C., K. Vijayaraghavan, K. Lohman, P. Karamchandani and C. Scott, 2004. Global source attribution for mercury deposition in the United States. Environmental Science and Technology, 38:555-569.

Selin, N.E., D.J. Jacob, R.J. Park, R.M. Yantosca, S. Strode, L. Jaegle and D. Jaffe, 2007. Chemical cycling and deposition of atmospheric mercury: Global constraints from observations. Journal of Geophysical Research, 112:D02308.

Sellers, P., C.A. Kelly and J.W.M. Rudd, 2001. Fluxes of methylmercury to the water column of a drainage lake: The relative importance of internal and external sources. Limnology and Oceanography, 46:623-631.

Sellers, P., C.A. Kelly, J.W.M. Rudd and A.R. MacHutchon, 1996. Photodegradation of methylmercury in lakes. Nature, 380:694-697.

Semiletov, I., O. Dudarev, V. Luchin, A. Charkin, K.-H. Shin and N. Tanaka, 2005. The East Siberian Sea as a transition zone between Pacific-derived waters and Arctic shelf waters. Geophysical Research Letters, 32:L10614.

Semkin, R.G., G. Mierle and R.J. Neureuther, 2005. Hydrochemistry and mercury cycling in a High Arctic watershed. Science of the Total Environment, 342:199-221.

Serreze, M.C., J.E. Walsh, F.S. Chapin, T. Osterkamp, M. Dyurgerov, V. Romanovsky, W.C. Oechel, J. Morison, T. Zhang and R.G. Barry, 2000. Observational evidence of recent change in the northern high-latitude environment. Climatic Change, 46:159-207.

Serreze, M.C., A.P. Barrett, A.G. Slater, R.A. Woodgate, K. Aagaard, R.B. Lammers, M. Steele, R. Moritz, M. Meredith and C.M. Lee, 2006. The large-scale freshwater cycle of the Arctic. Journal of Geophysical Research, 111:C11010.

Sharma, S., D.A. Jackson, C.K. Minns and B.J. Shuter, 2007. Will northern fish populations be in hot water because of climate change? Global Change Biology, 13:2052-2064.

Shepler, B.C., N.B. Balabanov and K.A. Peterson, 2007. Hg+Br → HgBr recombination and collision-induced dissociation dynamics. Journal of Chemical Physics, 127:164304.

Shia, R.-L., C. Seigneur, P. Pai, M. Ko and N.D. Sze, 1999. Global simulation of atmospheric mercury concentrations and deposition fluxes. Journal of Geophysical Research, 104:23,747-723,760.

Shibata, Y., M. Morita and K. Fuwa, 1992. Selenium and arsenic in biology: Their chemical forms and biological functions. Advances in Biophysics, 28:31-80.

Shiklomanov, A.I., T.I. Yakovleva, R.B. Lammers, I.P. Karasev, C.J. Vorosmarty and E. Linder, 2006. Cold region river discharge uncertainty – estimates from large Russian rivers. Journal of Hydrology, 326:231-256.

Shotyk, W., M.E. Goodsite, F. Roos-Barraclough, R. Frei, J. Heinemeier, G. Asmund, C. Lohse and T.S. Hansen, 2003. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve". Geochimica et Cosmochimica Acta, 67:3991-4011.

Shotyk, W., N. Givelet, A.K. Cheburkin, M.E. Goodsite and F. Roos-Barraclough, 2005a. Response to Comment on "Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the High Arctic of Canada recorded by peat hummocks". Environmental Science and Technology, 39:910-912.

Shotyk, W., 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 and C. Lohse, 2005b. Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands. Geochimica et Cosmochimica Acta, 69:1-17.

Shuter, B.J. and K.K. Ing, 1997. Factors affecting the production of zooplankton in lakes. Canadian Journal of Fisheries and Aquatic Sciences, 54:359-377.

Siegel, F.R., J.H. Kravitz and J.J. Galasso, 2001. Arsenic and mercury contamination in 31 cores taken in 1965, St. Anna Trough, Kara Sea, Arctic Ocean. Environmental Geology, 40:528-542.

Siegel, G.J., R.W. Albers, S.T. Brady and D.L. Price, 2006. Basic Neurochemistry. Molecular, Cellular and Medical Aspects. 7th Edn. Elsevier.

Sierszen, M.E., M.E. McDonald and D.A. Jensen, 2003. Benthos as the basis for arctic lake food webs. Aquatic Ecology, 37:437-445.

Silver, S. and T.K. Misra, 1988. Plasmid-mediated heavy-metal resistances. Annual Review of Microbiology, 42:717-743.

Simoneau, M., M. Lucotte, S. Garceau and D. Laliberte, 2005. Fish growth rates modulate mercury concentrations in walleye (*Sander vitreus*) from eastern Canadian lakes. Environmental Research, 98:73-82.

Simpson, W.R., L. Alvarez-Aviles, T.A. Douglas, M. Sturm and F. Domine, 2005. Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime. Geophysical Research Letters, 32:L04811.

Simpson, W.R., R. von Glasow, K. Riedel, P. Anderson, P. Ariya, J. Bottenheim, J. Burrows, L.J. Carpenter, U. Friess, M.E. Goodsite, D. Heard, M. Hutterli, H.W. Jacobi, L. Kaleschke, B. Neff, J. Plane, U. Platt, A. Richter, H. Roscoe, R. Sander, P. Shepson, J. Sodeau, A. Steffen, T. Wagner and E. Wolff, 2007a. Halogens and their role in polar boundary-layer ozone depletion. Atmospheric Chemistry and Physics, 7:4375-4418.

Simpson, W.R., D. Carlson, G. Honninger, T.A. Douglas, M. Sturm, D. Perovich and U. Platt, 2007b. First-year sea-ice contact predicts bromine monoxide (BrO) levels at Barrow, Alaska better than potential frost flower contact. Atmospheric Chemistry and Physics, 7:621-627.

Skaare, J.U., E. Degre and P.E. Aspholm, 1994. Mercury and selenium in Arctic and coastal seals of the coast of Norway. Environmental Pollution 85:153-160.

Skov, H., J.H. Christensen, M.E. Goodsite, N.Z. Heidam, B. Jensen, P. Wahlin and G. Geernaert, 2004. Fate of elemental mercury in the arctic during atmospheric mercury depletion episodes and the load of atmospheric mercury to the arctic. Environmental Science and Technology, 38:2373-2382.

Skyllberg, U., J. Qian, W. Frech, K. Xia and W.F. Bleam, 2003. Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. Biogeochemistry, 64:53-76.

Skyllberg, U., 2010. Chapter 13 – Mercury biogeochemistry in soils and sediments. Developments in Soil Science, 34:379-410.

Slemr, F., E.G. Brunke, R. Ebinghaus, C. Temme, J. Munthe, I. Wängberg, W.H. Schroeder, A. Steffen and T. Berg, 2003. Worldwide trend of atmospheric mercury since 1977. Geophysical Research Letters, 30:1516.

Smith, T.G., 1987. The ringed seal, *Phoca hispida*, of the Canadian western Arctic. Canadian Bulletin of Fisheries and Aquatic Sciences, 216:81.

Smith, T.G. and F.A.J. Armstrong, 1978. Mercury and selenium in ringed and bearded seal tissues from Arctic Canada. Arctic 31:75-84.

Smith, L.C., Y. Sheng, G.M. MacDonald and L.D. Hinzman, 2005a. Disappearing Arctic lakes. Science, 308:1429.

Smith, S.L., M.M. Burgess, D. Riseborough and F.M. Nixon, 2005b. Recent trends from Canadian permafrost thermal monitoring network sites. Permafrost and Periglacial Processes, 16:19-30.

Smith, L.C., Y. Sheng and G.M. MacDonald, 2007. A first-pan-Arctic assessment of the influence of glaciation, permafrost, topography and peatlands on Northern Hemisphere lake distribution. Permafrost and Periglacial Processes, 18:201-208.

Smol, J.P., A.P. Wolfe, H.J.B. Birks and 23 others, 2005. Climate-driven regime shifts in the biological communities of arctic lakes. Proceedings of the National Academy of Sciences of the United States of America, 102:4397-4402.

Smol, J.P. and M.S.V. Douglas, 2007a. Crossing the final ecological threshold in high Arctic ponds. Proceedings of the National Academy of Sciences of the United States of America, 104:12395-12397.

Smol, J.P. and M.S.V. Douglas, 2007b. From controversy to consensus: making the case for recent climate change in the Arctic using lake sediments. Frontiers in Ecology and the Environment, 5:466-474.

Sokal, R.R. and F.J. Rohlf, 1981. Biometry. The Principles and Practice of Statistics in Biological Research. 2nd Ed. 859 pp. Freeman & Co.

Sommar, J., K. Gårdfeldt, X. Feng and O. Lindqvist, 1999. Rate coefficients for gas-phase oxidation of elemental mercury by bromine and hydroxyl radicals. Paper presented at Mercury as a Global Pollutant – 5th International Conference. CETEM – Center for Mineral Technology, Rio de Janerio, Brazil, May 23-28.

Sommar, J., K. Gardfeldt, D. Stromberg and X.B. Feng, 2001. A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury. Atmospheric Environment, 35:3049-3054.

Sommar, J., I. Wangberg, T. Berg, K. Gardfeldt, J. Munthe, A. Richeter, A. Urba, F. Wittrock and W.H. Schroeder, 2004. Circumpolar transport and air-surface exchange of atmospheric mercury at Ny-Alesund (79°N), Svalbard, spring 2002. Atmospheric Chemistry and Physics Discussions, 4:1727-1771.

Sommar, J., I. Wangberg, T. Berg, K. Gardfelt, J. Munthe, A. Richter, A. Urba, F. Wittrock and W.H. Schroeder, 2007. Circumpolar transport and air-surface exchange of atmospheric mercury at Ny-Alesund (79 degrees N), Svalbard, spring 2002. Atmospheric Chemistry and Physics, 7:151-166.

Sommar, J., M.E. Andersson and H.-W. Jacobi, 2010. Circumpolar measurements of speciated mercury, ozone and carbon monoxide in the boundary layer of the Arctic Ocean. Atmospheric Chemistry and Physics, 10:5031-5045.

Sonne, C., 2010. Health effects from long-range transported contaminants in Arctic top predators: An integrated review based on studies of polar bears and relevant model species. Environment International, 36:461-491.

Sonne, C., R. Dietz, P.S. Leifsson, G. Asmund, E.W. Born and M. Kirkegaard, 2007. Are liver and renal lesions in East Greenland polar bears (*Ursus maritimus*) associated with high mercury levels? Environmental Health, 6:11

Sonne, C., M. Dam, P.L. Leifsson and R. Dietz, 2010. Liver and renal histopathology of North Atlantic long-finned pilot whales (*Globicephala melas*) contaminated with high concentrations of heavy metals and organochlorine compounds. Toxicological and Environmental Chemistry 92:969-985.

Sou, T. and G. Flato, 2009. Sea Ice in the Canadian Arctic Archipelago: Modeling the past (1950-2004) and the future (2041-60). Journal of Climate, 22:2181-2198.

Springer, A.M., C.P. McRoy and M.V. Flint, 1996. The Bering Sea green belt: shelf-edge process and ecosystem production. Fish Oceanography, 5:205-223.

Sprovieri, F., N. Pirrone, M. Landis and R.K. Stevens, 2005. Oxidation of gaseous elemental mercury to gaseous divalent mercury during 2003 polar sunrise at Ny-Alesund. Environmental Science and Technology, 39:9156-9165.

St Louis, V.L., J.W.M. Rudd, C.A. Kelly, R.A. Bodaly, M.J. Paterson, K.G. Beaty, R.H. Hesslein, A. Heyes and A.R. Majewski, 2004. The rise and fall of mercury methylation in an experimental reservoir. Environmental Science and Technology, 38:1348-1358.

St Louis, V.L., M.J. Sharp, A. Steffen, A. May, J. Barker, J.L. Kirk, D.J.A. Kelly, S.E. Arnott, B. Keatley and J.P. Smol, 2005. Some sources and sinks of monomethyl and inorganic mercury on Ellesmere island in the Canadian High Arctic. Environmental Science and Technology, 39:2686-2701.

St Louis, V.L., H. Hintelmann, J.A. Graydon, J.L. Kirk, J. Barker, B. Dimock, M.J. Sharp and I. Lehnherr, 2007. Methylated mercury species in Canadian High Arctic marine surface waters and snowpacks. Environmental Science and Technology, 41:6433-6441.

Stange, K., A. Maage and J. Klungosoyr, 1996. Contaminants in fish and sediments in the North Atlantic ocean. TemaNord 1996:522. Nordic Council of Ministers, Copenhagen.

Stanley, J.B., P.F. Schuster, M.M. Reddy, D.A. Roth, H.E. Taylor and G.R. Aiken, 2002. Mercury on the move during snowmelt in Vermont. Eos, Transactions, American Geophysical Union, 83:45, 47-48.

Steen, A.O., T. Berg, A.P. Dastoor, D.A. Durnford, L.R. Hole and K.A. Pfaffhuber, 2009. Dynamic exchange of gaseous elemental mercury during polar night and day. Atmospheric Environment, 43:5604-5610.

Steen, A.O., T. Berg, A.P. Dastoor, D.A. Durnford, L.R. Hole and K.A. Pfaffhuber, 2010. Natural and anthropogenic atmospheric mercury in the European Arctic: a speciation study. Atmospheric Chemistry and Physics Discussions, 10:27255-27281.

Steffen, A., 2009. Mercury measurements at Alert. In: Smith, S., J. Stow and J. Edwards (Eds.). Synopsis of Research Conducted under the 2008-2009 Northern Contaminants Program, pp. 58-64, Minister of Northern Affairs and Development, Ottawa.

Steffen, A., W. Schroeder, J. Bottenheim, J. Narayan and J.D. Fuentes, 2002. Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the Canadian Arctic during Alert 2000. Atmospheric Environment, 36:2653-2661.

Steffen, A., W. Schroeder, R. Macdonald, L. Poissant and A. Konoplev, 2005. Mercury in the Arctic atmosphere: An analysis of eight years of measurements of GEM at Alert (Canada) and a comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada). Science of the Total Environment, 342:185-198.

Steffen, A., T. Douglas, M. Amyot, P. Ariya, K. Aspmo, T. Berg, J. Bottenheim, S. Brooks, F. Cobbett, A. Dastoor, A. Dommergue, R. Ebinghaus, C. Ferrari, K. Gardfeldt, M.E. Goodsite, D. Lean, A.J. Poulain, C. Scherz, H. Skov, J. Sommar and C. Temme, 2008a. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. Atmospheric Chemistry and Physics, 8:1445-1482.

Steffen, A., T. Douglas, M. Amyot, P. Ariya, K. Aspmo, T. Berg, J. Bottenheim, S. Brooks, F. Cobbett, A. Dastoor, A. Dommergue, R. Ebinghaus, C. Ferrari, K. Gardfeldt, M.E. Goodsite, D.R.S. Lean, A.J. Poulain, C. Scherz, H. Skov, J. Sommar and C. Temme, 2008b. A synthesis of atmospheric mercury depletion event chemistry linking atmosphere, snow and water. Atmospheric Chemical and Physical Discussions, 7:10837-10931.

Stein, R. and R.W. Macdonald (Eds.), 2004. The Organic Carbon Cycle in the Arctic Ocean. 336 pp. Springer.

Stein, R. and R.W. Macdonald, 2004. Organic carbon budget: Arctic Ocean vs global ocean. In: Stein, R. and R.W. Macdonald (Eds.). The Organic Carbon Cycle in the Arctic Ocean, pp. 315-322, Springer.

Stein, J.N., C.S. Jessop, T.R. Porter and K.T.J. Chang-Kue, 1973. Fish Resources of the Mackenzie River Valley. Interim report II. 260 pp. Fisheries Service of Environment Canada.

Steinacher, M., F. Joos, T.L. Frölicher, G.K. Plattner and S.C. Doney, 2008. Imminent ocean acidification projected with the NCAR global coupled carbon cycle-climate model. Biogeosciences Discussions, 5:4353-4393.

Steinnes, E. and T.E. Sjobakk, 2005. Order-of-magnitude increase of Hg in Norwegian peat profiles since the outset of industrial activity in Europe. Environmental Pollution, 137:365-370.

Steinnes, E., T. Berg and T.E. Sjøbakk, 2003. Temporal and spatial trends in Hg deposition monitored by moss analysis. Science of the total Environment, 304:215-219.

Stemmler, I. and G. Lammel, 2009. Cycling of DDT in the global environment 1950-2002: World ocean returns the pollutant. Geophysical Research Letters, 36:L24602.

Stern, G.A. and L. Lockhart, 2009. Mercury in beluga, narwhal and walrus from the Canadian Arctic: status in 2009. In: Smith, S., J. Stow and J. Edwards (Eds.). Synopsis of Research Conducted under the 2008/2009 Northern Contaminant Program, R71-64-2009E, pp. 108-122. Indian and Northern Affairs Canada, Ottawa, Canada.

Stern, G.A. and R.W. Macdonald, 2005. Biogeographical provinces of total and methyl mercury in zooplankton and fish from the Beaufort and Chukchi Seas: Results from the SHEBA drift. Environmental Science and Technology, 39:4707-4713.

Stern, G.A., H. Sanei, P. Roach, J. Dalaronde and P.M. Outridge, 2009. 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. Environmental Science and Technology, 43:7684-7690.

Stevick, P.T., B.J. McConnell and P.S. Hammond, 2002. Patterns of movement. In: Hoelzel, A.R. (Ed.). Marine Mammal Biology: An Evolutionary Approach, pp. 185-216. Blackwell Science.

Stewart, D.B. and L.M.J. Bernier, 1982. An aquatic resource survey of islands bordering Viscount Melville Sound, District of Franklin, Northwest Territories. Background Report 2, 108 pp. Environment

Canada, Lands Directorate, Indian and Northern Affairs Canada, Northern Environment Branch.

Stewart, R.E.A., S.E. Campana, C.M. Jones and B.E. Stewart, 2006. Bomb radiocarbon dating calibrates beluga (*Delphinapterus leucas*) age estimates. Canadian Journal of Zoology, 84:1840-1852.

Stirling, I., N.J. Lunn and J. Iacozza, 1999. Long-term trends in the population ecology of polar bears in western Hudson Bay in relation to climatic change. Arctic, 52:294-306.

Stohl, A., T. Berg, J.F. Burkhart, A.M. Fjæraa, C. Forster, A. Herber, Ø. Hov, C. Lunder, W.W. McMillan, S. Oltmans, M. Shiobara, D. Simpson, S. Solberg, K. Stebel, J. Ström, K. Tørseth, R. Treffeisen, K. Virkunnen and K.E. Yttri, 2007. Arctic smoke – record high air-pollution in the European Arctic due to agricultural fires in Eastern Europe in spring 2006. Atmospheric Chemistry and Physics, 7:511-534.

Streets, D.G., Q. Zhang and Y. Wu, 2009. Projections of global mercury emissions in 2050. Environmental Science and Technology, 43:2983-2988.

Strode, S.A., L. Jaegle, N.E. Selin, D.J. Jacob, R.J. Park, R.M. Yantosca, R.P. Mason and F. Slemr, 2007. Air-sea exchange in the global mercury cycle. Global Biogeochemical Cycles, 21: GB1017.

Strode, S., L. Jaeglé and N. Selin, 2009. Impact of mercury emissions from historic gold and silver mining: Global modeling. Atmospheric Environment, 43:2012-2017.

Stroeve, J., M.M. Holland, W. Meier, T. Scambos and M. Serreze, 2007. Arctic sea ice decline: Faster than forecast. Geophysical Research Letters, 34:L09501.

Stroeve, J., M. Serreze, S. Drobot, S. Gearheard, M. Holland, J. Maslanik, W. Meier and T. Scambos, 2008. Arctic sea ice extent plummets in 2007. Eos, Transactions, American Geophysical Union, 89:12-14.

Sun, L.G., X.B. Yin, X.D. Liu, R.B. Zhu, Z.Q. Xie and Y.H. Wang, 2006. A 2000-year record of mercury and ancient civilizations in seal hairs from King George Island, West Antarctica. Science of the Total Environment, 368:236-247.

Sunderland, E.M. and R.P. Mason, 2007. Human impacts on open ocean mercury concentrations. Global Biogeochemical Cycles, 21:GB4022.

Sunderland, E.M., D.P. Krabbenhoft, J.W. Moreau, S.A. Strode and W.M. Landing, 2009. Mercury sources, distribution, and bioavailability in the North Pacific Ocean: Insights from data and models. Global Biogeochemical Cycles, 23:GB2010.

Sundseth, K., J.M. Pacyna, E.G. Pacyna, J. Munthe, M. Belhaj and S. Astrom, 2010. Economic benefits from decreased mercury emissions: Projections for 2020. Journal of Cleaner Production, 18:386-394.

Swartzendruber, P.C., D.A. Jaffe, E.M. Prestbo, P. Weiss-Penzias, N.E. Selin, R. Park, D.J. Jacob, S. Strode and L. Jaegle, 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. Journal of Geophysical Research-Atmospheres, 111:D24301.

Tackett, P.J., A. Cavender, A.D. Keil, P.B. Shepson, J.W. Bottenheim, S. Morin, J. Deary, A. Steffen and C. Doerge, 2007. A study of the vertical scale of halogen chemistry in the Arctic troposphere during polar sunrise at Barrow, Alaska. Journal of Geophysical Research, 112:D07306.

Tape, K., M. Sturm and C. Racine, 2006. The evidence for shrub expansion in Northern Alaska and the Pan-Arctic. Global Change Biology, 12:686-702.

Tarasick, D.W. and J.W. Bottenheim, 2002. Surface ozone depletion episodes in the Arctic and Antarctic from historical ozonesonde records. Atmospheric Chemistry and Physics, 2:197-205.

Temme, C., J.W. Einax, R. Ebinghaus and W.H. Schroeder, 2003. Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the south Atlantic Ocean during polar summer. Environmental Science and Technology, 37:22-31.

Temme, C., P. Blanchard, A. Steffen, C. Banic, S. Beauchamp, L. Poissant, R. Tordon and B. Wiens, 2007. Trend, seasonal and multivariate analysis study of total gaseous mercury data from the Canadian atmospheric mercury measurement network (CAMNet). Atmospheric Environment, 41:5423-5441.

Therriault, T.W. and D. Schneider, 1998. Predicting change in fish mercury concentrations following reservoir impoundment. Environmental Pollution, 101:33-42.

Thompson, D.R., 1996. Mercury in birds and terrestrial mammals. In: Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (Eds.). Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations. SETAC Special Publication Series., pp. 341-356, Lewis Publishers.

Thyen, S., P.H. Becker and H. Behmann, 2000. Organochlorine and mercury contamination of little terns (*Sterna albifrons*) breeding at the western Baltic Sea, 1978-96. Environmental Pollution, 108:225-238.

Tian, W., G.M. Egeland, I. Sobol and H.M. Chan, 2011. Mercury hair concentrations and dietary exposure among Inuit preschool children in Nunavut, Canada. Environment International, 37:42-48.

Tilbury, K.L., J.E. Stein, C.A. Krone, R.L. Brownell, S.A. Blokhin, J.L. Bolton and D.W. Ernest, 2002. Chemical contaminants in juvenile gray whales (*Eschrichtius robustus*) from subsistence harvest in Arctic feeding grounds. Chemosphere, 47:555-564.

Timoney, K.P. and P. Lee, 2009. Does the Alberta tar sands industry pollute? The scientific evidence. The Open Conservation Biology Journal, 3:65-81.

Tinggi, U., 2003. Essentiality and toxicity of selenium and its status in Australia: a review. Toxicology Letters, 137:103-110.

Tokos, J.J.S., B. Hall, J.A. Calhoun and E.M. Prestbo, 1998. Homogeneous gas-phase reaction of $Hg^0$ with $H_2O_2$, $O_3$, $CH_3I$, and $(CH_3)_2S$: Implications for atmospheric Hg cycling. Atmospheric Environment, 32:823-827.

Tranter, M., P. Brimblecombe, T.D. Davies, C.E. Vincent, P.W. Abrahams and I. Blackwood, 1986. The composition of snowfall, snowpack and meltwater in the Scottish Highlands – evidence for preferential elution. Atmospheric Environment, 20:517-525.

Travnikov, O., 2005. Contribution of the intercontinental atmospheric transport to mercury pollution in the Northern Hemisphere. Atmospheric Environment, 39:7541-7548.

Travnikov, O., J.E. Jonson, A.S. Andersen, M. Gauss, A. Gusev, O. Rozovskaya, D. Simpson, V. Sokovyh, S. Valiyaveetil and P. Wind, 2009. Development of the EMEP global modelling framework: Progress report. Available: http://www.msceast.org/publications.html.

Travnikov, O., C.-J. Lin and A. Dastoor, 2010. Global and regional modeling. In: Pironne, N. and T. Keating (Eds.). Hemispheric Transport of Air Pollution 2010. Part B: Mercury, pp. 97-144, Economic Commission for Europe.

Tremblay, A., M. Lucotte and R. Schetagne, 1998. Total mercury and methylmercury accumulation in zooplankton of hydroelectric reservoirs in northern Québec (Canada). Science of the Total Environment, 213:307-315.

Tseng, C.M., C. Lamborg, W.F. Fitzgerald and D.R. Engstrom, 2004. Cycling of dissolved elemental mercury in Arctic Alaskan lakes. Geochimica et Cosmochimica Acta, 68:1173-1184.

Tsui, M.T.K. and W.X. Wang, 2004. Uptake and elimination routes of inorganic mercury and methylmercury in *Daphnia magna*. Environmental Science and Technology, 38:808-816.

Tucker, S., W.D. Bowen and S.J. Iverson, 2007. Dimensions of diet segregation in grey seals *Halichoerus grypus* revealed through stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$). Marine Ecology Progress Series, 339:271-282.

Tvinnereim, H.M., R. Eide and T. Riise, 2000. Heavy metals in human primary teeth: some factors influencing the metal concentrations. Science of the Total Environment, 255:21-27.

UN ECE, 2000. Joint EMEP/ CORINAIR Atmospheric Emission Inventory Guidebook. United Nations Economic Commission for Europe.

UNEP, 2002. Global Mercury Assessment. United Nations Environment Programme, Geneva.

UNEP, 2008. The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport. 42 pp. United Nations Environment Programme – Chemicals Branch, Geneva.

UNEP, 2009. Climate Change Science Compendium. McMullen, C.P. (Ed.). United Nations Environment Programme, 68 pp.

US EPA, 1997. Mercury study report to Congress. Vol. VII: Characterization of human health and wildlife risks from mercury exposure in the United States. 152 pp. U.S. Environmental Protection Agency.

US EPA, 2006. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control. US Environmental Protection Agency EPA-600/R-06/008.

US EPA, 2008. Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-pollutant Control. US Environmental Protection Agency EPA-600/R-08/077.

USGS, 2006. Mercury statistics. http://minerals.usgs.gov/ds/2005/140/mercury-use.pdf. United States Geological Survey.

Vadeboncoeur, Y., E. Jeppesen, M.J. Vander Zanden, H.H. Schierup, K. Christoffersen and D.M. Lodge, 2003. From Greenland to green lakes: Cultural eutrophication and the loss of benthic pathways in lakes. Limnology and Oceanography, 48:1408-1418.

Van Metre, P.C. and C.C. Fuller, 2009. Dual-core mass-balance approach for evaluating mercury and Pb-210 atmospheric fallout and focusing to lakes. Environmental Science and Technology, 43:26-32.

Vandal, G.M., R.P. Mason and W.F. Fitzgerald, 1991. Cycling of volatile mercury in temperate lakes. Water, Air and Soil Pollution, 56:791-803.

Verbyla, D., 2008. The greening and browning of Alaska based on 1982-2003 satellite data. Global Ecology and Biogeography, 17:547-555.

Verta, M., S. Rekolainen and K. Kinnunen, 1985. Causes of increased fish mercury levels in Finnish reservoirs. Publications of the Water Research Institute, National Board of Waters, Finland, 65:32-43.

Verta, M., S. Salo, M. Korhonen, P. Porvari, A. Paloheimo and J. Munthe, 2010. Climate induced thermocline change has an effect on the methyl mercury cycle in small boreal lakes. Science of the Total Environment, 408:3639-3647.

Visschedijk, A.J.H., H.A.C. Denier van der Gon, M. van het Bolscher and P.Y.J. Zandveld, 2006 Study to the effectiveness of the UN ECE Heavy Metals (HM) Protocol and cost of additional measures. TNO report No. 2006-A-R0087/B.

Vogt, R., P.J. Crutzen and R. Sander, 1996. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. Nature, 383:327-330.

von Storch, H., C. Hagner, M. Costa-Cabral, F. Feser, J. Pacyna, E. Pacyna and S. Kolb, 2002. Reassessing past European gasoline lead policies. EOS, Transactions, American Geophysical Union, 83:Number 36; 33 September 2002.

Vörösmarty, C., L. Hinzman, B. Peterson, D. Bromwich, L. Hamilton, J. Morison, V. Romanovsky, M. Sturm and R. Webb, 2002. Arctic-CHAMP: A program to study arctic hydrology and its role in global change, EOS, Transactions. American Geophysical Union, 83:241-249.

Wagemann, R. and R.E.A. Stewart, 1994. Concentrations of heavy-metals and selenium in tissues and some foods of walrus (*Odobenus rosmarus rosmarus*) from the eastern Canadian Arctic and sub-Arctic, and associations between metals, age, and gender. Canadian Journal of Fisheries and Aquatic Sciences, 51:426-436.

Wagemann, R., E. Trebacz, G. Boila and W.L. Lockhart, 1998. Methylmercury and total mercury in tissues of arctic marine mammals. Science of the Total Environment, 218:19-31.

Walker, G., 2007. Climate Change 2007: A world melting from the top down. Nature, 446:718-722.

Wallace, J.M. and D.S. Gutzler, 1981. Teleconnections in the geopotential height field during the northern hemisphere winter. Monthly Weather Review, 109:784-812.

Walsh, J.E., 2008. Climate of the arctic marine environment. Ecological Applications, 18:S3-S22.

Walsh, C.T., M.D. Distefano, M.J. Moore, L.M. Shewchuk and G.L. Verdine, 1988. Molecular-basis of bacterial-resistance to organomercurial and inorganic mercuric-salts. FASEB Journal, 2:124-130.

Wang, A., D. Barber and C.J. Pfeiffer, 2001. Protective effects of selenium against mercury toxicity in cultured Atlantic spotted dolphin (*Stenella plagiodon*) renal cells. Archives of Environmental Contamination and Toxicology, 41:403-409.

Wang, D., S.M. Henrichs and L. Guo, 2006. Distributions of nutrients, dissolved organic carbon and carbohydrates in the western Arctic Ocean. Continental Shelf Research, 26:1654-1667.

Wang, F., R.W. Macdonald, G.A. Stern and P.M. Outridge, 2010. When noise becomes the signal: Chemical contamination of aquatic ecosystems under a changing climate. Marine Pollution Bulletin, 60:1633-1635.

Wängberg, I., J. Munthe, R. Ebinghaus, K. Gardfeldt, A. Iverfeldt and J. Sommar, 2003. Distribution of TPM in northern Europe. Science of the Total Environment, 304:53-59.

Wängberg, I., J. Munthe, T. Berg, R. Ebinghaus, H.H. Kock, C. Temme, E. Bieber, T.G. Spain and A. Stolk, 2007. Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area. Atmospheric Environment, 41:2612-2619.

Wängberg, I., K. Aspmo Pfaffhuber, T. Berg, H. Hakola, K. Kyllönen, J. Munthe, P. Porvari and M. Verta, 2010. Atmospheric and catchment mercury concentrations and fluxes in Fennoscandia. Nordic Council of Ministers.

Watras, C.J. and N.S. Bloom, 1992. Mercury and methylmercury individual zooplankton-implications for bioaccumulation. Limnology and Oceanography, 37:1313-1318.

Watras, C.J., R.C. Back, S. Halvorsen, R.J.M. Hudson, K.A. Morrison and S.P. Wente, 1998. Bioaccumulation of mercury in pelagic freshwater food webs. Science of the Total Environment, 219:183-208.

Watras, C.J., K.A. Morrison, A. Kent, N. Price, O. Regnell, C. Eckley, H. Hintelmann and T. Hubacher, 2005. Sources of methylmercury to a wetland-dominated lake in northern Wisconsin. Environmental Science and Technology, 39:4747-4758.

Webber, H.M. and T.A. Haines, 2003. Mercury effects on predator avoidance behavior of a forage fish, golden shiner (*Notemigonus crysoleucas*). Environmental Toxicology and Chemistry, 22:1556-1561.

Weihe, P., J.C. Hansen, K. Murata, F. Debes, P. Jørgensen, U. Steuerwald, R.F. White and P. Grandjean, 2002. Neurobehavioral performance of Inuit children with increased prenatal exposure to methylmercury. International Journal of Circumpolar Health, 61:41-49.

Weihe, P., U. Steuerwald, S. Taheri, O. Færø, A.S. Veyhe and D. Nicolajsen, 2003. The human health programme in the Faroe Islands, 1985-2001. In: Deutch, B. and J.C. Hansen (Eds.). AMAP, Greenland and the Faroe Islands, 1997-2001.Volume 1 Human Health. Ministry of Environment, Denmark.

Weiss-Penzias, P., D.A. Jaffe, P. Swartzendruber, W. Hafner, D. Chand and E. Prestbo, 2007. Quantifying Asian biomass burning sources of mercury using the Hg/CO ratio in pollution plumes observed at the Mount Bachelor Observatory. Atmospheric Environment, 41:4366-4379.

Welch, H.E. and J. Kalff, 1974. Benthic photosynthesis and respiration in Char Lake. Journal of the Fisheries Research Board of Canada, 31:609-620.

Wennberg, M., T. Lundh, I.A. Bergdahl, G. Hallmans, J. Jansson, B. Stegmayr, H.M. Custodio and S. Skerfving, 2007. Time trends in burdens of cadmium, lead, and mercury in the population of northern Sweden. Environmental Research, 100:330-338.

Whalin, L., E.-H. Kim and R.P. Mason, 2007. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. Marine Chemistry, 107:278-294.

Wheatley, B. and M.A. Wheatley, 1988. Methylmercury in the Canadian Arctic environment past and present – natural or industrial? Arctic Medical Research 47:163-167.

WHO, 1990. Methylmercury. International Programme on Chemical Safety. Environmental Health Criteria 101. World Health Organization, Geneva.

WHO, 1998. Summary and Conclusions: Joint FAO/WHO Expert Committee on Food Additives. Presented at the 51st meeting. World Health Organization.

Wiener, J.G. and D.J. Spry, 1996. Toxicological significance of mercury in freshwater fish. In: Beyer, W.N., G.H. Heinz and A.W. Redmon-Norwood (Eds.). Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations, pp. 297-339. CRC Press.

Wiener, J.G., D.P. Krabbenhoft, G.H. Heinz and A.M. Scheuhammer, 2003. Ecotoxicology of mercury. In: Hoffman, D.J., B.A. Rattner, G.A.J. Burton and J.J. Cairns (Eds.). Handbook of Ecotoxicology. Second Edition, pp. 409-463. Lewis Publishers.

Wilhelm, S.M., L. Liang, D. Cussen and D.A. Kirchgessner, 2007. Mercury in crude oil processed in the United States (2004). Environmental Science and Technology, 41:4509-4514.

Williams, M.W. and J.M. Melack, 1991. Solute chemistry of snowmelt and runoff in an alpine basin, Sierra-Nevada. Water Resources Research, 27:1575-1588.

Wilson, S.J., F. Steenhuisen, J.M. Pacyna and E.G. Pacyna, 2006. Mapping the spatial distribution of global anthropogenic mercury atmospheric emission inventories. Atmospheric Environment, 40:4621-4632.

Witze, A., 2008. Climate change: Losing Greenland. Nature, 452:798-802.

Wolfe, M.F., S. Schwarzbach and R.A. Sulaiman, 1998. Effects of mercury on wildlife: A comprehensive review. Environmental Toxicology and Chemistry, 17:146-160.

Woo, M.K., 1983. Hydrology of a drainage-basin in the Canadian High Arctic. Annals of the Association of American Geographers, 73:577-596.

Woo, M.K. and R. Thorne, 2003. Streamflow in the Mackenzie Basin, Canada. Arctic, 56:328-340.

Woshner, V.M., 2000. Concentrations and interactions of selected elements in tissues of four marine mammal species harvested by Inuit hunters in arctic Alaska, with an intensive histologic assessment, emphasizing the beluga whale. PhD Dissertation. University of Illinois.

Woshner, V.M., T.M. O'Hara, G.R. Bratton, R.S. Suydam and V.R. Beasley, 2001a. Concentrations and interactions of selected essential and non-essential elements in bowhead and beluga whales of arctic Alaska. Journal of Wildlife Diseases, 37:693-710.

Woshner, V.M., T.M. O'Hara, G.R. Bratton and V.R. Beasley, 2001b. Concentrations and interactions of selected essential and non-essential elements in ringed seals and polar bears of arctic Alaska. Journal of Wildlife Diseases, 37:711-721.

Woshner, V.M., T.M. O'Hara, J.A. Eurell, M.A. Wallig, G.R. Bratton, R.S. Suydam and V.R. Beasley, 2002. Distribution of inorganic mercury in liver and kidney of beluga and bowhead whales through autometallographic development of light microscopic tissue sections. Toxicologic Pathology, 30:209-215.

Woshner, V., K. Knott, R. Wells, C. Willetto, R. Swor and T. O'Hara, 2008. Mercury and selenium in blood and epidermis of bottlenose dolphins (*Tursiops truncatus*) from Sarasota Bay, FL: Interaction and relevance to life history and hematologic parameters. Ecohealth, 5:360-370.

Wrona, F., T. Prowse, J. Reist, R. Beamish, J.J. Gibson, J. Hobbie, E. Jeppesen, J. King, A. Korhola, R.W. Macdonald, M. Power, V. Skvortsov, G. Koeck, W. Vincent and L. Levesque, 2005. Freshwater ecosystems. In: Arctic Climate Impact Assessment, pp. 353-452. Cambridge University Press.

Xu, C.H., L.D. Guo, F.G. Dou and C.L. Ping, 2009. Potential DOC production from size-fractionated Arctic tundra soils. Cold Regions Science and Technology, 55:141-150.

Yamamoto-Kawai, M., F.A. McLaughlin, E.C. Carmack, S. Nishino and K. Shimada, 2009. Aragonite undersaturation in the Arctic Ocean: Effects of ocean acidification and sea ice melt. Science, 326:1098-1100.

Yokoo, E.M., J.G. Valente, L. Grattan, S.L. Schmidt, I. Platt and E.K. Silbergeld, 2003. Low level methylmercury exposure affects neuropsychological function in adults. Environmental Health, 2:8.

Young, J.F., W.D. Wosilait and R.H. Luecke, 2001. Analysis of methylmercury deposition in humans utilizing a PBPK model and animal pharmacokinetic data. Journal of Toxicology and Environmental Health A, 63:19-52.

Young, B., L. Loseto and S. Ferguson, 2010. Diet differences among age classes of Arctic seals: evidence from stable isotope and mercury biomarkers. Polar Biology, 33:153-162.

Zaccone, C., A. Santoro, C. Cocozza, R. Terzano, W. Shotyk and T.M. Miano, 2009. Comparison of Hg concentrations in ombrotrophic peat and corresponding humic acids, and implications for the use of bogs as archives of atmospheric Hg deposition. Geoderma, 148:399-404.

Zauke, G.P., V.M. Savinov, J. Ritterhoff and T. Savinova, 1999. Heavy metals in fish from the Barents Sea (summer 1994). Science of the Total Environment, 227:161-173.

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

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

Zhong, H. and W.-X. Wang, 2009. Controls of dissolved organic matter and chloride on mercury uptake by a marine diatom. Environmental Science and Technology, 43:8998-9003.

# Abbreviations and Acronyms

| | |
|---|---|
| $\delta^{13}C$ | Stable carbon isotope |
| $\delta^{15}N$ | Stable nitrogen isotope |
| [..] | Concentration, e.g. [Hg] = total Hg concentration |
| ACI | Activated carbon injection |
| AMAP | Arctic Monitoring and Assessment Programme |
| AMDE | Atmospheric mercury depletion event |
| ASGM | Artisanal and small-scale gold mining |
| BMDL | Benchmark dose lower limit |
| Br | Bromine |
| bw | Body weight |
| C | Carbon |
| Cd | Cadmium |
| C-DOM | Colored dissolved organic matter |
| $CH_4$ | Methane |
| $CO_2$ | Carbon dioxide |
| Cu | Copper |
| DOC | Dissolved organic carbon |
| DOM | Dissolved organic matter |
| dw | Dry weight |
| ESPs | Electrostatic precipitators |
| EXEC | 'Extended Emissions Control' emissions scenario |
| Fe | Iron |
| FFs | Fabric filters |
| FGD | Flue gas desulfurization |
| HC | Hydrocarbon |
| HCH | Hexachlorocyclohexane |
| Hg | Mercury |
| IPCC | Intergovernmental Panel on Climate Change |
| LOAEL | Lowest observed adverse effect level |
| LRTAP | UNECE Convention on Long-range Transboundary Air Pollution |
| MFTR | 'Maximum Feasible Technological Reduction' emissions scenario |
| N | Nitrogen |
| NAO | North Atlantic Oscillation |
| NMDA | N-methyl-D-aspartate |
| NOEL | No Observed Effect Level |
| ODE | Ozone depletion event |
| Pb | Lead |
| $pCO_2$ | Partial pressure of carbon dioxide |
| PNA | Pacific North American |
| POC | Particulate organic carbon |
| POM | Particulate organic matter |
| POP | Persistent organic pollutant |
| RfD | Reference dose |
| RFSL | Russian food safety limit |
| S2 | Methodologically-defined component of carbon (S1 and S2 components are mostly algal-derived kerogen; S3 is oxygen-bearing organic matter. See Carrie et al., 2010) |
| SCR | Selective catalytic reduction |
| Se | Selenium |
| SQ | 'Status Quo' emissions scenario |
| Ti | Titanium |
| TOC | Total organic carbon |
| TWI | Tolerable weekly intake |
| UNEP | United Nations Environment Programme |
| USD | U.S. Dollar |
| USEPA | U.S. Environmental Protection Agency |
| USFDA | U.S. Food and Drug Administration |
| UV | Ultraviolet |
| ww | Wet weight |
| Zn | Zinc |

**Models**

| | |
|---|---|
| DEHM | Danish Eulerian Hemispheric model |
| GEOS-Chem | Goddard Earth Observing System – chemical transport model |
| GLEMOS | Global EMEP Multi-media Modelling System |
| GRAHM | Global/Regional Atmospheric Heavy Metal model |

**Mercury terminology**

| | |
|---|---|
| DGM | Dissolved gaseous mercury |
| DMHg | Dimethylmercury |
| FPM | Fine particulate mercury |
| GEM | Gaseous elemental mercury |
| GOM | Gaseous oxidized mercury |
| Hg(II) | Inorganic divalent mercury |
| Hg(0) | Elemental mercury |
| HgP / PHg | Particulate mercury |
| HgT / THg | Total mercury |
| HgR / RGM | Reactive gaseous mercury |
| MeHg | Methylmercury |
| MMHg | Monomethylmercury |
| RGM / $Hg_R$ | Reactive gaseous mercury |
| TGM | Total gaseous mercury |
| THg / HgT | Total mercury |
| TPM | Total particulate mercury |