**Atmospheric
Chemistry
and Physics**

A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow

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Abstract. It was discovered in 1995 that, during the spring time, unexpectedly low concentrations of gaseous elemental mercury (GEM) occurred in the Arctic air. This was surprising for a pollutant known to have a long residence time in the atmosphere; however conditions appeared to exist in the Arctic that promoted this depletion of mercury (Hg). This phenomenon is termed atmospheric mercury depletion events (AMDEs) and its discovery has revolutionized our understanding of the cycling of Hg in Polar Regions while stimulating a significant amount of research to understand its impact to this fragile ecosystem. Shortly after the discovery was made in Canada, AMDEs were confirmed to occur throughout the Arctic, sub-Artic and Antarctic coasts. It is now known that, through a series of photochemically initiated reactions involving halogens, GEM is converted to a more reactive species and is subsequently associated to particles in the air and/or deposited to the polar environment. AMDEs are a means by which Hg is transferred from the atmosphere to the environment that was previously unknown. In this article we review Hg research taken place in Polar Regions pertaining to AMDEs, the methods used to collect Hg in different environmental media, research results of the current understanding of AMDEs from field, laboratory and modeling work, how Hg cycles around the environment after AMDEs, gaps in our current knowledge and the future impacts that AMDEs may have on polar environments. The research presented has shown that while considerable improvements in methodology to measure Hg have been made but the main limitation remains knowing the speciation of Hg in the various media. The processes that drive AMDEs and how they occur are discussed. As well, the role that the snow pack and the sea ice play in the cycling of Hg is presented. It has been found that deposition of Hg from AMDEs occurs at marine coasts and not far inland and that a fraction of the
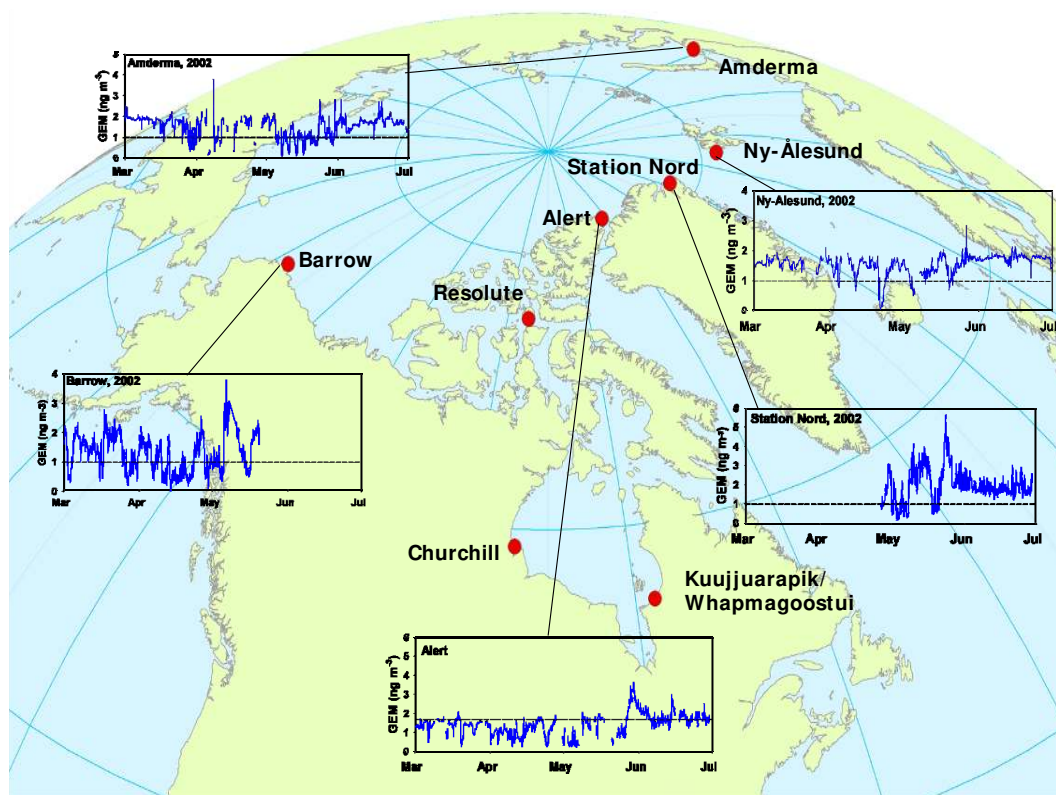
Fig. 1. Map of sampling sites for mercury research undertaken in the Arctic (and sub-Arctic) including time series of GEM concentrations at Amderma, Barrow, Ny-Ålesund, Station Nord and Alert during spring 2002. These time series demonstrate that during the Arctic spring, all sites show occurrence of AMDEs by concentrations going below 1 ng/m^3 (as indicated by the dashed line).

deposited Hg does not remain in the same form in the snow. Kinetic studies undertaken have demonstrated that bromine is the major oxidant depleting Hg in the atmosphere. Modeling results demonstrate that there is a significant deposition of Hg to Polar Regions as a result of AMDEs. Models have also shown that Hg is readily transported to the Arctic from source regions, at times during springtime when this environment is actively transforming Hg from the atmosphere to the snow and ice surfaces. The presence of significant amounts of methyl Hg in snow in the Arctic surrounding AMDEs is important because this species is the link between the environment and impacts to wildlife and humans. Further, much work on methylation and demethylation processes has occurred but these processes are not yet fully understood. Recent changes in the climate and sea ice cover in Polar Regions are likely to have strong effects on the cycling of Hg in this environment; however more research is needed to understand Hg processes in order to formulate meaningful predictions of these changes.

1 Introduction

The first continuous measurements of surface level atmospheric mercury (Hg) concentrations began at Alert, Canada in 1995 (Fig. 1). To the astonishment of the investigators, they observed rapid episodically very low concentrations of gaseous elemental Hg (GEM) between March and June. To appreciate the significance of these results it should be understood that until that time there was general agreement that the atmospheric residence time of GEM was 6–24 months (Schroeder and Munthe, 1995) and little variation in the atmospheric concentration of Hg was reported from any other location. Even though the episodes of low GEM concentrations strongly correlated with similar periods of low ground level ozone that were reported at the same location (Barrie et al., 1988), it took several years of consecutive measurements before the investigators felt convinced that this was a real phenomenon and reported their observations (Schroeder et al., 1998). It is now well established that these low GEM concentrations, termed atmospheric mercury depletion events (AMDEs), are an annual recurring spring time phenomenon (Steffen et al., 2005). Furthermore, the occurrence of AMDEs has now been observed throughout Polar Regions (see Fig. 1) at Ny-Ålesund, Svalbard 78°54′ N 11°53′ E

(Berg et al., 2003a); Pt. Barrow, Alaska 71°19′ N 156°37′ W (Lindberg et al., 2001); Station Nord, Greenland 81°36′ N 16°40 E (Skov et al., 2004); Kuujjuarapik, Quebec 55°16′ N 77°45′ W (Poissant and Pilote, 2003); Amderma, Russia 69°45′ N 61°40′ E (Steffen et al., 2005) and Neumeyer, Antartica 70°39′ S 8°15′ W (Ebinghaus et al., 2002), resulting in over 200 publications on the topic in the 5 years after the first report.

The depletion events demonstrate the existence of mechanisms representing the very fast removal of Hg from the atmosphere. However, surface based observations do not show a total removal of Hg from the atmosphere in the vertical column. In fact, the depletions appear to be limited vertically from the terrestrial or ocean surface up to a surface boundary layer of usually less than 1 km depth (Banic et al., 2003; Tackett et al., 2007). Even though these AMDEs are confined to the boundary layer, it is estimated that they can lead to the deposition of up to 300 tonnes of Hg per year to the Arctic (Ariya et al., 2004; Skov et al., 2004). It is known that a unique series of photochemically initiated reactions involving ozone and halogen compounds, largely of marine origin, and especially bromine oxides (BrO_x, Br, BrO), lead to the destruction of ozone (Simpson et al., 2007). Given the close correlation between ozone depletion events (ODEs) and AMDEs (see Fig. 2), it has been hypothesized that BrO_x, in turn, oxidizes GEM to reactive gaseous mercury (RGM) that is readily scavenged by snow and ice surfaces (Schroeder et al., 1998). AMDEs are only reported during polar springtime suggesting that sea ice or, more specifically, refreezing ice in open leads provides a halogen source that drives AMDE chemistry (Lindberg et al., 2002; Kaleschke, 2004; Simpson et al., 2007; Brooks et al., 2006).

In 1996, a review was published that clearly identified mercury as a heavy metal of great concern because of its anthropogenic mobilization during the last century and its ability to bioaccumulate and biomagnify Arctic marine wildlife (Macdonald and Bewers, 1996). This paper further recommended that work was urgently needed to verify trends of mercury in various media including the atmosphere, the oceans, the water system and the biota. While the discovery of AMDEs in 1995 initiated almost a decade of intense study of atmospheric Hg processes, there have been many studies of Hg Polar Regions prior to this discovery. This work was driven by the fact that Hg has strongly toxic properties, readily bioaccumulates in food webs, is found in elevated levels in arctic marine mammals and, in some locations, is above acceptable levels in the cord blood of mothers (Wagemann et al., 1998; Arnold et al., 2003; Lockhart et al., 2005a; Lockhart et al., 2005b). For example, elemental Hg entering the environment can be converted to bioavailable oxidized Hg which can then be converted to a methylated Hg species through a variety of abiotic and biotic processes. For biota, exposure to MeHg causes central nervous system effects, including a loss of coordination, inability to feed, a reduced responsiveness to stimuli and starvation. MeHg is a contam-
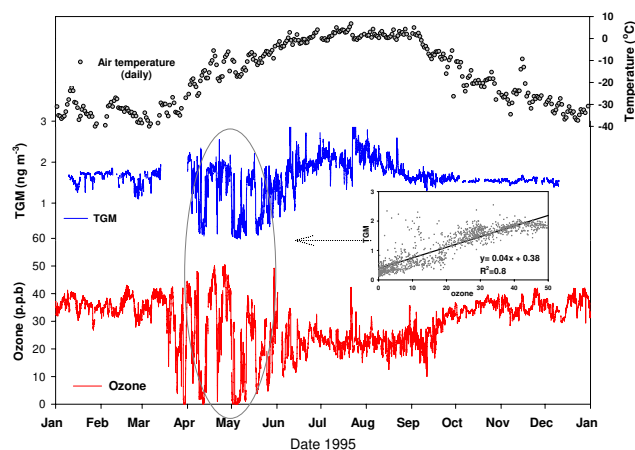

Fig. 2. Annual time series of TGM and ozone concentrations and air temperature from Alert 1995. Insert: linear correlation between TGM and ozone during an AMDE time period (adapted from Schroeder et al., 1998).

inant of grave concern because it can cross the blood brain barrier and can also act as an immunosuppressant rendering animals and humans more susceptible to disease (Eisler, 1987; Thompson, 1996; Derome et al., 2005). Subtle health effects are occurring in certain areas of the Arctic due to exposure to Hg in traditional food, and the dietary intake of Hg has, at times, exceeded established national guidelines in a number of communities (Johansen et al., 2000; Johansen et al., 2004). Evidence suggests that the greatest concern is for fetal and neonatal development. For example, evidence of neurobehavioral effects in children have been reported in the Faroe Islands (Grandjean et al., 1997) and in Inuit children in northern Quebec (Saint-Amour et al., 2006) who have been exposed to Hg through the consumption of country food. It has also been shown that the effects of Hg in the Arctic can have adverse economic effects in this region (Hylander and Goodsite, 2006).

Mercury has unique characteristics that include long-range atmospheric transport, the transformation to more toxic methylmercuric compounds and the ability of these compounds to biomagnify in the aquatic food chain. This has motivated intensive research on Hg as a pollutant of global concern. As well, interest in Hg in Polar Regions was accelerated with the discovery of AMDEs and this led to interest in snow measurements that yielded the highest reported concentrations of Hg in snow in a remote pristine ecosystem (Schroeder et al., 1998; Douglas et al., 2005). In 2006 alone, more than 40 publications have appeared relating to Hg in the Arctic. Hg is on the priority list of a large (and increasing) number of international agreements, conventions and national advisories aimed at environmental protection including all compartments, human health and wildlife (e.g. The Arctic Monitoring and Assessment Programme (AMAP), United Nations – Economic Commission

for Europe: Heavy Metals Protocol (UN-ECE), The Helsinki Commission (HELCOM), The OSPAR convention and many others).

The objective of this review article is to provide a comprehensive synthesis of the available science behind AMDEs and the research that has been undertaken in the arena of Hg in Polar Regions in the ten years since the discovery of AMDEs. This review article will first examine features of the environmental importance of Hg with a focus on issues of special importance for Polar Regions. This will be followed by sections outlining the measurement techniques used in field and laboratory experiments and a summary of results from field and laboratory based investigations of atmospheric processes. In addition, reviews of the modeling efforts that have been undertaken to better predict deposition and storage scenarios will be presented. The review will conclude by identifying gaps in our current understanding of mercury in polar environments and offering an outlook of potential future directions of Hg research in Polar Regions.

2   Mercury in the environment

Mercury behaves exceptionally in the environment due to its volatility, its potential to be methylated and its ability to bioaccumulate in aquatic food webs. Mercury is emitted into the atmosphere from a number of natural and anthropogenic sources. Experimental field data and model estimates indicate that anthropogenic Hg emissions are at least as great as those from natural sources (Mason et al., 1994; Fitzgerald et al., 1998; Martinez-Cortizas et al., 1999; Mason and Sheu, 2002; Pacyna et al., 2006). The change of the global atmospheric pool of Hg over time and the resulting concentration levels of gaseous elemental Hg are poorly defined. It is believed that anthropogenic emissions are leading to a general increase in Hg on local, regional and global scales and that the increase in global deposition to terrestrial and aquatic ecosystems since pre-industrial times is about a factor of 3 ± 1 (Lindberg et al., 2007). While the observed increase in Hg concentrations following the planet's industrialization has been documented, it is more difficult to understand the natural Hg cycle without the influence of anthropogenic activities. Ice cores provide a record for examining Hg deposition during changing climatic cycles (ice cores can reach up to 900 000 years in Antarctica, 150 000 years in Greenland). For example, Vandal et al. (1993) showed that for samples from the past 34 000 years, Hg concentrations were higher during the last glacial maximum, when oceanic productivity may have been higher than it is today. They therefore suggest that the oceans were the principal pre-industrial source of Hg to the atmosphere.

Hg participates in a number of complex environmental processes and interest has largely focused on the aquatic, biological and atmospheric cycles. Environmental cycling of Hg can be described as a series of chemical, biological and physical transformations that govern the distribution of Hg in and between different compartments of the environment. Hg can exist in a number of different chemical species, each with their own range of physical, chemical and ecotoxicological properties. These properties are of fundamental importance for the environmental behaviour of Hg (UNEP, 2002).

The three most important species of Hg known to occur in the environment are as follows (Schroeder and Munthe, 1998):

- Elemental mercury (Hg) [Hg^0 or Hg(0)] which has a high vapour pressure and a relatively low solubility in water. Of the Hg species found in the atmosphere, Hg(0) is the most stable and dominant and is subject to undergo long range transport;

- Divalent inorganic mercury [Hg^{2+} or Hg(II)] which is thought to be the principle form in wet deposition, is more soluble in water than Hg(0) and has a strong affinity for many inorganic and organic ligands, especially those containing sulphur;

- Methyl mercury [CH_3Hg^+ or MeHg] which is toxic and is strongly bio-accumulated by living organisms.

2.1   Mercury pollution in the Polar Regions

Polar ecosystems are generally considered to be the last pristine environments on earth. The Arctic, for example, is not densely populated and has, relative to temperate regions, little industrial activity (except select areas in the Russian Arctic (Bard, 1999) and mining in Svalbard) and is therefore perceived to be relatively unaffected by human activity. Antarctica is considered to be even less affected than the Arctic by anthropogenic influences because of its isolated location far from industrial activities which are predominantly located in the northern hemisphere. However, long distance atmospheric transport brings anthropogenic contaminants from mid- and low latitude sources to both Polar Regions (Bard, 1999).

Polar Regions contain fragile ecosystems and unique conditions that make the impact of external pollutants a larger threat than in other regions (Macdonald et al., 2005). In the Arctic, Hg levels are shown to be higher in the upper layers of marine sediment indicating that Hg input to the Arctic is post-industrially driven (Hermanson, 1998). Evidence from ice core samples confirms this. While this is not unique to the Arctic, it is often taken as evidence that industrialization is present in this region although some have suggested that this may not always be the case (Gobeil et al., 1999). Ice core studies from Greenland (Boutron et al., 1998; Mann et al., 2005) observed higher Hg concentrations in snow between the late 1940s to the mid 1960s, when industrial activities that produced considerable Hg were high, than in more recent snow. This trend has also been observed in other environmental media such as peat from Southern Greenland (Shotyk et al., 2003).

Reports have found that some marine mammals in the Canadian Arctic exceed human consumption guidelines and that Hg has been recorded above acceptable levels in the cord blood of mothers (Wagemann et al., 1998; Arnold et al., 2003; Lockhart et al., 2005a). Perhaps most striking is that Hg levels recorded in some northerners living in the Arctic are higher than those recorded in people from more temperate, industrialized regions where most of the Hg originates (Arnold et al., 2003). Mercury readily bioaccumulates in freshwater ecosystems and in marine wildlife but the pathways by which Hg is introduced to these environments are not well understood. The unpredictability in the spatial and temporal trends of Hg levels in marine wildlife throughout the Arctic indicates that the high Hg concentrations found in some species are likely driven by local or regional influences (Riget et al., 2007). The traditional way of life for northerners relies heavily on the consumption of country food (the wildlife) and this is of concern because much of these foods contain elevated Hg levels.

There are four major pollutant groups (listed below) that are well known to migrate to high latitudes. Three have been well known for more than a decade while the fourth group, a new and emerging group of organic contaminants, is of growing concern:

1. acidifying gases (SO_x) from Eurasian smelters and industry (Barrie et al., 1989)

2. heavy metals, including Hg, from fossil fuel combustion, industry and mining (Akeredolu et al., 1994)

3. classical persistent organic pollutants (POPs) including pesticides and polychlorinated biphenyls (Muir et al., 1992), and

4. emerging POPs, such as brominated flame retardants (BFRs) and polyfluorinated compounds (PFOA, PFOS) (Giesy and Kannan, 2001; Smithwick et al., 2005).

These contaminants are of concern because most of them biomagnify through the marine food chain to elevated levels in top predators, including humans, which may create adverse physiological effects (Dewailly et al., 1991; Bacon et al., 1992; Bossi et al., 2005). POPs and the other semi-volatile pollutants mentioned above are known to be transported to the Arctic via the "grasshopper effect" (Wania and Mackay, 1996). Both POPs and Hg are subject to partitioning onto particles and deposition from the atmosphere, however, unlike POPs much of the deposition of Hg in the Arctic results from photochemical reactions. Since Hg can exist in the atmosphere in various forms for long periods of time, there are several pathways by which Hg can arrive in remote locations.

Rapid changes in global atmospheric circulation systems also play key roles in how the pristine environment of the Arctic becomes contaminated (Barrie, 1986; Heidam et al., 2004). The Arctic troposphere is characterized by stable stratification and minimal vertical mixing in the winter and spring periods (Raatz, 1992). During the Arctic summer, the troposphere is well mixed which prevents the accumulation of atmospheric pollutants. In the winter and spring, pollutants accumulate in the Arctic because of a combination of robust stratification, resulting from strong surface temperature inversions inhibiting turbulent transport, and the atmospheric transport of pollutants from mid-latitudes. This pole ward transport of pollutants is due to the geographic position of a meteorological phenomenon known as blocking (Iversen and Joranger, 1985). Mid-latitude pollutant source regions undergo periods of atmospheric stagnation resulting in weather conditions that reduce contaminant scavenging rates and thus permit accumulation of pollutants over these source areas (Dastoor and Pudykiewicz, 1996). If a cyclonic system approaches a blocking high in these mid-latitudes, a strong pressure gradient builds and forces polluted air masses northward. If the transport path persists long enough, these polluted air masses can reach the Arctic troposphere within 2 to 10 days (Raatz and Shaw, 1984; Oehme, 1991; Weller and Schrems, 1996). Once atmospheric contaminants reach the Polar Regions, their lifetime in the troposphere is then controlled by local removal processes. The fate of transported Hg to the Arctic is discussed further in Sect. 6.

2.2 Mercury in the atmosphere

The long residence time of GEM in the atmosphere is about one year (Schroeder and Munthe, 1995) and is thus sufficient to allow for homogeneous mixing, at least within the hemisphere of origin. Since anthropogenic sources of Hg emissions into the atmosphere are primarily located in the northern hemisphere, a concentration gradient between the two hemispheres should be expected. Indeed, the global background concentration (the average sea-level atmospheric concentration of Hg(0) at remote sites) is generally 1.5–1.7 ng/m^3 in the northern hemisphere and 1.1–1.3 ng/m^3 in the southern hemisphere (Ebinghaus et al., 2002; Slemr et al., 2003; Temme et al., 2004; Kock et al., 2005). The lifetime of Hg in the atmosphere also depends on its chemical form. Gaseous elemental mercury can be transported globally while oxidized forms of Hg are more reactive and travel much shorter distances before they are scavenged or deposited. Temporal variations in deposition can result from changes in Hg emission rates, changes in local and regional sources (e.g. NO_x and SO_2) and, potentially, from changes in climate (e.g. changes in precipitation amounts, air temperature, sea ice coverage) (Macdonald et al., 2005). An increase of O_3 concentrations and aerosol loadings will also impact the atmospheric residence time and deposition fluxes of elemental and oxidized mercury (Lindberg et al., 2007). It is likely that global mercury cycling has changed over time not only by anthropogenic emissions but by increases in the oxidation potential of the atmosphere itself since the industrial revolution (Lindberg et al., 2007).

Table 1. Continental Hg emission trends from 1990 to 2000 and related uncertainties based on (Pacyna et al., 2006) and adopted from (Lindberg et al., 2007).

Continent	1990–1995 (tones/yr)	1995–2000 (tones/yr)	Uncertainty
Africa	2-fold increase: 200 to 400	constant level: 400	±50%
Asia	2-fold increase: 600 to 1200	constant level: 1200	±40%
Australia	2-fold increase: 50 to 100	constant level: 100	±30%
Europe	decline: 550 to 300	further reduction to 200	±30%
North America	slight decline: 220	fairly constant: 200	±27%
South America	30% increase: 55 to 80	fairly constant: 80	±50%

The most prevalent species of Hg in the atmosphere include gaseous elemental mercury (GEM) or Hg(0); oxidized reactive gaseous mercury (RGM), consisting of Hg(II) or Hg(I) compounds, and particle-bound Hg(II or I) mercury (PHg). Due to the methods used to measure these atmospheric species (see Sect. 3) and the lack of current analytical standards other than for GEM, information on the speciation/fractionation of these different chemical and physical forms is limited. As a consequence, RGM and PHg are considered operationally defined for this publication.

The reactive forms of Hg (e.g. RGM and some PHg) have short lifetimes in the atmosphere and are deposited from the atmosphere close to emission sources. However, the existence of reactive Hg in a particular air sample does not necessarily imply the existence of a local emission source but can be the result of atmospheric chemical reactions involving GEM transported from distant sources (Gauchard et al., 2005; Bottenheim and Chan, 2006; Lindberg et al., 2007). Experimental evidence demonstrating the presence and production of RGM and PHg at remote locations ranging from Polar Regions to the open ocean will be discussed in more detail in Sect. 4 (Schroeder et al., 1998; Lindberg et al., 2002; Berg et al., 2003a; Temme et al., 2003; Laurier et al., 2003; Skov et al., 2004).

2.3 Worldwide anthropogenic mercury sources

The onset of the major industrial activities since the 1940's has altered the global Hg cycle via the anthropogenic transfer of large quantities of Hg from deep geological stores to the Earth's surface and atmosphere (Ebinghaus et al., 1999; Ferrara, 1999; Shotyk et al., 2003). Several historic sediment and peat bog records from remote sites in both the northern and the southern hemispheres indicate a 2–4 fold increase in Hg deposition since pre-industrial times (Engstrom and Swain, 1997; Bindler et al., 2001; Lamborg et al., 2002; Shotyk et al., 2003; Givelet et al., 2004; Fitzgerald et al., 2005; Shotyk et al., 2005). North American and European Hg emissions are decreasing while those in Asia and Africa are increasing but the latter changes are less well documented and thus carry a larger uncertainty (see Table 1). Slemr et al. (2003) attempted to reconstruct the worldwide trend of at-

mospheric Hg concentrations from long-term measurements at 6 sites in the northern hemisphere, 2 sites in the southern hemisphere and multiple intermittent ship cruises over the Atlantic Ocean since 1977. They suggest that Hg concentrations in the global atmosphere have increased since the first measurements in 1977 to a maximum in the 1980s, subsequently decreased to a minimum in 1996 and then remained at a constant level of about $1.7 \, \text{ng/m}^3$, in the northern hemisphere, until 2001. However, this assessment and analysis includes several significant assumptions and an alternative hypothesis has been proposed that suggests that the total gaseous Hg concentration in the northern hemisphere remained virtually unchanged since 1977 (Lindberg et al., 2007). As mentioned in the previous section, factors including the change in the oxidation potential of the atmosphere over the past several decades (Schimel, 2000) may partially account for the discrepancy between measurement trends of atmospheric Hg (either constant or decreasing) and Hg emission inventories (increasing: Lindberg et al., 2007). Further, Lindberg et al. (2007) conclude that reductions in anthropogenic inputs will not produce a linear decrease in Hg deposition, especially at remote locations that are dominated by the global pool. A further understanding of atmospheric Hg chemical kinetics and deposition (re-emission) processes (in Polar Regions and elsewhere) is warranted to truly understand the impacts of global emission reductions of Hg on atmospheric Hg concentrations.

2.4 Mercury in snow and air and snow and ice interactions

Mercury can be deposited onto snow surfaces through both wet and dry deposition. Dry deposition in Polar Regions mainly corresponds with the deposition of RGM formed during AMDEs (Lu et al., 2001; Lindberg et al., 2002; Ariya et al., 2004). Mercury in snow is mainly found in its oxidised form (e.g. Hg(II)) with concentrations that can range from a few up to hundreds of ng/L (Lalonde et al., 2002; Lindberg et al., 2002; Steffen et al., 2002; Berg et al., 2003a; Ferrari et al., 2004a; Ferrari et al., 2005; Lahoutifard et al., 2006). AMDEs can lead to increased Hg concentrations in the surface snow (Lu et al., 2001; Lindberg et al., 2002; Brooks et al., 2006), however, it has also been observed that within

24 h after deposition of Hg from the atmosphere, a fraction is re-emitted as GEM back to the atmosphere (Lalonde et al., 2002; Dommergue et al., 2003a). Polar snow packs themselves have been investigated for their role as a chemical reactor that leads to the formation of active oxidants/reductants (Dominé and Shepson, 2002). Hence it appears that snow packs can act both as a sink and a source of Hg to the atmosphere depending on the environmental conditions (e.g. temperature, irradiation, presence of water layers around snow grains) and the chemical composition of the snow (e.g. presence of halogens, organic substances) (Lalonde et al., 2002; Dommergue et al., 2003b; Dommergue et al., 2003a; Lalonde et al., 2003; Fain et al., 2006a).

The concentration of MeHg within the snow pack has been reported at 3 orders of magnitude lower than total Hg in polar snow samples within the range of 10–200 pg/L (Ferrari et al., 2004b; Lahoutifard et al., 2005; St. Louis et al., 2005). The fraction of mercury that is detected by a luminescent bioreporter, also known as the "bioavailable" fraction of Hg, in Arctic snow at Barrow was reported to be approximately 45% of the total Hg just prior to annual melt (Scott, 2001). The author proposed that the fraction of bioavailable Hg had increased in the surface snow between polar sunrise and spring melt due to deposition ascribed to AMDEs (Scott, 2001).

There is much discussion about the fate of the deposited Hg to polar snow packs through AMDEs during and after snow melt. The reduction and subsequent re-emission of a fraction of Hg from the snow pack is largely believed to occur through photochemical processes (Lalonde et al., 2002). King and Simpson (2001) have shown that solar irradiation can effectively penetrate the first few centimeters of the snow pack, possibly leading to photoreduction of Hg complexes contained therein. The interaction of microbes within the surface grains of the snow pack and the Hg contained therein is also of interest during this critical period (Amato et al., 2007). Research has been undertaken to further investigate the interaction of micro-organisms within the water layer around the snow grains that can form strong complexes with metals (Döppenschmidt and Butt, 2000; Ariya et al., 2002a; Krembs, 2006). The resultant melt water will then likely contain Hg bound to organic material that could thereafter enter the food chain. Finally, measurement techniques such as investigating the presence of Hg in polar firn (compressed snow) and ice cores provide essential environmental archives for studying the global Hg cycle (Vandal et al., 1993; Boutron et al., 1998; Mann et al., 2005).

Mercury is a contaminant of concern that is found in many different media in the polar environment. To address this, considerable work has been undertaken to develop methodologies to investigate the processes by which it transforms and cycles in this challenging environment. The following section outlines the many different methodologies that are employed to investigate Hg specifically in Polar Regions.

3 Methodology employed to measure mercury in Polar Regions

3.1 Atmospheric mercury methodology

Gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle associated mercury (PHg) are the most commonly measured and monitored Hg species (at times termed fractions) in Polar Regions because they play a role in the AMDE process and associated deposition to the snow and sea ice surface. GEM is the most predominant (90–99%) of these forms of Hg found in the air (Schroeder and Munthe, 1995; Lin and Pehkonen, 1998). Currently, Hg(0) is the only gaseous Hg component that is easily and accurately measured in the field. The oxidized forms of Hg (including RGM and PHg) exhibit different characteristics than Hg(0) in toxicity, transport and deposition to ecosystems and play an important role in understanding the fate and impact of Hg on the environment. Currently, RGM and PHg are operationally defined and no unambiguous identification has been possible to date.

Nearly all analyses of atmospheric Hg, independent of fractionation or speciation, are performed using atomic absorption spectroscopy (AAS) or atomic fluorescence spectroscopy (AFS) as the principle method of detection. AAS instruments are simple, fairly inexpensive and small and are thus relatively mobile. AFS instruments, which tend to require more facilities (e.g. AC power and argon carrier gas), have greater sensitivity (Baeyens, 1992) allowing for an absolute detection limit as low as 0.1 pg (Tekran Inc., Toronto, Canada). At times, this advantage in sensitivity is forsaken for applicability and practicality when sampling in Polar Regions.

Many recent advances in measurement techniques of these species have occurred in the last ten years to support investigations of AMDEs. The current state of the art in measurement techniques for these two species will be covered in this section. Table 2 provides a summary of the polar site locations and methods employed to measure atmospheric Hg species.

3.1.1 Gaseous Elemental Mercury (GEM)

Elemental mercury's ability to form alloys, especially amalgams, with noble metals offers a convenient way to collect air samples (Williston, 1968; Fitzgerald and Gill, 1979). Presently, amalgamation with gold is exclusively the principle method used to collect GEM (Schroeder and Munthe, 1995) for atmospheric measurements in Polar Regions. The basic principle of operation is i) pre-concentration of GEM onto a trap; ii) removal of the Hg from the trap by thermal desorption and iii) detection and quantification of the Hg. This method has been previously presented in many publications, for example: (Ebinghaus et al., 1999; Munthe et al., 2001; Landis et al., 2002; Aspmo et al., 2005). Calibration

Table 2. Summary of measurement sites, methodologies employed and atmospheric Hg species measured.

Location	Analyte	Analytical method/ Instrumentation	Reference
Alert	GEM HgP, RGM TAM Hg-Flux TFM TPM	Tekran 2537A Tekran 2537A/1130/1135 Tekran 2537A/ CRPU Gradient-micrometeorology Manual TPM/TFM minisampler	(Schroeder et al., 1998; Lu et al., 2001; Steffen et al., 2002; Banic et al., 2003; Slemr et al., 2003; Steffen et al., 2003a; Steffen et al., 2003b; Ariya et al., 2004; Lu and Schroeder, 2004; St. Louis et al., 2005; Steffen et al., 2005; Cobbett et al., 2007)
Amderma	GEM	Tekran 2537A	(Steffen et al., 2005)
Barrow	GEM, RGM HgP, RGM RGM Flux	Tekran 2537A, manual denuders Tekran 2537A/1130/1135 REA developed system	(Lindberg et al., 2001; Lindberg et al., 2002; Skov et al., 2006; Tackett et al., 2007; Brooks et al., 2006)
Ny-Ålesund	GEM, HgP, RGM TAM GEM	Gardis Tekran 2537/1130/1135, CRPU TGM (manual gold trap) RGM (manual) KCl coated denuders HgP (manual) filters	(Berg et al., 2003a; Berg et al., 2003b; Wangberg et al., 2003; Aspmo et al., 2005; Ferrari et al., 2005; Gauchard et al., 2005; Sprovieri et al., 2005a, 2005b; Fain et al., 2006b; Fain et al., 2006a; Sommar et al., 2007)
Resolute	GEM	Tekran 2537A	(Lahoutifard et al., 2005)
Station Nord	GEM	Tekran 2537A Gardis	(Ferrari et al., 2004a; Ferrari et al., 2004b; Skov et al., 2004)
Neumayer	GEM, RGM	Tekran 2537A Tekran 2537A /130 (prototype)	(Ebinghaus et al., 2002; Temme et al., 2003)
Terra Nova	GEM, RGM	Tekran 2537A/1130	(Sprovieri et al., 2002)
North Atlantic Ocean	GEM, RGM, HgP	Tekran 2537A/1130/1135	(Aspmo et al., 2006)
Sub-Arctic	GEM	Gardis Tekran 2537A/1130/1135	(Dommergue et al., 2003b; Dommergue et al., 2003a; Gauchard et al., 2005; Steffen et al., 2005; Kirk et al., 2006; Lahoutifard et al., 2006)

of GEM is well documented (Schroeder and Munthe, 1995; Aspmo et al., 2005; Temme et al., 2007); the instruments are calibrated by injecting a known quantity of Hg(0) from an external source maintained at a known temperature and pressure.

The method currently used in polar research to collect and measure GEM in ambient air is as follows: air is drawn through a quartz tube filled with gold beads or gold wires where the Hg amalgamates to the gold in the trap (Schroeder and Munthe, 1995). The gold trap is then thermally desorbed to a temperature greater than 500°C releasing the GEM from the trap into a carrier gas (usually ultra high purity argon or air). The Hg is then carried into a spectrometer (either AFS or AAS) for detection. In polar regions, some researchers re-

port ambient air collected with this method as total gaseous mercury (TGM) which includes both the GEM and RGM species (Ebinghaus et al., 2002), however, if a filter (usually Teflon) is placed at the inlet of the sample line, it is most likely that RGM is removed and thus only GEM is collected (Steffen et al., 2002). Since the discovery of AMDEs, the research undertaken to collect and analyse GEM has predominantly employed the Tekran automated 2537A™ (AFS) instrument or the automated Gardis (AAS) instrument (Lindberg et al., 2002; Sprovieri et al., 2002; Steffen et al., 2002; Dommergue et al., 2003a; Skov et al., 2004; Aspmo et al., 2005). Both these aforementioned instruments are automated and collect continuous or semi-continuous measurements, respectively.

3.1.2 Reactive Gaseous Mercury (RGM)

Through the years, several efforts have been made to develop methods to accurately sample and quantify low concentrations of RGM, an inorganic Hg species, in the atmosphere (Brosset, 1987; Stratton and Lindberg, 1995; Xiao et al., 1997; Feng et al., 2000). The methods currently used in Polar Regions to measure RGM are outlined in the following paragraph.

The detailed methodology for collecting RGM (in Polar Regions) is described in Feng et al. (2000) and Landis et al. (2002). Briefly, KCl coated annular denuders are employed to collect RGM (primarily $HgCl_2$ and/or $HgBr_2$) from ambient air at a flow rate of 10 litres per minute for a minimum sampling time of 1 h. For the commercial automated Tekran system, once the RGM is collected, the denuder is heated to 500°C in a stream of Hg free air. The thermally released Hg is passed over a quartz chip pyrolysis chamber (maintained between 525°C and 800°C). The manual method for analysis of RGM is similar to this process without the quartz chip pyrolysis chamber (Aspmo et al., 2005). The RGM in the sample is thermally decomposed to Hg(0) and is transferred to a gold trap, usually inside a Tekran 2537A. This Hg(0) is then analysed and detected by AFS (as described above). RGM is usually detected in the low pg/m^3 concentration range but at times during polar spring, concentrations can increase to the low ng/m^3 range.

Calibration of this technique and the elucidation of the chemical speciation of RGM are part of ongoing discussions within the polar research community. Feng et al. (2003) evaluated a diffusion-type device to calibrate the denuder based system described above and found that this system, if modified, could be used for calibration. However, to the best of the authors' knowledge, no calibration system is available that can be used by the research community in Polar Regions to establish the accuracy of the RGM collected using this technique. Therefore, this significant limitation in the analytical capabilities of RGM detection must be prudently identified and considered when reporting information about RGM concentrations in Polar Regions. In addition, while KCl denuders are known to collect HgX_2 (X = halogen), the chemical speciation of RGM has yet to be determined. Therefore, at this time, RGM must be considered, at best, an operationally defined atmospheric species as presented in this publication.

3.1.3 Particle associated Mercury (HgP)

In general, the concentration of Hg on particles accounts for only a few percent of the total atmospheric Hg pool but some Arctic studies have shown that this few percent rises to approximately 40% during the springtime in Polar Regions (Lu et al., 2001; Steffen et al., 2003a). To collect HgP in Polar Regions, air is passed through a suitable filter medium that traps the airborne particles (Schroeder and Munthe, 1995). At present, filter methods are most commonly applied whereby a variety of different filter materials are used, including Teflon, cellulose, quartz and glass fibre (Lu and Schroeder, 1999). Further, wet digestion (Keeler et al., 1995) or pyrolysis (Schroeder and Munthe, 1995; Lu et al., 1998) is used to release the captured HgP, followed by detection using CV-AFS or AFS, respectively. For atmospheric Hg speciation in Polar Regions, quartz filters are commonly used. The procedure using the commercially developed Tekran 1135 is as follows: HgP is collected onto a quartz filter and is thermally released from the filter by heating it to approximately 800°C. The released sample is pyrolysed by passing the air stream through quartz chips also maintained at 800°C (Landis et al., 2002). Manual methods for analysis have also been employed with a similar procedure except the quartz chips chamber is not employed (Aspmo et al., 2005). The thermal decomposition to GEM is followed by AFS detection (Lu et al., 1998; Landis et al., 2002).

3.1.4 Total Atmospheric Mercury (TAM)

TAM species present in ambient air are determined by pyrolysing the air prior to introducing the air stream into a Hg analyzer. A cold regions Pyrolysis unit (CRPU) was specially designed to measure TAM under Arctic conditions as a front end unit to the Tekran 2537A (Steffen et al., 2002; Banic et al., 2003; Aspmo et al., 2005). Incoming air is heated and maintained at 900°C in a quartz tube filled with quartz chips. All gas-phase Hg (both GEM and RGM) and most particle associated organic and inorganic Hg are converted to GEM within the CRPU and are then detected and analysed using AFS (Steffen et al., 2002; Steffen et al., 2003a; Lu and Schroeder, 2004).

3.2 Flux measurement methods

The exchange of Hg to and from a surface is termed a "flux". Fluxes of RGM or GEM are expressed as emission or deposition rates, generally in nanograms per meter squared per unit of time (usually seconds or hours). Typical sign convention treats an emission as a positive flux and a deposition as a negative flux. From the flux and air concentration information, a deposition velocity can be calculated and Hg transformation mechanisms are then analysed. Several flux measurement methods have employed micro meteorological techniques to measure air-snow surface exchange of GEM (Lindberg et al., 2002; Cobbett et al., 2007; Brooks et al., 2006) and air-snow surface exchange of RGM (Lindberg et al., 2002; Skov et al., 2006). As well, indicative methods such as flux chambers (Schroeder et al., 2003; Ferrari et al., 2005; Sommar et al., 2007) and vertical gradient measurements have been employed to infer the direction of fluxes in Polar Regions (Steffen et al., 2002; Schroeder et al., 2003; Sommar et al., 2007).

3.2.1 Micrometeorological methods

There are three primary micrometeorological (micromet) methods employed to measure the atmospheric flux of trace compounds: i) the eddy covariance method; ii) relaxed eddy accumulation (REA) and iii) flux gradient methods including the modified bowen ratio (MBR) method – most commonly used in Hg measurements. Micromet methods involve the measurement of fluctuations in wind speed and wind direction to determine turbulent transfer coefficients which are referred to as "eddy diffusivities". Micromet methods assume that turbulent mixing dominates over simple diffusion and combines the measured vertical transport rates in near surface air (turbulence), in methods i) and ii), with concentration fluctuations and, in method iii), gradient of Hg species. In this way the average surface fluxes over an area around the sampling location known as the flux footprint or fetch are calculated.

The most direct of these methods is eddy covariance which involves the measurement of instantaneous high frequency fluctuations in wind speed about its mean in the vertical using a fast-response sonic anemometer and simultaneously measuring high frequency fluctuations in the concentration of a trace species called "eddy correlation". This is not possible for Hg given the lack of fast or high frequency measurement methods. Recent advances in applications of optical atmospheric methods such as LIDAR for the determination of atmospheric Hg fluxes (Bennet et al., 2006) or MAX-DOAS for BrO (Hönninger and Platt, 2002) may lead to future application of this sensitive technique to Hg. At present, these optical methods can only be applied in areas with high Hg(0) concentrations (i.e. near chlor-alkali plants) and are therefore not suitable for Polar Regions.

The second micromet method, relaxed eddy accumulation (REA), was applied toward measuring Hg(0) fluxes (Cobos et al., 2002; Olofsson et al., 2005). The technique has been employed for RGM fluxes in the Arctic at Barrow, Alaska and Station Nord, Greenland (Lindberg et al., 2002; Goodsite, 2003; Skov et al., 2006). REA "relaxes" the requirement for instantaneous gas analysis by differentially collecting the trace compound in air over time followed by analysis of the compound. In the case of RGM, the collector used is a manual or automated KCl denuder sampling system. For GEM the collector is a gold trap as described earlier in Sect. 3.1.1. The limitation of the REA and the MBR methods is that Hg is accumulated over time and thus fast or high frequency information of the species is forsaken.

The third method, flux gradient, assumes that turbulence transports all gaseous species equally. Using this assumption, the measurement of a concentration gradient of Hg at two or more heights above a surface concurrently with micromet measurements can be used to quantify the vertical turbulence mixing rate. These variables are combined to calculate the flux of Hg between a surface and the atmosphere. This method has been successfully employed in the Arctic

for measuring the flux of GEM between the air and the snow pack (Cobbett et al., 2007). A type of flux gradient method, the modified Bowen ratio technique, calculates a fast eddy correlation flux measurement for an easily measured tracer flux (e.g. carbon dioxide, water vapour), a gradient of the eddy correlation tracer and the Hg species at the same heights in order to calculate the flux. This method and has been successfully employed in the Arctic (Skov et al., 2006; Brooks et al., 2006) for Hg flux measurements between the snow pack and the atmosphere.

3.2.2 Chamber methods

The use of chambers to measure the flux processes of Hg in Polar Regions is beneficial because they are sensitive to environmental conditions and also to instrumental parameters such as the flushing flow rate (Wallschlager et al., 1999) and ventilation, and thus may be applied to measurements over the snow surface (Ferrari et al., 2005). Chamber methods employ a small encapsulated surface area (e.g. the snow pack) and determine the rate of change of the Hg emissions in the head space with time. There are some limitations with using chamber methods in Polar Regions which include a limited chamber footprint (the area that the chamber covers), isolation of the surface from the effects of atmospheric turbulence and the chamber may act as a greenhouse and modify the temperature and humidity of the snow surface thus altering the properties of the snow and the natural behaviour of Hg within that medium.

To further the study of snow to air transfers of GEM, laboratory manipulation studies have involved the collection of bulk snow from polar areas and subjected them to a variety of parameters (e.g. solar radiation and temperature) within a controlled environment to determine effects of these parameters on the flux of Hg from the snow (Lalonde et al., 2002; Poulain et al., 2004; Lahoutifard et al., 2006; Dommergue et al., 2007). These atmospheric laboratory and modelling methods will be discussed in subsequent sections.

3.3 Aqueous Hg measurement techniques employed in the Arctic

Mercury is usually measured in polar aquatic systems at ultra-trace levels. Table 3 provides a summary of aqueous measurements that have been made at various locations in the Arctic, including a brief overview of the analytical method used for each study.

3.3.1 Total mercury in water samples

Total mercury (THg) concentrations in surface water have been reported in levels ranging from subnanogram to more than 1 nanogram per litre in the North Atlantic Ocean (Mason et al., 1998), Arctic Russian estuaries (Coquery et al., 1995b) and a high Arctic watershed (Semkin et al., 2005). Maximum concentrations have been measured around 10

Table 3. Summary of aqueous mercury measurement methods in the Arctic.

Analyte & associated reference	Sampling source	Location	Analytical method	Detection limit
Total-Hg				
(Semkin et al., 2005)	Lake	Amituk Lake, Cornwallis Island, Nunavut, Canada	oxidation by hydrogen peroxide, reduction by sodium borohydride, trapping on gold coated sand, AFS detection	0.08 ng/L
(Aspmo et al., 2006)	Ocean	North Atlantic, 75–85° N	preservation with HCl, digestion by BrCl, reduction by stannous chloride, AFS detection	0.05 ng/L
(Sommar et al., 2007)	Fjord	Kongfjorden, Svalbard, Norway	Preservation with HCl	
(Mason et al., 1998)	Ocean	North Atlantic, 50–70° N	acidified sample (HCl), allowed for digestion (72h), reduction with $SnCl_2$, CVAFS detection	
(Loseto et al., 2004a)	Lake	8 lakes north of Resolute Bay, Cornwallis Island, Nunavut, Canada	Preservation with BrCl, $SnCl_2$ reduction, CVAFS (EPA Method 1631)	0.25 ng/L
(Hammerschmidt et al., 2006a)	Lake	4 lakes near Toolik Field Station, Arctic Alaska, US	analysis within 25 h of collection, digestion with BrCl, CVAFS detection	0.01 ng/L
(St. Louis et al., 2005)	Pond and lake	Northern Ellesmere Island, Nunavut, Canada	Preservation with conc. trace-metal grade HCl equal to 0.2% (vol.), CVAFS detection with Tekran 2500	0.05 ng/L
(Coquery et al., 1995a)	River and estuary	Ob, Yenisei and Lena river and their estuaries to Kara Sea and Laptev Sea, Siberian Arctic, Russia	reduction by $NaBH_4$, double gold amalgamation, CVAFS detection	0.14 ng/L
DGM				
(Sommar et al., 2007)	Fjord	Kongfjorden, Svalbard, Norway	purge and trap with inert gas ($0.3\,L\,min^{-1}$), collected on Au-trap, CVAFS detection	
(Mason et al., 1998)	Ocean	North Atlantic Ocean, 50–70° N	purge and trap on gold trap, CVAFS detection	0.04 ng/L
(Fitzgerald et al., 2005)	Lake	5 lakes near Toolik Field Station, Arctic Alaska, US	purge and trap with Hg-free N_2 gas in borosilicate bubbler to gold-coated sand trap, detection by CVAFS	
(Tseng et al., 2004)	Lake	Ten lakes, Arctic Alaska, US	semiautomatic purge and trap ($1\,L\,min^{-1}\,N_2$), two-stage amalgamation and flow-injection technique, AFS-detection	6 pg/L
Hg(II) – reactive				
(Mason et al., 1998)	Ocean	North Atlantic, 50–70° N	direct reduction with acidic (2.6 N HCl) 10% stannous chloride, CVAFS detection	0.35 pM
MeHg				
(Loseto et al., 2004a)	Lake	8 lakes north of Resolute Bay, Cornwallis Island, Nunavut, Canada	SPE on sulfide columns, acidic KBr elusion, GC with AFS detection	0.02 ng/L
(Mason et al., 1998)	Ocean	North Atlantic Ocean, 50–70° N	Distillation, ethylation with sodium tetraethylboarate, GC with AFS detection	0.5 pM
(Demuth and Heumann, 2001)	Ocean	North Atlantic Ocean	Ethylation/propylation, purging, cryofocussing, GC-ICP-IDMS	0.03 pg/mL
(Hammerschmidt et al., 2006a)	Lake	Toolik Lake, Arctic Alaska, US	Ethylation, concentration on Tenax, flow injection GC CVAFS	0.004 ng/L
(St. Louis et al., 2005)	Ponds and lake	Northern Ellesmere Island, Nunavut, Canada	Preserve with concentrated trace metal grade HCl (0.2% vol.), distillation, aqueous phase ethylation, CVAFS	0.02 ng/L
(Leitch et al., 2007)	Lake	Lower Mackenzie River, Canada	Capillary GC-AFS	0.02 ng/L
Me_2Hg				
(Mason et al., 1998)	Ocean	North Atlantic, 50–70° N	Purge and trap on Carbotrap column, CVAFS detection	10 fM
Photoreduction/photooxidation				
(Amyot et al., 1997)	lake	Amituk Lake, Merreta Lake, North Lake, Arctic wetland, Cornwallis Island, Nunavut, Canada	Time series of DGM in bottles incubated under solar radiation, and submitted to various treatments (filters, H_2O_2, fulvic acids)	
(Poulain et al., 2004)	pond	Cornwallis Island, Nunavut, Canada	Time series of DGM in bottles incubated under solar radiation.	
(Tseng et al., 2004)	lake	10 lakes, Arctic Alaska, US		

nanograms per litre in Canadian Arctic ponds and lakes (Loseto et al., 2004b; St. Louis et al., 2005). In general, water samples are collected in Teflon or glass bottles containing a 0.4–0.5% acidic solution of HCl in order to reduce contamination and to preserve the Hg in the sample (Parker and Bloom, 2005). As well, samples can be collected using high density polyethylene bottles (Hall et al., 2002) should Teflon not be available. BrCl is added to the sample after collection to digest the Hg in the water followed by reduction of the Hg with stannous chloride ($SnCl_2$). Pre-concentration of Hg onto gold traps by sparging the sample to release Hg(0) from the solution follows this reduction and the Hg contained in this sample is then detected using CVAFS (Loseto et al., 2004a; Aspmo et al., 2006; Hammerschmidt et al., 2006b). Semkin et al. (2005) used hydrogen peroxide for oxidative digestion and both Semkin et al. (2005) and Coquery et al. (2005) reduced Hg(II) species with sodium borohydride. Detection limits ranging from 0.01 to 0.25 ng/L are reported in the aforementioned papers.

3.3.2 Monomethyl mercury and dimethyl mercury in water samples

Aqueous monomethyl mercury (MeHg) concentrations are reported in levels from a few tenths of a picogram per litre in Arctic Lakes (St. Louis et al., 2005; Hammerschmidt et al., 2006a) and the Mackenzie river basin and mainstream (Leitch et al., 2007) to several hundreds of picograms per litre in small Arctic ponds (St. Louis et al., 2005) and the North Atlantic Ocean (Mason et al., 1998).

In most applications MeHg was determined by aqueous phase ethylation with sodium tetraethylborate, subsequent concentration either by cryofocusing with liquid nitrogen (Demuth and Heumann, 2001) or by collection on Tenax traps (Hammerschmidt et al., 2006a), separation by capillary gas chromatography and finished by AFS detection (Mason et al., 1998; St. Louis et al., 2005; Leitch et al., 2007). Solid phase extraction on sulfide columns followed by acidic KBr elution before GC separation with AFS detection has been employed (Loseto et al., 2004a). In addition, propylation instead of ethylation was successfully used coupled with ICP/GC where the method detection limits were reported in the range of 20 pg/L (Demuth and Heumann, 2001).

Me_2Hg was analyzed by purge and trap technique on Carbotrap® columns and subsequent thermal desorption, separation by gas chromatography and AFS detection (Mason et al., 1998).

3.3.3 Dissolved gaseous mercury and reactive mercury in water samples

Dissolved gaseous mercury (DGM) can be produced in freshwater and marine environments through biotic and abiotic processes. DGM is composed of volatile Hg species similar to Hg(0) and Me_2Hg, both of which are characterized by relatively high Henry's law coefficients (Schroeder and Munthe, 1995). Reported concentrations of DGM in Arctic Alaskan lakes (Tseng et al., 2004; Fitzgerald et al., 2005), the North Atlantic Ocean (Mason et al., 1998) and a Spitsbergen fjord (Sommar et al., 2007) range between 10 to more than 100 pg/L . In general, DGM is collected and measured by purging water samples with an inert gas which releases the volatile Hg species from the water sample. The Hg is then pre-concentrated onto a gold adsorber (purge & trap technique) and analyzed by CVAFS (Mason et al., 1998; Tseng et al., 2004; Fitzgerald et al., 2005; Sommar et al., 2007). Gårdfeldt et al. (2002) show some promising methodologies employing an in situ impinger technique for continuous automatic measurements for DGM and compared them with manual methods.

Reactive Hg in water samples consists of the fraction of Hg that is directly reduced from the water sample by stannous chloride and subsequently analysed by purge & trap. When corrected for the presence of DGM, it is designated as Hg(II) because the sample consists largely of inorganic Hg complexes (Mason et al., 1998). Further, Tseng et al. (2004) defines another Hg species in water samples as dissolved labile Hg (DLM). This DLM is found in $<0.45\,\mu m$-filtered aliquots and is reduced by stannous chloride.

3.4 Air-water exchange

There has been only a small number of air-water exchange studies of Hg conducted in Polar Regions. Considering the strong seasonal and spatial variation in the magnitude and direction of Hg fluxes, it is certainly an important component. There are many different approaches to measuring flux and some are more qualitative rather than quantitative. The most commonly used technique to measure the Hg air-surface flux is eddy correlation described in Sect. 3.2. However, this micrometeorological method requires air sensors with a response time of at least several Hz. A feasible sensor for measuring the air-water exchange of Hg(0) has been reported (Bauer et al., 2002; Bauer et al., 2003). Micrometeorological techniques (MBR or REA) have been implemented in the field to measure air surface fluxes of GEM and RGM from various surfaces (e.g. Meyers et al., 1996; Cobos et al., 2002; Olofsson et al., 2005; Skov et al., 2006).

3.5 Photoreduction and photooxidation in fresh and sea water

Photoredox experiments are usually carried out using batch or flow-through incubations. Batch incubations are conducted by incubating water samples under solar radiation in Teflon bottles (or quartz tubes) for short periods of time (between 1 and 8 h). During such incubations, some samples are wrapped in various light filters, or kept in the dark, in order to isolate the effect of different wavebands (UV-A, UV-B, visible). Samples are occasionally spiked with reactive oxy-

gen species (Amyot et al., 1997), dissolved organic carbon (Amyot et al., 1997); humic acids (Costa and Liss, 2000) or other compounds potentially involved in photoreduction reactions such as Fe(III) (Zhang and Lindberg, 2001). Photoreduction and photooxidation are known to occur simultaneously. Since photoreduction is usually the dominant reaction, these studies primarily report apparent photoreduction rates ($k_{\text{apparent}}=k_{\text{reduction}}-k_{\text{oxidation}}$). Typically, a plateau in the concentration of Hg(0) over time is observed after a few hours of incubation, when equilibrium is reached between reduction and oxidation. Some studies have modified the samples with aqueous Hg(0) at the start of the incubation in order to calculate a photooxidation rate – $k_{\text{oxidation}}$ (Lalonde et al., 2004). The flow-through samples are exposed to solar radiation and are continuously purged of their Hg(0) which allows the calculation of actual photoreduction rates – $k_{\text{reduction}}$ (Costa and Liss, 2000; O'Driscoll et al., 2006). Indeed, since Hg(0) is removed for quantification as the reaction proceeds, there is no substrate for oxidation; thus the reduction rate can be calculated. The emergence of analytical systems for the in situ continuous analysis of DGM will provide another way to relate DGM production and loss to solar radiation (Amyot et al., 2001; Gårdfeldt et al., 2002).

Other mechanistic reaction kinetic studies have also been performed in order to discriminate between oxidation and reduction reactions that may occur simultaneously in this environment (Gårdfeldt et al., 2001; Gårdfeldt and Jonsson, 2003). Reactions between Hg(0) and $O_{3(\text{aq})}$, as well as $Br_{2(\text{aq})}$ and $Cl_{2(\text{aq})}$, have been studied in the laboratory by relative rate (scavenger) hydrolysis titration techniques (Munthe, 1992; Lin and Pehkonen, 1998; Wang and Pehkonen, 2004). Finally, Hg(0) photoradical aqueous reactions between Hg(0)+OH have been studied under laboratory conditions and are reported to be fast (Lin and Pehkonen, 1998; Gårdfeldt et al., 2001).

3.6 Snow sampling and analytical methods

Snow and ice provide the substrate upon which Hg is transferred from the atmosphere to polar ecosystems. Thus, a better understanding of the scavenging, storage and ultimate fate of Hg in the polar snow pack is a major research focus. Snow or ice sample collection in Polar Regions generally makes use of the "*clean hands – dirty hands*" protocol as described by Patterson and Settle (1976). Special attention must be paid to minimise contamination of the samples by the sampling personnel, their equipment and the surrounding environment (e.g. building influence, biological matter). Tests in the field for recovery and blanks are performed to ensure that the sampling procedure is free of contamination. In all cases, clean nitrile or latex powder free gloves and dust-free clothing must be worn throughout the sample collection period. Utmost care must be taken to ensure that snow sampling personnel cover their mouths, hair and noses to prevent contamination.

Snow surface sampling does not require any additional specific precautions but sampling from a snow pit to recover specific snow layers, precipitation or wind events requires further preparation. Prior to collecting snow samples a series of detailed measurements should be made to characterize the snow pack and determine what is represented at a given location (Sturm and Liston, 2003). A snow measuring pit, roughly two square meters, should be excavated to the desired depth and heterogeneity can be assessed by excavating several pits in a given area. Snow layer measurements are collected where each identifiable layer is characterized by its thickness, lateral consistency and snow grain features. The type and size of snow grains from each layer can be characterised using a 20X optical microscope. The most widely accepted classifications for snow have been documented (Colbeck, 1986; Jones et al., 2001). Following identification of unique snow layers and grain types a sampling plan is developed. Once the snow pack and snow layer characteristics have been identified, samplers put on their clean protective gear and move 100 m upwind of the initial snow pit location to excavate a pit from which trace element samples may be collected.

Ice and ice core sampling is performed with drills. To reduce contamination from the drill on the sample, the outer layers of the core are mechanically scraped off in a cold lab in clean room conditions (Planchon et al., 2004). Samples should be stored in glass, Teflon or sometimes high density polyethylene bottles that have been rigorously cleaned according to United States Environmental Protection Agency protocols (EPA, 1996) and in Parker and Bloom (2005).

Once snow has been collected using the above outlined clean procedures, Hg species are analysed by several techniques that have been well described in the literature (Gill and Fitzgerald, 1987; Bloom and Fitzgerald, 1988; Amyot et al., 2004; Planchon et al., 2004). The low levels of Hg species in snow and ice require the use of sensitive and reproducible techniques. These techniques employ chemical treatment of the sample followed by chemical transformation and detection. The most common Hg species that are found in polar snow will be described in detail in Sect. 6. Samples are melted and analysed by the same techniques as those applied to fresh and sea water samples described in Sect. 3.3.1 (Amyot et al., 2004). Reactive mercury, methyl mercury (MeHg) and total mercury (THg) are measured in water from melted snow and ice samples using ultra-sensitive detectors such as CVAFS (Gill and Fitzgerald, 1987; Bloom and Fitzgerald, 1988) and, more recently, with inductively coupled plasma mass spectrometry (Eyrikh et al., 2003; Planchon et al., 2004; Mann et al., 2005). Prior to detection, reactive and total Hg samples are chemically treated. Reactive Hg is first reduced with $SnCl_2$ to form Hg(0) which is separated through sparging from the matrix. The Hg content in the sample is then measured with the techniques presented above. Mercury that is strongly bound to particles (i.e. organic matter and that which is not reduced by the application

of SnCl$_2$) is treated with BrCl prior to SnCl$_2$ treatment to allow for the measurement of THg in the sample. Methyl mercury is measured by coupling gas chromatography with inductively coupled plasma (Jitaru et al., 2003) or atomic fluorescence spectrometry following a solid-phase extraction on sulfydryl-cotton fibre (SCF) and an acidic-potassium bromide elusion (Lahoutifard et al., 2005) based on Cai et al. (2000).

As well, GEM in the interstitial snow pack air can be measured by a variety of techniques. For example, inserting Teflon tubing into the snow pack (Steffen et al., 2003b), using Teflon probes (Dommergue et al., 2003c) or sniffers (St. Louis et al., 2005). Using these samplers at different depths within the snow pack and coupling the measurements with ancillary information (e.g. temperature), the variation of GEM in the air of the snow can be determined.

4 Atmospheric Mercury in Polar Regions and Atmospheric Mercury Depletion events (AMDEs)

4.1 Trends of atmospheric mercury

Long-term measurements of atmospheric Hg suggest that concentrations increased from the late 1970s to a peak in the 1980s, decreased to a minimum around 1996 and have been nearly constant since that time (Slemr et al., 2003). The long-term data used for the reconstruction of the worldwide trend of GEM since 1977 were collected at several global background sites in both hemispheres. Continuous long-term TGM measurements in Polar Regions using highly time-resolved automatic monitors (described in Sect. 3.1) have been carried out exclusively at several observatory sites within the Northern Hemisphere. For this discussion, only time series from Polar Regions with more than 5 years of continuous measurements are considered. These include measurements from Ny-Ålesund, Norway (1994–2000 [manual samples]; 2000–2002 [automated samples]) and Alert, Canada (1995–2002/5) (Berg et al., 2004; Temme et al., 2004; Kim et al., 2005; Steffen et al., 2005; Temme et al., 2007). Techniques of series analysis such as seasonal decomposition and statistical tools for trend analysis were applied to these datasets. Both of these time series showed no evidence of annual long-term trends during each respective monitoring period. In the springtime, highly variable GEM concentrations as well as the lowest median concentrations of all the seasons are reported by Steffen et al. (2005) for each observed year. This trend in the springtime concentration is a result of AMDEs that are known to occur in these regions. While the low springtime median concentrations at Alert revealed no significant trend (95% CI) from 1995 to 2002, the summer GEM concentrations indicated a statistically significant (95% CI) decrease from 1995 to 2002. Mercury concentrations measured in the summer were higher than the springtime at Alert perhaps due to the emission of Hg from tundra and snow surfaces (Steffen et al., 2005). This decreasing summer trend in GEM concentration is in contrast to a more recent report of a trend at Alert, between 1995 and 2005, where it is shown that no statistically significant trend for each season was found (Temme et al., 2007). The authors hypothesize that this change in trends may be due to higher re-emission from the oceans coupled with effects from rising air temperatures during Arctic summer and effects from decreasing European emission rates during that time period.

Currently, there are no other long term measurements published of Hg in the atmosphere from Polar Regions. The authors encourage more long term measurements of GEM and other atmospheric Hg species in Polar Regions as these measurements can yield critical information to better understand the processes involved in the cycling of Hg in the polar atmosphere. Further, two major drivers of Hg deposition to the Arctic are currently undergoing dramatic change. Firstly, the climate is warming which is changing the timing and extent of sea ice and its coverage (Serreze et al., 2003; Stroeve et al., 2005). The effects of shifts in sea ice on Hg scavenging by snow and ice and on halogen emission from open water and sea ice regions are unknown. Warming is also dramatically affecting the seasons with winter coming later and spring melt coming earlier. Thus, the amount of time between Hg deposition during AMDEs and Hg mobilization during spring melt are shrinking. This could affect the amount of reemission of Hg from the snow pack but no models or measurements investigating this have been made. Secondly, coal and fossil fuel combustion in Asia, a major global source of Hg, is expected to increase up to 350% between 1990 levels and 2020 (van Aardenne et al., 1999). The effects of these increasing emissions on AMDE processes and the long term deposition of Hg to the Polar Regions will only be discernible if long term measurements are collected at numerous locations.

4.2 Atmospheric Mercury Depletion Events (AMDEs)

The first annual time series of high-resolution atmospheric Hg vapour data was collected in the Arctic at Alert, Nunavut, Canada in 1995 (Schroeder et al., 1998) as shown in Fig. 2. It was found that after sunrise the GEM concentrations underwent extraordinary fluctuations, decreasing at times from values approximately 1.7 ng/m^3 to values less than 0.1 ng/m^3 within periods of 24 h or less. This behaviour runs counter to what is expected for an air pollutant characterized by a long atmospheric residence time (Schroeder and Munthe, 1995). The unique environmental condition at Alert that appeared to initiate this unusual behaviour was the sudden exposure to solar radiation in early March after approximately 5 months of total darkness. Further measurements at Alert in 1996 (to the present present) corroborated the distinctive behaviour of GEM after polar sunrise and revealed a strong correlation between GEM and ground level ozone concentrations as shown in Fig. 2 (Schroeder et al., 1998). During and after polar
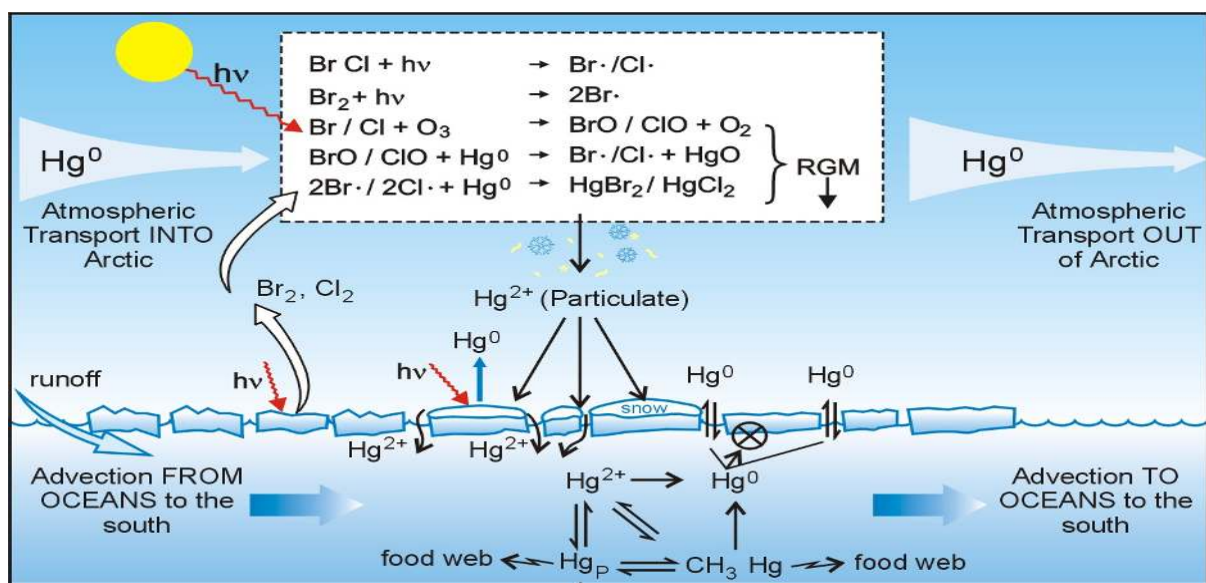
Fig. 3. Schematic of the cycling of mercury in Polar Regions (modified from MacDonald et al., 2005).

sunrise, GEM and ozone concentrations were found to deplete at the same time with excellent correlations during the period between late March and mid-June (correlation coefficient [r^2] between GEM and O_3 is ~0.8). This relationship between ozone and GEM appears endemic to other locations in Arctic Regions (Lindberg et al., 2001; Berg et al., 2003a; Skov et al., 2006) and the sub-arctic (Poissant and Pilote, 2003)[1]. Soon after the first publication of AMDEs (Schroeder et al., 1998), continuous highly time resolved measurements of total gaseous mercury (TGM) were also carried out at the German Antarctic research station Neumayer between January 2000 and February 2001 (Ebinghaus et al., 2002). These measurements corroborated the hypothesis that AMDEs do also occur in the Antarctic, giving evidence that both Polar Regions are impacted by an enhanced atmospheric Hg deposition during polar springtime.

At Alert in 1998, Lu et al. (2001) and Lu and Schroeder (2004) reported an anti-correlation between measured gas phase Hg and the concentration of HgP during AMDEs. They suggested that GEM was being converted to total particulate and reactive gas phase mercury (RGM) when AMDEs occurred. This hypothesis that RGM is produced during AMDEs was confirmed in 2000 through direct measurements by Lindberg et al. (2001) at Barrow, Alaska, USA. Steffen et al. (2002) measured TAM at Alert in 2000 and showed that during depletion events other forms of Hg species exist in the air besides GEM. This study also demonstrated that, during depletion events, on average only 50% of the converted GEM remains in the air during AMDEs. It was

proposed that the remainder of the converted Hg is deposited onto the nearby snow and ice surfaces. Figure 3 shows a summary schematic of the cycling of Hg resulting from AMDEs around Polar Regions.

4.2.1 How and where do AMDEs occur?

It is now thought that the chemistry that causes the well known ozone depletion events (ODEs) (Bottenheim et al., 1986; Barrie et al., 1988; Simpson et al., 2007) is similar to what drives AMDEs (Lindberg et al., 2001; Ariya et al., 2002b; Lindberg et al., 2002; Calvert and Lindberg, 2004b; Goodsite et al., 2004). The depletion of GEM in the polar atmosphere is thought to be caused by the oxidation of GEM by reactive halogens; namely Br atoms or BrO radicals (Ariya et al., 2004; Calvert and Lindberg, 2004a; Goodsite et al., 2004; Skov et al., 2004) (see Sect. 4.3 for more detail). The reaction (oxidation) of Hg(0) with this reactive halogen yields inorganic RGM, Hg(II). While there are mechanisms and theoretical calculations that suggest that RGM is predominantly a bromide compound (Calvert and Lindberg, 2004a), its identity has not been directly elucidated and thus RGM is operationally defined. The reactive halogen species oxidizing Hg are assumed to be generated from open water regions such as leads or polynyas from refreezing sea ice forming on open waters and UV radiation. High column densities of BrO clouds above areas of AMDEs have been seen in the air column by the GOME satellite throughout the Arctic and the Antarctic as shown in Fig. 4 (Lu et al., 2001; Ebinghaus et al., 2002; Lindberg et al., 2002; Wangberg et al., 2003; Sprovieri et al., 2005a). Bottenheim and Chan (2006) reported that ODEs observed at Arctic measurement
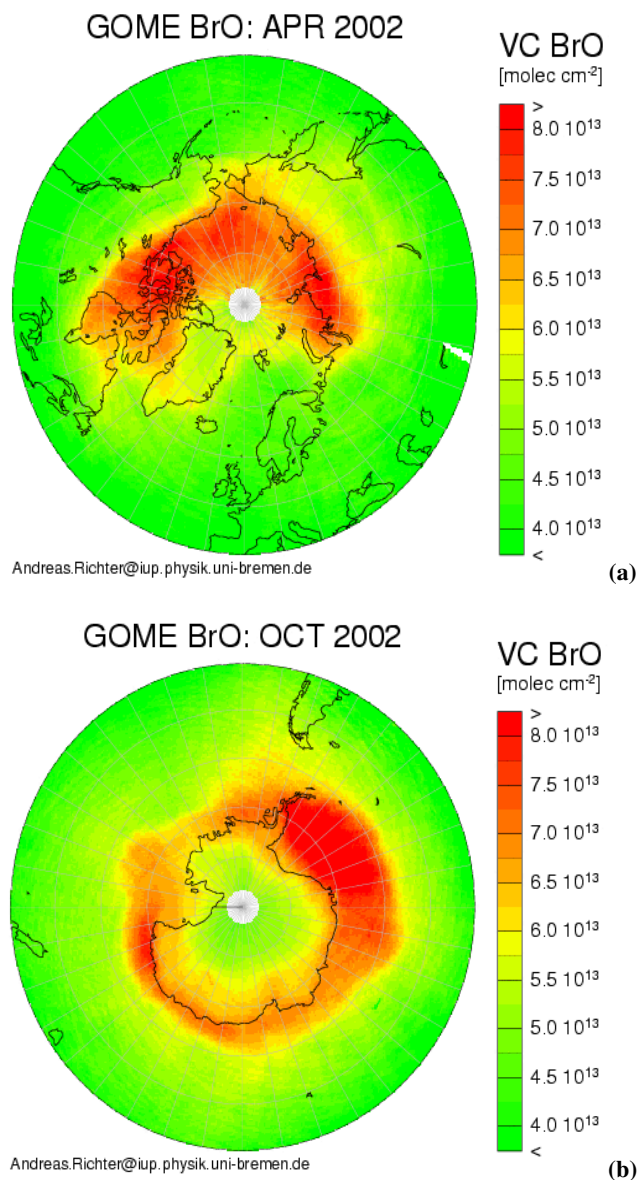
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[1] The geographic scope of the discussion in *this* section has been limited to Polar Regions (north and south of 60°) and does not include work conducted in sub-polar regions

GOME BrO: APR 2002

Andreas.Richter@iup.physik.uni-bremen.de

(a)

GOME BrO: OCT 2002

Andreas.Richter@iup.physik.uni-bremen.de

(b)

Fig. 4. GOME BrO measurements over **(a)** the Arctic April 2002 and **(b)** the Antarctic October 2002. The values given are in molecules/cm^2. Green areas correspond to low BrO concentration values and the red areas correspond to higher BrO concentration values.

sites originate over the Arctic Ocean near marginal ice zones where high concentrations of BrO are observed. In addition, in-situ measurements of BrO were made in Alert and showed that an increase in the BrO concentration is matched by a decrease in GEM (Steffen et al., 2003b). BrO was measured in the layer near the earth's surface at 1±0.5 km (Hönninger and Platt, 2002). This observation matches well with vertical profile measurements (Banic et al., 2003) that showed AMDEs are limited to the surface up to a maximum of 1 km and by Tackett et al. (2007), who showed that the most active

halogen chemistry affecting Hg is within the first 100–200 m from the snow surface. Further experiments by Steffen et al. (2002) showed that depletion events occur immediately at the snow surface (less than 2 m) and within the first few centimetres of the snow pack. Studies at the Ny-Ålesund station, where GEM levels were measured at two heights (12 m a.s.l and 474 m a.s.l) in the spring time during AMDEs, showed that GEM concentrations during AMDEs are comparable (Berg et al., 2003b; Temme et al., 2004; Sprovieri et al., 2005b; Sommar et al., 2007) but concentration differences between the two elevations were reported prior to AMDEs. In addition, at 12 m a.s.l., GEM concentrations following AMDEs were found to be higher in magnitude and displayed higher variability in comparison to results reported at 474 m a.s.l (Berg et al., 2003b; Sprovieri et al., 2005a; Sommar et al., 2007). These results imply that there is a cycling of mercury that occurs near the surface and the air masses are not well mixed within the boundary layer to be measured at heights of 474 m a.s.l.

4.2.2 Mercury speciation and AMDEs

Lindberg et al. (2001, 2002) reported the first and highest measured concentration levels of RGM (up to 900 pg/m^3) during AMDEs at Barrow and showed a strong correlation between RGM production and UV-B irradiation. The increase of UV-B over the springtime period also correlated well with an increase in surface snow Hg concentrations. Similar observations were made in the Beaufort Sea on the SHEBA ship in 1997 (Lu et al., 2001). RGM (and PHg) have a higher deposition velocity (Skov et al., 2006) and is more hygroscopic (Lin and Pehkonen, 1999) than GEM (Lindberg et al., 2001; Cobos et al., 2002; Skov et al., 2004; Brooks et al., 2006) and thus are readily deposited onto the snow and ice surfaces.

Both RGM and PHg have been measured during AMDEs at many Arctic sites (Lindberg et al., 2002; Berg et al., 2003a; Steffen et al., 2003a; Aspmo et al., 2005; Gauchard et al., 2005; Sprovieri et al., 2005a). Mercury species measurements in the Antarctic have only been made during the Antarctic summer at Terra Nova Bay from November to December 2000 (Sprovieri et al., 2002) and at Neumayer Station between December 2000 and February 2001 (Temme et al., 2003). Maximum RGM concentrations (exceeding 300 pg/m^3) were observed during the Antarctic summer and a process other than the halogen chemistry suggested above for the oxidation of GEM was proposed (Sprovieri et al., 2002).

The relative distribution of these two atmospheric species differs between locations. RGM can exist in the gas phase but will be readily sorbed onto aerosols present in the air because of its hygroscopic properties (Ariya et al., 2004). At Alert, the overall predominant species in spring is PHg (Steffen et al., 2003b) but a clear shift from the predominance of PHg to RGM is observed during the spring (Kirk et

al., 2006; Cobbett et al., 2007). At Barrow, RGM is the predominant species observed (Lindberg et al., 2002). Several studies at Ny-Ålesund have shown that, in general, there is no predominance of either RGM or PHg (Gauchard et al., 2005; Sprovieri et al., 2005a, b). Some researchers have suggested that the distribution of the RGM and PHg is an indication of the age of an air mass (Lindberg et al., 2002; Steffen et al., 2003a; Sprovieri et al., 2005a) while others suggest that the distribution is an indication of local versus transported events (to the measurement site) (Wangberg et al., 2003; Gauchard et al., 2005). The presence of UV radiation is also thought to contribute to the distribution of RGM and PHg as suggested by Lindberg et al. (2002). During low levels of UV the RGM present in the air is sorbed onto aerosol bound Br and/or Cl but at higher levels of UV this aerosol is rapidly decomposed and RGM becomes the predominant species. This hypothesis was later used by Sprovieri et al. (2005a) and found the same results at Ny-Ålesund in 2003.

4.2.3 Mercury deposition to snow caused by AMDEs

Studies have shown that the concentration of Hg in the snow increases during and following AMDEs where oxidized atmospheric Hg is thought to have been deposited (Lu et al., 2001; Lindberg et al., 2002; Steffen et al., 2002; Sommar et al., 2007). The fate of this deposited Hg is under debate in the scientific Hg community in terms of how much of this deposited Hg is emitted as GEM through photoreduction and how much remains in the snow (this is further discussed in Sect. 6, post deposition scenarios). Atmospheric profile measurements of GEM collected in 2000 (Steffen et al., 2002) showed that after AMDEs, some Hg was emitted from the snow surface. As the depletion event aloft continued, this emitted Hg(0) then appeared to be oxidized right at the snow surface. This data demonstrated a cycling of Hg that occurs immediately near the snow surface (and within the snow pack). This was attributed to a combination of snow/air temperature as well as solar radiation (Lu et al., 2001; Lindberg et al., 2002; Steffen et al., 2002).

In Barrow, Lindberg et al. (2002) measured concentrations of up to 90 ng/L in the snow, which is higher than the concentration of Hg found in snow from background regions. Also at Barrow, Scott (2001) reported a post polar sunrise increase in bioavailable Hg in the surface snow and an increasing ratio of bioavailable to THg as the springtime slowly progressed to annual snowmelt. In Svalbard, Ferrari et al. (2005) demonstrated that of seven AMDEs recorded, no increase in the concentration of Hg in the surface snow was observed. The authors suggest that the origin of the AMDE plays a significant role in the amount of Hg deposition that is observed. Thus, deposition of Hg onto the snow surfaces in the Arctic, as a result of AMDEs, are not spatially homogeneous and the factors affecting such deposition must be well understood to address the impacts of AMDEs on the Arctic environment.

4.2.4 Mass Balance and the deposition of mercury

To the date of this review, an annual mass balance does not exist for Hg in Polar Regions or at any specific measurement sites. Brooks et al. (2006) recently published a mass balance for Hg in the Arctic springtime showing a net surface gain during a 2 week period from data collected at Barrow, AK. However, there are many limitations associated with calculating such a mass balance that the applicability of their reported techniques cannot be applied to annual mass balances over the whole region. Such limitations include the lack of knowledge of Hg speciation in the atmosphere, the potential for inter-compartmental transfer of Hg in Polar Regions and the lack of a circumpolar network collecting Hg measurements. During a meeting of experts in 2003, the need to establish the emission proportion of Hg from the surface after deposition from AMDEs, or release to other compartments, was identified and must be agreed upon before true mass balance estimates could be made (Schroeder et al., 2003). Further, an experts meeting in 2006 (AICI) determined that despite intense trans-arctic springtime field campaigns this remains an issue to be resolved. Several lines of evidence, based on atmospheric measurements and models, have shown strong net deposition of Hg to Arctic areas as a result of AMDEs. Lu et al. (2001) estimated a total deposition of 50 tons year^{-1} over northern waters. Lindberg et al. (2002) estimated that between 100 and 300 tons of Hg will be deposited from the atmosphere in polar spring. Banic et al. (2003) estimated a total deposition resulting from AMDEs of 100 tons year^{-1} over areas north of 70° (15 times the area of Lu et al.) Ariya et al. (2004) estimated that 225 tons year^{-1} of Hg is deposited in the Arctic (and a portion of the sub-Arctic) without considering AMDEs and an additional 135 tons year^{-1} was estimated to be deposited as a result of AMDEs. Further analysis showed that the highest deposition of Hg was found in the European part of the Arctic while the lowest were over the Canadian Arctic and Greenland. Another model calculated an estimated load of 208 tons year^{-1} of Hg to the Arctic (this model did not consider emission from the snow surface) (Skov et al., 2004). There have been no reported deposition estimates for the Antarctic. These depositional estimates should be carefully compared and reviewed with estimates provided by measurements made in environmental archives in the Arctic. For example, Hg concentration measurements and age dating of peat from the Canadian Arctic show that the natural "background" Hg accumulation rate is relatively constant (ca. 1 microgram per sq. m per yr.) throughout the past 6000 years (Givelet et al., 2004).

4.3 Mechanisms of AMDEs

It is important to understand the kinetics and thermodynamics of the elementary and complex reactions of GEM in the

atmosphere to truly comprehend the chemical and physical transformation of Hg in Polar Regions. Several review articles have been published on the transformation of Hg in the atmosphere and have addressed the properties, sources, sinks and fluxes of Hg (Lindqvist and Rodhe, 1985; Schroeder et al., 1991; Lin and Pehkonen, 1999). However, following the discovery of AMDEs, the search for an explanation of how the conversion of Hg occurs in the Polar troposphere began. Because AMDEs follow the same pattern as ODEs (Schroeder et al., 1998), it was thought that the production of a reactive gas phase species of Hg may be attributed to the same photochemically initiated reaction mechanisms (Lu et al., 2001; Lindberg et al., 2002). Further, the reaction of Hg with halogen oxide radicals drew attention to satellite "BrO" column measurements that began to surface around that time (Richter et al., 1998; Müller et al., 2002; van Roozendael et al., 2002), see Fig. 4. Several publications have shown the coincidence of increased BrO concentration measured from satellites around areas of strong AMDE occurrences (Lu et al., 2001; Ebinghaus et al., 2002; Lindberg et al., 2002; Wangberg et al., 2003; Skov et al., 2004; Sprovieri et al., 2005a; Brooks et al., 2006). Calvert and Lindberg (2004a) modeled the homogeneous component of halogen-mercury-ozone-chemistry and found that Br-BrO can explain the observed processes occurring in the Polar springtime atmosphere. They also suggested that products such as HgO, HgBr$_2$, BrHgOBr and BrOHgOBr should be considered as potential components of RGM and PHg produced during AMDEs. In a companion paper, Calvert and Lindberg (2004b) investigated the influence of iodine on the chemistry of AMDEs. They confirmed their earlier conclusions in regard to the role of Br and concluded that depletions of Hg can be enhanced by the presence of photochemically active iodine compounds. Goodsite et al. (2004) proposed a homogeneous mechanism for Hg-Br chemistry in the troposphere based on theoretical kinetic calculations and showed that gas phase oxidation of GEM by Br atoms could explain AMDEs in the Arctic springtime boundary layer. Brooks et al. (2006) report direct evidence of a link between Br and Hg chemistry as a direct source for RGM in Alaska. Holmes et al. (2006) conclude that uncertainties in the kinetic data, especially for reactions involving HgBr as a reactant, need to be resolved in order to more narrowly constrain the lifetime of Hg(0) and the Hg(II) product distribution.

The studies described above do not represent experimental research but rather models of mechanisms between Hg and halogens. There are few experimental studies that have reported reactions between halogens and halogen oxides with mercury. The limited number of experiments is primarily due to the complexity of these reactions and their side reactions. Recent studies by Ariya et al. (2002a) show extensive kinetic and product analysis on the reactions of GEM with molecular and atomic halogens (X/X$_2$ where X=Cl, Br) and the results from these and others are summarized in Table 4 (Donohoue et al., 2005; Sumner, 2005; Donohoue et al., 2006). These

different experiments report more than an order of magnitude difference in reaction rates of Br and Cl with elemental mercury. While each technique has advantages and disadvantages it is recommended that future studies are targeted to these reactions and that an intercomparison between experimental studies be made to provide more information on reaction kinetics.

As discussed above, BrO is thought to be a key player in the oxidation of GEM during AMDEs yet experimental studies of such XO reactions are very scarce and, to the best knowledge of the authors, there has been only one published laboratory kinetic study on the reaction of BrO with elemental mercury (Raofie and Ariya, 2003). Calculated reaction rates from this study are reported as a bimolecular rate constant for BrO+Hg(0)$_{(g)}$ and are shown in Table 4. The estimated value implies that BrO is a significant potential contributor to AMDEs reported in Polar Regions. Raofie and Ariya (2004) published the first experimental product study of BrO initiated oxidation of GEM where the reaction products were analysed in the gas phase, on suspended aerosols and on wall deposits. In this study, the products were identified to be HgBr, HgOBr or HgBrO and HgO. The existence of a stable Hg(I), in the form of HgBr and Hg(II), upon a BrO-initiated oxidation of Hg(0), emphasizes the importance to selectively quantify various mercury species in aerosols and deposits in field studies. While most of the products containing mercury were identified as deposits, aerosols did account for a substantial portion of products.

Existing kinetic results indicate that the direct Br reaction with GEM is more important than BrO (Raofie and Ariya, 2003; Goodsite et al., 2004). While modeling studies (Ariya et al., 2004; Skov et al., 2004) support this conclusion further studies are required to examine the GEM and Br reaction in order to explain elemental Hg depletion in Polar Regions. While Calvert and Lindberg (2004a, b) suggest the importance of iodine in AMDEs, there exist no laboratory studies on the kinetics and products of I$_2$, I and IO with GEM. The authors encourage additional studies in this domain to expand our understanding of tropospheric iodine chemistry further.

Despite the recent positive trend in the number of laboratory and theoretical studies of gas-phase elemental Hg, focused kinetic, thermo-chemical and mechanistic studies of Hg(0) are still relatively scarce and somewhat inconsistent. These studies are needed in order to further our understanding of the atmospheric chemistry of Hg during the polar spring. It is pivotal to provide kinetic, product and thermochemical studies on complex reactions. A detailed review of ab-initio thermochemical and kinetic studies of Hg reactions has been reported by Ariya and Peterson (2005) and details of the methods and values important for this review are discussed in more detail in other publications (Balabanov et al., 2005; Shepler et al., 2005). Finally, experimental studies on the uptake and kinetics of heterogeneous reactions of Hg on various environmentally relevant surfaces such as ice, snow,

Table 4. Available literature of rate constants for selected atmospheric mercury reactions (at room Temperature (296+/−2 K)).

Reaction	Rate constants (molecule/cm^3 s^1)	Reference	Comments
$Hg^0 + O_3 \rightarrow$ products	$(3\pm2)\times10^{-20}$	(Hall, 1995)	
	$(7.5\pm0.9)\times10^{-19}$	(Pal and Ariya, 2004)	Temperature dependence is evaluated
	$(6.4\pm2.3)\times10^{-19}$	(Sumner, 2005)	
$Hg^0 + HO \rightarrow$ products	$(8.7\pm2.8)\times10^{-14}$	(Sommar et al., 2001)	
	$(9.3\pm1.3)\times10^{-14}$	(Pal and Ariya, 2004)	Temperature dependence is evaluated at 100 and 400 Torr He and air
	$<10^{-13}$	(Bauer et al., 2003)	
$Hg^0 + Cl \rightarrow$ products	$(1.0\pm0.2)\times10^{-11}$	(Ariya et al., 2002b)	
	$(1.5)\times10^{-11}$	(Horne et al., 1968)	120–170°C
	2.8×10^{-11}	(Khalizov et al., 2003)	Theoretical
	7.6×10^{-13}	(Donohoue et al., 2005)	Second-order rate was calculated at 260 K and 760 Torr
$Hg^0 + Cl_2 \rightarrow$ products	$(2.7\pm0.2)\times10^{-18}$	(Ariya et al., 2002a)	
	$(2.5\pm0.9)\times10^{-18}$	(Sumner, 2005)	
$Hg^0 + Br \rightarrow$ products	$(3.2\pm0.3)\times10^{-12}$	(Ariya et al., 2002a)	
	$(2.7)\times10^{-13}$	(Grieg et al., 1970)	120–170°C
	2.0×10^{-12}	(Khalizov et al., 2003)	Theoretical – calculated at 298 K, 760 Torr
	1.1×10^{-12}	(Goodsite et al., 2004)	Theoretical – calculated at 298 K, 760 Torr
	3.6×10^{-13}	(Donohoue et al., 2006)	
$Hg^0 + BrO \rightarrow$ products	$1\times10^{-15}<k<1\times10^{-13}$	(Raofie and Ariya, 2003)	
	1×10^{-14}	(Sumner, 2005)	
$Hg^0 + Br_2 \rightarrow$ products	$\leq(9\pm2)\times10^{-17}$	(Ariya et al., 2002a)	
	No reaction	(Sumner, 2005)	No reaction was observed under experimental conditions employed
$Hg^0 + F_2 \rightarrow$ products	$(1.8\pm0.4)\times10^{-15}$	(Sumner, 2005)	
$Hg^0 + NO_3 \rightarrow$ products	$\leq4\times10^{-15}\leq7\times10^{-15}$	(Sommar et al., 1997; Sumner, 2005)	
$Hg^0 + H_2O_2 \rightarrow$ products	$\leq8\times10^{-19}$	(Tokos et al., 1998)	
$Hg(CH_3)_2 + HO \rightarrow$ products	$(1.97\pm0.23)\times10^{-11}$	(Niki et al., 1983b)	
$Hg(CH_3)_2 + Cl \rightarrow$ products	$(2.75\pm0.3)\times10^{-10}$	(Niki et al., 1983a)	
$Hg(CH_3)_2 + NO_3 \rightarrow$ products	$(7.4\pm2.6)\times10^{-14}$	(Sommar et al., 1996)	

and aerosols are, as of yet, unexplored domains that should be undertaken in future research.

4.4 Transects of mercury away from the edge of the ocean

As discussed above, it is assumed that sea ice is a necessary ingredient in the recipe for producing AMDEs as sea ice is a source of the reactive halogens required to facilitate AMDE reactions (Richter et al., 1998; Wagner and Platt, 1998; Lindberg et al., 2002; Ariya et al., 2004; Frieß et al., 2004; Simpson et al., 2007). As well, the snow pack may be both a source and a sink for reactive halogens thereby providing a wide spatial region over which reactive halogen chemistry can occur (Simpson et al., 2005). Further evidence

linking sea ice with AMDEs is that they are not reported at lower latitudes and they are only reported in regions near the coast (Lu et al., 2001; Garbarino et al., 2002) or within 200 kilometers of sea ice (Snyder-Conn et al., 1997; Lu et al., 2001; Douglas and Sturm, 2004). Along the northern Canadian coast, Lu et al. (2001) reported the highest mercury concentrations in snow were collected between 70 and 75° N with lower concentrations around Hudson's Bay (55 to 65° N). Their results also show that snow collected near open sea ice regions yields greater Hg deposition rates. Investigations of Hg in coastal and inland snow in the Alaskan Arctic (Snyder-Conn et al., 1997; Garbarino et al., 2002) provide further information suggesting that the highest Hg concentrations in the Arctic are found in coastal snow. These studies
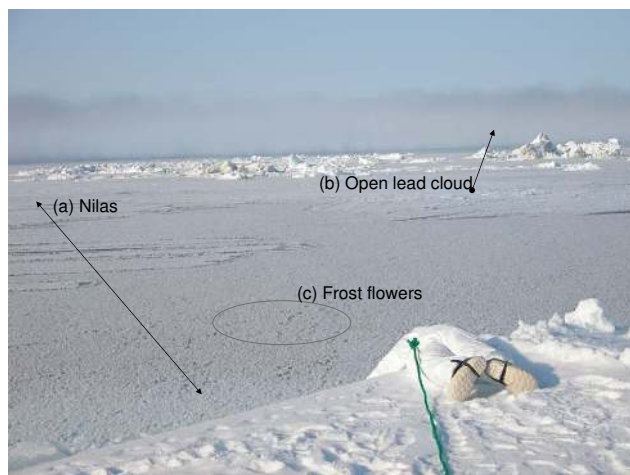
Fig. 5. Photo describing ice features from a location on the ice near Barrow, Alaska during the Arctic spring where samples have been collected for mercury. Shown in this photo are **(a)** nilas (new sea ice); **(b)** an open lead – evident by the gray cloud and **(c)** a newly formed frost flower field.

used cores of the entire snow pack collected in May that represent a full year of snow accumulation. Thus, AMDE deposition active in the March to May timeframe is likely diluted by pre-AMDE snow with a low Hg concentration (approximately 5–8 ng/L or lower). Elevated Hg concentrations were measured in coastal snow cores from three out of the four transect reported. Snow cores collected on sea ice yielded far greater Hg concentrations (100–214 ng/L) than those collected at coastal (3–83 n/L) or inland (0.1–7.2 ng/L) locations. This may partially be attributed to a smaller fraction of the low concentration pre-AMDE snow pack being represented in the sea ice cores. Since the sea ice develops in December or January any snow that fell earlier in the winter would not be preserved in the snow pack on the sea ice. Snow on sea ice generally contains a higher halogen ion content than terrestrial snow (Simpson et al., 2005). Snow on sea ice generally contains a higher halogen ion content than terrestrial snow (Simpson et al., 2005) and this may promote AMDE chemistry on sea ice but this hypothesis has never been tested. More work needs to be done to address the differences in AMDE Hg deposition to snow on sea ice or land as these two ecosystems may promote different processes in the polar biochemical cycle of Hg.

The snow collection sites were all more than 75 km from the coast and yielded total Hg concentrations ranging between 0.5 and 2 ng/L. The concentration of Hg from the site closest to the Arctic Ocean coast (75 km) increased from 3 to 6 ng/L between pre- and post- AMDE conditions. Typical Hg concentrations in surface snow collected along the Arctic Ocean Coast near Barrow during an AMDE range between 12 and 100 ng/L (Lindberg et al., 2002; Douglas et al., 2005). The lower values further inland indicate that snow

located near the coast receives the greatest AMDE Hg signature while inland snow receives minimal AMDE Hg deposition. A similar study was conducted in the sub-Arctic on the shore of Hudson's Bay that showed Hg concentrations in the snow increased after AMDEs and was inversely proportional to distance from the bay (Constant et al., 2007).

4.5 The role of sea ice in AMDE chemistry

Sea ice leads and polynyas provide a unique link between warm sea water and the cold overlying Arctic air. In Polar Regions during late winter and spring ambient air is typically colder than seawater and this creates convection cells in the lower atmosphere above exposed ocean water (Alam and Curry, 1995; Muench et al., 1995; Pinto and Curry, 1995; Pinto et al., 1995). These convection cells transfer heat from exposed ocean water to the lower 1 km of the atmosphere (Pinto and Curry, 1995; Pinto et al., 1995). A dark grey cloud of saturated moisture commonly forms above open water regions (Fig. 5 of sea ice lead). Water vapour density measured in the boundary layer above sea ice in the Arctic and Antarctic is almost always near ice saturation due to the exposure of warm sea water in leads and polynyas (Andreas et al., 2002) and thus crystals that form near sea ice and leads are commonly formed from the vapour phase. Diamond dust (ice crystal precipitation that falls under cold clear skies below −20°C (Girard and Blanchet, 2001)) and surface hoar (faceted, feather shaped clusters of ice that grow when the near surface relative humidity is at saturation with respect to ice (Andreas et al., 2002)) are commonly observed near sea ice leads. Thus, sea ice provides a location where enhanced crystallization and scavenging of moisture from the vapour phase may occur.

Douglas et al. (2005), collected surface hoar crystals formed near leads that yielded Hg concentrations up to 820 ng/L. These values are greater than previously reported maximum values for snow collected following AMDEs that typically range between 80 and 100 ng/L (Lu et al., 2001; Lindberg et al., 2002). Douglas et al. (2005) proposed two hypotheses to explain the reported high Hg concentrations near leads: 1) convective processes promoted halogen transfer to the air above the leads and this led to enhanced AMDE chemistry, and/or 2) the convection process and supersaturated air above the lead promoted enhanced active growth of snow and ice crystals from the vapour phase that readily scavenged available RGM. Results from a recent study investigating mercury deposition to a range of snow and ice crystal types (Douglas et al., 2008) suggest that enhanced scavenging of Hg by condensing ice crystals is the most likely source of elevated Hg near leads. Ice crystals grown from the vapor phase like surface hoar (up to 975 ng/L) and diamond dust (92 to 1370 ng/L) yield the highest mercury concentrations reported to date. Frost flowers are formed from a combination of brine and vapor condensation and they yield mercury concentrations ranging from 140 to 180 ng/L (Douglas

et al., 2008). More work needs to be done to investigate how unique crystal forms may scavenge Hg differently but, of most importance, is a better understanding of the ultimate fate of Hg scavenged by snow and ice crystals following spring melt. Stable mercury isotopes provide a potentially promising tool to track Hg from deposition to melt and into ecosystem pools.

The sea ice environment is also enhanced in halogen concentration from the fractionation of halogen rich brines to the sea ice surface during ice growth. Halogen concentrations are elevated in snow on sea ice (Simpson et al., 2005; Simpson et al., 2007) and this may lead to enhanced AMDE chemistry near sea ice. Frost flowers on newly formed brine rich sea ice have been suggested as a potential source of halogens to initiate depletion chemistry in the sea ice lead environment (Rankin et al., 2002; Kaleschke, 2004; Jacobi et al., 2006) because these delicate crystals commonly form on young ice growing on refreezing sea ice leads and are enhanced in halogens (approximately 3 times higher than seawater). However, frost flowers grow in regions that once included open water and contained nilas (new ice) that promotes the fractionation of salty brine upward to the ice surface. In addition, the snow pack on sea ice and land may be both a source and a sink for reactive halogens (Simpson et al., 2005) or a location where active halogen chemistry could occur. The snow pack covers a greater surface area than frost flower fields and is not dependent on sea ice processes and, therefore, may have a greater spatial and temporal impact on the extent of atmospheric chemistry relating to AMDEs. Further evidence linking sea ice with elevated Hg concentrations in nearby ecosystems is provided by a recent study in Antarctica where soils, lichens and mosses down wind of an open water polynya in Antarctica have yielded higher Hg concentrations than were at control sites far from the polynya (Bargagli et al., 2005). These results suggest that the processes driving elevated Hg deposition near open water regions of sea ice may affect nearby ecosystems.

Taken in total, it is apparent that sea ice plays a major role in AMDEs. Mercury concentrations in snow on sea ice are elevated compared to terrestrial snow nearby. Further, sea ice leads provide a unique location where vapour phase crystals may scavenge Hg at greater rates than typical snow precipitation. Though brine rich sea ice, snow and frost flower crystals are likely implicated in AMDE processes near leads their relative contribution to AMDE physical and chemical processes is largely unknown. A greater understanding of: 1) the role sea ice plays in Hg scavenging; 2) the connection between halogens on sea ice and Hg and 3) the relationship between snow and ice crystal formation processes and Hg scavenging must be achieved.

The discovery of AMDEs has altered our understanding of how Hg processes occur in Polar Regions. Because of this unique atmospheric transformation of Hg, we have been forced to consider the changes in the physical pathways by which Hg transfers from the atmosphere to the rest of the ecosystem. The atmosphere is the first medium in which pollutants are found and this section has described the work undertaken to understand the mechanisms and processes of how Hg transforms in this medium.

5 Modeling of mercury into and within the Arctic region

Due to the lack of long term spatial and temporal measurements of Hg in Arctic regions there is a reliance on modeling to estimate Hg loading rates. Further, modeling the response of deposition processes to changing Hg fluxes from different source regions has become increasingly relevant as North American emissions decrease while Eurasian industrial sources increase. Modeling can help see into the future as the changing source regions are combined with climate warming to challenge our predictive capabilities for assessing future deposition and storage regimes.

5.1 Modeling of the transport of mercury to the Arctic

Mercury is transported into the Arctic from global natural sources which include emission from oceanic, continental and previously deposited Hg sources and from current anthropogenic sources. Transport pathways of Hg to the Arctic are influenced by atmospheric circulation patterns on time scales ranging from a day to millennia (Raatz, 1984; Mayewski et al., 1997). The most prominent circulation patterns affecting the transport of Hg to the Arctic are the Pacific North America (PNA) and the North Atlantic Oscillations (NAO) (Wallace and Gutzler, 1981; Barnston and Livezey, 1987; Macdonald et al., 2005). Mid-latitude atmospheric blocking (Iversen and Joranger, 1985) also plays a major role in the transportation of pollutants to the Artic. Modeling shows a strong influence of NAO on pollution transport into the Arctic, particularly in the winter and spring seasons (Eckhardt et al., 2003). Mid-latitude blocking at the scale of 5–15 days is associated with elevated levels of Arctic inflow (Raatz, 1984) and is most frequent during the winter and spring seasons.

Transportation pathways of Hg to Alert, Nunavut have been modeled (Cheng and Schroeder, 2000). This model suggests possible source regions include Eastern Europe, the Northeast Coast of North America and central Siberia. A more recent model by Travnikov (Travnikov, 2005) examined the contribution of Northern hemispheric Hg emissions to the Hg deposition in the Arctic and reported the following distribution of Hg source regions: 24% from global oceanic sources, 33% from Asia, 22% from Europe, 10% from North America, 4% from Africa and 7% from the Southern Hemisphere. This study concluded approximately half of the Hg deposited in the Arctic is from recent anthropogenic sources where Asia and Europe are the largest contributors. Further, a comprehensive GRAHM model developed by Dastoor and

Larocque (2004) examined source regions of Hg to the Arctic and also highlighted the seasonal distribution of Hg in the Arctic. Dastoor and Larocque (2004) showed frequent episodes of Hg transport from Eurasian sources to the Arctic in winter due to the location of these sources northward of the Polar front. In addition, they also found trans-Pacific transport of Hg from East Asian sources in spring (predominantly) and in winter entering the Arctic. In contrast, during the summer, Dastoor and Larocque (2004) demonstrated that weak airflow movements and a confined polar front (north of 70°) prevent significant advection of Hg from mid-latitude regions to the Arctic. The main transport pathway of Hg to the Arctic during the spring and summer occurs through the ascent of air masses close to source regions, mediated by cyclones, followed by high-altitude transport and then a slow descent of the air mass into the Arctic, due to radiative cooling (Stohl, 2006). Finally, Jaffe et al. (2005) showed that long-range transport episodes of Hg from Asia to the North Pacific and North America are observed to be most frequent during the spring. This last finding is especially important to note when attempting to understand the role that spring time AMDEs play in Hg pollution in the Arctic environment.

5.2 Modeling of atmospheric processes of mercury in the Arctic

Chemical processes of Hg necessary for representation in atmospheric Hg models for Polar Regions include ambient gas phase chemistry, aqueous phase chemistry and chemistry on snow and ice surfaces. The necessary physical processes addressed by these models include dry deposition onto the ice and snow, aqueous phase deposition and Hg scavenging by cloud ice particles and snowfall.

Currently, there are two hemispheric Hg models including the Danish Eulerian Hemispheric Model (DEHM) (Christensen et al., 2004) and the Meteorological Synthesizing Centre-East hemispheric mercury model (MSCE-Hg-Hem) (Travnikov and Ryaboshapko, 2002) and one global Hg model: Global/Regional Atmospheric Heavy Metals Model (GRAHM) (Dastoor and Larocque, 2004) to represent Arctic mercury processes. GEM, RGM and PHg are the three Hg species simulated by these models. All models include current anthropogenic sources of Hg. MSCE-Hg-Hem and GRAHM also include oceanic and land based natural (including re-emission of previously deposited mercury) sources of Hg.

In addition to the representation of free tropospheric Hg chemistry, these models reply on a simplified parameterization of the AMDE related Arctic boundary layer chemistry in the springtime due to the lack of sufficient knowledge of these chemical reactions. There are several differences between these 3 models and each model exhibits some shortcomings to truly representing the behaviour of AMDEs in Polar Regions. Christensen et al. (2004) in the DEHM included a linear fast oxidation of GEM by ozone in the

boundary layer over sea ice during sunny conditions during Polar Sunrise. Although, the main features of AMDEs were reproduced by this model, it was not able to represent the high Hg concentrations in air following the depletion events or in the summertime. GRAHM included halogen oxidation processes of Hg based on the experimentally determined reaction rates (Ariya et al., 2002b) in the presence of sea ice. The Travnikov and Ryaboshapko MSCE-Hg-Hem model (Travnikov, 2005) included the GEM oxidation during AMDEs in the coastal regions during sunlight by converting GEM to RGM and PHg within the lowest 1 km near the surface. The models have been compared in Europe in a model intercomparison (Ryaboshapko et al., 2007). There is no direct comparison available in the Arctic region but the published independent studies on these models show (Ariya et al., 2004; Christensen et al., 2004; Travnikov, 2005) that they all capture the springtime depletion to some degree but fail to simulate the above average mercury concentrations observed following the AMDEs at some sites.

Dry deposition of GEM over ice and snow is neglected in the Hg models due to its low solubility characteristic (Lin and Pehkonen, 1999). The dry deposition of RGM and PHg is calculated by estimating the deposition velocities based on the resistance method capable of reproducing diurnal and seasonal variations (Wesely, 1989; Wang and Pehkonen, 2004). Deposition velocity in the resistance scheme is defined as the inverse of total resistance, where total resistance consists of the sum of aerodynamic resistance, quasi-laminar sub layer resistance and surface resistance. RGM surface resistance characteristics are assumed to be similar to that of nitric acid because of their similar solubility (Petersen et al., 1995). The dry deposition velocity for PHg is also a function of particle size and density.

Mercury deposition as RGM and PHg to the water is included in all the models. The oceanic emission of Hg(0) is also included in the models which depends on the surface temperature and the distribution of primary production activity in the oceans. The scavenging of soluble forms of Hg (RGM and PHg) by in-cloud ice and below-cloud snow is defined using scavenging coefficients similar to the scavenging coefficients for nitric acid (Petersen et al., 1995) in GRAHM and MSCE-Hg-Hem and similar to sulphate in DEHM (Christensen et al., 2004). Currently, Hg models do not include heterogeneous chemistry on the surface of snow and ice due to the lack of laboratory data required to generate accurate models. GRAHM and MSCE-Hg-Hem also consider the evaporation of precipitation which releases Hg to the atmosphere below the clouds.

In GRAHM, re-emission of Hg from snow and ice in the Arctic is treated as GEM as a fraction of the annual deposition of Hg in the Arctic (Ariya et al., 2004). However, the dynamic linkage between the Hg deposition during MDEs, photo-reduction of mercury in the snow pack or re-emission were not represented in the model due to the lack of thorough understanding of these processes. Re-emission from snow

and ice is neglected in the other two models (Travnikov and Ryaboshapko, 2002; Christensen et al., 2004) as well. This is considered a large gap in information and future modeling efforts should focus on incorporating re-emission of Hg from snow and ice. All models estimated an upper limit of the contribution of Hg deposition by AMDEs and were unable to determine the true net accumulation of Hg to the Arctic because of the lack of adequate representation of Hg re-emission from snow and ice surfaces.

While models play a crucial role in understanding the present and predicting the future transport of Hg to the Arctic, their current limitations lie with our knowledge gaps about Hg processes in this region. Future modeling efforts should focus on ensuring deposition and re-emission of Hg from surfaces is incorporated within the models. The following section addresses the current state of knowledge about what happens to the Hg that is deposited to the environmental surfaces during AMDEs.

6 Post-deposition scenarios

6.1 Mercury deposition and re-emission to and from the snow

6.1.1 Flux studies

Since the first observations of AMDEs (Schroeder et al., 1998) there has been a large amount of interest in determining the air-surface exchanges (fluxes) of Hg species to better understand the springtime cycling of Hg in Polar Regions. In the high Arctic, the focus has mainly been on dry deposition of Hg because the climate is generally dry with little annual precipitation. Fluxes of Hg have been inferred from micrometeorology and chamber methods (See Sect. 3.2). The exchange of Hg between the air and snow pack associated with AMDEs are bi-directional and are dominated by RGM deposition resulting from the rapid in-situ oxidation of GEM. At Barrow, the MBR and REA micrometeorological methods have been used to determine the emission of photo-reduced GEM (Brooks et al., 2006) and the fluxes of RGM (Skov et al., 2006), respectively. At Alert, the micrometeorological flux gradient method has been used to determine emission and deposition fluxes of GEM (Cobbett et al., 2007). In Ny-Ålesund, chamber methods have been used to calculate GEM surface emission rates from the change in GEM concentrations in the head space within the chamber (Ferrari et al., 2005). As well, in Ny-Ålesund gradient methods have been used to calculate GEM fluxes during AMDEs (Berg et al., 2003b; Sommar et al., 2007).

While the deposition flux of RGM to the snow pack may be inferred from the springtime increases of total Hg in surface snow (from near detection limits prior to polar sunrise to, occasionally, several hundred ng/L Hg prior to snow melt), direct micrometeorological measurements of RGM

deposition directly to the snow pack was attempted by Skov et al. (2006) at Barrow. This work, between 2001 and 2004, employed REA techniques (Businger and Oncley, 1990; Oncley et al., 1993) and measured RGM on paired KCl denuders. This task is complicated because the lifetime of RGM is short (Lindberg et al., 2002) and it will rapidly dry deposit to the snow surface, react and/or adsorb onto particles to form HgP or reduce again to GEM. As well, while the surface aerodynamic resistance of Hg to deposition increases with colder air temperatures it decreases with wind speed (Brooks et al., 2006). The Skov et al. (2006) measurements showed that RGM deposition fluxes primarily occurred with occasional RGM emissions, yet it is not certain if these were a sampling artifact. In addition, multi-year RGM-REA flux measurements have shown that the snow pack intermittently acts as a source of RGM (Skov et al., 2006). In general, while RGM deposition rates are highest in the afternoon and GEM emissions are highest in the late morning and mid-day, the magnitude of these fluxes vary greatly with episodic fluxes of GEM dominating emissions (Brooks et al., 2006). During a continuous five month study at Alert between January and June 2005 GEM emission fluxes were the highest during the polar night (Cobbett et al., 2007). During the transition period from polar night to polar day, the GEM emission flux was approximately zero and not until June, when the snow was melting quickly and the tundra was visible, were there any significant GEM emission fluxes. These dynamic deposition and re-emission episodes underscore the delicate balance of the Arctic Hg phenomenon between atmospheric oxidation and deposition on the one hand and snow pack photo-reduction and emission on the other. Seasonal studies at Barrow (Brooks et al., 2006) indicate a springtime RGM deposition of roughly 34 mg (Hg) m^{-2} and GEM emission of ~8 mg (Hg) m^{-2}, netting a surface gain of 26 mg (Hg) m^{-2}. This is contrary to some publications suggesting a net emission of GEM following depletion events (Lahoutifard et al., 2005; Kirk et al., 2006). At Alert, this hypothesis was investigated with no evidence that there is a net emission of GEM after AMDEs (i.e. GEM emission fluxes are approximately zero following AMDEs). While these limited studies have indicated that roughly one third of the deposited mercury may become available to biota via melt water (Lindberg et al., 2001), disparate sampling times and frequencies, along with inter-annual variability and the representative factors of the measurements, places into question the spatial and temporal extrapolations of these results.

Emission of Hg(0) from snow surfaces appears to be enhanced by sunlight and temperature (Steffen et al., 2002; Ferrari et al., 2005). In 2003, at Ny-Ålesund, Hg emission fluxes were reported to range between 0 to 50 ng/m^{2}h using flux chamber techniques. The peak GEM emission flux was recorded after an AMDE but surprisingly, this peak in GEM did not correspond to any commensurate change in Hg concentration in the surface snow (Ferrari et al., 2005). During periods when AMDEs were not active Ferrari et al. (2005)

reported that the GEM emission fluxes resulted from the production of GEM within the interstitial snow pack air (between 15–50 ng/m^{2}h in the surface and 0.3–6.5 ng/m^{2}h in the deeper snow layers). During a short field campaign in 2002 in Ny-Ålesund, emission fluxes of GEM were observed around AMDE's. The average flux was 8 ng/m^{2}h and a high mid-day peak was reported as 70 ng/m^{2}h (Berg et al., 2003b; Sommar et al., 2007).

Quantifying Hg fluxes is essential to understanding the fate of mercury in the Arctic. Based on current knowledge of atmospheric chemistry of Hg in the Arctic, measuring the GEM flux is insufficient to determine chemical mechanisms. The need for continuous, high resolution fluxes of RGM and HgP remains. This is a new area of field research in its beginning stages of development (Skov et al., 2006); as analytical methods improve so will the ability to measure and interpret Hg fluxes.

6.1.2 Mercury in the snow pack

The fate of Hg, once deposited onto snow and ice packs, is poorly understood and not well studied. This is surprising considering the snow pack acts as a transitional environment between the atmospheric reservoir and ecosystem uptake. In Arctic regions, the snow pack contains a variety of impurities contributed by anthropogenic sources of the northern industrialized countries (Douglas and Sturm, 2004; Poulain et al., 2004; Poulain et al., 2007c). This reservoir of adsorbed or dissolved compounds is not inert but rather plays an active role in photochemical reactions in the snow (Dominé and Shepson, 2002). Snow packs offer large surfaces for which the exchange of Hg between the air at the lowest point of the atmosphere and the air within the snow pack can occur. Dominé and Shepson (2002) estimate that, considering the global snow cover on the Earth's surface, an air volume equivalent to the volume of the atmosphere passes through snow packs every 4 months. Additionally, snow packs act like a reaction chamber promoting heterogeneous and photochemical reactions. For instance, well known reactions involving NO$_x$ and HCHO within the snow pack have been demonstrated (Honrath et al., 1999; Sumner and Shepson, 1999). As a result, reactions that occur within the snow affect both the composition of the snow and the overlying atmosphere.

Both inorganic and organic forms of Hg are found in snow. The inorganic forms include Hg(0) and complexes of Hg(II). Total Hg consists of all inorganic forms of Hg measured yet the fraction of Hg(0) is small (approximately 1 percent of THg is Hg(0)) (Poulain et al., 2004). Reported concentrations of total Hg in snow are low during polar winter, ranging from 0.1 and 1 ngL^{-1} in Antarctica (Sheppard et al., 1991) and between <1 ng/L and 5 ng/L in the Arctic (Steffen et al., 2002; Aspmo et al., 2005; Ferrari et al., 2005). During AMDEs, at polar sunrise, typical total mercury concentrations in surface snow increase up to maximum values rang-

ing between 20 and 100 ng/L (Lu et al., 2001; Lindberg et al., 2002; Steffen et al., 2002; Berg et al., 2003a; Poulain et al., 2004; Lahoutifard et al., 2005; Lahoutifard et al., 2006). The highest concentration of total Hg ever reported in polar ecosystem snow (820 ng/L) was found in surface hoar crystals formed directly from the vapour phase (Douglas et al., 2005).

The only organic form of Hg currently reported in polar snow is methyl mercury (MeHg), although Me$_2$Hg has recently been measured in seawater, no such measurements have been made in snow, though its presence in snow is suspected (Kirk, 2006). Kirk and St. Louis (2006) theorize that Me$_2$Hg produced at ocean depths is transported to the surface by ocean upwelling, where it is volatilized, and could be deposited to coastal snow packs (Kirk, 2006; Kirk et al., 2006). Reported levels of MeHg in snow of the Canadian high Arctic range from 0.02 to 0.28 ng/L (Kirk, 2006; Kirk et al., 2006) and may represent a significant fraction of the pool of total mercury. MeHg was hypothesized to be partly of marine origin, based on correlations between chloride and MeHg levels (St. Louis et al., 2005). Similarly, Constant et al. (2007) measured MeHg in the snow on the shore of Hudson's Bay and found a positive correlation between MeHg, sulfate and chloride in the snow. The authors suggest that marine aerosols are a source of MeHg the snow pack in this area.

6.1.3 Hg(0) emissions from polar snow packs

It has become clear that the snow pack is a potential source of GEM to the atmosphere (Steffen et al., 2002; Brooks et al., 2006). Steffen et al. (2002) were one of the first to report measurements of GEM from interstitial air in the snow (a few centimeters below the surface) and showed that the snow pack releases GEM (Steffen et al., 2002). Further field measurements confirmed that GEM emissions were strongly correlated with solar irradiation by demonstrating that diurnal cycles of GEM existed in the interstitial air over a period of several days . In addition, Lahoutifard et al. (2005) found a pronounced diel pattern with GEM concentration gradients between 20 and 150 cm above the snow pack suggesting concentration gradients were sufficient to sustain rapid fluxes between the atmosphere and the snow. Evidence of GEM production within the interstitial air in the snow was observed throughout the Arctic via interstitial air measurements, snow sampling or a combination of both methods in Barrow, US (Lindberg et al., 2002), Station Nord, Greenland , Ny-Ålesund, Svalbard (Ferrari et al., 2004b; Ferrari et al., 2005; Fain et al., 2006b; Fain et al., 2006a; Sommar et al., 2007) Resolute Bay, Canada (Ariya et al., 2004; Poulain et al., 2004; Lahoutifard et al., 2005), Kuujjuarapik (a subarctic site in Canada) (Dommergue et al., 2003a; Lahoutifard et al., 2006) and on Ellesmere Island, Canada. Concentration of GEM in interstitial snow pack air reported from these studies ranges between 0.4 to 5 ng/m^3 yet concentrations up

to 30 ng/m^3 have been observed in the high Arctic (see references above).

Many uncertainties remain about GEM production in the snow pack due to the poor understanding of light penetration inside the snow pack. In the case of UV and visible light, these wavelengths are poorly absorbed but tend to be scattered by the snow. King and Simpson (2001) estimate that 85% of the photochemical reactions occur in the top 10 cm of the snow pack. However, this estimate is dependent on the physical shape and temperature of the snow. The presence of GEM in the lower layers of the snow pack was examined by Lahoutifard et al. (2005) who found vertical GEM gradients that suggested transport of mercury to and from the snow pack. The coefficients for molecular diffusivity of Hg were too low to account for the observed gradients, therefore, the movement of mercury in the snow pack was concluded to be enhanced by the presence of hydrogen peroxide (Lahoutifard et al., 2005).

The continuous production of GEM and its subsequent evasion from the snow may lead to a decrease of the Hg content of Arctic snow packs over the course of the winter and spring. This has important ramifications in our ability to link Hg deposition to the snow pack with Hg available for methylation or ecosystem uptake during spring melt. For example it has been shown that surface snow could lose up to 90% of its total Hg content within 48 h (Poulain et al., 2004) and that emission fluxes could be in the range of a few to hundreds of ng/m^{2}h (Ferrari et al., 2005). The importance of snow to air transfers of GEM cannot be assessed through short-term studies because it depends on time dependent factors that include solar irradiation, the chemical composition of the snow, the site characteristics and the snow pack characteristics. Further, as snow melt begins, high GEM emissions in interstitial snow pack air increase to concentration values of more than 10 times that above the surface (Dommergue et al., 2003b; Dommergue et al., 2003a; Cobbett et al., 2007) and this may have an impact on the atmospheric concentration of GEM (Lindberg et al., 2001).

6.2 Redox processes, transformations in snow and photoreduction and photooxidation in fresh and sea water

Once deposited by dry/wet deposition or AMDEs, Hg species in snow can potentially undergo redox reactions and methylation/demethylation processes. Methylation processes will be discussed below in Sect. 6.3. Reduction of Hg(II) in snow proceeds mostly through photochemical reactions (Lalonde et al., 2002; Lalonde et al., 2003; Dommergue et al., 2007) as polychromatic experiments indicate major effects within the UV-B wave band. The importance of the reductive process has been exemplified in the Arctic by rapid Hg losses in the irradiated surface snow layers (Poulain et al., 2004). Since adsorption/desorption processes of Hg(0) are quite unlikely (Bartels-Rausch et al., 2002), resulting diel cycles of Hg(0) in interstitial air bring strong evidence for an

important post reduction snow to air transfer (Dommergue et al., 2003a; Ferrari et al., 2005). It has been recently suggested that Hg reduction in snow mostly occurs in the snow crystal quasi-liquid layer and is therefore highly dependent on temperature (Ferrari et al., 2005). However, there is a need for further physical and chemical characterization of this so-called quasi-liquid layer. There have been accounts of Hg(II) reduction in snow during the night and at depth in the snow pack (Ferrari et al., 2004b). HO$_2^{\cdot}$ has been proposed as a reducing agent of Hg(II) during the day and at night (Dommergue et al., 2003a; Ferrari et al., 2004b). In contrast, an experimental thermochemical study by Gårdfeldt and Jonsson (2003) showed that Hg(II) is reduced by neither HO$_2$ nor O$_2^-$ under ambient conditions. Direct photolysis of some Hg complexes has also been proposed. Oxidation of newly formed Hg(0) in snow has been reported and was attributed to photochemical processes (Poulain et al., 2004). Based on studies conducted on temperate snow samples, it is likely that this photooxidation is controlled by the presence of halogen radicals in snow (Ariya et al., 2004) and is therefore of importance in coastal snow packs. This reaction is mainly driven by UV-A and UV-B wavebands (Poulain et al., 2004). Studies have also proposed that hydrogen peroxide formed in snow could oxidize Hg under acidic conditions (Lahoutifard et al., 2006). Further, the significance of biological redox processes in snow has recently been suggested (Hennebelle et al., 2006) and data from arctic ponds formed by snow melt, coastal lagoons and seawater indicate the presence of bacteria that express resistance to Hg via reduction (Poulain et al., 2007b).

Observations made by Ferrari et al. (2004b) and Fain et al. (2006a, b) in the field showed that Hg(0) can be significantly depleted inside the snow pack. Other studies indicate that some radicals (HO, Cl, Br), first produced by irradiation, may be responsible for Hg(0) oxidation (Poulain et al., 2004; Fain et al., 2006b; Fain et al., 2006a). However, oxidants leading to the Hg(0) destruction in the snow-pack are not yet identified.

Finally, if chemical processes have been observed in the snow pack at the surface of the snow grains, microbiological interactions can also take place especially when snow melt starts (Amato et al., 2007). Water layers around the snow grains (Döppenschmidt and Butt, 2000) that are enriched in ions and organic substances are locations where chemistry is enhanced (Takenaka et al., 1992). In these layers, microorganisms can develop efficiently (Ariya et al., 2002a; Amato et al., 2007) and interact with Hg by adsorption onto the cell or cell walls, as long as genetic material of the microorganism is available for this process (Hennebelle et al., 2006). During the melting period, micro-organisms can generate exopolysaccharides (E.P.S) (Krembs, 2006) which can form strong complexes with metals (Loaec et al., 1998) such as lead, cadmium and zinc (Loaec et al., 1998). The resultant melt water will then likely contain Hg bound to organic material that could then enter the food chain.

The oxidation of Hg can take place in fresh and sea waters (Lalonde et al., 2001; Poulain et al., 2007a). In its oxidized form, Hg is water soluble and will readily deposit to aqueous systems from the atmosphere through dry and wet processes (e.g. AMDEs). Once the Hg is transferred into this oxidised state, it can be methylated and is thus available for bioaccumulation. Therefore, it is necessary to identify the lifetime and end products of photodegradation of Hg in fresh and sea waters. Gårdfeldt et al. (2001) and Lin and Pehkonen (1998) reported that Hg(0) photoradical aqueous reactions such as Hg(0)+OH are fast. As well, reduction of Hg(II) to Hg(0) in natural aerated waters, e.g. melted snow, may proceed thermally or under actinic radiation in the presence of a suitable inorganic (e.g. sulphite) or organic (e.g. oxalate) ligands. In these cases, intramolecular transfer of $2e^-$ charge from ligand to metal, possibly involving fragmentation of the ligand, can occur (Van Loon et al., 2000; Van Loon et al., 2001; Gårdfeldt and Jonsson, 2003). Other possible monomeric radical intermediates Hg(I)/HgX from redox processes are efficiently scavenged in aerated solutions by molecular oxygen yielding divalent Hg species (Lyu et al., 1983; Horvath and Vogler, 1993). Because aqueous phase chemistry of Hg plays an important role in the removal of Hg from the atmosphere, studies such as those described above must be considered when trying to understand cycling of Hg in Polar Regions.

6.3 Methylation of Hg in Polar Regions

Although most of the measurements for mercury in Arctic ecosystems have been for total Hg, it is MeHg that is the most toxic and environmentally relevant form that biomagnifies in food chains leading to humans. While MeHg shows a direct bioaccumulation of at least 10 000 times between water and particulate material (Watras et al., 1995), the increase in subsequent trophic levels is typically 4 to 6 times (Cabana and Rasmussen, 1994). The fraction of MeHg to total Hg also increases progressively with increasing trophic levels (Wagemann et al., 1997).

MeHg production in the Arctic has been documented in wetland soils and streams (Loseto et al., 2004a), in freshwater ponds (St. Louis et al., 2005) and lakes in tundra watersheds (Hammerschmidt et al., 2006b). Sulfate reducing bacteria (SRB) are considered to be the main Hg methylators in aquatic temperate ecosystems and may play a role in the Arctic soils, streams and lakes; however this assumption requires further testing. Loseto et al. (2004b) collected sediments in Arctic wetlands prior to spring thaw. The MeHg concentration in the frozen sediments was low when they were transported to the laboratory (average 0.065 ng/g) but after incubation at 6 and 8°C for 30 and 60 days, values increased up to 100 fold in some samples. Although sulfate reduction occurred, SRB abundance was generally low and showed no relationship with MeHg formation. The dissimilar sulfate-reductase gene specific for SRB was found at only one site

where the SRB abundance was low. This implies another mechanism for MeHg formation may be operating. Iron reducing bacteria is also thought to form MeHg (Flemming et al., 2006) and photochemical (Siciliano et al., 2005) or abiotic formation from methyl donors such as methyl cobalamin, methyl tin or methyl lead are also possible (Celo and Scott, 2005; Celo et al., 2006). Loseto et al. (2004a) further reported a peak in MeHg concentration immediately following snowmelt in Resolute and found that this peak occurred in drainage basins that were located both in and out of wetlands. This peak of MeHg concentration was also found in the streams during peak runoff. This result was surprising because if the MeHg is formed in wetlands then maximum MeHg levels would be expected later in the season during the time of lowest flow where minimal dilution in the water would occur. This finding can be of great importance in the context of climate change. Thus, it was concluded that MeHg is either formed in the snow or deposited to the snow. In contrast to the high levels of THg in the snow are associated with AMDEs (>30 ng/L), the concentration of THg in runoff was low (<2 ng/L) in wetlands, streams and lakes.

After measuring high MeHg concentrations in high Arctic snow (up to 280 pg/L), St. Louis et al. (2005) proposed that MeHg may also be produced abiotically from the photochemical breakdown of Me_2Hg evaded from the ocean. This latter pathway was also demonstrated under laboratory conditions (Niki et al., 1983a) but the relative magnitude of this source of MeHg to high latitude ecosystems has not been quantified. MeHg can be produced upon irradiation and in the presence of dissolved organic matter in surface water of temperate lakes (Siciliano et al., 2005). Hence, continuous daylight combined with the presence of biogenic organic matter from heterotrophic activity may lead to the production of MeHg in polar environments.

MeHg may also potentially be biologically formed in aerosols or in snow. Constant et al. (2007) suggest that MeHg levels reported on the shore of Hudson's Bay are a result of methylation of THg (at 8–9 ng/L) in snow because of a positive correlation between the high levels measured (200 pg/L) and heterotrophic bacteria plate counts and particulate material in the snow. Also, It has been suggested that MeHg may be formed in the atmosphere through a reaction between labile Hg(II) complexes and an unknown methylating agent(s), potentially acetate or similar molecules (Hammerschmidt et al., 2007). These authors propose that available Hg(II) limits the reaction and increased atmospheric loadings of Hg could lead to enhanced MeHg in precipitation. Indeed, the heterotrophic activity of bacteria and fungi was demonstrated in aerosols and in snow from Spitzbergen (Norway) and at the South Pole. Together with the observation that high levels of bioavailable Hg were found in snow following AMDEs and considering alternative pathways for MeHg methylation to those occurring in anoxic conditions, one can expect methylation to occur. In coastal/marine areas, the production of MeHg and Me_2Hg by macroalgae from Kongs-

fjord on Spitzbergen,was reported (Pongratz and Heumann, 1998).

Demethylation of MeHg has been historically attributed to bacterial processes and photodegradation. In polar areas, Hammerschmidt et al. (2006) provided evidence for an important role of photodemethylation in controlled pools of MeHg in lakes. The role of microbial demethylation is supported by the expression of *mer*-operon functions, namely *mer*A genes, in microbial biomass collected from coastal/marine environments.

The impact of the springtime pulse of MeHg to the high arctic is an important mechanism to understand because of the toxic effects that MeHg may have on the availability of MeHg for marine mammal uptake. Further, the influence of climate changes (e.g. warming, thinning and melting of sea ice) on net MeHg production, most likely through changes in the organic carbon cycle, must be quantified to fully understand the link to this increase in MeHg production and any connection to the uptake of this pollutant by marine mammals. Perhaps there is sufficient total Hg in the environment to fuel the methylation process for decades to come because the production of MeHg will, no doubt, increase with temperature.

6.4   Mercury in polar waters

The ocean plays a key role in the biogeochemical cycling of Hg (Mason and Sheu, 2002) yet there is limited information about the processes occurring with Hg in Arctic coastal and marine waters (Aspmo et al., 2006) and their contribution to elevated levels of Hg in Polar Regions. It is now recognized that there is MeHg in Arctic snow close to marine locations (St. Louis et al., 2005) yet the importance of this MeHg from marine waters as a source to aquatic food chains has not been established. Leitch et al. (2007) calculated that 15 kg per year of MeHg and 2.2 tonnes per year of THg were transported from the Mackenzie River to the Beaufort Sea during the spring freshet. The authors suggest that this river plays a major role in the elevated Hg concentrations in marine mammals in the Beaufort Sea (Leitch et al., 2007). Other studies have reported THg concentrations averaging 160.5 ± 88.3 pg/L from samples collected in the North Atlantic Ocean; more than 400 pg/L of THg in surface waters of Toolik Lake, Alaska (Tseng et al., 2004) and more than 35 pg/L DGM on the North Atlantic at latitudes $>74°$ N and/or regions where the ocean was mostly covered with sea ice (Aspmo et al., 2006). In the latter study, the authors hypothesized that Hg was exported from melting sea-ice to the surface ocean water. After abiotic and/or biotic reduction during Arctic summer, Hg(0) accumulated under the sea ice cover and parts of it were re-emitted from water surfaces to the atmosphere during summer. It is not clear from these results if elevated GEM and DGM concentrations reported are the direct consequence of strong input pulses of Hg to the Arctic Ocean during AMDEs in the months before. In addi-

tion to MeHg being reported in polar oceans Me$_2$Hg has been measured in the Arctic Ocean and in Hudsons Bay (Kirk, 2006). Me$_2$Hg concentrations were highest in the deepest water samples and almost equal to the level for MeHg, which was also reported higher in the deeper samples. Values were low, near detection limits, in surface samples and thus it remains a challenge to explain the mechanism for transport from deep water to the atmosphere where photodegradation to MeHg can occur.

The oceans play one of the most significant roles in Polar Regions both in spatial breadth and processes and yet information about dynamics of Hg around these environments is scarce. Considering that the Arctic Ocean contains a large, vulnerable ecosystem exposed to this toxic pollutant, the vast number of processes that occur in the water column, sediments and ice (e.g. concentrating and methylation of Hg) and that change in climate will primarily affect this ocean and beyond, the authors recommend that future research must focus on this area.

7   Conclusions and future directions

During the last decade a great leap in our understanding of Hg transformation in the Arctic and the Antarctic atmosphere has occurred, especially in measurement, laboratory and modeling studies. The goal of this review article is to provide a comprehensive assessment of the state of the Hg science in Polar Regions since the discovery of AMDEs. Taken in total, these studies frame our current understanding of the roles that atmospheric chemistry, Hg speciation, Hg deposition, snow and ice processes and photochemical reactions play in driving the fascinating Hg cycling in this environment. Prioritizing future research directions is difficult because of the interdisciplinary nature of Polar Hg studies that incorporate work from atmospheric chemists, sea ice and snow chemists, modelers, laboratory experimentalists and ecosystem biogeochemists. Here we will attempt to summarize where the current state of knowledge lies with an eye to the future research efforts and results that are needed to move the state of knowledge further. We will first start with what is generally considered well known and then will transition toward the major gaps in our knowledge base. As earlier stated, the changing climate and emissions sources over the next 20 years will dramatically affect the source, deposition and long term fate of Hg deposited to Polar Regions. The effects of these changes on the AMDE processes that deposit Hg to the Arctic and Antarctic are, as of yet, unknown.

It is well understood that AMDEs occur throughout Polar Regions close to marine locations each spring. Further, research has shown that the initiation of AMDEs requires Hg in the atmosphere, sunlight and reactive halogens. Sea ice or snow may provide a large pool of halogens to feed the photochemical reactions. Several lines of evidence confirm that Hg is able to undergo fast kinetic reactions with halogen radicals

such as Br and BrO although IO and I have not been ruled out as players. It is agreed that GEM is converted to an inorganic gas phase Hg species, termed RGM, during AMDEs and this RGM is either associated with aerosols (termed PHg) and/or deposited to the snow pack. The fate of this deposited Hg species is less clear. Some of the deposited RGM is reduced to GEM and subsequently re-emitted to the atmosphere while some remains or is re-oxidised at or within the snow pack. Photochemistry studies of Hg within the snow pack have shown that reactions occur within the first few centimeters. Flux measurements have shown that there is a net deposition of Hg to the snow in early spring followed by a net emission of Hg in the summer. Gas phase Hg has been measured in interstitial snow pack air and in the atmosphere during non-AMDE periods.

Several models have been developed to incorporate AMDEs into regional and global Hg assessments. Both process and transport models describe the cycling of Hg within and into Polar Regions. All the models agree that AMDEs affect the amount of annual Hg deposited to Polar Regions. With the addition of more long term stations measuring atmospheric Hg species throughout the Arctic and the Antarctic the models can be greatly refined. However, the largest gap in the current models is a solid understanding of the chemical processes that drive deposition and re-emission of Hg in this environment.

Because of the link the snow pack has to the local environment, considerable research on the deposition to and processes within this medium have been done. This work covers a wide spatial extent as research sites in numerous Arctic and Antarctic locations have been employed. However, few of these studies are part of long term study sites. This research has demonstrated the heterogeneity of Hg distribution in the snow pack and that both physical conditions and chemical processes must be accounted for in the assessment of the fate of Hg within the snow pack. Transects inland away from the ocean demonstrate higher Hg concentrations in the snow at locations closer to marine water. Of great significance, MeHg has been found at elevated levels in snow close to marine waters and this may represent a significant fraction of the pool of total Hg. Whatever the source of MeHg in the Arctic, it is recognized that substantial amounts of it exist in polar environments but the link to the aquatic and marine food chains has yet to be resolved. Further, Hg and MeHg may be available as a large pulse emitted from the snow pack during spring melt events. Many studies have focused on the primary deposition of Hg to snow and ice and the link to atmospheric chemical processes. Some of these have been coupled to re-emission measurements that suggest much of the Hg deposited during AMDEs is lost to the atmosphere during photochemical reduction and, perhaps, also during snow melt and snow metamorphism. However, detailed investigations tracking Hg in the snow pack and surface water before and after spring melt are needed. Further, lake, tundra and marine sediments and ice cores provide a long term record

of Hg deposition that can be used to compare pre- and post-industrial revolution deposition rates. More work to incorporate these studies for long term background Hg deposition in order to compare future Hg deposition rates, in light of climate warming and changing emissions sources, will be required. The study of methylation processes occurring in Polar Regions has been put in the forefront of importance and is gaining momentum within the research community. It is clear that the formation of MeHg may be intimately linked to a warming climate because both the processes of methylation and demethylation will be altered by this change, thus every attempt should be made to understand what is controlling these methylation processes and establish what drives these controls in order to determine the impacts of climate change on the polar environment.

The role of the sea ice in the cycling of atmospheric Hg has been closely studied and has shown to provide a viable source of halogens and a location for AMDE chemistry to occur. Some research on Hg in and into the Arctic Ocean and Hudson's Bay indicates that these bodies of water are vital to the Hg cycle. Initial work has begun on the microbiological transformations of Hg in aquatic systems and their effect on Hg distribution in Polar Regions. Since microbiological processes likely drive the methylation and biological uptake of Hg these studies must be continued both in the field and in laboratory controlled environments.

While there has been a tremendous amount of research undertaken since the discovery of AMDEs, several key questions remain that limit a complete understanding Hg cycling in Polar Regions. In the following paragraphs, the authors present suggestions on where future research should be directed in order to gain this desired comprehensive understanding of Hg cycling in this region.

One critical gap of knowledge is the lack of proper field methodology for atmospheric Hg speciation in environmental matrices, including air, snow and aerosols. Of most significance is the identification of the exact chemical structure of the Hg species produced during AMDEs. This is essential to know before properly addressing the global cycling of Hg, including the Polar Regions, in order to know which species are involved in the chemical, physical and biological transformations in the environment. We strongly recommend development of novel techniques to efficiently address Hg speciation in Polar Regions (as well as within other environmental conditions). Additionally, it is vital to understand exactly how and where the atmospheric products are produced not only in the boundary layer but also throughout the free troposphere. This is very relevant to understanding the impact of a rapidly changing climate in Polar Regions and the effect these changes will have on the availability of Hg to enter this ecosystem. Stable mercury isotopes provide a promising tool to monitor Hg deposition processes and to track Hg methylation and incorporation into ecosystems. Studies that make use of stable Hg isotopes may be able to link atmospheric, cryospheric and biologic processes and as

a consequence their further refinement and application are encouraged.

Modeling and predicting the loading of Hg to polar ecosystems is challenging because there are several drivers of the Hg cycle currently undergoing rapid change. Firstly, the source regions of Hg in the Northern hemisphere are shifting from North America and Western Europe to Asia and Eastern Europe. Models have shown that air currents from Asia occur in the springtime when atmospheric Hg chemistry is in full swing and any increases in the amount of Hg from this important source region will, no doubt, affect the Hg cycle of the Arctic. Secondly, and very importantly, is that the extent of sea ice is in marked decline in certain Arctic regions and the degree to which this decline occurs is predicted to be high. Sea ice drives the major meteorological components of the Arctic system (precipitation, temperature, winds, and regional circulation) and these parameters largely control the entry and subsequent scavenging of atmospheric contaminants including Hg. Changes in the timing and extent of sea ice will no doubt affect AMDE dynamics. It is essential to fully comprehend the role that sea ice plays in AMDE chemistry and subsequent deposition to the ocean. Thus, field campaigns, as well as laboratory and theoretical calculations, must continue to further elucidate the sea ice Hg interactions and its potential global impact. As well, the changing dynamics of this aspect of Hg chemistry in the Arctic will only be understood with a denser network of long term Hg monitoring sites.

A significant gap in our understanding of Hg cycling in Polar Region lies in our understanding of how mercury enters the upper ocean water from the atmosphere. One third of the Artic is covered by the oceans yet we know very little about their role in Hg cycling. How the deposition of Hg to the oceans from the atmosphere (and how that material is further fed into this vulnerable ecosystem) will be altered by change in ice climate is of great significance and relies almost completely on water-column work that has not been undertaken. Further, more work on the biological uptake of Hg by the ecosystem from the air/snow and water is required.

Human dynamics investigations have increasingly shown that people in the Arctic have elevated Hg in their country food diets. MeHg is the toxic form of Hg that dictates the accumulation of mercury in polar environments. While an influx of research on the subject of the processes under which MeHg is produced in polar environments have surfaced, these processes remain not well understood. Some have suggested microbiological transformations of mercury in aquatic systems, others have suggested photochemical reactions and Me_2Hg evolution from the ocean, yet no direct conclusions have been made. In light of new evidence on the role of biological aerosols the redox reaction of Hg around these bioaerosols is an area of interest for future research. Atmospheric redox mechanisms of Hg at the air-snow interface, in clouds and fog and in melting snow are desired because they are also not fully understood. It may be possible

to employ Hg as an environmental tracer to gain a better understanding of fundamental ecosystem processes. This is an arena where Hg isotopes may provide new and novel information.

Multidisciplinary investigations combining soil and ice microbiology, atmospheric chemistry, oceanography and laboratory investigations may provide the greatest breakthroughs in assessing the long term fate of Hg in the Polar ecosystems. These types of studies are likely the most sorely needed as they will move the current research across disciplines to provide a better understanding of Polar Regions processes and the fate of contaminants. Results from focused investigations of Hg deposition and ecosystem processes are likely to yield new and novel information on many unique processes in the Polar Regions. Similarly, investigations tracking the sources and fate of other contaminants such as POPs and other trace metals are likely to yield critical information in atmospheric chemical processes, snow and sea ice melt processes and trophic level relationships.

It is essential to quantify transfer functions from the atmosphere to snow and ice and from melt runoff to soil and aquatic microbiology to gain a better assessment of how the Arctic will respond to changing source regions and a warming climate. We will move the state of understanding forward when the entire system is investigated and a series of synthesis efforts are combined into a strong cohesive assessment of the Polar Region as a whole. Future research on Hg in Polar Regions must focus on discussing the processes and pathways of this contaminant in the context of climate change. With the onset of the International Polar Year, the next ten years of Hg chemical investigations in the Polar Regions will be exciting and will no doubt incorporate investigators representing many research disciplines. In the end, the authors hope that the next decade will move the science toward a better overall comprehension of arctic system processes.

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