Mercury in the Arctic Atmosphere

Springtime Cycling Near and Over the Sea Ice

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Abstract

The objective of the work described in this thesis is to improve our understanding of factors that affect the depletion of gaseous elemental mercury (GEM) from the atmosphere during the Arctic springtime. This was accomplished through research undertaken and described in three publications. Atmospheric mercury depletion events (AMDEs) are now an established phenomenon in the high Arctic whereby the long-lived GEM is oxidized in the air through a series of photochemically-initiated reactions involving halogens and ozone. This chemistry produces reactive gaseous mercury (RGM) and particulate bound mercury (PHg) which both have shorter atmospheric residence times than GEM and deposit more readily to the snow and ice surfaces. This is a means by which mercury can be transferred from the atmosphere to the Arctic environment that was unknown prior to 1995 when AMDEs were discovered. An extensive review paper was completed that summarizes mercury work in the high Arctic in the ten years following the discovery of AMDEs. This review was followed by two papers investigating the processes around atmospheric mercury in the Arctic springtime.

The review provided a synthesis of currently used methodologies to measure mercury in the Arctic, research results related to AMDEs from field, laboratory and modeling work, and information about how mercury cycles around the environment after AMDEs. This review concluded that bromine oxide and bromide (BrO/Br) radicals oxidize GEM to RGM and/or PHg and that these are readily scavenged by snow and ice surfaces. However, the fate and total amount of the RGM and PHg produced by an AMDE remained unclear. Some of the deposited RGM/PHg was found to be reduced to GEM and subsequently re-emitted to the atmosphere while some remained (or was re-oxidised) at or within the snow pack. Flux measurements of GEM found there to be a net deposition of mercury to the snow in the dark winter, a net zero emission during the spring followed by a net emission of mercury in the summer. The presence of significant amounts of methyl mercury in snow in the Arctic surrounding AMDEs was considered important because this species is the link between the environment and impacts to wildlife and humans. Further, despite research on methylation and demethylation of mercury, these processes are not yet fully understood. The role of the sea ice in the cycling of atmospheric mercury was studied and showed that the sea ice offers an environment enhanced in halogen concentration due to the fractionation of

halogen rich brines to the sea ice surface during ice growth. Snow and frost flowers on newly formed brine-rich sea ice were suggested as a potential source of halogens to initiate depletion chemistry in the sea ice environment. Regional and global models predicting the transport and deposition of mercury began to incorporate AMDEs in their chemistry and agreed that AMDEs increase the amount of annual mercury deposited to Polar Regions. Several gaps of information were identified in the review and recommendations for future research were highlighted. The most significant gap, which remains today, was the lack of identification of the exact chemical species of mercury compounds produced during AMDEs. Several additions to the models were recommended including fully incorporating the chemical processes that drive mercury deposition and re-emission. Thus, it was recommended that field campaigns, as well as laboratory and theoretical calculations, must continue to further elucidate the sea ice mercury interactions and their potential global impact. With the addition of more long term stations measuring atmospheric mercury species throughout the Arctic and the Antarctic the models can be greatly refined. The two papers that followed in this thesis served to address some of the gaps of knowledge identified in this review.

Ten years of atmospheric mercury speciation data and 14 years of mercury in snow data from Alert, Canada were examined in the second paper of this thesis. In each of the ten years of sampling, PHg increased steadily from January through March and was higher than RGM. This pattern began to change in April with very high levels of PHg and increasing RGM. In May, RGM transitioned to be significantly higher than PHg and continued to be high into June whereas, during that time, PHg dropped sharply down. The transition from higher PHg to higher RGM from April to May was thought to be driven by a combination of air temperature and particle availability. In February through April, partitioning of RGM onto aerosols to produce PHg was favoured by low temperatures and elevated concentrations of particles that are principally the result of Arctic Haze and some sea salts. In the snow, the concentrations of mercury peaked in May for all years. The highest deposition of mercury to the snow in the spring at Alert was during and after the transition of PHg to RGM in the atmosphere. This indicated that the conditions in the atmosphere may drive the timing of mercury springtime deposition to the Arctic surfaces.

The third paper described results from a field campaign on the Beaufort Sea ice near Barrow, USA in March 2009 as part of the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) and OASIS-Canada International Polar Year Programs. For the first time, measurements of GEM, RGM and PHg were successfully collected directly over the sea ice. Concentrations of PHg were significantly higher than RGM and GEM was depleted for a significant portion of the study. Ozone (O_3) and BrO chemistry were active during the study and positive linear relationships between GEM and O_3 and RGM and BrO were reported. This suggested that similar bromine chemistry that drives springtime O_3 depletions was also at play with mercury. Further, GEM was measured simultaneously over the tundra and the sea ice and revealed significantly higher re-emission of GEM following AMDEs over the tundra. Elevated chloride levels in snow over sea ice were proposed to be the cause of lower GEM emissions over the sea ice. This finding suggested that the sea ice retains more deposited mercury than inland snow and that current estimates of mercury deposition over the Arctic Ocean may be underestimated.

This thesis is a summary of research undertaken to increase our understanding of AMDEs in order to use this information to assess the impacts of these processes on the cycling of mercury. The Arctic Ocean is rapidly changing, as is the overlying and surrounding atmosphere. In order to predict how mercury in the Arctic environment will change, the processes that it undergoes with the current conditions must be understood. The research presented here has improved our understanding of several processes impacting AMDEs and the entry of mercury to the Arctic ecosystem. The global community has recently combined efforts to develop a treaty (the Minimata Convention) for the reduction of global mercury emissions in order to reduce the impact of this toxic chemical on humans and wildlife. The work presented here has and will play a role on assessing future impacts of global emissions on the biogeochemical cycling of mercury in this sensitive and remote region.

Acknowledgements

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To the most amazing group of friends a girl could as for: I thank you for your friendship, advice, understanding, long talks and many cocktails over the past six years. I have been put through the wringer in my life but without this strong support system onto which I have been able to rely, this thesis would not have been possible.

Finally to my family: I thank my awesome sisters who have my back and my parents who are my solid grounding and who are always there when I need them. Mum, thank you for carving a path for woman in science (especially me) that was very easy to follow and Papa for always encouraging education. I love you all and am grateful to be surrounded by such a supportive family, busses.

Well…
I think I won the bet Papa!

Table of Contents

Chapter 1: Introduction and background

Mercury is a natural element commonly known as quicksilver and was originally termed *hydrargyrum* from the Greek words for "liquid" and "silver." Mercury is predominantly found naturally as cinnabar (HgS). Known as the only metal in liquid form at room temperature, mercury has fascinated scientists for centuries. Mercury is considered a "heavy metal" with a density of 13.5 g cm^{-3} (Schroeder and Munthe, 1998) which can allow heavy materials, such as steel, to float on its surface. Mercury has many common uses in devices such as thermometers, barometers, electrical switches, fluorescent light bulbs and in dental amalgams. Mercury has been used as a preservative in vaccines; as an anti-fungal agent in cosmetics; it has been employed to cure syphilis and has been used to clean felt in hats. While mercury has many useful properties, it is also a toxic chemical that is ubiquitous in the environment. Mercury is a potent neurotoxin when in the methylated form and has the ability to cross the protective blood brain barrier and affect the central nervous system (EC and HC, 2010).

1.1 Mercury in the environment

Mercury is released to the environment through three types of emissions: natural, anthropogenic (new) sources and re-emission (of previously deposited mercury of both anthropogenic and natural origin) (UNEP and AMAP, 2013). Natural sources of mercury include forest fires, volcanoes, ocean emissions and weathering of the earth's surfaces. Mercury is released anthropogenically to the environment through processes such as coal burning, metals smelting, gold/silver mining and from chlor-alkali plants. As well, mercury is emitted from incinerators, flooding caused by dams and through the production, breakage and disposal of mercury-containing products. Re-emission comprises both natural and anthropogenic mercury re-released to the environment. The current breakdown of these releases to the global pool is: 80-600 tons per year from natural emissions; 2000 tons per year from anthropogenic emissions and 400-6300 tons per year from re-emission (UNEP and AMAP, 2013). Mercury is volatile, has a long atmospheric residence time and, thus, can be transported from source regions and travel around the world, which makes it a global pollutant. Mercury is generally released to the atmosphere as an inorganic species (Hg^0 or Hg^{2+}) but has the potential to be methylated in the environment and, in that form, can bioaccumulate in the aquatic food chain (Schroeder and Munthe, 1998). The primary exposure path to humans of mercury is through the consumption of aquatic and marine food (Driscoll et al., 2013). In Canada, a significant portion of fish consumption advisories are regarding methyl mercury levels (EC and HC, 2010). Historical records show that mercury levels significantly increased due to emissions in the environment during industrial times (Lindberg et al., 2007), began to level off in the mid 1990s but have started to show an increase since 2005 (UNEP and AMAP, 2013). It is important to note that the predominant source regions of emissions have changed from Europe and North America to Asia (Driscoll et al., 2013). The shift in source regions can impact interpreting long term trends produced from measurements (Cole et al., 2013).

1.2 Mercury in the atmosphere

Mercury in the atmosphere is transformed by physical and chemical processes. The different properties of the Hg species determine how and where they are deposited to the surface. Gaseous elemental mercury (GEM) has the longest lifetime in the air of the mercury species and can be transported globally (within tens of thousands of kilometres) while reactive gaseous mercury (RGM) and particulate mercury (PHg) are generally scavenged or deposited in the region of emission sources (within a few tens to hundreds of kilometres) either directly or following atmospheric chemical transformations/reactions (Schroeder and Munthe, 1998). The residence time of GEM in the atmosphere is estimated to be within 6 and 24 months (Schroeder and Munthe, 1998; Steffen et al., 2008) and can therefore be mixed in the troposphere globally within one year (Driscoll et al., 2013). GEM is the dominant form of mercury in the atmosphere and represents about 95−98% of total global atmospheric mercury. RGM is approximately 0.2−1% of the total and PHg represents the balance from 0.2 to 2% (Schroeder and Munthe, 1998; Peterson et al., 2009; Rutter et al., 2009). The average northern hemispheric total gaseous mercury (TGM = GEM + RGM) concentration has been reported to be approximately 1.7 ng m^{-3} in 2003 (Slemr et al., 2003) with more recent reports showing lower concentrations at some sites (Ebinghaus et al., 2011; Slemr et al., 2011). Recently, the rate of decrease of TGM was reported from several sites to be higher in mid latitudes than in the high Arctic (Cole et al., 2013). Shorter lived atmospheric mercury species such as RGM and PHg are either emitted directly from emission sources or the result of conversion of GEM and/or partitioning of RGM onto atmospheric particles. These latter two mercury species are more readily deposited from the air than GEM as shown by their higher dry deposition velocities (RGM>PHg>>GEM) (Zhang et al., 2009) and higher solubility/precipitation scavenging efficiency. Mercury is removed from the atmosphere through wet and dry deposition at a rate that depends on the species of Hg, the local meteorology, the type of surface and the presence of atmospheric oxidants. Wet deposition (scavenging of the gas phase mercury or PHg) is believed to account for a large portion of atmospheric mercury deposition (Prestbo and Gay, 2009). Dry deposition of Hg from the air to the surface is predominantly modeled (Dastoor and Larocque, 2004; Zhang et al., 2012) but some direct measurements have been reported (Graydon et al., 2008).

Chemical transformation of mercury occurs in the atmosphere through oxidation/reduction and photochemistry (Steffen et al., 2012a). These reactions can occur in the gas phase or through heterogeneous reactions in the aqueous phase of cloud droplets and at various air/water/aerosol surfaces. There are currently very limited data on heterogeneous reactions at the molecular scale for mercury (Subir et al., 2011, 2012). Gas-phase redox chemistry is dominated by the oxidation of Hg^0. The oxidants responsible include, but are not limited to, ozone (O_3), hydroxyl radical ($OH^\bullet$), hydrogen peroxide (H_2O_2) and reactive halogens such as Cl, Cl_2, Br, Br_2, BrO, I and I_2. While most of these reactions are possible, it is believed that the dominant global oxidants of mercury are halogen radicals (predominantly Br) and involve photochemistry (Holmes et al., 2006; Driscoll et al., 2013). The reduction of Hg^{2+} back to Hg^0 is also important for the atmospheric Hg cycle and is generally assumed to take place in the aqueous phase (because of the solubility of Hg^{2+}) and results in volatile Hg^0 as the product. There is not a lot of evidence for reduction of Hg in the gas phase (Lindberg et al., 2007). In the aqueous phase, the primarily identified reductants are HSO_3^-, $HO_{2(aq)}$, $O_2^-{}_{(aq)}$. Other photo-reduction pathways of Hg^{2+} involve various halides and organo-Hg^{2+} complexes. Evidence of photo-reduction in the snow has been presented (Lalonde et al., 2003; Poulain et al., 2004) but little is known about the reactants involved in these reduction reactions or their rates (Subir et al., 2011, 2012).

1.3 Mercury in the Arctic

The Arctic is an ecosystem different than any other in the world and is very susceptible to foreign inputs of chemicals and pollution. Mercury has been a priority issue for the Arctic for many years and recently, to reflect that importance to circumpolar governments, two comprehensive assessment reports exclusively on mercury in the Arctic have been published (AMAP, 2011; NCP, 2012). These reports are as follows: "Mercury in the Arctic – AMAP Assessment 2011" and "Mercury in Canada's North – the Canadian Arctic Contaminants Assessment Report III – 2012". Both reports comprehensively assess current scientific investigations of mercury in the air, terrestrial and aquatic environments and include discussions on the levels in biota. The reason that such work was undertaken is that mercury is found at elevated levels in some Arctic wildlife and indigenous people (AMAP, 2005) and can affect their health. Through the consumption of country food, northern people are exposed to toxic pollutants such as mercury. Country food, which includes food such as whale muktuk, ringed seal liver, fish and caribou, is part of the northern traditional life and has many health benefits. While northerners are encouraged to continue to consume country foods, there have been advisories on certain populations at risk, such as pregnant woman and young children, to reduce consumption of species known to contain high levels of mercury.

Mercury is delivered to the Arctic primarily through the atmosphere and through ocean currents. The atmospheric contribution is significant and results primarily from non-Arctic source regions. However, the input of mercury to the Arctic is controlled by its physical and chemical processes. The Arctic environment and overlying atmosphere is currently in transition because of the rapid rate of change induced by climate warming (NCP, 2012). Several factors such as increasing air temperature, changing precipitation patterns, melting of permafrost and sea ice changes can have impacts on the cycling of mercury in the Arctic. For this reason, the processes that mercury undergoes in and how it is removed from the atmosphere are important to understand. The work described in this thesis focuses on the cycling of mercury in the atmosphere and its impact on the deposition and emission back to the air.

1.4 Atmospheric mercury depletion events

Gaseous elemental mercury (GEM) is characterized by its long atmospheric residence time of 6-24 months (Schroeder and Munthe, 1998). However, during polar spring, GEM is known to undergo extraordinary fluctuations in concentration and is, at times, nearly completely removed from the atmosphere within hours. This was first observed in 1995 in Alert, Canada where the concentration of GEM in the air decreased from background concentration values of approximately 1.5 ng m^{-3} to less than 0.1 ng m^{-3} within periods of 24 hours or less (Schroeder et al., 1998). The unique environmental condition at Alert that appeared to initiate this unusual behaviour was the sudden exposure to solar radiation in after five months of total darkness. The phenomenon of near complete removal of GEM from the air is termed an Atmospheric Mercury Depletion Event (AMDE) and has been found to occur around coastal regions in both the Arctic and Antarctic (Lindberg et al., 2001; Lu et al., 2001; Ebinghaus et al., 2002; Berg et al., 2003; Poissant and Pilote, 2003; Temme et al., 2003; Skov et al., 2004; Kirk et al., 2006; Steffen et al., 2008). Smaller scale observations in the Dead Sea of GEM depletion have also been reported in regions of high airborne sea salt (Obrist et al., 2011). As well, during this springtime period, tropospheric O_3 depletes from the atmosphere (Barrie et al., 1988; Simpson et al., 2007) and at the same rate as GEM (Schroeder et al., 1998; Steffen et al., 2008). This atmospheric chemistry has sparked the interest of over a decade of scientific research studies throughout the Polar Regions and has led to much discovery on how, where and why AMDEs occur.

Mercury cannot be created nor destroyed, it is only converted. It has been found that as GEM is depleted from the air, it is transformed to other mercury species (Steffen et al., 2002). During a field study at Alert in 2000, it was found that during AMDEs, approximately 50% of the transformed GEM remains in the air (as other mercury species) and it was suspected that the remainder was deposited onto the snow and ice surfaces (Steffen et al., 2002). In the same study, it was confirmed that snow samples collected after AMDEs were higher in mercury than those collected before. Further research confirmed that some of the mercury that is deposited during AMDEs is reduced back to elemental and some of it is retained by the snow and is available to enter the ecosystem (Lalonde et al., 2002; Steffen et al., 2002; Kirk, 2006; Durnford and Dastoor, 2011; Douglas et al., 2012). While there are several oxidants available to transform GEM in the polar atmosphere, it is generally thought that the springtime oxidation of GEM is by reactive halogens (Simpson et al., 2007; Steffen et al., 2008; Steffen et al., 2012a). Hg^0 is oxidized to an Hg^{2+} species as shown in Figure 1 of the general cycling of atmospheric mercury in the Arctic spring.

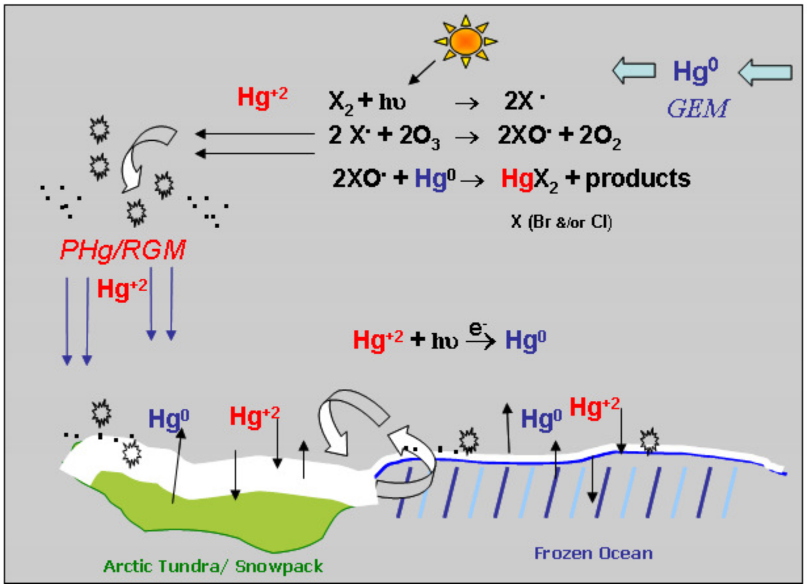

Figure 1: A general schematic of the atmospheric mercury cycle during AMDEs in the Arctic Springtime

The oxidation of Hg^0 by these reactive halogens is believed to yield inorganic Hg^{2+} compounds, though the exact products have not been determined. They are therefore grouped as RGM. RGM is more easily removed from the atmosphere either as a gas or associated to particles as PHg as they both have higher dry deposition velocities than GEM (Zhang et al., 2009). The reactive halogen species oxidizing mercury are assumed to be generated from UV radiation and halogens produced through open water regions such as leads or polynyas or refreezing sea ice (Simpson et al., 2007). High column densities of BrO clouds have been seen by the GOME satellite above areas of AMDEs and throughout the Arctic (Lu et al., 2001; Ebinghaus et al., 2002; Lindberg et al., 2002; Wangberg et al., 2003; Sprovieri et al., 2005). The conditions that are associated with AMDEs are low temperatures, air that has recently touched the sea ice, a strong inversion layer, sunlight and available sea salts. There has been some discussion over the actual amount of mercury deposited to the Arctic as a result of AMDEs. Given that there are limited kinetic data on the oxidation of mercury in the atmosphere, current models rely on observational information to constrain the accuracy of the parameters put into the models. While model simulations have predicted 200-325 Mg of mercury is deposited annually in the Arctic and ~20-60% of this deposition is attributed to AMDEs; more recent runs suggest net annual deposition between 60 and 140 Mg per year, depending on the model and the area represented (Kirk et al., 2012). There still remain limitations in the accuracy of the model predictions from the atmospheric mercury side because the processes that GEM undergoes in the Arctic system are not fully realized, the changes in the Arctic climate are continually occurring and the exact chemical identity of RGM and PHg remain unknown.

1.5 Policy drivers for mercury

Mercury continues to be a risk to the health of humans and wildlife all around the world. The main exposure route of mercury is through consumption of fish or marine mammals. The Arctic is an area that is vulnerable to this risk and thus there is a need for governmental input into regulating and decreasing mercury exposure when possible. In 2003, the United Nations Environment Program (UNEP) governing council decided that there was enough evidence that mercury causes global impacts and warranted international action to reduce risks to human health and the environment (AMAP, 2011). There currently exist international agreements that address mercury issues including the United Nations Economic Commission for Europe–Long-range Transboundary Air Pollution (UNECE-LRTAP), United Nations Environment Program (UNEP) Heavy Metals Protocol, UNEP Fate and Transport partnerships and the currently negotiated Minimata Convention on Mercury that will be open for signature in the fall of 2013. These international agreements are intended to limit emissions of mercury and will hopefully, in turn, reduce the contamination of mercury within the Arctic region.

1.6 Research objectives

The overall objective of the research presented in this thesis was to investigate processes in the Arctic air that can impact atmospheric mercury depletion events (AMDEs). Figure 2 shows the locations of the pertinent research undertaken for this work at Barrow, USA and Alert, Canada. This project began with an assessment of the current understanding of atmospheric mercury in Polar Regions with an emphasis on the springtime chemistry. Gaps in our understanding of the cycling of speciated mercury around the sea ice and over long periods of time were identified and some questions resulting from these gaps were addressed in the remainder of the project.

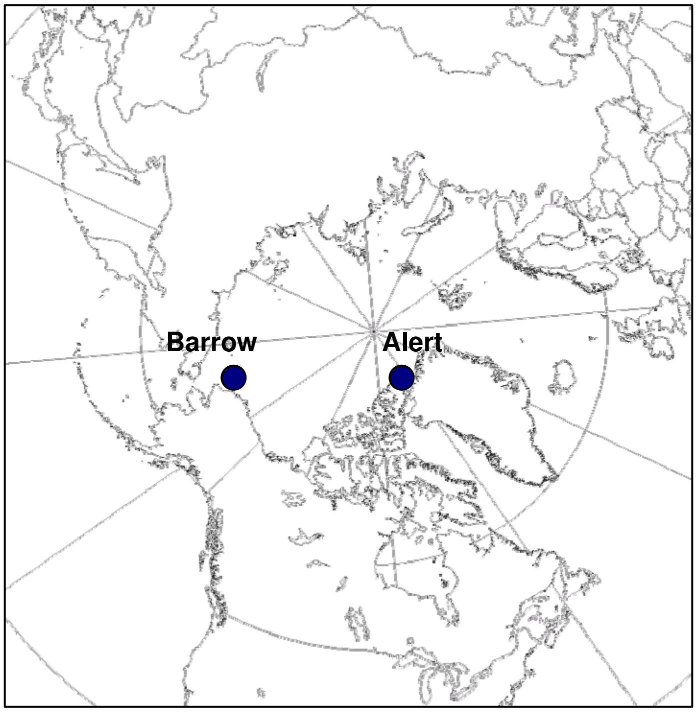

Figure 2: Map of locations of study sites: Barrow, Alaska, US and Alert, Nunavut, Canada

The first question was what can be learned about the AMDE chemistry and processes from atmospheric speciated mercury information over time? This was addressed by collecting and investigating long term atmospheric mercury data from Alert, Nunavut in order to ascertain what factors impact the springtime behaviour over time. There are few atmospheric mercury data available from the high Arctic over long time periods and this extensive data set provided significant insight into recurring annual processes that occur. Another question that was addressed with the long term data set was under what conditions is mercury is transferred to the snow during AMDEs? The mercury data from Alert was coupled with meteorological, aerosol and snow data which enabled an in-depth investigation of the springtime chemistry for almost ten seasons.

An additional question identified in the review paper was, since there exists little to no information about it, how do atmospheric conditions influence the atmospheric speciation of mercury over the sea ice where AMDE chemistry was thought to originate? The need for improvements of field techniques to collect atmospheric mercury data over the sea ice was acknowledged and the International Polar Year (IPY) provided a perfect opportunity to undertake this type of investigation because a significant amount of work in the Arctic was being funded. Under the IPY, the Ocean-Atmosphere-Sea-Ice-Snowpack (OASIS) program conducted a month long field campaign in and off the coast of Barrow, Alaska on the Chukchi Sea. The goal of this study was to determine whether the sea ice surface characteristics affect the overlying mercury behaviour. For the first time, speciated atmospheric mercury measurements were collected over freshly formed sea ice along with O_3, meteorological and other data. Overcoming the logistics of this task was an accomplishment in itself and considerable work was undertaken to be able to collect the data in this challenging environment. This work enabled an assessment of whether there were differences in the chemistry over the sea ice in comparison to inland (where most previous measurements have been reported) and to investigate physical and chemical processes right at the sea ice surface.

The papers included in this thesis focus on the atmospheric contribution to the cycling of mercury in the high Arctic and the specific goals of each paper are as follows:

Paper #1: A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow

The objective of this review article was to provide a comprehensive synthesis of the currently available science behind AMDEs and the research that occurred in the ten years following the discovery of AMDEs. This paper examined features of the environmental importance of Hg in Polar Regions and outlined the measurement techniques used in both the Arctic field and laboratory experiments. A summary of results from investigations into Arctic atmospheric processes was presented and included current modeling efforts to better predict deposition. The review concluded by identifying gaps in our current understanding of mercury in polar environments and offered an outlook of potential future directions of Hg research in Polar Regions. The gaps identified that are relevant to the remainder of this thesis include: the need for improvements of field techniques to collect atmospheric mercury data, the need to increase our understanding of the impacts of sea ice changes on AMDEs, understand how mercury enters the upper ocean water from the atmosphere, the need to improve knowledge of the processes that drive deposition and re-emission of mercury in the Arctic and the need for more intensified long term monitoring throughout the Arctic.

Paper #2: Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada

The objective of this paper was to provide insight into the springtime processes that govern the transformation and deposition of mercury to the high Arctic through long term atmospheric mercury speciation measurements. Further, this paper aimed to assess if there exist links between atmospheric parameters such as aerosols, air temperature and humidity on the speciation and deposition of mercury in the springtime. This research also set out to understand the link between the levels of mercury in the atmosphere and in the surrounding snow.

Paper #3: Atmospheric mercury over sea ice during the OASIS-2009 campaign

The objective of this paper was to assess if atmospheric mercury speciation measurements could be made out on the sea ice and if so, how does speciated mercury behave over the sea ice? This was done by developing a system that could be brought out on the ice and make the appropriate measurements. The OASIS field study provided the opportunity to use this system on the sea ice and collect novel information about mercury speciation. This paper also set out to assess if there are the differences between GEM behaviour over the tundra snow pack and sea by making simultaneous measurements at two locations throughout the campaign.

The overall aim of these three papers is to further our understanding of what factors affect the depletion of GEM in the springtime and therefore the cycling of mercury in the high Arctic.

Chapter 2: Experimental

There are many methods employed to measure mercury in the environment. Paper #1: *A Synthesis of Atmospheric Mercury Depletion Event Chemistry in the Atmosphere and Snow* provides a summary of the methods used to determine mercury levels in air, water and snow throughout arctic studies. The section below describes the locations and experimental procedures used in the studies of atmospheric mercury and snow in the high Arctic outlined in Paper #2: *Understanding Atmospheric Mercury Speciation and Mercury in Snow over Time at Alert, Canada* and Paper #3: *Atmospheric Mercury over Sea Ice during the OASIS-2009 Campaign.*

2.1 Sampling locations

The long term atmospheric measurements at Alert were collected using both the Tekran 2537A mercury vapour analyser and the Tekran 2537/1130/1135 system. Alert, Nunavut, Canada is located at 82.5ºN and 62.3ºW, 800km from the geographic North Pole. The mercury instrumentation is located at the Dr. Neil Trivett Global Atmospheric Watch (GAW) Observatory on the north eastern edge of Ellesmere Island. The laboratory is located approximately 8km from the shore of the Lincoln Sea and is at an elevation of 195m a.s.l. The Tekran systems are located on an outside walk up tower approximately 3 metres above the ground (Figure 3a). The tables from which the snow samples were collected are located approximately 200 m south of the laboratory (Figure 3a). The Barrow, Alaska, USA study was mostly undertaken over the Chukchi Sea near the town of Barrow located at 71.29ºN and 156.85ºW. The instruments were housed in aluminum boxes (called the "Out On The Ice" (OOTI) system) and were towed on specially designed sleds behind snowmobiles onto the Arctic sea ice and placed as closely as possible to open leads. The inlet of the Hg speciation system was approximately 15 cm above the snow pack or ice surface (Figure 3b). The second mercury system was located inland with an inlet height of 85 cm from the snow surface.

2.2 Atmospheric measurements

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, 1998) for atmospheric measurements.

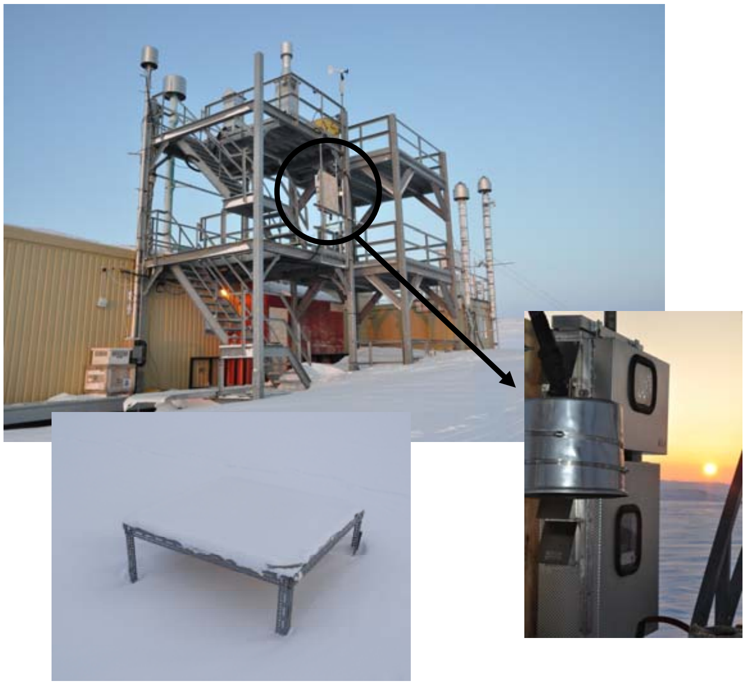

Figure 3a: Atmospheric mercury measurement sample system and snow sampling table (bottom left) at Alert, Nunavut

Figure 3b: Atmospheric mercury measurement sample system employed at Barrow, Alaska

The basic principle and sequence of operation is initially pre-concentration of GEM onto a trap, the removal of the GEM from the trap by thermal desorption and detection and quantification using spectroscopic methods. Calibration of GEM is well documented (Schroeder and Munthe, 1998; Aspmo et al., 2005; Temme et al., 2007) and employs injecting a known quantity of saturated mercury vapour that is maintained at constant temperature. A vapour pressure versus temperature relationship is then used to determine the injected amount (Gustin and Jaffe, 2010).

The automated semi-continuous Tekran 2537A coupled with the Tekran 1130/1135 systems has been employed to measure atmospheric mercury species GEM, RGM and PHg. To measure GEM alone the Tekran 2537A instrument can be used. This instrument operates by drawing in air using an internal pump through a quartz tube filled with gold beads where the mercury in the air amalgamates to the gold in the trap. After the system collects the air for a preset amount of time (usually 5-30 minutes), the gold trap is heated to a temperature around 500ºC which releases the GEM from the trap into a carrier gas of ultra high purity argon. The desorbed mercury is carried into a cold vapour atomic fluorescence spectrometer for detection and the instrument quantifies the mercury using an internal calibration system. The system provides continuous measurements because there are two gold traps used; while one trap collects the sample, the other is being analysed. Some researchers report ambient air collected with this method as total gaseous mercury (TGM) which includes both the GEM and RGM species (Ebinghaus et al., 2002), however, because a filter was placed at the inlet of the sample lines for this type of sampling, it is most likely that RGM is removed by this filter and thus only GEM is collected (Steffen et al., 2002). Thus, for work presented in this thesis, GEM is the reported mercury species when only the Tekran 2537A instrument is used.

To measure GEM, RGM and PHg together, the Tekran 2537A system is used along with two additional units that are placed at the front end of the instrument to separate RGM and PHg mercury species sequentially. GEM samples are collected continuously on 5 minute intervals while RGM/PHg are collected for longer and then analyzed over a period of an hour. Thus, the data collected with this system is not continuous. The RGM species are physically separated by a KCl coated denuder and PHg is removed from the air using a quartz fibre filter. RGM is thought primarily to be either $HgCl_2$ and/or $HgBr_2$ which are both known to adhere to KCl (Landis et al., 2002). The inlet of this system includes an impactor and elutriator where air is pulled through the inlet and only particles below 2.5μm are allowed to enter the sampling system. Air is pulled into the system at 10 litres per minute; the RGM and PHg are sampled at this flow rate and collected for 1-2 hours while, at the same time, GEM is sampled at a flow rate of 1 litre per minute. A diagram of the system is shown in Figure 4. The separation of the three species is as follows: the air is pulled into the system where RGM adheres to the KCl coated denuder, PHg is trapped on the quartz fibre filter and GEM is allowed to pass through the system and is measured each 5 minutes. GEM is reported as a concentration in nanograms of mercury per cubic metre of air by the Tekran 2537A. After the preset sampling period is complete, the instrument switches to analysis mode where mercury-free air is pushed through to remove any residual GEM and provide a blank sample for quality control purposes. At this point the sequential analysis of PHg and RGM is undertaken. The system contains a pyrolysis chamber consisting of broken quartz that is first heated and maintained at 800°C. The purpose of this chamber is to pyrolyse (thermally decompose) all mercury compounds to elemental Hg (GEM) so that the sample is detected as GEM by the Tekran 2537A. The pyrolyser is heated for 5 minutes and then the quartz filter is heated to 800°C so that the mercury on the particles is driven off the filter, flows over the quartz chips in the pyrolyser and the mercury in the air is analysed by the Tekran 2537A. The system desorbs the quartz filter for 15 minutes to ensure complete removal of the PHg. The system then begins to heat the denuder to 500°C where the RGM is driven off the KCl coating, passes through the pyrolyser and goes to the Tekran 2537A for analysis. The denuder is heated for 15 minutes to ensure all RGM is removed. Finally, the system is cooled down and mercury free air is passed through for 10 minutes to provide a second blank for the samples. All concentrations of RGM and PHg are reported as total elemental mercury. A scale factor is applied to this total to reflect the volume of air sampled by the denuder and quartz filter and produces a concentration in picograms of mercury per cubic metre of air.

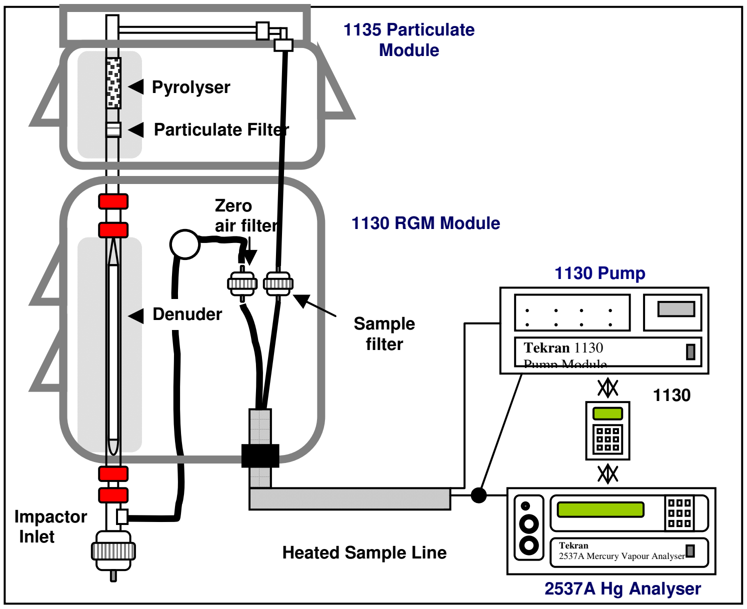

Figure 4: A schematic of the Tekran 2537/1130/1135 sampling instrument

The GEM measurements are calibrated using an external standard and these calibrations are well documented (Temme et al., 2007). Calibration of RGM and PHg remain part of ongoing discussions within the research community (Aspmo et al., 2005; Gustin and Jaffe, 2010). Feng et al. (2003) evaluated a diffusion-type device to calibrate the denuder based system for RGM sampling and found that this system, if modified, could be used for calibration. However, no calibration system is currently available that can be used by the research community to establish the accuracy of the RGM and PHg. Therefore, this significant limitation in the analytical capabilities of RGM and PHg detection must be prudently identified and considered when reporting information about RGM/PHg concentrations. For this reason, rigorous quality control (QC) and quality assurance (QA) protocols on the data sets have been developed and applied using the instrument function parameters and desorption cycles as the feedback on the instrument performance. This does not negate the need for standards but it allows for some confidence in interpreting the RGM/PHg data relative to each other. Flagging criteria were developed for data collected with the Tekran 2537A/1130/1135 systems and are described in Steffen et al. (2012b). Using knowledge and experience of instrument performance and data fluctuations, an automated computer program was developed to apply the same criteria to each data point. These criteria identify variations and outliers in the recorded instrument parameters and variations in the measured concentrations. The software program employs algorithms that apply the flagging criteria to all the data. Flags represent a shorthand code that is applied to the data based on established QC criteria and are characterized as either valid or invalid. Invalid flags represent data that fall outside the specified criterion or are non-representative values within the dataset. Data that are flagged invalid are not included in the final QCed dataset. Valid flags represent data deemed questionable according to the established QC criteria. The valid flags act as tools to highlight questionable data which signals the person reviewing the data. The data is investigated in detail so that each valid and invalid flag is reviewed and assessed for validity. This is a time consuming process but allows for greater confidence in the data presented and allows for intercomparison between collected data sets.

2.3 Snow measurements

As part of this thesis, snow samples were collected at several locations during the research. For the measurements collected at Alert, the snow was collected both on PTFE-coated tables and from the ground located behind the GAW lab (Steffen et al., 2008; Steffen et al., 2013b). Snow samples are collected on a snow event basis when the local operator is available to collect the sample. Samples are collected in glass jars using gloved hands, a PTFE scraper and a scoop made from a PTFE bottle. The snow is collected into a pile with the scraper and scooped into glass jars from the snow tables. The tables are divided into three sections and each area of sample collected is measured. When the samples have been collected, the remainder of snow is scraped off so that the table is left blank and ready to collect the next snowfall. Using a very similar procedure, ground samples are collected close to the tables. The surface snow (approximately 1cm deep) is scraped into a pile using a Teflon scraper. The snow is then scooped into the glass sample jars. Snow samples are kept in the jars in sealed zip locked bags, in coolers and are kept frozen. The coolers are filled with snow and hand carried from Alert to Toronto where they remain frozen until analysis. During the Barrow study the snow samples were collected from the surface of the snow pack using precleaned high density polyethylene (HDPE) jars and a precleaned HDPE scoop. Both sets of samples were maintained frozen and brought from the Arctic to laboratories where they were analysed for total mercury and some ions.

Chapter 3: Research Summary, Discussion and Conclusions

This thesis project combined a synthesis of available research on atmospheric mercury depletion events (AMDEs) with novel research that has significantly contributed to scientific knowledge on the cycling of atmospheric mercury in the Arctic during springtime. Since the discovery of AMDEs in 1995, how mercury behaves in the air has been studied by many. The research presented here has provided a unique perspective on this chemistry because it made use of the longest available atmospheric mercury data set that exists and collected data from directly over the Arctic Ocean which had never been done before. The highlighted results of this thesis are discussed in the following sections while the details of the research are given in the individual papers.

The highlights are divided as follows:
3.1 The background and synthesis of available research on AMDEs ten years following the discovery
3.2 Atmospheric mercury speciation over time and the impact of atmospheric parameters on its distribution
3.3 The impact of the atmosphere on mercury levels in snow
3.4 Atmospheric mercury over the sea ice

3.1 The background and synthesis of available research ten years following the discovery of AMDEs

The first continuous measurements of surface level atmospheric mercury (Hg) concentrations began at Alert, Canada in 1995. Between March and June, episodically very low concentrations of gaseous elemental mercury (GEM) were observed (Schroeder et al., 1998). It was found that after polar 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 hours or less. To appreciate the significance of these results, it should be understood that until that time the atmospheric residence time of GEM was thought be 6-24 months (Schroeder and Munthe, 1998) and little variation had been reported. 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 five months of total darkness. These episodes of low GEM concentrations were strongly correlated with similar periods of low ground level O_3. The phenomenon of low episodic springtime GEM concentrations, termed atmospheric mercury depletion events (AMDEs), are an annually recurring spring time phenomenon (Steffen et al., 2005) and have been reported throughout Polar Regions (Steffen et al., 2008). It is known that a unique series of photochemically initiated reactions involving ozone and halogen compounds, largely of marine origin and especially bromine oxides, lead to the destruction of O_3 (Simpson et al., 2007). It is believed that the BrO/Br radicals, produced through multiphase chain reactions, oxidize GEM to reactive gaseous mercury (RGM) and/or mercury associated to particles as particulate mercury (PHg) that are readily scavenged by snow and ice surfaces (Schroeder et al., 1998; Ariya and Ryzhkov, 2003; Simpson et al., 2007; Poissant et al., 2008). While there are mechanisms and theoretical calculations that suggest that RGM is predominantly a bromide compound (Calvert and Lindberg, 2004), its identity has not been directly elucidated and thus RGM and PHg are operationally defined. The occurrence of AMDEs demonstrates that there are mechanisms of fast removal of mercury from the atmosphere that require the presence of mercury, sunlight, ozone and reactive halogens.

The fate of the RGM and PHg produced during an AMDE, including how much is deposited to the snow and ice, is unclear. Reports of elevated levels of total mercury in snow around depletion events at coastal sites range between 20 and 100 ng L^{-1} (Lu et al., 2001; Lindberg et al., 2002; Steffen et al., 2002; Berg et al., 2003; Poulain et al., 2004; Lahoutifard et al., 2005). This work covered a wide spatial extent as research was made at numerous Arctic and Antarctic locations; however, few of these measurements were part of long term studies. Some of the deposited RGM/PHg was found to be reduced to GEM and subsequently re-emitted to the atmosphere while some remained or was re-oxidised at or within the snow pack. Flux measurements showed that there was a net deposition of mercury to the snow in the dark, a net zero emission during the spring followed by a net emission of mercury in the summer (Steffen et al., 2005; Cobbett et al., 2007). Further, several studies reported a loss of mercury from the snow pack within days of deposition of mercury after an AMDE (Poulain et al., 2004; Ferrari et al., 2005). The review paper concluded that the importance of snow to air transfers of GEM should not be assessed through short-term studies because of time-dependent factors including solar irradiation, the chemical composition of the snow, the site characteristics and the snow pack characteristics. Further, as snow melt begins, GEM in interstitial snow pack air was found to increase to concentration values of more than ten times that above the snow surface (Dommergue et al., 2003b; Dommergue et al., 2003a) which can impact the atmospheric concentration of GEM (Lindberg et al., 2001). Aqueous and gaseous redox process studies showed that reduction can occur in the snow pack and may have an impact on the levels of mercury in melt water in the latter part of the spring (Dommergue et al., 2003a; Gardfeldt and Jonsson, 2003; Ferrari et al., 2004). Although most of the measurements for mercury in Arctic ecosystems have been for total mercury, it is methyl mercury that is the most toxic and environmentally relevant form because it biomagnifies in food chains. After measuring high levels of methyl mercury in high Arctic snow (up to 280 pg L^{-1}), St Louis *et al.* (2005) proposed that methyl mercury may be produced abiotically from the photochemical breakdown of dimethyl mercury from the ocean. They further suggested that it is possible that increased atmospheric loadings of mercury (RGM/PHg) could lead to enhanced methyl mercury in precipitation. Increases in bioavailable mercury following AMDEs were found but a direct link to AMDEs and methyl mercury concentrations in the snow were not made. Whatever the source of methyl mercury in the Arctic, it was 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.

The role of the sea ice in the cycling of atmospheric mercury was studied. The sea ice offers an environment enhanced in halogen concentrations from the wicking of halogen rich brines to the sea ice surface during ice growth. Snow and 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; Simpson et al., 2005; Jacobi et al., 2006a, b; Simpson et al., 2007). The ocean plays a key role in the biogeochemical cycling of mercury (Mason and Sheu, 2002) yet there is limited information about the processes occurring with mercury in Arctic coastal and marine waters (Aspmo et al., 2006). There are elevated levels of methyl mercury in Arctic snow close to marine locations and AMDEs are thought to be driven by the sea ice yet the role that the Arctic Ocean plays in the mercury cycle remained a large unknown. Figure 5 shows the overall schematic of mercury cycling presented in this paper.

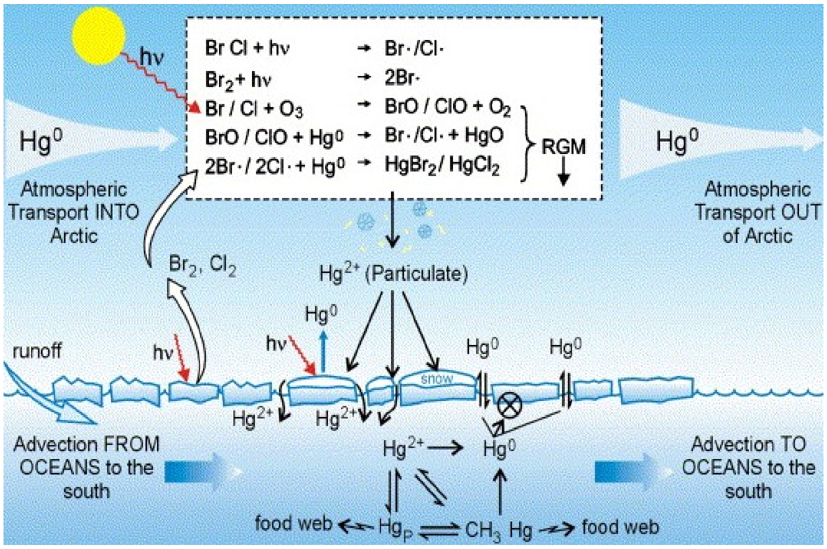

Figure 5: A schematic of the overall cycling of mercury in Polar Regions (from Steffen *et al.*, 2008)

Regional and global models of the transport and deposition of mercury have incorporated AMDEs and indicate that AMDEs affect the amount of annual mercury deposited to Polar Regions. The modeling studies reported that long range transport of mercury to the Arctic can occur and that the source regions mainly include Eurasia, Europe and North America (Dastoor and Larocque, 2004; Jaffe et al., 2005; Travnikov, 2005). A comparison of the existing models for mercury (including some processes during AMDEs) was done and found that all the models capture the springtime depletion to some degree but fail to simulate the above average mercury concentrations observed following the AMDEs at some sites indicating that a thorough understanding of the processes was still lacking (Ryaboshapko et al., 2007). Some of the missing processes include re-emission of mercury after a depletion event and deposition of mercury during depletion events.

Several gaps of information were identified and highlighted recommendations for future research. The most significant gap, which remains today, was the lack of identification of the exact chemical species of mercury produced during AMDEs (*i.e.* the identity of RGM and PHg). This identification is vital to quantitatively assessing the current and future impacts of AMDEs on the Arctic ecosystem. Several additions to the models were recommended including fully incorporating the chemical processes that drive mercury deposition and re-emission. Further, it was recommended that field campaigns, as well as laboratory and theoretical calculations, must continue to elucidate the sea ice mercury interactions and their potential global impact. With the addition of more long term stations measuring atmospheric Hg species throughout the Arctic and the Antarctic, the models can be greatly refined. Another significant gap identified was how mercury enters the upper ocean water from the atmosphere. Given that one third of the Arctic is covered by the Arctic Ocean, how this material is fed into this system was deemed important to understand. As well, because methyl mercury is the toxic form that dictates the accumulation of mercury in polar environments, the processes under which methyl mercury is produced in polar environments need to be better understood. Finally, multidisciplinary investigations combining soil and ice microbiology, atmospheric chemistry, oceanography and laboratory investigations provide the greatest breakthroughs in assessing the long term fate of mercury in the Polar ecosystems. Therefore, it was deemed 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. This paper concluded that with the onset of the International Polar Year (2007-2009), the next ten years of mercury chemical investigations in the Polar Regions will move the science toward a better overall comprehension of Arctic system processes.

Several of the recommendations from this review paper served as the bases for the scientific questions investigated in this thesis. These questions include what can be learned about the AMDE chemistry and processes from atmospheric speciated mercury information over long periods of time, under what conditions is mercury transferred to the snow during AMDEs, how do atmospheric conditions influence the atmospheric speciation of mercury over the sea ice and is there a difference in mercury in the air over the sea ice than inland?

3.2 Atmospheric mercury speciation over time and the impact of atmospheric parameters on its distribution

The atmospheric processes that dominate the springtime oxidation and deposition of mercury can drive transported mercury onto the Arctic surface. During the polar spring, GEM oxidizes to RGM (Schroeder et al., 1998; Lindberg et al., 2001). RGM can either remain in the air as a gas or adsorbed to particles (PHg). The decrease in GEM is generally coincidental with an increase in speciated mercury (PHg and RGM) (Lindberg et al., 2001; Lindberg et al., 2002; Aspmo et al., 2005; Kirk et al., 2006; Cobbett et al., 2007; Dastoor et al., 2008; Steffen et al., 2008; Steen et al., 2011). Few data sets of speciated atmospheric mercury in the high Arctic have looked at processes in the high Arctic over the long term. Hence, an analysis of ten years of mercury sampling in air coupled with atmospheric meteorological and particle measurements from Alert was performed.

Alert is a high Arctic site, located at the tip of Ellesmere Island, Nunavut, Canada. Long term atmospheric measurements of GEM have been undertaken since 1995 (Schroeder et al., 1998; Cole and Steffen, 2010) and speciation data have been collected since 2002. The lifetime of atmospheric mercury depends on its chemical form and is considered to be GEM>>PHg>RGM (Schroeder and Munthe, 1998). The complete data sets of GEM, PHg and RGM concentrations from Alert are shown by month in Figure 6 and reveal distinct seasonal signatures for all three species. The descriptive statistics for the PHg and RGM data are reported in Table 1. This information clearly reflects the springtime depression of GEM and the increases of PHg and RGM. Most interestingly, Figure 6 shows the clear decrease in GEM in March concurrent with a notable increase in PHg followed by an increase in RGM in May. PHg reaches its maximum in April and then trails off. In May, the RGM concentrations are highest and trail off into June when GEM concentrations begin to increase again.

This transition from PHg to RGM was previously reported for individual years (Kirk et al., 2006; Cobbett et al., 2007) but this research shows it occured each year for ten years within the same two week time period and thus warranted further investigation. Relative humidity, air temperature and particle concentration were investigated for their possible roles in the fractionation and transition of mercury species at Alert.

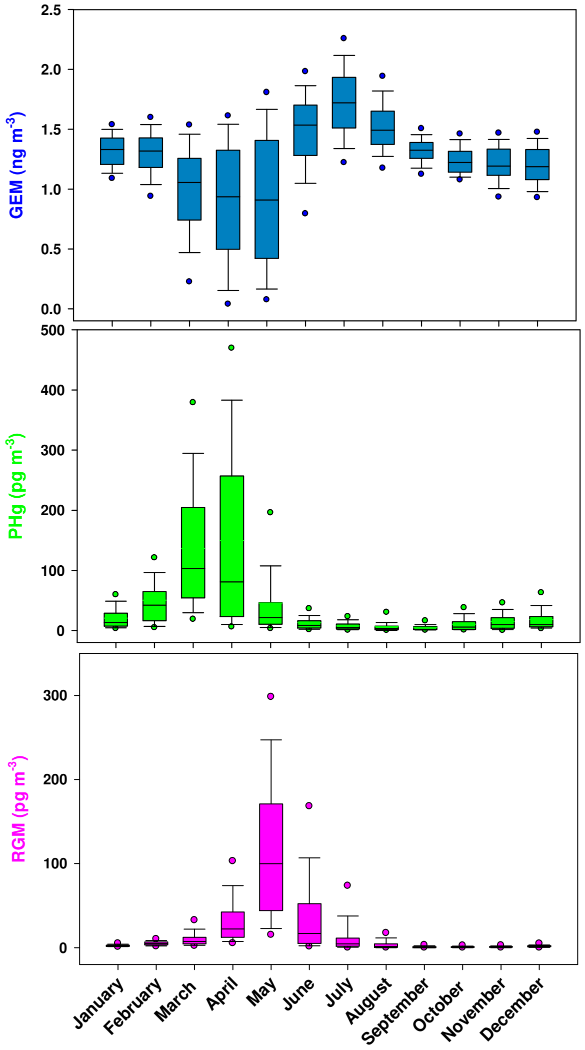

Figure 6: Box and whisker plots of monthly gaseous elemental mercury (GEM- blue), particulate mercury (PHg-green) and reactive gaseous mercury (RGM-pink) from Alert, 2002-2011. GEM is in ng m^{-3} and PHg and RGM are in pg m^{-3}
(Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set)

PHg	Mean	Median	Std Dev	Maximum	Air Temp
January	20.4	13.39	18.08	99.26	-28.0
February	50.26	41.87	53.31	520.54	-30.3
March	136.67	102.60	110.38	541.51	-30.5
April	149.58	80.56	154.48	748.69	-22.8
May	45.46	21.15	71.74	698.03	-10.6
June	12.76	8.40	15.45	153.33	-0.18
July	7.36	4.66	7.10	40.98	+4.3
August	6.22	3.38	9.55	85.76	+2.2
September	5.30	4.54	5.39	48.26	-7.39
October	10.25	5.46	12.37	70.40	-16.5
November	15.25	9.61	17.46	122.30	-23.2
December	18.35	9.58	21.91	135.62	-27.4
Overall	41.3	11.3	82.3	748.69	

RGM	Mean	Median	Std Dev	Maximum
January	2.36	2.13	1.22	7.79
February	5.25	4.98	2.92	37.57
March	11.35	7.40	15.63	220.56
April	33.96	22.20	35.78	331.87
May	120.11	99.88	94.67	877.85
June	41.09	16.76	62.13	718.02
July	14.78	4.60	30.77	260.95
August	4.35	1.46	8.75	108.82
September	1.01	0.71	1.37	13.93
October	0.88	0.70	0.90	7.99
November	1.08	0.94	0.99	10.71
December	1.86	1.71	1.98	20.72
Overall	22.6	3.17	51.99	877.85

Note Minimum values for PHg ranged from 0 to 1.6 and for RGM 0 to 0.4

Table 1: Descriptive statistics of PHg (top) and RGM (bottom) for monthly data and overall data between 2002 and 2011 at Alert, Canada. All concentrations for mean, median, standard deviation (std dev) and maximum are reported in pg m^{-3}

It was concluded that relative humidity, relating to water absorption by aerosols, may affect the transition of PHg to RGM from April to May; however, we suggest that other factors impact the transition more effectively. The dependence of the transition on the air temperature was investigated by looking at the fraction of PHg relative to the total oxidized mercury (RGM+PHg). The results show that there is an inverse correlation of the PHg fraction with air temperature; at lower air temperature there is a higher fraction of PHg in the air. This relationship was investigated for six years (data gaps in four of the years prevented analysis of all ten) and was found to be significant for most of the years as shown in Figure 7. In the years where there was not as significant a relationship anomalous PHg concentrations were reported in June. Before the transition (March to April), when the fraction was predominantly PHg, the median air temperature was -24.8°C and after the transition, when the fraction was predominantly RGM, it was -5.8°C. Thus, these results show that PHg is predominant at lower temperatures and suggests that the lower temperatures drive the partitioning of oxidized mercury from RGM towards PHg. Studies have predicted that in colder air masses the predominant Hg^{2+} fraction will be PHg rather than RGM (Rutter and Schauer, 2007a; Amos et al., 2012) and these results confirm these predictions. It was concluded that temperature is a significant driver in the transition of PHg to RGM at Alert during the spring.

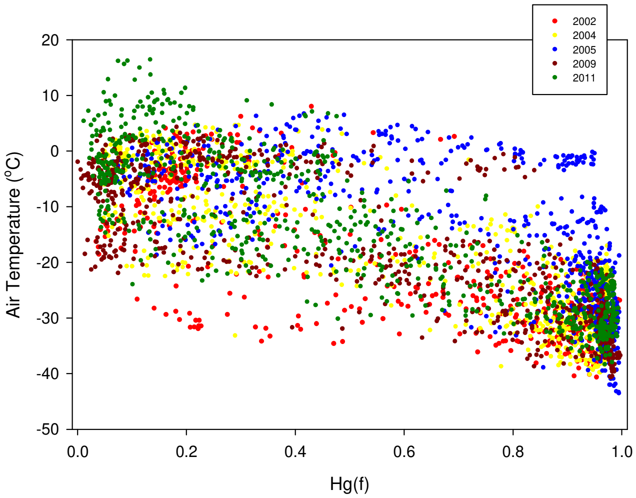

Figure 7: Springtime Air Temperature (°C) versus the fraction of mercury in the particulate phase (PHg/RGM+PHg)

Aerosol particles have been studied at Alert since 1980 (Barrie, 1986; Barrie et al., 1989; Gong et al., 1997; Sirois and Barrie, 1999; Sharma et al., 2004). Arctic Haze results from polluted air masses originating from anthropogenic emissions in Europe, North America and the former Soviet Union, that are transported to and trapped in the Arctic air. The haze primarily consists of sulphate and carbonaceous particles, maximizing in March and April (Sharma et al., 2004; Quinn et al., 2007). The potential impact of the atmospheric aerosol loading on the speciation transition from PHg to RGM was the last factor investigated. The aerosol levels were investigated in two ways: 1) by using the particle light back scattering measurements to measure the surface area of submicron aerosols and 2) by the concentration of the sub-500 nm diameter particles. Results from this analysis from years

2004-2010, Figure 8, showed that from January to April both the backscattering and PHg fraction are relatively steady. In May, when the transition from PHg to RGM occurs, the PHg fraction decreases to lower values concurrent with a significant decrease in the backscattering.

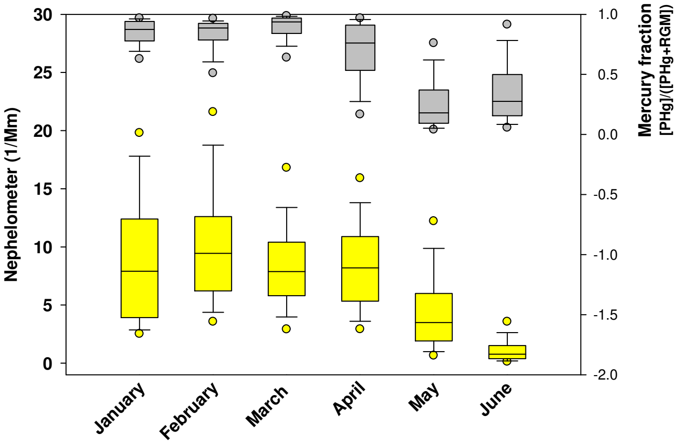

Figure 8: Box and whisker plots of monthly fraction of mercury as PHg (top) and backscattering to measure the surface area of submicron aerosols (bottom)
(Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set)

In 2011 only, PHg concentration was investigated with the total volume concentration of particles less than 500 nm during March through June. It was found that higher PHg concentration is associated with higher particle volume for March and April, May is a transition month to lower particle volume and June shows no association with PHg. That result is consistent with the trend of backscattering and PHg fraction reported, indicating that a larger PHg fraction is associated with higher concentrations of particle surface area and volume. Since PHg is believed to be due to RGM adherence to particles in the air (Sheu and Mason, 2004) it is conceivable that, during AMDE season, the presence of more particle surface area or volume in the air may contribute to a shift of RGM to PHg from March to April. Higher particle volume concentrations from January to April are linked with Arctic Haze (Barrie, 1986) and it is hypothesized that the presence of Arctic haze is a significant contributor to the increased levels of PHg during this period. Other aerosols such as sea salts and ice crystals are also common during the spring at Alert. Both these aerosols are effective scavengers of RGM and have been associated with elevated levels of PHg and total mercury in the snow (Rutter and Schauer, 2007b; Douglas et al., 2008; Malcolm et al., 2010; Steffen et al., 2013a). Partitioning of gas-phase mercury to particles can be dependent on the composition of the aerosol (Rutter and Schauer, 2007b). Particles containing sodium nitrate and sea salt components have shown the highest partition coefficients. Each year PHg at Alert begins to increase in March and then climbs to a maximum in April, concurrent with sea salt and arctic haze particle increases. Further study is required to identify which types of particles dominate both the atmospheric transition and deposition of mercury in the spring.

Ten years of atmospheric speciated mercury measurements at Alert reveal strong seasonality as well as significant variability within the spring season. It is concluded that the transition in mercury speciation between particle phase and gas phase is primarily due to a combination of air temperature and particle concentration. These two factors may be changing over the next few decades as a result of climate change and increased pollution emissions. Consequently, these new process findings on the cycling of mercury during AMDEs need to be incorporated into mercury models to better predict the chemistry and total deposition of mercury in the high Arctic.

3.3 The impact of the atmosphere on mercury levels in snow

Mercury can be deposited onto the snow and ice surfaces enabling its distribution into the environment. All three forms of mercury can deposit from the atmosphere to the snow surface and it has been shown that there is an increase in total mercury concentration in snow around following AMDEs (Steffen et al., 2008). A review of the behaviour of mercury species in snow concluded that PHg deposited to snow is likely to remain in the snow pack, GEM is immediately re-emitted and RGM undergoes several processes including photo reduction, emission and oxidation in the snow and thus its fate is uncertain (Durnford and Dastoor, 2011). Since 1998, snow samples have been collected repeatedly on a table and nearby snow surface at Alert in the spring just after snow events to examine total mercury concentration. The snow sampling was undertaken to investigate springtime chemistry and thus occurred only during the months of February to June. Collecting snow on a table in this manner may provide a more accurate representation of Hg that is removed from the atmosphere by snow. Surface samples are generally collected from the first 1 cm of the snow pack but accurately limiting the sampling to that level is challenging and in any case may well contain some older snow which would bias the concentrations. Furthermore, surface/ground snow samples can be compromised by contribution from blowing snow, multiple snow events and loss of deposited material to deeper layers of the snow pack. Results from this long term study reveal that there is significantly lower Hg concentrations observed from the ground samples in comparison to the table samples, reinforcing the use of snow table sampling to isolate the atmospheres influence on the levels of mercury in the snow. Results of this analysis show that there are small but slowly increasing amounts of Hg in the snow from February to April and that the levels peak in May and then trail off in June. There have been reports of similar observations from short term field studies (Lu et al., 2001; Durnford and Dastoor, 2011) but nothing this extensive over such a long period of time.

As discussed in Section 3.2, there is a transition in the spring from PHg to RGM in the air at Alert. The relationship between the level of mercury in the snow and the atmosphere was explored. Figure 9 shows the mercury concentration in snow from the table sampling (2002-2011) plotted together with PHg and RGM concentrations from February to June (averaged for each Julian day for all data from 2002 to 2011). This figure shows that when the PHg to RGM transition occurs in the atmosphere, there is an increase in mercury levels in the snow. This was found to repeat each year without fail, when snow samples were collected, over the ten-year period. We conclude that the highest deposition of mercury to the snow in the Arctic depends on what form of mercury is present in the atmosphere and the atmospheric conditions that lead to the presence of a given mercury fraction in the air. PHg is scavenged by snow (Amos et al., 2012) which will aid in the deposition of PHg to the snow surface. The decrease in PHg, and drop in particle numbers, in late April/early May coincides with the initial increase of Hg in the snow. Subsequently, the levels of mercury in snow keep rising (and falling) concurrently with the concentration of RGM. RGM is known to have a high dry deposition velocity (Zhang et al., 2009) and can readily deposit onto the snow surfaces which could explain these trends.

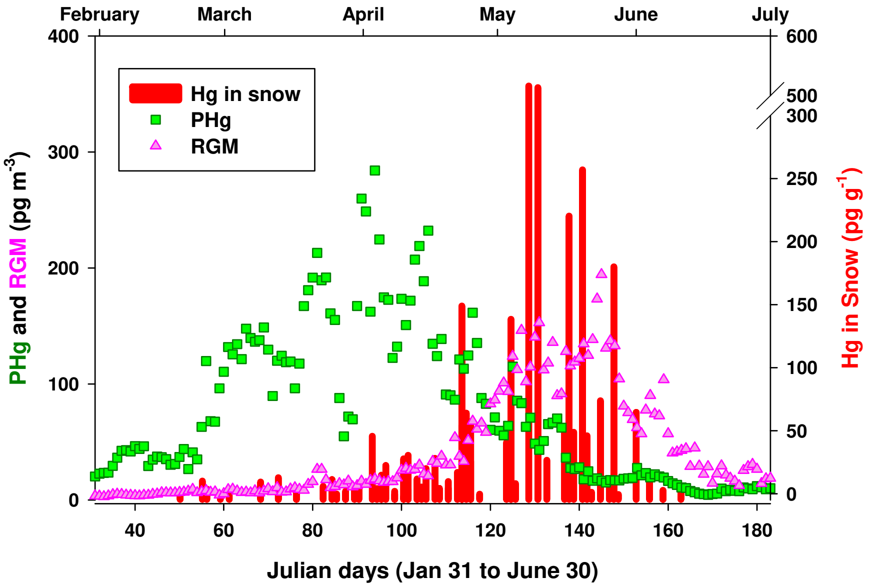

Figure 9: Atmospheric mercury speciation concentration data PHg and RGM (pg m^{-3}) and Hg concentration (pg g^{-1}) from the snow (table) from February to June for all data from 2002 to 2011. The atmospheric data has been averaged per Julian day over all the years

The results show that there are elevated levels of mercury in the snow in the Arctic spring during AMDE season. As well, the highest deposition to the snow in the spring at Alert is during and after the transition of PHg to RGM in the atmosphere. This latter finding is significant because current models that estimate the total deposition of mercury from the atmosphere are validated using measurements that have been reported at many different times throughout the spring. These results indicate that there is a specific time period in the spring, when certain atmospheric conditions are met, when the deposition of mercury to the snow pack primarily occurs. Thus, atmospheric mercury speciation during AMDE chemistry season needs to be incorporated into mercury models to better predict the total deposition of mercury to the high Arctic.

3.4 Atmospheric mercury over the sea ice

Measurements of GEM, RGM and PHg as well as O_3, bromine oxide (BrO) and meteorological data were collected on the Beaufort Sea ice near Barrow, Alaska in March 2009 as part of the OASIS and OASIS-Canada International Polar Year Programs. These results represent the first successful atmospheric mercury speciation measurements collected on the sea ice. The goal of this research study was to enhance our understanding of how atmospheric mercury species behave over the sea ice by collecting measurements on freshly formed sea ice and over the tundra.

Concentrations of RGM and PHg vary by location and season and there are significant differences reported between temperate background sites and high Arctic sites (Cole et al., 2013). While background concentrations for temperate locations range between approximately 2-25 and 1-54 pg m^{-3} for RGM and PHg, respectively (Poissant et al., 2005; Lynam and Keeler, 2006; Lyman and Gustin, 2008), concentrations at Alert range between approximately 0-340 and 0-700 pg m^{-3} for RGM and PHg, respectively, in the spring (Cobbett et al., 2007). Coastal observations have reported periodic near complete conversion of GEM to RGM and/or PHg during the Arctic springtime; nevertheless, few to no data have been published from similar measurements collected on Arctic Ocean sea ice. It is believed that the majority of the O_3 depletion events occur over the Arctic Ocean and those reported at coastal measurement sites are a result of depleted air masses that have travelled from the ocean to the site and not from local chemistry (Bottenheim and Chan, 2006). This conclusion is important because it is believed that AMDEs and O_3 depletions are both initiated by halogens from over the ice and thus it is likely that AMDEs also originate over the ocean. Until recently, logistical and technical challenges limited our ability to collect reliable atmospheric mercury speciation data immediately over the Arctic Ocean surface. This study took place near Barrow, Alaska March 5 to April 4, 2009. Most of the experiment was undertaken over the Chukchi Sea near the town of Barrow where the instruments were housed in special boxes towed behind snowmobiles on specially designed sleds onto the Arctic sea ice as close as possible to open leads. This setup was termed the "Out On The Ice" (OOTI) system (Figure 3b). During the study, the mean GEM concentration was 0.59 ± 0.40 ng m^{-3} indicating that for most of the time an AMDE was occurring. The PHg concentration averaged 393 ± 237 pg m^{-3} with a maximum of 900 pg m^{-3} and the mean RGM concentration was significantly lower at 30 ± 24 pg m^{-3} with a maximum value of 105 pg m^{-3}. Similar to what has been reported at Alert when AMDEs occur, GEM levels decreased coincidentally with an increase in PHg and RGM levels. A high particle load was confirmed by MAX-DOAS to be present in the lower surface air at the OOTI site during the campaign and several lines of evidence show that the particles are likely sea salt sulphate, non sea salt sulphate, arctic haze and/or diamond dust (Douglas et al., 2008; Domine et al., 2011; Seguin et al., 2011). It is likely that low temperatures and the availability of particles enabled the RGM formed in the atmosphere during AMDEs to adsorb onto particles and result in such a predominance of PHg measured over the sea ice. This finding is significant as the majority of mass balance calculations investigating the impact of AMDEs over the whole Arctic have relied on data collected inland or at coastal sites where sea salts may not be as predominant as over the ocean. Thus, current mass balance calculations may not accurately reflect the concentration of PHg over the sea ice.

Several factors were investigated to understand what influences the atmosphere would have on mercury speciation over the sea ice. A strong relationship between RGM and solar radiation was found which indicates that RGM is derived through photochemical reactions. PHg concentrations do not peak with solar radiation but lag behind by a few hours suggesting that this fraction of mercury is not directly formed by photochemical processes. To assess other factors the data was divided into specific meteorological events according to the air pressure and wind direction. Three distinct events during the study were evident. Table 2 summarises the data collected during each event and during the whole study, Events 1 and 3 showed the strongest contrasting behaviour and were both air masses having travelled over the sea ice (60^o and 15^o, respectively); Event 2 resulted from an air mass originating from the tundra (150^o) and is thus not discussed here (see paper #3 for full details).

During Event 1 PHg was above the total mean concentration and RGM was below whereas during Event 3, RGM was above its total mean and PHg was well below. The average RH during Event 1 was below 75% (high PHg) and Event 3 was above 75% (high RGM). The deliquescence point of NaCl is at 75% RH (Chen and Lee, 2001) which could indicate that above this level, the significant amount of sea salt particles could have absorbed water, grown to where they could be more readily removed from the air at this point or are too large to be sampled through our system (cutoff at 2.5μm).

	Units	Total	Event 1	Event 3
Dates		March 14-26	March 14-19	March 25-26
Wind direction Centre (range)	Degree	210-330	60 (30-90)	15 (0-30)
Air pressure Mean (range)	mbar	1035 (1012-1042)	1035 (1026-1041)	1019 (1012-1035)
PHg concentration Mean (range)	pg m^{-3}	393.5 (47.1-900.1)	**449.8** (123.1-898.9)	**255.5** (140.2-319.6)
RGM concentration Mean (range)	pg m^{-3}	30.1 (3.5-105.4)	**18.3** (3.5-71.8)	**42.9** (7.4-95.7)
% relative humidity mean (range)	percent	74.8 (61.3-82.3)	71.5 (61.7-78.7)	80.7 (78.2-81.9)
R^2 with Ozone PHg / RGM	n/a	0.61 / 0.10	0.82 / 0.01	0.58 / 0.29
R^2 with BrO GEM / PHg / RGM	n/a	0.48/0.1/0.36	0.58 / 0.08 / 0.74	0.03 / 0.03 / 0.37
Number of data points	n/a	96-101	37-44	10-12

Table 2: Summary information for data collected over the sea ice for the total study period and Events 1 and 3

These results show that there may be a relationship between the concentration of either PHg or RGM and RH, although this relationship was deemed not significant in Paper #2. The distance between sampling location and refrozen leads/open water was estimated using MODIS satellite images. During Event 1 when GEM was depleted and PHg enhanced, the air measured emerged from the direction of this refrozen lead located 1.2 -1.8 km away. During Event 3, the open leads were somewhat close (12.5 km away) GEM was depleted and RGM was enhanced. These results suggest that both open leads and recently frozen sea ice may be associated with GEM loss and with the differences in RGM and PHg concentration levels. The relationship between GEM and O_3 has been well documented during AMDEs and thus was investigated with the mercury speciation data (Schroeder et al., 1998; Ebinghaus et al., 2002; Berg et al., 2003; Poissant and Pilote, 2003; Skov et al., 2004). The correlation between GEM and O_3 has suggested that common chemistry is responsible for the depletion of both. Linear regressions were performed on GEM, PHg and RGM with O_3 for the whole study period and for each Event (Table 2). As expected, GEM and O_3 show a strong linear relationship over the sea ice (r^2=0.76). While there is a reasonable linear relationship between PHg and O_3 over the study period (r^2=0.61), the strongest relationship was reported during Event 1 (r^2=0.82) and there was little relationship between O_3 and RGM in this data. Interestingly, when the same analysis was undertaken with BrO data, a positive correlation with RGM was reported for Events 1 and 3 (r^2=0.74 and 0.37) but none was reported for BrO with PHg. The lifetimes of BrO and RGM in the air are quite different which makes a direct analysis of these chemicals challenging; however, given their high correlation during Events 1 and 3, the lifetime of RGM may be closer to that of BrO under some Arctic conditions. These results show that the chemistry of AMDEs is complex over the sea ice and that there are different factors that drive the distribution of atmospheric mercury speciation under these conditions.

The difference between GEM concentrations over the sea ice and inland over the snow-covered tundra was also investigated and the results are shown in Figure 10. The time series from GEM measurements inland over the tundra are shown by the grey circles and from over the sea ice by the blue circles. The mean GEM concentration, with 95% confidence interval, over the tundra was significantly higher (0.79 ± 0.11 ng m^{-3}) than that recorded over the sea ice (0.59 ± 0.08 ng m^{-3}). The minimum concentration at both locations was the same but the maximum over the tundra was higher than over the ice (2.92 and 1.51 ng m^{-3}, respectively).

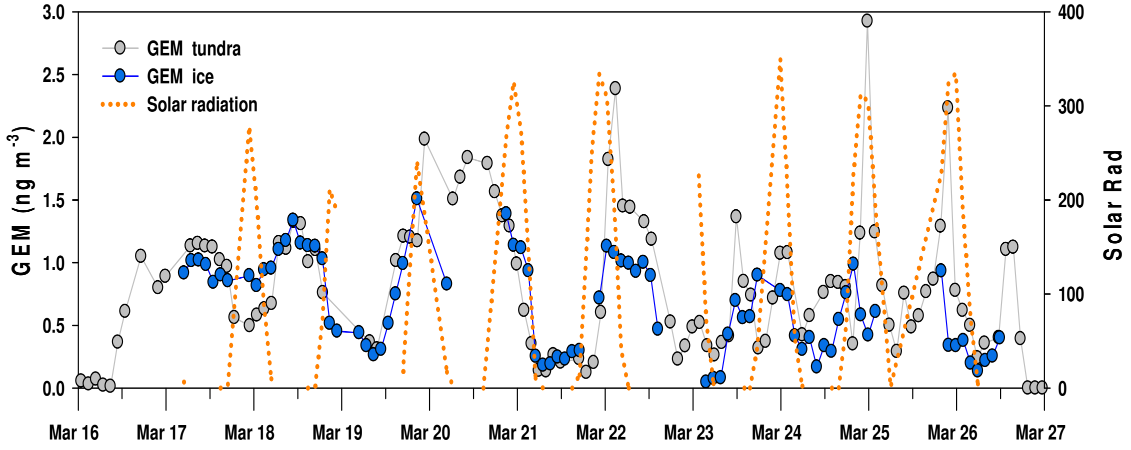

Figure 10: GEM measurements over tundra inland (grey circles), over the sea ice (blue circles), solar radiation (orange)

The results in Figure 10 show that both sites experience depletion events around the same time and to the same level throughout most of the study. The striking difference between these two data sets was the strong peaks of GEM at the tundra site following the end of a depletion event which are not concurrently observed over the ocean. GEM concentrations generally do return to background after depletion through mixing, generally from aloft. However, it has also been shown that some GEM is emitted from the snow pack following depletion events (Steffen et al., 2002; Poulain et al., 2004; Kirk et al., 2006), likely due to photoreduction processes of oxidised mercury (Lalonde et al., 2002; Poulain et al., 2004; Durnford and Dastoor, 2011). The strong peaks of GEM at the tundra site at the end of an AMDE indicates that the amount of GEM returning to the air was much higher (nearly double in concentration) than that over sea ice. These results suggest that emission of GEM from the tundra snow pack occurs with a different magnitude than the emission recorded over the sea ice. It was hypothesized that the lower GEM spikes over the sea ice were due to the large amounts of NaCl in the snow over the ocean surface. Poulain et al. (2004) and St. Louis et al. (2007) suggested that the photoreduction of oxidized Hg can be suppressed by the presence of chloride. When the snow was examined from both sites, the major ion data show that the chloride levels were six times higher in the snow over the sea ice than the tundra and bromide concentrations were twice as high in snow over the sea ice than the tundra. Higher concentration of chloride in the snow over the sea ice supports the hypothesis that the lower emission of GEM over the sea ice (in comparison with the tundra) can be caused by a suppression of the photoreduction of RGM/PHg by chloride. These results indicate that the sea ice snow can retain substantially more mercury than surface snow inland and this significant finding needs to be factored into the current models investigating the cycling of mercury in the Arctic Ocean region.

As the sea ice on the Arctic Ocean rapidly moves toward a greater fraction of more dynamic first year ice with more open leads, enhanced sea salt particle formation and increasingly halogen- and sea salt-rich ice, the impact of these changes on the distribution and deposition of mercury is important to know (Douglas et al., 2012; Nghiem et al., 2012). Thus, the present (and future) Arctic Ocean may be a larger sink for atmospherically deposited mercury than had previously been realised from field and modeling activities. As well, any potential for snow enriched in sea salts to move from the sea ice to the land in coastal environments will have higher mercury retention and thus a stronger impact of AMDEs on the coastal ecosystems.

Chapter 4: Future Directions

This cumulative thesis is a summary of research undertaken to improve our understanding of the processes that lead to AMDEs in order to assess the impacts of this phenomenon on the cycling of mercury. The Arctic is rapidly changing and with this change comes significant uncertainty as to the impacts of toxic chemicals, such as mercury, on such a fragile ecosystem. The research presented here has improved our understanding of several processes impacting AMDEs and the entry of mercury to the Arctic ecosystem; however, there still remains much to learn. The discussion below includes how the information from this thesis can be used by others and also includes suggestions for future research in this area.

The primary findings in this thesis include identifying the factors in the atmosphere that drive oxidation and deposition of mercury during the Arctic springtime and the discovery that the sea ice snow retains more mercury than the snow inland. Using these findings, global and regional models, such as GRAHM and GEOS-CHEM, can be better constrained to simulate the distribution and input of mercury in the Arctic. With that ability, the models will have improved predictive capabilities to assess the impact of various global and regional mercury emission scenarios. With the newly created *United Nations Environment Programme's Minimata Convention on Mercury* aimed to reduce global mercury emissions, accurate predictive models are crucial for forecasting the impacts of such reductions on places like the Arctic environment. Further, long term measurements, such as those made at Alert, are vital in order to directly assess whether the levels of mercury in the air are changing with emission control initiatives.

There still remain many parts of research in this area that require investigation in order to gain a stronger knowledge base of all the processes driving mercury in this environment. Some suggestions for future research are listed below:

1. With the Arctic changing so rapidly and temperatures around this area increasing each year, there is a need to fully assess how much mercury is emitted from the melting tundra.
2. Since methyl mercury is the link to toxicity in humans and wildlife, an improvement in our ability to predict how and where mercury will methylate in the changing Arctic is crucial. Increasing temperatures, changes in the carbon cycle and possible changes in bacterial composition may be happening which can impact methylation rates. These processes need to be well understood.
3. Serious efforts need to be made to know what the identities of RGM and PHg are in order to accurately assess the impact of AMDE chemistry on the Arctic.
4. The effect of aerosol composition on the deposition of Hg to the snow needs to be better constrained. There is a change in the distribution of particles that is coincident with the distribution of mercury but the exact identity (and origin) of these particles was not made. As well, other types of particles are reported throughout the rest of the year and the impact of these particles on the mercury cycle should be ascertained.
5. GEM measurements inland and over the sea ice were compared but further study on the behaviour of RGM and PHg at these different locations will also help to further assess the distribution and deposition of mercury on a larger spatial scale.
6. The impact of the changing sea ice on the depletion and replenishment of mercury in over the sea ice needs full understanding. As we head to a system of less multi year ice and overall sea ice coverage, the impact of these changes on AMDEs needs to be better understood.
7. Increased monitoring of atmospheric mercury is required throughout the Arctic especially in western Russia and the US where there are currently no national programs funding this type of research. The value of long term measurements at Alert exemplifies the immediate need to initiate action from governing bodies to implement monitoring programs.

These recommendations are reasonably straightforward to accomplish with support from research institutes and government agencies. The capability and knowhow currently exist within the mercury research community to accomplish these goals; it is simply a matter of gaining support from the funding agencies so that they can be initiated.

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Appendix A: Declarations to the individual papers

This cumulative thesis is based on three scientific papers which have all been published in international peer-reviewed journals.

Paper #1: A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow.

Primary author: Alexandra Steffen

Co-authors and contributors: Thomas Douglas, Marc Amyot, Parisa Ariya, Katrine Aspmo, Torunn Berg, Jan Bottenheim, Steve Brooks, Frank Cobbett, Ashu Dastoor, Aurelien Dommergue, Ralf Ebinghaus, Christophe Ferrari, Katarina Gardfeldt, Michael E. Goodsite, David Lean, Alexandre J. Poulain, Christina Scherz, Henrik Skov, Jonas Sommar and Christian Temme

Status: Published in Atmospheric Chemistry and Physics, 2008, 8, 1445-1482.

Selected presentations:

- Understanding atmospheric mercury in the world of ozone and halogens over the Arctic Ocean SOLAS Open Science Conference, Barcelona, Spain, November 2009 (invited oral presentation)
- Mercury and climate change in the Canadian Arctic air 5th SETAC World Congress, Sydney, Australia, August 2008 (oral presentation)

Paper #2: Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada

Primary author: Alexandra Steffen

Co-authors: Jan Bottenheim, Amanda Cole, Ralf Ebinghaus, Greg Lawson and Richard Leaitch

Status: Published as a discussion paper in Atmospheric Chemistry and Physics Discussions, 13, 17021-17052, 10.5194/acpd-13-17021-2013, 2013.

Selected presentations:

- Mercury in the Arctic air; a long term look at what we know and don't know. The 10th International Conference on Mercury as a Global Pollutant, Halifax, Canada, July 2011 (oral presentation)
- Long term records of pollutants in the Arctic air: The mercury and POPs stories. The International Polar Year 2012 Conference, Montreal, Canada, April 2012 (poster presentation)

Paper #3: Atmospheric mercury over sea ice during the OASIS-2009 campaign

Primary author: Alexandra Steffen

Co-authors: Jan Bottenheim, Amanda Cole, Thomas A. Douglas, Ralf Ebinghaus, Udo Friess, Stoyka Netcheva, Son Nghiem, Holger Sihler and Ralf Staebler

Status: Published in Atmospheric Chemistry and Physics, 13, 7007-7021, 2013.

Selected presentations:

- Atmospheric Mercury in an Arctic OASIS (Ocean-Atmosphere- Sea Ice-Snow Pack). The American Geophysical Union Fall Meeting, San Francisco, USA, December 2009 (oral presentation)
- Mercury over the sea ice as part of the Ocean-Atmosphere-Sea Ice-Snow pack (OASIS) - Canada IPY program. The International Polar Year Oslo Science Conference, Oslo, Norway, June 2010 (oral presentation)
- The role of the arctic ocean in mercury chemistry as part of the ocean-atmosphere-sea-ice-snow pack (OASIS) – Canada IPY program. The International Polar Year 2012 Conference, Montreal, Canada, April 2012 (oral presentation)
- Understanding the role of the atmosphere around the Arctic Ocean during atmospheric mercury depletion events. The 9th International Conference on Mercury as a Global Pollutant, Guiyang, China, June 2009 (oral presentation)

Appendix B: Academic publications relevant to this thesis

1. A comparison of data quality control protocols for atmospheric mercury speciation measurements (2012) **Steffen, A**., Scherz, T., Olson, M.L., Gay, D.A. and Blanchard, P., Journal of Environmental Monitoring, 14: 752-765.

2. Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude sites (2012). Cole, A. S., **Steffen, A.**, Aspmo Pfaffhuber, K., Berg, T., Pilote, M., Poissant, L., Tordon, R. and Hung, H. Atmos. Chem. Phys. Discuss., 12, 20209-20237.

3. Nghiem, S., Rigor, I., Richter, A., Burrows, J. P., Shepson, P. B., Bottenheim, J., Barber, D. G., **Steffen, A**., Latonas, J., Wang, F., Stern, G., Clemente-Colón, P., Martin, S., Hall, D. K., Kaleschke, L., Tackett, P., Neumann, G., and Asplin, M. J.: Field and satellite observations of the formation and distribution of Arctic atmospheric bromine above a rejuvenated sea ice cover, Journal of Geophysical Research D: Atmospheres, 117, D00S05, 2012.

4. Mercury in Arctic marine ecosystems: Sources, paths and exposure (2012). Kirk, J. L., Lehnherr, I., Andersson, M., Braune, B., Chan, L., Dastoor, A., Durnford, D., Gleason, A. L., Loseto, L. L., **Steffen, A**., and St Louis, V. L., Environmental Research, 119, 64-87.

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7. Trends in long-term gaseous mercury observations in the Arctic and effects of temperature and other atmospheric conditions (2010) Cole, A. S. and **Steffen, A**. Atmospheric Chemistry and Physics 10: 4661-4672.

8. GEM fluxes and atmospheric mercury concentrations (GEM, RGM and HgP) in the Canadian Arctic at Alert, Nunavut, Canada (February – June 2005). (2007) Cobbett, F, **Steffen, A**, Lawson, G and Van Heyst, B. (2007). Atmospheric Environment, 41(11), 2270-2282.

9. Mercury in the arctic atmosphere: an analysis of eight years of measurements of GEM at Alert (Canada) and a comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada). (2005). **Steffen A**, Schroeder WH, Macdonald R, Poissant L and Konoplev A. STOTEN; 342: 185-198.

10. Measurements of atmospheric mercury species during an international study of mercury depletion events at Ny-Alesund, Svalbard, spring 2003. (2005) How reproducible are our present methods? Aspmo, K, Gauchard, P-A, **Steffen, A**, Temme, C, Berg, T, Bahlman, E, Banic, C, Dommergue, A, Ebinghaus, R, Ferrari, C, Pironne, N, Sprovieri, F Wibetoe, G. Atmospheric Environment, 39: 7607-7619
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12. Worldwide Trend of Atmospheric Mercury since 1977. (2003) Slemr, F, Brunke, E, Ebinghaus, R, Temme, C, Munthe, J, Wangberg, I, Schroeder, WH, **Steffen, A** and Berg, T. Geophysical Research Letters; Vol. 30 (10) 1516.

13. Mercury throughout polar sunrise 2002 (2003) **Steffen, A**, Schroeder, WH, Edwards, G and Banic, C. Journal de Physique IV France; (107) 1267-1270.

14. Atmospheric Mercury Concentrations: Measurements and Profiles near Snow and Ice Surfaces in the Canadian Arctic during Alert 2000. (2002) **Steffen, A**, Schroeder, WH, Bottenheim, J, Narayan, J, and Fuentes, JD. Atmospheric Environment, 36: 2653-2661.

15. Magnification of atmospheric mercury deposition to Polar Regions in springtime: the link to tropospheric ozone depletion chemistry. (2001) Lu, JY, Schroeder, WH, Barrie, LA, **Steffen, A**, Welch, HE, Martin, K, Lockhart, WL, Hunt, RV, Boila, G, and Richter, A. Geophysical Research Letters; Vol. 28 (17) 3219-3222.

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Relevant technical reports:

1. **Steffen, A**., Cole, A., Dastoor, A., Antoniadis, M., Ariya, P., and Morrison, H.: Atmospheric Mercury, in: Canadian Arctic Contaminants Assessment Report III: Mercury in Canada's North., edited by: Braune, B., and Chetelat, J., Northern Contaminants Program (NCP), Aboriginal Affairs and Northern Development Canada, Ottawa, 276 pp., 2012.

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Cumulative thesis

Paper #1

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

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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

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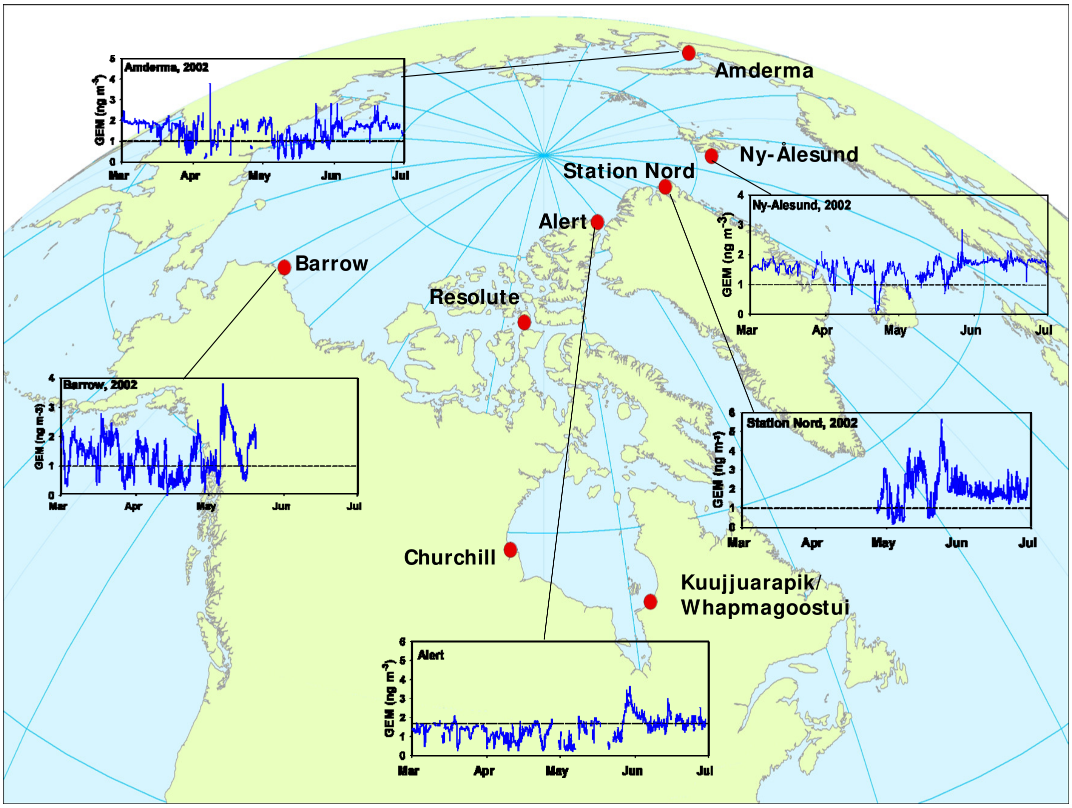

Fig. 1. Map of sampling sites for mercury research undertaken in the Arctic (and sub-Arctic) including time series of GEM concentrations at Amderma, Barrow, Ny-Ålesund, Station Nord and Alert during spring 2002. These time series demonstrate that during the Arctic spring, all sites show occurrence of 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 contaminant 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).

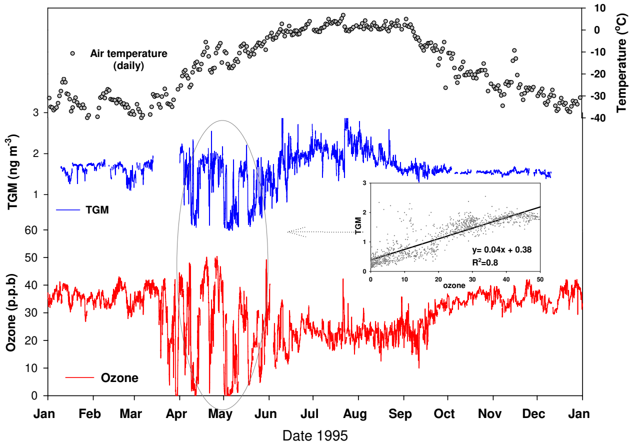

Fig. 2. Annual time series of TGM and ozone concentrations and air temperature from Alert 1995. Insert: linear correlation between TGM and ozone during an AMDE time period (adapted from Schroeder et al., 1998).

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 $\mathrm{ng/m^3}$ in the northern hemisphere and 1.1–1.3 $\mathrm{ng/m^3}$ 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 atmospheric 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 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 report 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$^{\mathrm{TM}}$ (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 oxygen 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 $O_{3(aq)}$, as well as $Br_{2(aq)}$ and $Cl_{2(aq)}$, 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

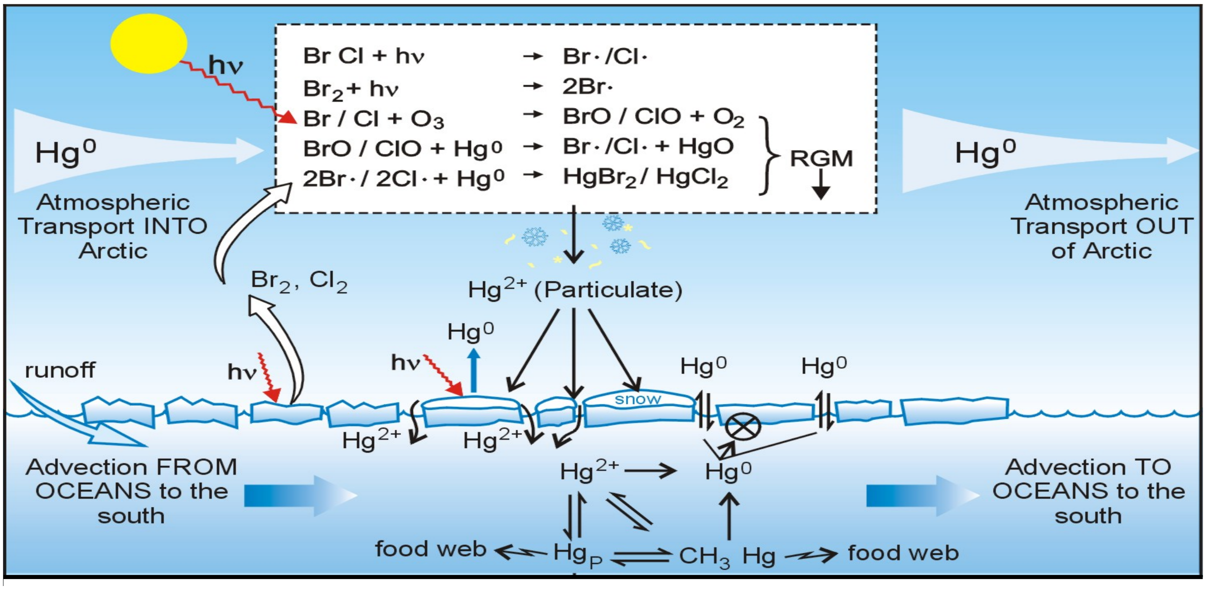

Fig. 3. Schematic of the cycling of mercury in Polar Regions (modified from MacDonald et al., 2005).

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 $\sim$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

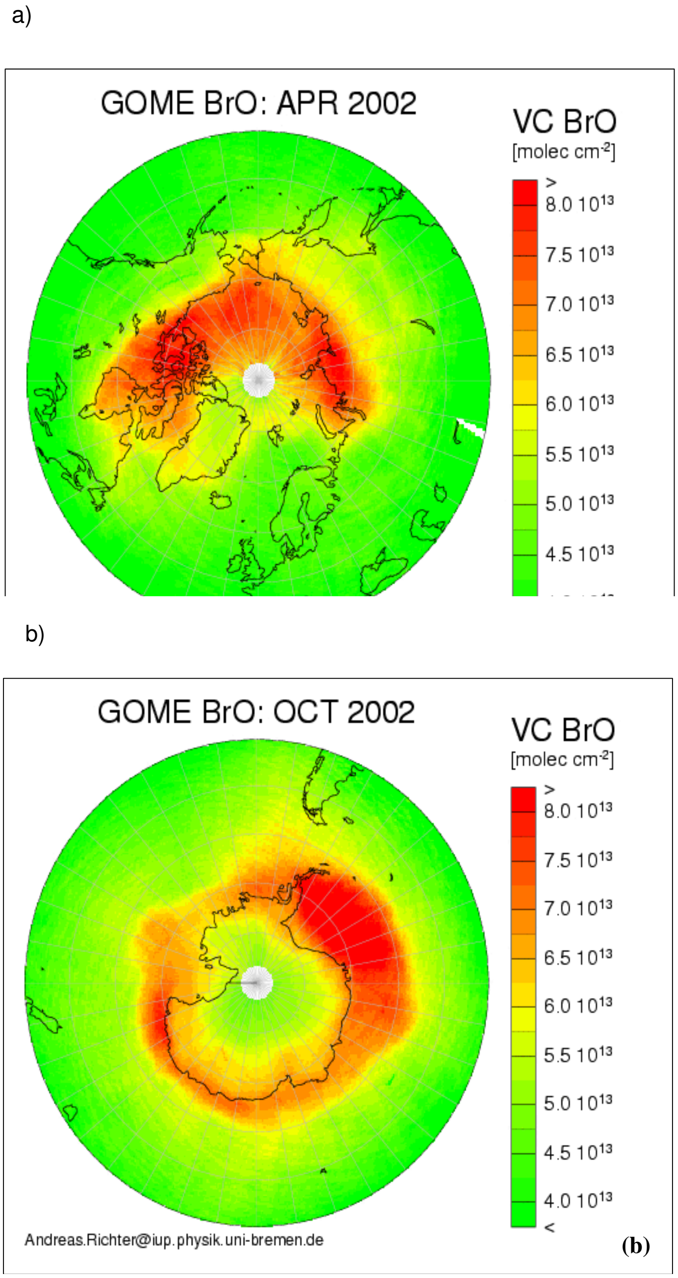

Fig. 4. GOME BrO measurements over **(a)** the Arctic April 2002 and **(b)** the Antarctic October 2002. The values given are in molecules/cm^2. Green areas correspond to low BrO concentration values and the red areas correspond to higher BrO concentration values.

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

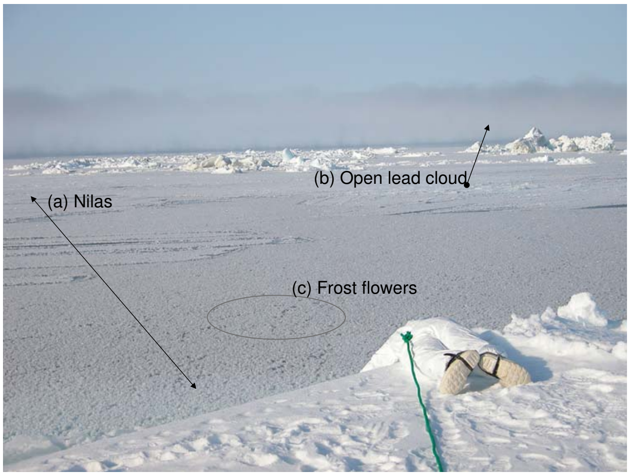

Fig. 5. Photo describing ice features from a location on the ice near Barrow, Alaska during the Arctic spring where samples have been collected for mercury. Shown in this photo are **(a)** nilas (new sea ice); **(b)** an open lead – evident by the gray cloud and **(c)** a newly formed frost flower field.

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 $\sim$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^2h 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 ranging 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_2Hg 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_2Hg 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, micro-organisms 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 micro-organism 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 Kongsfjord 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 addition to MeHg being reported in polar oceans Me_2Hg has been measured in the Arctic Ocean and in Hudsons Bay (Kirk, 2006). Me_2Hg 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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Paper #2

Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada

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Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada

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Abstract

Ten years of atmospheric mercury speciation data and 14 yr of mercury in snow data from Alert, Nunavut, Canada are examined. The speciation data, collected from 2002 to 2011, includes gaseous elemental mercury (GEM), particulate mercury (PHg) and reactive gaseous mercury (RGM). During the winter-spring period of atmospheric mercury depletion events (AMDEs), when GEM is close to being completely depleted from the air, the concentrations of PHg and RGM rise significantly. During this period, the median concentrations for PHg is 28.2 $\mathrm{pgm^{-3}}$ and RGM is 23.9 $\mathrm{pgm^{-3}}$ from March to June in comparison to the annual median concentrations of 11.3 and 3.2 $\mathrm{pgm^{-3}}$ for PHg and RGM, respectively. In each of the ten years of sampling, PHg increases steadily from January through March and is higher than RGM. This pattern begins to change in April with very high levels of PHg and increasing RGM. In May, RGM transitions to be significantly higher than PHg and continues into June whereas PHg sharply drops down. The transition is thought to be driven by a combination of air temperature and particle availability. Firstly, the ratio of PHg to RGM is favoured by low temperatures suggesting that oxidized mercury may partition to available particles to form PHg. Prior to the transition, the median air temperature is -24.8°C and after the transition the median air temperature is -5.8°C. Secondly, high aerosol levels in the spring are a strong driver for the high PHg concentrations. In February through April, partitioning of oxidized mercury to produce PHg was favoured by increased concentrations of particles that are principally the result of Arctic Haze and some sea salts. In the snow, the concentrations of mercury peak in May for all years. The highest deposition of mercury to the snow in the spring at Alert is during and after the transition of PHg to RGM in the atmosphere.

1 Introduction

Mercury has created quite a stir in the high Arctic air over the past two decades because of its interesting springtime atmospheric chemistry and its impact on the environment. Since there are virtually no local sources of mercury in the Arctic, its presence is thought to be due to long range transport from Asia, Russia, North America and Europe (Durnford et al., 2010). The atmospheric processes that dominate the springtime oxidation and deposition of mercury can drive some of this long range transported mercury onto the Arctic surface. It has been demonstrated that, during the polar spring, gaseous elemental mercury (GEM) oxidizes to shorter lived mercury species known as reactive gaseous mercury (RGM) (Schroeder et al., 1998; Lindberg et al., 2001). RGM can either be in the air as a gas or adsorbed to particles and be reported as particulate mercury (PHg). Many studies have reported the decrease in GEM and a coincidental increase in speciated mercury (PHg and RGM) and the association of this chemistry with spring time ozone and halogen chemistry (Lindberg et al., 2001; Lindberg et al.,2002; Aspmo et al., 2005; Kirk et al., 2006; Cobbett et al., 2007; Dastoor et al., 2008; Steffen et al., 2008; Steen et al., 2011). There are few long term data sets of speci- ated atmospheric mercury that have looked at processes in the high Arctic, with the exception of Cole et al. (2013) who reported on the long term trends at Alert.

Alert is a high Arctic site, located at the tip of Ellesmere Island, Nunavut, Canada.Long term atmospheric measurements of GEM have been undertaken since 1995 (Schroeder et al., 1998; Cole and Steffen, 2010) and speciation data have been col- lected since 2002. The unique GEM annual signature from Alert has been previously published (Schroeder et al., 1998; Steffen et al., 2005; Cobbett et al., 2007; Cole and Steffen, 2010) showing northern hemispheric background levels in the fall and winter, low concentrations in the spring and higher concentrations in the summer. The life- time of atmospheric mercury depends on its chemical form and is considered to be GEM $\gg$ PHg > RGM (Schroeder and Munthe, 1998). The dry deposition velocities of these species have been modeled to be RGM > PHg > GEM (Zhang et al., 2009).

The fractionation of these Hg species depends on location and chemistry with GEM being the predominant species in the air in most locations (generally the sum of all Hg species consists of 98 % GEM, 1.5 % RGM and 0.5 % PHg, Peterson et al., 2009). However, at locations in the Arctic (and Antarctic) this fractionation changes during the spring months; at Alert for example, to 88.5 % GEM, 4.5 % RGM and 7 % PHg (from 2002 to 2011 using mean concentrations) or 95.6 % GEM, 2 % RGM and 2.4 % PHg (using median concentrations). It is well known that a series of photochemically initi-ated reactions can oxidize GEM to an Hg^{2+} inorganic species (Simpson et al., 2007;Ariya et al., 2008; Obrist et al., 2011) either in the gas phase (as RGM) or associated to particles (as PHg). These reactions result in atmospheric mercury depletion events (AMDEs) and refer to the depletion of GEM from the troposphere. This loss has been explained as conversion of GEM to other mercury species and/or a loss to the snow surface (Steffen and Cole, 2008).

Currently, the actual chemical identity of RGM and PHg are not well determined, they are operationally defined as the fraction of gaseous mercury that can be separated from the air by a KCl coated denuder and mercury associated with particles collected on a quartz filter, respectively (Sheu and Mason, 2004; Gustin and Jaffe, 2010). Analysis methods for RGM and PHg include separation of the species and quantification as GEM. While there are reasonably reliable reference standards for GEM (Temme et al., 2007), there exist none to accurately quantify and elucidate RGM and PHg (Temme et al., 2007; Gustin and Jaffe, 2010). The data set used for the current study was obtained using sampling protocols, quality control and analysis as described by Steffen et al. (2012). The data were collected over a 10 yr period were compared from year to year to observe recurring patterns and potential processes.

Aerosol particles have been studied at Alert since 1980 (Barrie, 1986; Barrie et al., 1989; Gong et al., 1997; Sirois and Barrie, 1999; Sharma et al., 2004). The well known phenomenon of Arctic Haze is due to air masses originating from anthropogenic emissions in Europe, North America and the former Soviet Union, that are transported to and trapped in the Arctic air.

The haze primarily consists of sulphate and carbonaceous particles, maximizing in March and April (Sharma et al., 2004; Quinn et al., 2007).

This study reports an analysis of ten years of mercury sampling in air and fourteen years of mercury sampling of the snow coupled with atmospheric meteorological and particle measurements from Alert.

2 Methods

2.1 Sample location

Alert, Nunavut, Canada is located at 82.5° N and 62.3° W, 800 km from the geographic North Pole. The instrumentation is located at the Dr. Neil Trivett Global Atmospheric Watch (GAW) Observatory on the north eastern edge of Ellesmere Island. The laboratory is located approximately 8 km from the shore of the Lincoln Sea and is at an elevation of 195 m a.s.l. The atmospheric mercury speciation and particulate instruments are located on an outside walk up tower approximately three and five metres above the ground, respectively. The tables from which the snow samples were collected are located approximately 200 m south of the laboratory.

2.2 Atmospheric mercury speciation

GEM, PHg and RGM were collected using the Tekran 2537A/1130/1135 automated mercury vapour analyzer system. The methods have been described in detail elsewhere (Landis et al., 2002; Steffen and Cole, 2008). In short: air is pulled into the analyzer through a Teflon® coated elutriator and impactor designed to remove particles and snow > 2.5 µm at flow rates of 10.0 L min^{-1} (particle size cut off varies with flow rate). The sample air flows via a KCl coated quartz denuder to trap RGM in the 1130 unit, and then passes over a quartz particulate filter to trap PHg in the 1135 unit. GEM passes through both the 1130 and 1135 units and is carried into the 2537 analyzer (at a flow rate of 1 L min^{-1}) for analysis.

GEM is reported as ng m^{-3} of mercury. The samples are analysed by first heating an inline pyrolyzer to 800 °C. The quartz filter is then heated to desorb the PHg and sent through the pyrolyzer to break all PHg to GEM which is then analysed by the 2537A instrument. The denuder is then heated to 600 °C to release the RGM and passes over the pyrolyzer to break down all RGM to GEM which is analysed by the 2537A instrument. PHg and RGM are reported as pg m^{-3} of mercury. Mercury free zero air is passed through the system before and after these desorption cycles as blanks. At Alert, air samples were originally collected for 3 h to ensure there was enough mercury collected for analysis and once verified the sampling time was reduced to 2 h. Rigorous procedures during and after sample collection/analysis have been established for Alert to ensure consistency from year to year and are described in detail in Steffen et al. (2012).

The analytical detection limits of the Tekran® 2537 analyzer (< 0.1 ng m^{-3}, from the manufacturer, or 0.75 pg of mercury collected based on a 7.5 L sample volume) are more than an order of magnitude below ambient GEM concentrations (typically > 1 ng m^{-3}). For the PHg and RGM data collected at Alert, the detection limits are calculated to be three times the standard deviation of the two post desorption blanks. The detection limits for PHg and RGM at Alert for each year from 2002 to 2011 are shown in Table 1.

2.3 Meteorological data

The air temperature is measured at the GAW station at a 1 Hz frequency using a Campbell 107F thermistor (USA). Prior to 2004, relative humidity (RH) is calculated from the dew point measured with a custom Atmospheric Environmental Services Type E dew cell (AES Drawing series 0306) at the Alert station (station #2400300, 82°31′4″ N, 62°16′50″ W, 30.48 m). All RH measurements after 2004/06/26 are from a Vaisala RH sensor (model HMP45C212) at the Alert Climate station (2400305, 82°30′ N, 62°20′ W,65.4 m). Data are obtained from the Environment Canada National Climate Data and Information Archive (http://climate.weatheroffice.gc.ca/contacts/index_e.html).

2.4 Aerosol particle volume and light scattering

The ambient aerosol is pulled into the laboratory through a 3 m long, 10 cm diameter stainless steel vertical manifold at a flow rate of about 1000 L min^{-1}. Particles are sampled out of the manifold from near the center of the flow stream, about 30 cm up from the bottom of the manifold. From there the particles are delivered to the sampling devices via stainless steel tubing. The mean total residence time of a particle from outside to its measurement point is approximately 3 s and, at this point, the particle at approximately room temperature and the relative humidity (RH) is < 50 %. Particle size distributions from 20 nm to 500 nm are measured with a TSI 3034 Scanning Mobility Particle System (SMPS) which is calibrated on site using monodisperse particles of polystyrene latex and of ammonium sulphate generated with a Brechtel Manufacturing Incorporated (BMI) Scanning Electrical Mobility Spectrometer (SEMS). Particle volumeconcentrations in the size range of 20 nm to 500 nm are derived from the integration of the SMPS size distribution assuming spherical particles.

Particle volume dry scattering coefficients (σ_{sp}) in < 1 and < 10 µm sizes are mea- sured by a 3-λ Integrating Nephelometer (TSI Model 3563). The instrument is calibrated by using high purity dry CO_2 and drift in the calibration is checked weekly. Measurement uncertainties of the TSI nephelometer have been described in detail elsewhere (Ander-son and Ogren, 1998; Anderson et al., 1999; Sheridan et al., 2002). The nephelometer data used in this paper are particle light scattering coefficients (b_{sca}) at 550 nm wave- length and represents particles greater than 500 nm in diameter (from 2004–2006 there was no size selection so all particles were collected, post 2006 a 10 µm cut-off was employed).

2.5 Snow sampling

One litre wide-mouth glass jars are used for sample collection. PTFE lined polypropylene (PP) lids were used until 2001 and then replaced with solid PFA Teflon lids (Savillex). The snow is collected on tables and the ground located behind the GAW lab. Snow samples are collected on a snow event basis when the local operator is available to collect the sample. There are two tables approximately 1 m × 1 m each from which the samples are collected. The tables are made of a wooden platform covered with a 1/32” thick PTFE sheet that is attached to the table surrounded by a 1” × 1” PTFE edge. The platform is mounted on Dexion steel strips and the legs are dug into the tundra for stability. When there is a layer of snow on the tables, three bottles of snow are collected using gloved hands, a PTFE scraper and a scoop made from a PTFE bottle. The snow is collected into a pile with the scraper and scooped into glass jars from the snow tables. The tables are divided into three sections and each area of sample collected is measured. When the samples have been collected, the remainder of snow is scraped off so that the table is left blank and ready to collect the next snowfall. Using a very similar procedure, ground samples are collected close to the tables. The surface snow (approximately 1 cm deep) is scraped into a pile using a Teflon scraper. The snow is then scooped into the glass sample jars. Snow samples are kept in the jars in sealed zip locked bags, in coolers and are kept frozen. The coolers are filled with snow and hand carried from Alert to Toronto where they remain frozen until analysis.

2.6 Snow analysis

The sample jars and lids are cleaned in a multi-stage process: soap bath, concentrated hydrochloric acid, concentrated nitric acid, then air dried in a clean-lab. Jars are numbered and pre-weighed before they are packed in coolers and sent to Alert. Blank water is generated using a multi-stage purification process: reverse osmosis, distillation, passage through two Milli-Q systems with UV-digestion.

Bromine monochloride (0.1 N BrCl) is prepared using low-Hg hydrochloric acid (HCl; JT Baker Instraanalyzed), bromic acid (Sigma) and potassium bromate (Alfa Aesar). Alkaline stannous sulphate is produced from stannous sulphate (Alfa Aesar and Sigma) and low-Hg sodium hydroxide (Anachemia Science).

Prior to analysis, sample jars are weighed and 0.1N BrCl is added to the thawing snow samples to give a final concentration of 0.4 %. Total-Hg in the melted snow is determined by direct cold-vapor atomic fluorescence detection after reduction with alkaline stannous sulphate. The detection limits of this method are typically 0.05 pg mL^{-1}, based on three times standard deviation of the analytical blanks. The analytical sys- tem couples an autosampler (Gilson 222) and an atomic fluorescence detector (Tekran 2500) and uses a chromatography interface and software for signal capture and peak integrations. The phase separator was built in-house and made of PFA Teflon with a polyethylene gas bubbler and actively pumped liquid inlet and outlets. A gas phase drier (Nafion) removes water from the sample gas before it passes into the AFS detector.

Quality assurance and control samples included laboratory, bottle, trip and field blanks. In all cases, 250 mL of ultra-pure blank water is added to the blank jars, along with 0.1 N BrCl to give the same concentration as the samples. The 250 mL value is selected because it was close to the average volume of the melted snow samples. Standard reference water is run alongside samples during analyses. All samples are pre-screened by running 10 mL single samples to determine general THg concentrations. The samples are split into low and high samples to fit calibration standards with equivalent concentration ranges. The final analytical runs determined samples as duplicates or triplicates and spike recoveries were determined every eight to ten samples. Analytical blank results are not subtracted from sample results, since the blank water is independent of the sample results and reagents used have been determined to be be- low the detection limits of the method. These blank results are used as a base value for the various other blanks determined. Field blank averages are used to correct sample results, after conversions to average mass per jar values.

17029

3 Results and discussion

3.1 Long-term speciation data

Ten years of gaseous elemental mercury (GEM), reactive gas phase mercury (RGM) and particulate mercury (PHg) concentration measurements from Alert, Canada from 2002 to 2011 are shown in Fig. 1. Measuring accurate and reliable atmospheric GEM, RGM and PHg has its challenges (Gustin and Jaffe, 2010) especially in the remote high Arctic. Few long term mercury speciation measurements have been reported around temperate regions and only one for the Arctic (Cole et al., 2013). This time series shows that the annual signature of mercury species repeats from year to year. The years 2003, 2006 and 2010 are not anomalous but reflect instrumental problems and hence a lack complete data sets for those years.

Figure 2 shows box plots of the monthly concentrations of GEM, RGM and PHg over the 10 yr period. The middle line in the box indicates the median concentration; the bottom and top of the box represent the 25th and 75th percentiles; the whiskers above and below the box indicate the 90th and 10th percentiles and the dots indicate the maximum and minimum values in the data set. A distinct annual cycle for all three species is highlighted in this figure. Annual statistics of PHg and RGM show considerable variability among years. The monthly and overall statistics of PHg and RGM are presented in Table 2. The overall PHg and RGM median concentrations for the 10 yr period are 11.3 and 3.2 pg m^{-3}, respectively, but as is clear from Fig. 2, there are considerable changes in the concentrations throughout the year. PHg is very low in the months June through October (median < 8.4 pg m^{-3}) but begins to increase in November through February (median range ∼ 9–42 pg m^{-3}). This pattern is seen each year and is not considered anomalous. High variability in all the data is observed from March to May and the springtime chemistry is evident in the elevated March to May PHg levels (median range 21–103 pg m^{-3}). The increase in PHg over the winter is not considered to be reflective of AMDE chemistry but may be a product of transport association with winter particle pollution (Arctic haze).

17030

In contrast, RGM is very low from August to February (median range 0.7–5.3 pg m^{-3}), slightly elevated in March and July (median 7.4 and 4.6 pg m^{-3}, respectively) and high April to June (median range 17– 100 pg m^{-3}). It has been reported that AMDEs stop when the temperature is sustained above 0 °C (Steffen et al., 2005), however there appears to be production of RGM well into July where air temperatures are above 0 °C. This annually occurring higher level of RGM in July is variable in concentration and unexpected but is not considered to be a result from AMDE chemistry. This study focuses on the springtime chemistry from March to June inclusive. Further in depth investigations into the annual cycling of PHg and RGM at Alert must be undertaken to explain these patterns.

Finally, Fig. 2 shows the clear decrease in GEM in March concurrent with a notable increase in PHg followed by an increase in RGM in May. PHg reaches its maximum in April and then trails off. In May, the RGM concentrations are highest and trail off into June where GEM concentrations begin to increase again. Cobbett et al. (2007), reported a transition of PHg to RGM in the spring of 2005 at Alert and we report here that this transition occurs each year around the same time (within a 2 week period) for the ten years of measurements. This transition from PHg to RGM was also observed in 2004 in Churchill, Canada on Hudson's Bay around the same time of the year (Kirk et al., 2006) and over a longer period at Ny-Alesund in 2007/08 (Steen et al., 2011).

3.2 Factors affecting the transition from PHg to RGM

Previous field and modeling studies have suggested that factors such as specific humidity, air temperature, wind speed and aerosol particle loadings impact the fractionation of mercury species (Cobbett et al., 2007; Rutter and Schauer, 2007a,b; Amos et al., 2012). Here relative humidity (RH), air temperature and particle concentration are investigated for their possible roles in the fractionation of mercury species at Alert. Monthly plots of air temperature (top) and RH (bottom) for years 2002–2011 and 2004– 2011, respectively, are shown in Fig. 3. The median RH increases substantially from April to May. Before the PHg to RGM transition, the April median RH is 74 % and after the transition the May RH is 85 %.

It has been suggested that a threshold of 75 % RH marks a decrease in the PHg concentrations in the Arctic spring (Steffen et al., 2013). Since RH is temperature dependant and describes the water content relative to saturation, absolute water content (AWC) is also plotted (middle). In Fig. 3, both RH and AWC follow the same pattern with temperature throughout the year and a similar steep increase in both parameters is shown March to May. It can be conceivable that the transition of PHg to RGM from April to May could be related to water absorption by aerosols. However, we suggest that other factors affect the transition of PHg to RGM more effectively and are described below.

The dependence of the transition on the air temperature was investigated by looking at the fraction of PHg relative to [PHg] + [RGM] or Hg(f) (f indicates fraction). Regressions of Hg(f) versus temperature (Fig. 4) indicate that a higher Hg(f) is associated with colder temperatures. The linear regression r^2 values and line slopes for each year from February to June are shown in Fig. 4. For this part of the study, data from the years 2003, 2006, 2007 and 2010 were not included because of large data gaps. The relationships in Fig. 4 are in keeping with the findings of Rutter and Schauer (2007b) who reported a linear relationship between the logarithm of inverse gas to particle partition- ing and inverse air and were later confirmed by Amos et al. (2012). The former study's data was limited to a minimum air temperature of −3 °C and the latter used temperatures down to −16.7 °C. Our study reflects a temperature range of −40 to +20 °C. Our data cannot be directly compared with these two studies, as there are no $PM_{2.5}$ data available from Alert to calculate the particle surface area so that the PHg data can be normalized over differently sized particle surfaces. However, the slopes of the linear regressions between years are very close (see Fig. 4) indicating the relationship between the air temperature and Hg(f) is similar each year. The years where this relationship is not reasonably significant between air temperature and PHg are 2005 and 2008 which shows a high Hg(f) at temperatures between −5 and 5 °C due to anomalously high PHg concentrations. We have no explanation for the elevated PHg at these times. Cole and Steffen (Cole and Steffen, 2010) reported a relationship between air temperature and the frequency of depletion events. They reported that there were higher frequencies of depleted GEM reported in March when temperatures were between −40 and −45 °C and between −25 and −20 °C in May and suggested that the latter temperature may be related to the initiation of bromine chemistry but did not provide a firm explanation for this relationship. Before the transition (March to April), when Hg(f) is greater than 0.5 (predominantly PHg), the median air temperature is −24.8 °C and after the transition, when Hg(f) is less than 0.5 (predominantly RGM), the median air temperature is −5.8 °C. Thus, results from this study show that PHg is predominant at lower temperatures and suggests that the lower temperatures drive the partitioning of oxidized mercury from RGM towards PHg. Further, the average temperature during the week of transition for all the years, except 2003 and 2010, is −15.6 ± 2.8 °C. Indeed, modelling studies have predicted that in colder air masses the predominant Hg^{+2} fraction will be PHg rather than RGM (Amos et al., 2012). We conclude that temperature is a significant driver in the transition of PHg to RGM at Alert during the spring.

The potential impact of the atmospheric aerosol loading on the speciation transition from PHg to RGM is also considered. The aerosol is represented here in two ways: (1) using the particle light scattering measurements from the nephelometer, which is approximately proportional to the surface area of the submicron aerosol, and (2) the volume concentration of the sub-500 nm diameter particles, which is proportional to the mass concentration of the aerosol. The light scattering data are available back to 2004, whereas the volume concentration data are only available since 2011; for the long-lived aerosol measured at Alert, these two quantities are also proportional to each other. Figure 5 shows monthly box and whisker plots of the particle light scattering co- efficient (b_{sca}) at 550 nm wavelength (yellow boxes) and Hg(f) (grey boxes) for January to June. From January to April both b_{sca} and Hg(f) are relatively steady. In May, when the transition from pHg to RGM occurs, Hg(f) decreases to lower values concurrent with a significant decrease in the b_{sca}. The slight increase in the PHg fraction in June is curious and may reflect the relatively low PHg and RGM concentrations in comparison to the high values in the previous months (Table 2) and thereby skewing the Hg(f).

Figure 6 shows PHg as a function of the total volume concentration of particles less than 500 nm for hourly averages during March through June 2011. These results show that PHg is associated with higher particle volume for March and April, May is a transition month to lower particle volume and June shows no association with PHg. That result is consistent with the trend of b_{sca} and Hg(f) in Fig. 5, indicating that a larger Hg(f) is associated with higher concentrations of particle surface area and volume. Since PHg is believed to be due to RGM adherence to particles in the air (Sheu and Mason, 2004),it is conceivable that the presence of more particle surface area or volume in the air may contribute to an increased shift of RGM to PHg during January to April at Alert. The higher particle volume concentrations during January to April are linked with Arctic Haze (Barrie, 1986) and we hypothesize that the presence of Arctic haze is a significant contributor to the increased levels of PHg during this period. This is not the first report of an influence of arctic haze on mercury as Douglas and Sturm (2004) linked mercury levels and arctic haze in the snow around northern Alaska. Other aerosols such as sea salts and ice crystals are also common during the spring at Alert. Both these aerosols are effective scavengers of RGM and have been associated with elevated levels of PHg and Hg in the snow (Rutter and Schauer, 2007a; Douglas et al., 2008; Malcolm et al.,2010; Steffen et al., 2013). Coarse particle Na^+, mostly sea salt derived, is elevated in February and the beginning of March at Alert (Leaitch et al., 2013) but drops off in April while the PHg levels remain high; ice crystals were not measured at Alert. Partitioning of gas-phase mercury to particles can be dependent on the composition of the aerosol (Rutter and Schauer, 2007a). Particles containing sodium nitrate and sea salt com- ponents have shown the highest partition coefficients. Each year PHg at Alert begins to increase in March and then climbs to a maximum in April and are concurrent with sea salts and arctic haze particle increases. Further study is required to identify which types of particles dominate both the atmospheric transition and deposition of mercury in the spring.

3.2.1 Mercury in snow at Alert

Mercury can be deposited onto the snow and ice surfaces enabling its distribution into the environment. All 3 forms of mercury can deposit from the atmosphere to the snow surface. While RGM and PHg have higher deposition velocities than GEM, GEM deposition is significant because of its much higher concentration in the atmosphere compared to the other mercury species (Lin, 2006). However, for this paper, we are focussing on the deposition of RGM and PHg in the context of AMDE occurrence at Alert. A review of mercury behaviour in snow concluded that PHg deposited to snow is likely to remain in the snow pack, while deposited GEM is immediately re-emitted (Durnford and Dastoor, 2011). RGM undergoes several processes including photo reduction and emission and oxidation in the snow and thus its fate is uncertain (Durnford and Dastoor, 2011). These authors conclude that, because of the heterogeneity of snow and mercury deposition around the Arctic, single field studies reporting concentration of mercury in the snow may not allow for extrapolation of deposition on a regional scale.

Since 1998, snow samples have been collected at Alert in the spring just after a snow event. The number of samples has depended on the number of snow events occurring in a given year and on local operator availability to sample the snow. Figure 7 shows box and whisker plots of the concentrations of Hg from Alert (1998–2011) in the snow (in pg g^{-1}) from both the table (top) and ground samples (bottom). It is evident that significantly lower Hg concentrations are observed from the ground samples in com- parison to the table samples, reinforcing the use of snow table sampling here. Snow sampling was undertaken to investigate springtime chemistry and thus occurred only during the months of February to June. To the authors' knowledge, this is the only data set of its kind from the Arctic. Collecting snow on a table in this manner is believed to give a reasonable measure of Hg that is removed from the atmosphere by snow. Sur- face samples are generally collected from the first 1 cm of the snow pack but accurately limiting the sampling to that level is challenging and in any case may well contain some older snow which would bias the obtained concentrations of its components.

Further-more, surface/ground snow samples can be compromised by contribution from blowing snow, multiple snow events and loss of deposited material to deeper layers of the snow pack.

Figure 7 shows the monthly distribution of Hg in snow from February to June from 1998 to 2011. These results show that there is a small but increasing amount of Hg in the snow in February, March and April and that levels peak in May and then trail off in June. There have been reports of similar observations from short term field studies or shorter times (Lu et al., 2001; Durnford and Dastoor, 2011) but nothing this extensive over such a long period of time.

The relationship between the level of Hg in the snow and the atmosphere (RGM and PHg) is explored in Fig. 8. We do not include GEM in this discussion because as mentioned earlier it is believed to be rapidly re-emitted from the snow. In this figure the mercury concentration in snow (2002–2011) is plotted together with PHg and RGM concentrations from February to June (averaged for each Julian day for all data from 2002 to 2011). It can be seen that when the PHg to RGM transition occurs in the atmosphere, there is an increase in Hg levels in the snow. This was found to repeat each year without fail, when snow samples were collected, over the ten-year period. We conclude that the highest deposition of mercury to the snow in the Arctic depends on what form of mercury is present in the atmosphere and the atmospheric conditions that lead to the presence of a given mercury fraction in the air. PHg is scavenged more efficiently by snow than RGM (Amos et al., 2012) which will aid in the deposition of PHg to the snow surface. As shown in Fig. 8, the decrease in PHg and drop in particle numbers in May coincides with the initial increase of Hg in the snow. Subsequently, the levels of mercury in snow keep rising (and falling) concurrently with the concentration of RGM. RGM is known to have a higher dry deposition velocity (Zhang et al., 2009) and can readily deposit onto the snow surfaces which could explain these trends. In any case, our data show that the highest deposition to the snow in the spring at Alert is during and after the transition of PHg to RGM in the atmosphere.

4 Conclusions

Atmospheric speciated mercury measurements reveal strong seasonality as well as significant variability within the spring season. Low PHg concentrations are found in the summer, increase towards the winter and peak in March and April. RGM concentration levels are lowest from August to February, peak in May and remain elevated until July. The most significant finding is the abrupt transition of PHg to RGM during April to May that is repeated over a ten-year period. Fourteen years of snow sampling data from Alert show that the concentrations of mercury in the snow increase as the spring season progresses, peak in May and decrease thereafter.

The results from considering atmospheric factors that may have an impact on the transition from PHg to RGM are as follows:

1. The partitioning of oxidized mercury shows a higher fraction of PHg at low temperatures. We hypothesize that this is due to increases partitioning of RGM to available particles at low temperatures. Prior to the transition from predominance of PHg, the median air temperature is $-24.8\,^{\circ}$C and after the transition the median air temperature is $-5.8\,^{\circ}$C. The average temperature over the transition period is$-15.6\pm2.8\,^{\circ}$C.
2. The availability of high levels of aerosols during the springtime is a strong driver for the high PHg concentrations repeatedly reported during the Alert springtime period. From February to April particles such as arctic haze and sea salts can provide the surface area for RGM adsorption. A strong decrease in the particle concentration in the air is concurrent with a sharp decline in PHg.
3. It is possible that the transition of PHg to RGM from April to May could be related to water absorption by aerosols. However, we suggest that other factors affect the transition of PHg to RGM more effectively and are described below.

We believe that the transition in mercury speciation between particle phase and gas phase is primarily due to a combination of air temperature and particle concentration.

More investigation is needed to determine the relative roles of air temperature and particle concentration and to understand if particle-bound water is a significant factor in this transition. Fourteen years of snow sampling at Alert show that the concentrations of mercury in the snow increase as the spring season progresses, peak in May and decrease thereafter. Ten years of data from the snow and atmospheric measurements are linked to show that during the PHg transition to RGM there is a concurrent increase in the concentration of mercury in the snow; subsequent to this transition, the concentration in snow appears to mirror the rise and fall in the concentration of RGM in the air. Thus, the highest deposition of mercury to the snow in the spring at Alert is during and after the transition of PHg to RGM in the atmosphere.

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Table 1. Detection limits for each year for annual and springtime measurements and the number of samples represented for each data point from 2002 to 2011 at Alert, Canada. Detection limits are reported in pg m^{-3}.

Detection Limit (pg m^{-3})	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Annual	10.50	5.50	2.08	1.80	0.73	5.39	1.16	2.25	1.10	1.47
Spring	1.33	6.24	3.08	2.63	1.17	7.89	1.32	3.61	1.93	1.88
No. of samples										
Annual	1954	2169	3525	3130	5232	4220	4262	4482	3070	3711
Spring	864	533	916	1000	1452	834	1176	1262	498	1208

Table 2. Descriptive statistics of PHg (top) and RGM (bottom) for monthly data and overall data between 2002 and 2011 at Alert, Canada. All concentrations for mean, median, standard deviation (std dev) and maximum are reported in pg m^{-3}. Number represents the number of data points included in the statistics. Mean monthly air temperature is reported in ^{o}C

PHg	**Mean**	**Median**	**Std Dev**	**Maximum**	**Number**	**Air Temp**
January	20.4	13.39	18.08	99.26	1023	-28.0
February	50.26	41.87	53.31	520.54	926	-30.3
March	136.67	102.60	110.38	541.51	1175	-30.5
April	149.58	80.56	154.48	748.69	1710	-22.8
May	45.46	21.15	71.74	698.03	1688	-10.6
June	12.76	8.40	15.45	153.33	1517	-0.18
July	7.36	4.66	7.10	40.98	1638	+4.3
August	6.22	3.38	9.55	85.76	1642	+2.2
September	5.30	4.54	5.39	48.26	924	-7.39
October	10.25	5.46	12.37	70.40	1194	-16.5
November	15.25	9.61	17.46	122.30	1297	-23.2
December	18.35	9.58	21.91	135.62	1349	-27.4
Overall	41.3	11.3	82.3	748.69	16083	

RGM	**Mean**	**Median**	**Std Dev**	**Maximum**	**Number**
January	2.36	2.13	1.22	7.79	942
February	5.25	4.98	2.92	37.57	837
March	11.35	7.40	15.63	220.56	1147
April	33.96	22.20	35.78	331.87	1714
May	120.11	99.88	94.67	877.85	1630
June	41.09	16.76	62.13	718.02	1516
July	14.78	4.60	30.77	260.95	1687
August	4.35	1.46	8.75	108.82	1732
September	1.01	0.71	1.37	13.93	1069
October	0.88	0.70	0.90	7.99	1452
November	1.08	0.94	0.99	10.71	1451
December	1.86	1.71	1.98	20.72	1410
Overall	22.6	3.17	51.99	877.85	16587

Note Minimum values for PHg ranged from 0 to 1.6 and for RGM 0 to 0.4

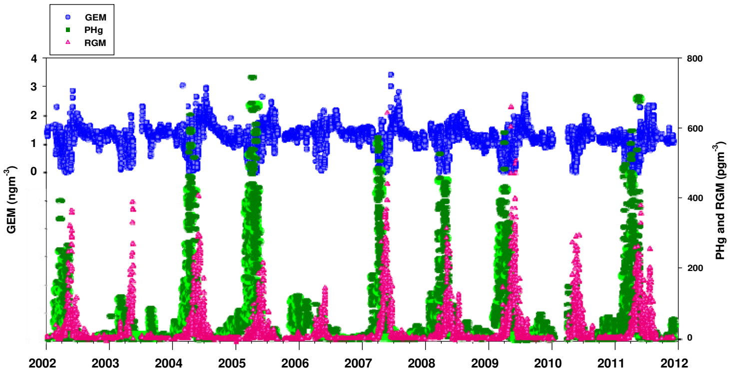

Fig. 1. Six hourly averaged data for gaseous elemental mercury (GEM – blue), particulate mercury (PHg-green) and reactive gaseous mercury (RGM – pink) from 2002 to 2011 at Alert Nunavut, Canada

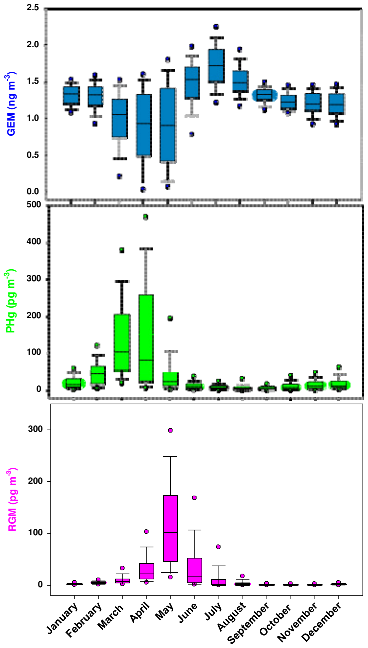

Fig. 2. Box and whisker plots of monthly gaseous elemental mercury (GEM – blue), particulate mercury (PHg – green) and reactive gaseous mercury (RGM – pink) from Alert, 2002–2011. GEM is in ng m^{-3} and PHg and RGM are in pg m^{-3}. Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set.

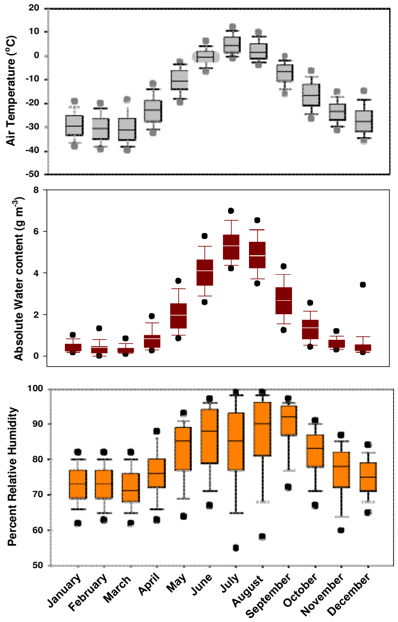

Fig. 3. Box and whisker plots of air temperature, absolute water content (AWC) and percent relative humidity (RH) data from Alert. (Air temperature and AWC are data from 2002–2011 and RH from 2004–2011). Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set.

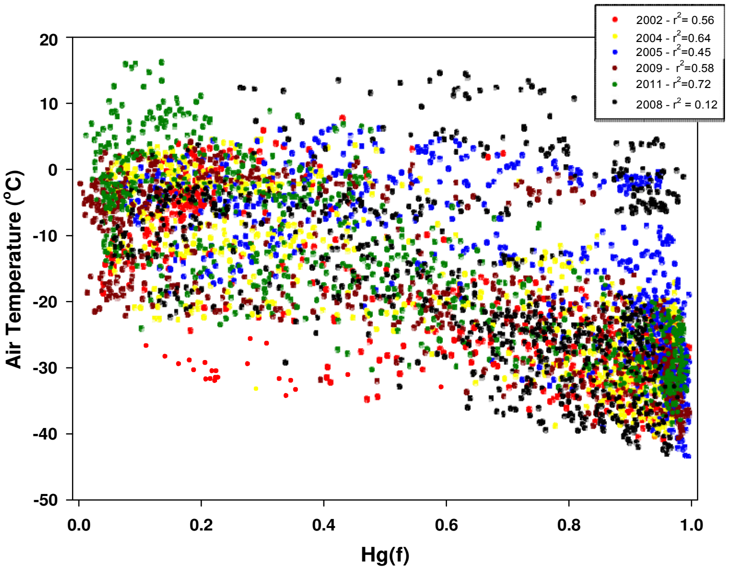

Fig. 4. Linear regression of Air Temperature versus Particulate Hg Fraction for March to June time period (Hg(f) = [PHg]/([PHg] + [RGM])). Slopes: **2002**: −27.7; **2004**: −29.4; **2005**: −29.4;

2008: −16.5; **2009**: −26.7; **2011**: −32.4. *Years 2003, 2006, 2007 and 2010 are not included due to large data gaps.*

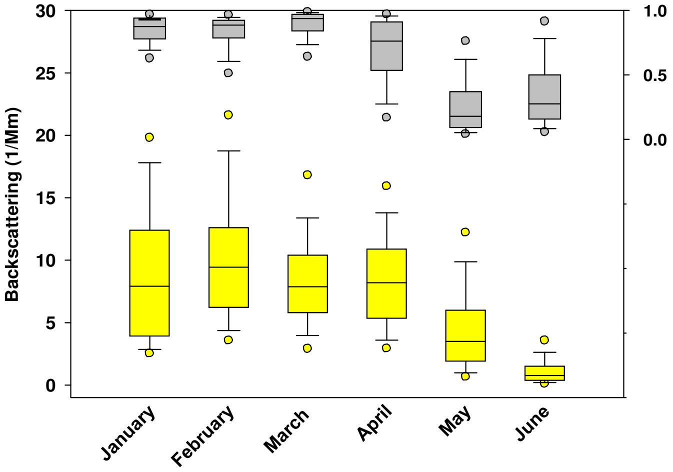

Fig. 5. Monthly box and whisker plot of backscattering (b_{sca}) and mercury fraction data from Alert. Nephelometer data is in (Mm-1) for 550 nm (yellow) from January to June 2004 to 2009. Mercury fraction data is unitless and is from January to June 2002 to 2011. Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set.

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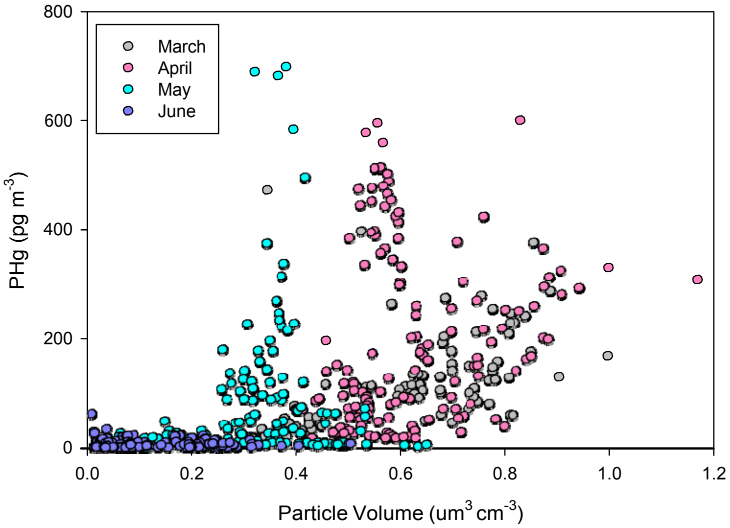

Fig. 6. Particulate mercury (PHg) concentration (pg m^{-3}) as a function of Total Volume Con- centration of Particles (< 500 nm) for the months March, April, May and June 2011 at Alert, Canada.

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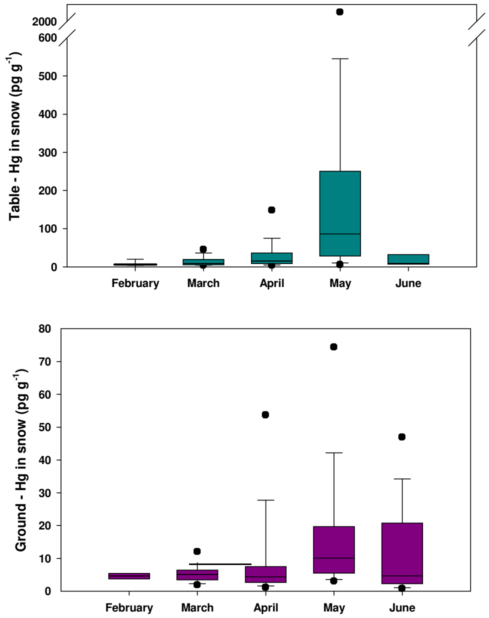

Fig. 7. Long term snow sampling measurements at Alert from 1998 to 2011 sampled on an event basis. Samples are expressed as concentration of mercury (pg g^{-1}) and were collected from a Teflon covered table (top – blue) and from the top layer of the snow pack (bottom – purple). Centre line in the box represents the median value, the boundaries of the box represent the 25th and 75th percentiles, the whiskers represent the 10th and 90th percentile and the dots represent the maximum and minimum values in the data set.

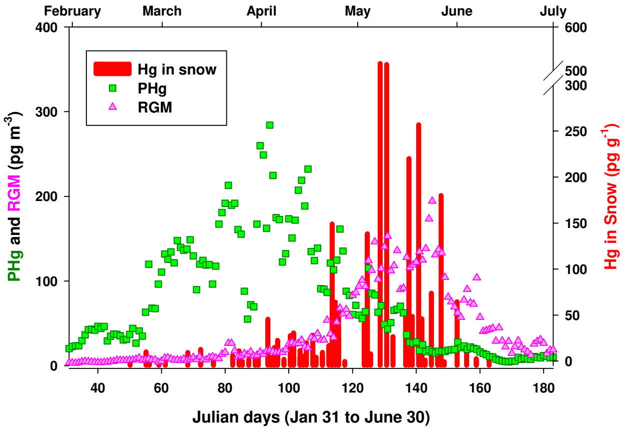

Fig. 8. Atmospheric mercury speciation concentration data PHg and RGM (pg m^{-3}) and Hg concentration (pg g^{-1}) from the snow (table) from February to June for all data from 2002 to 2011. The atmospheric data has been averaged per Julian day over all the years.

Paper #3

Atmospheric mercury over sea ice during the OASIS-2009 campaign

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Atmospheric mercury over sea ice during the OASIS-2009 campaign

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Abstract. Measurements of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate mercury (PHg) were collected on the Beaufort Sea ice near Barrow, Alaska, in March 2009 as part of the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) and OASIS-Canada International Polar Year programmes. These results represent the first atmospheric mercury speciation measurements collected on the sea ice. Concentrations of PHg averaged 393.5 pg m^{-3} (range 47.1–900.1 pg m^{-3}) and RGM concentrations averaged 30.1 pg m^{-3} (range 3.5–105.4 pg m^{-3}) during the two-week-long study. The mean concentration of GEM during the study was 0.59 ng m^{-3} (range 0.01–1.51 ng m^{-3}) and was depleted compared to annual Arctic ambient boundary layer concentrations. It is shown that when ozone (O_3) and bromine oxide (BrO) chemistry were active there is a positive linear relationship between GEM and O_3, a negative one between PHg and O_3, a positive correlation between RGM and BrO, and none between RGM and O_3. For the first time, GEM was measured simultaneously over the tundra and the sea ice. The results show a significant difference in the magnitude of the emission of GEM from the two locations, with significantly higher emission over the tundra. Elevated chloride levels in snow over sea ice are proposed to be the cause of lower GEM emissions over the sea ice because chloride has been shown to suppress photoreduction processes of RGM to GEM in snow. Since the snowpack on sea ice retains more mercury than inland snow, current models of the Arctic mercury cycle may greatly underestimate atmospheric deposition fluxes because they are based predominantly on land-based measurements. Land-based measurements of atmospheric mercury deposition may also underestimate the impacts of sea ice changes on the mercury cycle in the Arctic. The predicted changes in sea ice conditions and a more saline future snowpack in the Arctic could enhance retention of atmospherically deposited mercury and increase the amount of mercury entering the Arctic Ocean and coastal ecosystems.

1 Introduction

Mercury (Hg) is a toxic pollutant found in all compartments of the environment. Its presence in the environment derives from both natural and anthropogenic sources. At elevated levels, in a methylated form, mercury can be a neurotoxin to wildlife and humans. Thus, understanding how it enters and is distributed within ecosystems is crucial for the pro-tection of those living in them. The Arctic is vulnerable to mercury pollution and much has been published on its cy-cling in this unique environment (Steffen et al., 2008; Dou-glas et al., 2012b; Stern et al., 2012). The average northern hemispheric gaseous elemental mercury (GEM) concentration has been reported to be approximately 1.7 ng m^{-3} in 2003 (Slemr et al., 2003), with more recent reports showing

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lower concentrations at some sites (Ebinghaus et al., 2011; Slemr et al., 2011). The mean GEM concentration for the high Arctic site Alert has been reported to be 1.54 annually and $1.39\,\mathrm{ng\,m^{-3}}$ in the spring season (Steffen et al., 2005), though also declining in recent years (Cole and Steffen, 2010).

The Arctic atmosphere plays a key role in controlling mercury deposition to snow and ice surfaces. In the spring, through a series of photochemically initiated reactions, mercury is oxidized from its predominant form GEM (Hg(0)) in the air to inorganic Hg(II) species, either as a gas or associated to particles. These gaseous or particle-bound Hg(II) species are termed reactive gaseous mercury (RGM) or particulate mercury (PHg), respectively. While this oxidation process is not Arctic specific, the efficiency in the Arctic spring is remarkable whereby GEM is often depleted to levels below the detection limit. This process is termed an "atmospheric mercury depletion event" (AMDE) and is concurrent with the depletion of marine boundary layer ozone (O_3) (Steffen et al., 2008). Ozone is destroyed by bromine atoms that are produced through a series of photochemically initiated reactions from sea salts, and GEM is oxidized by bromine atoms either as Br or BrO (Simpson et al., 2007; Steffen et al., 2008). Both GEM and O_3 depletions require the presence of sea salts, sunlight, stable boundary conditions and cold temperatures. At this time, RGM and PHg are operationally defined as mercury that adsorbs to a KCl denuder (gas phase) and mercury that is associated to particles $< 2.5\,\mu\mathrm{m}$ and collected on quartz filters, respectively. Concentrations of RGM and PHg vary by location and season; however, there are significant differences reported between temperate background sites and high Arctic sites (Cole et al., 2013). Background concentrations for several North American studies have been reported to range from approximately 2 to 25 and 1 to $54\,\mathrm{pg\,m^{-3}}$ for RGM and PHg, respectively (Poissant et al., 2005; Lynam and Keeler, 2006; Lyman and Gustin, 2008). In contrast, in the high Arctic at Alert, concentrations of RGM and PHg can range from approximately 0 to 340 and 0 to $700\,\mathrm{pg\,m^{-3}}$ for RGM and PHg, respectively, in the spring (Cobbett et al., 2007), but are generally lower the remainder of the year. Coastal observations have reported periodic near-complete conversion of GEM to RGM and/or PHg during the Arctic springtime; nevertheless, few to no data have been published from similar measurements collected on Arctic Ocean sea ice. The fate of mercury in the coastal environment has been the object of investigation for over a decade. It is believed that the majority of the O_3 depletion events occur over the Arctic Ocean and those reported at coastal measurement sites are a result of depleted air masses that have travelled from the ocean to the site and not from local chemistry (Bottenheim and Chan, 2006). Strengthening the argument that this chemistry is initiated over the sea ice, near-complete O_3 depletion was observed over Arctic Ocean sea ice on a German icebreaker in 2003 and on a sailboat expedition in 2008 (Jacobi et al., 2006; Bottenheim et al., 2009). Ozone lidar measurements onboard the Amundsen icebreaker also observed that depleted layers were always connected to the surface and that the probability of low ozone concentrations increased with the amount of time the advected air masses had spent close to the surface in the preceding six days (Seabrook et al., 2011). Until recently, logistical and technical challenges limited our ability to collect reliable atmospheric mercury speciation (GEM, RGM and PHg) data immediately over the Arctic Ocean.

Over the springtime period, when GEM is converted in the air to RGM/PHg, there is often increased concentration of Hg in the underlying snowpack (Schroeder et al., 1998; Ebinghaus et al., 2002; Lindberg et al., 2002; Berg et al., 2003b; Skov et al., 2004; Steffen et al., 2008). It has been suggested that there are mechanisms within the top layer of the snowpack that release some of that deposited mercury back to the air as GEM, which then makes it again available for oxidation and deposition (Lalonde et al., 2002; Dommergue et al., 2003; Ferrari et al., 2004, 2005; Kirk et al., 2006; Cobbett et al., 2007; Constant et al., 2007; Dommergue et al., 2007; Durnford and Dastoor, 2011; Douglas et al., 2012b). Thus, it has been reported that the level of mercury drops off with time in the snowpack (following atmospheric deposition) as a result of photoreduction processes (Poulain et al., 2004; Kirk et al., 2006; Constant et al., 2007; Sherman et al., 2010; Durnford and Dastoor, 2011). A question that remains is how much of this deposited Hg is retained by snowpacks or entrained in melt water and how much is emitted to the air? Currently, modellers have made assumptions on the amount of GEM re-emitted from the snow surface in their simulation models. Fisher et al. (2012) use 60 % re-emission in their standard simulation, while others use 59 % and 60 % as the estimates (Dastoor et al., 2008; Holmes et al., 2010). In an in-depth study, Durnford et al. (2012) determined modelled re-emission rates of 67 % between 60° N and 66.5° N and 75 % from 66.5° N to 90° N as a result of the mechanisms discussed above. In a general review, Douglas et al. (2012b) estimated an overall re-emission of between 60 and 80 % of deposited Hg.

As part of the March 2009 International Polar Year (IPY) Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) international and OASIS-Canada campaigns in Barrow, Alaska, atmospheric mercury speciation measurements and a suite of meteorological, O_3 and bromine oxide (BrO) measurements including snowpack chemical composition measurements were made over the Arctic sea ice. Other studies have collected information from platforms in the high Arctic such as icebreakers (Aspmo et al., 2006; Chaulk et al., 2011), but none have measured atmospheric mercury species directly on the unperturbed ice near open leads or freshly formed sea ice. GEM measurements were made simultaneously over the tundra snowpack at an inland location for comparison. Results from this novel experiment provide new insights into the behaviour of atmospheric mercury in the Arctic Ocean environment.

2 Methods

2.1 Logistics and sites

The study took place near Barrow, Alaska, from 5 March to 4 April 2009. Most of the experiment described in this study was undertaken over the Chukchi Sea near the town of Barrow. The instrument boxes, called the "Out On The Ice" (OOTI) system, were towed on specially designed sleds behind snowmobiles onto the Arctic sea ice as close as possible to open leads. Figure 1a shows a map of the site locations and a satellite image of the sea ice conditions on 19 March. The first site (71.29° N, 156.85° W) was initially close to an open lead but the lead closed within the first day of sampling. The instruments were moved to other locations on two separate occasions on 19 March (71.36° N, 156.69° W) and 23 March (71.36° N, 156.66° W). The ice surface for the 3 sites can be described as follows: Site 1 – windblown snow over few-day-old frost flowers; Site 2 – snow over sea ice; and Site 3 – 1- to 2-day-old frost flowers (FFs). Sites 1, 2 and 3 were located 1.4, 2.9 and 2.2 km from the shoreline, respectively. The distance between sites 1 and 2, and sites 2 and 3 was approximately 10 and 1km, respectively. Figure 1b shows the experimental set-up on the sea ice. The instrumentation was housed in two separate aluminum boxes (Box 1 and Box 2) that were lined with insulating foam and maintained at a temperature above freezing either through instrument-generated heat or with a heated blanket. Box 1 housed the meteorological instrumentation, the ozone instruments and the mini-MAX-DOAS spectrometer. Attached to the top of the box was a telescope for the MAX-DOAS for scanning over the ice. Box 2 housed the mercury speciation instrumentation. All the instruments were powered using a 5 kW gas generator that was located approximately 17 m downwind of the sample inlets. Data was collected on a semi-continuous basis as per the instrument methodology, and data gaps occurred during site transfers or when the generator stopped working due to mechanical problems associated with the extremely cold conditions. Once the equipment was moved to a site, the systems were set up as shown in the photo in Fig. 1b. The inlet of the Hg speciation system was approximately 15 cm above the snowpack or ice surface, the ozone inlet was between at 1 and 10 cm above the surface, and the meteorological data were collected between 215 and 300 cm from the surface. A second mercury system was located inland with an inlet height of 85 cm from the snow surface. This "tundra" site was 1.2 km inland and 7.6 km from site 1, 4.6 km from site 2 and 4.5 km from site 3.

2.2 Atmospheric mercury

Atmospheric mercury was collected using a Tekran® (Toronto, Ontario, Canada) 2537A/1130/1135 mercury speciation system that measures the concentration of GEM, RGM and PHg. GEM is collected on gold traps, RGM is collected on KCl coated denuders and PHg is collected on quartz filters (2.5 µm cutoff from the impactor set-up). The method has been described in detail elsewhere (Landis et al., 2002; Steffen et al., 2008). GEM samples were collected continuously with 5 min intervals (using 2 traps), while RGM/PHg were collected hourly and then analysed over the subsequent hour. All the data were quality controlled manually but following protocols used by Environment Canada (Steffen et al., 2012b). Hourly averaged data were produced based on the start and end times of the Hg speciation collection (as it does not always start at the top of the hour). Thus, all ancillary data were averaged at the same start and end times as the Hg speciation for appropriate comparison of data. Measurements of GEM, RGM and PHg were made at the OOTI site. GEM was collected at the tundra site with another speciation system. RGM and PHg from the tundra site are not reported here due to instrument problems.

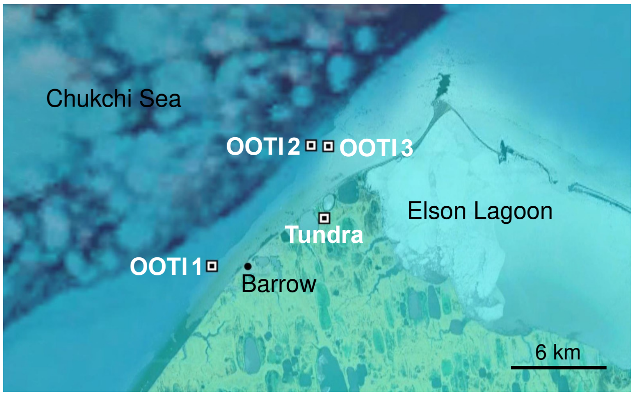

Fig. 1a. Field experimental sites around Barrow near the northernmost tip of Alaska. OOTI 1 at 71.29° N, 156.85° W; OOTI 2 at 71.36° N, 156.69° W; OOTI 3 at 71.36° N, 156.66° W; and Tundra at 71.32° N, 156.66° W. The MODIS Aqua satellite is translucently overlain to show sea ice conditions in the Chukchi Sea on 19 March 2009.

2.3 Meteorological information

Wind speed and direction were measured using a propeller anemometer (Model 05103, R. M. Young, Traverse City, MI, USA) at 3.0 m above the surface and a sonic anemometer (CSAT-3, Campbell Scientific, Logan, UT, USA) at 2.2 m. The orientation relative to absolute north was determined by hand-held GPS (Garmin Etrex). To determine temperatures, copper-constantan thermocouples were located inside passive radiation shields at 1.38, 0.1 m above and 0.05 m under the snow surface. A platinum resistance thermometer/relative humidity sensor (HMP45C, Campbell Scientific, Logan, UT, USA) inside a passive radiation shield was located at 2.3 m. Shortwave radiation (incoming and reflected) was monitored using silicon photovoltaic detectors (Li-190S, Li-200S, Li-Cor, Lincoln, NB, USA). Pressure was measured on site with a barometer (Model 61202V, RM Young).

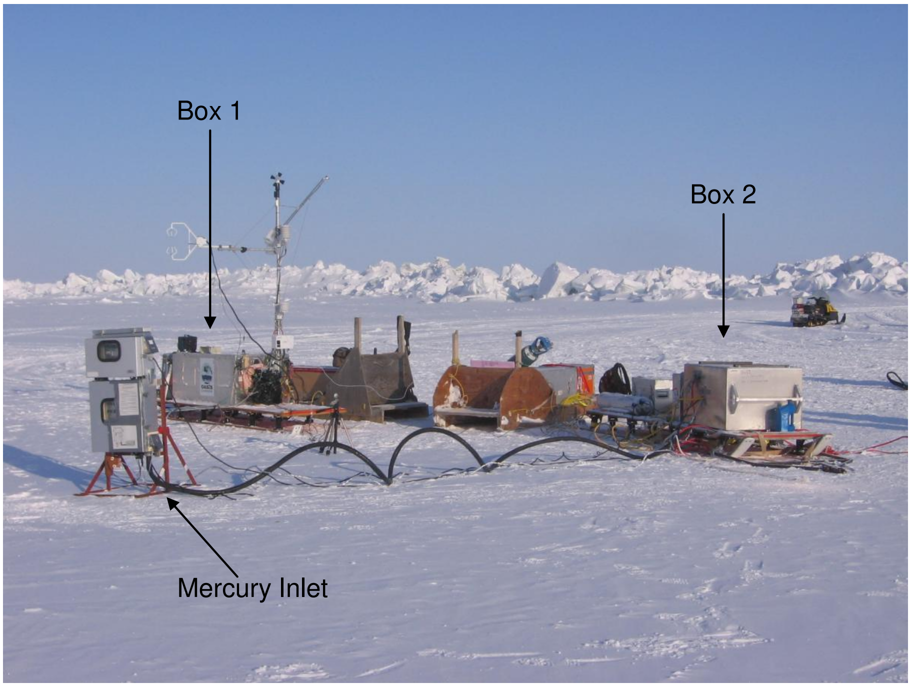

Fig. 1b. Experimental set-up of the Out On The Ice (OOTI) system. Box 1 housed the meteorological, MAX-DOAS and ozone instrumentation. Box 2 housed the mercury instrumentation. The inlet for the atmospheric mercury measurement is shown.

2.4 Ozone

At the OOTI site, a Model 205 dual-cell ozone monitor, manufactured by 2B Technology (Boulder, Colorado, USA), was used to measure surface-level ozone. Ambient air was sampled through $\frac{1}{4}$ " PFA tubing. A Teflon 2 µm-pore-sized filter was used to prevent penetration of any particles into the measuring cells. The instrument was calibrated at the beginning and end of the field campaign. Its zero was monitored for possible drift through regular zero measurements using an external ozone scrubber on the days when ozone was above a threshold of 10 ppb.

2.5 Bromine monoxide

Differential optical absorption spectroscopy (DOAS) can be used to quantify the column abundances of trace gases, such as bromine oxide (BrO), along a well-defined light path. These trace gases are determined using specific narrow-band absorption structures in the ultraviolet and visible spectral regions. The BrO measurements described in this paper were collected with a long-path DOAS (LP-DOAS) instrument (Platt and Stutz, 2008). The general set-up used in this study is described elsewhere (Frieß et al., 2011; Liao et al., 2011). The LP-DOAS telescope was located approximately 1 km inland on a building facing northwest. Two retro reflectors were installed 3623 m and 1074 m away from the telescope and provided a light path of 7246 m and 2148 m, respectively. The long light path was used under favourable meteorological conditions, whereas the short light path was used during periods of low visibility owing to fog, blowing snow or occasionally occurring mirages. Depending on meteorological conditions, spectra were recorded with integration times ranging between 1 and 50 s. The LP-DOAS light paths were almost parallel to the coast and are therefore are used to represent the same air mass. Liao et al. (2011) concluded that BrO is often distributed homogeneously on spatial scales of up to at least 4 km. Since the measurements from the LP-DOAS were collected within this distance, they are considered representative at the OOTI site.

2.6 Snow and ion chromatography samples

Samples for major ion analyses were[2] collected into pre-cleaned high-density polyethylene (HDPE) bags using pre-cleaned HDPE scoops. Samples were stored frozen until arrival at the laboratory where they were allowed to melt to room temperature and were filtered through trace-metal-grade nitric-acid-washed 0.45 mm polypropylene filters. Frost flower samples were diluted with 18 MΩ water 1000 times (by volume) prior to analysis. All sample dilutions were done in quadruplicate to assess cross-sample variation in the dilution process and were determined to be repeatable within 5 % of the concentration values. Cation and anion concentrations were quantified on a Dionex ICS-3000 ion chromatograph with an AS-19 anion column and CS-12 cation column (Dionex Corporation, Sunnyvale, California) at the Cold Regions Research and Engineering Laboratory

Alaska Geochemistry Laboratory. Each sample had a 10 mL injection volume. A gradient method using potassium hydroxide eluent ranged from 20 mM to 35 mM for anion analyses. Cation analyses used methane sulfonic acid eluent with a concentration of 25 mM in isocratic mode. The system flow rate was 1 mL min^{-1} and the operating temperature was 30 °C. The ion chromatograph was calibrated through repeat analysis of five calibration standards with concentrations ranging from 0.5 to 120 mg L^{-1} (within the range of analyses). Laboratory analytical anion and cation standards with values from 1 to 100 mg L^{-1} were analysed repeatedly to verify system calibration and assess analytical precision. Based on these analyses the calculated precision for the analyses is 5 %. Peaks were identified using Chromeleon (Dionex, Sunnyvale, California) and were verified visually.

2.7 MAX-DOAS

A mini-Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) system was used to record the aerosol extinction vertical profiles. This instrument is based on the Ocean Optics Inc. USB2000 miniature spectrometer (Hoffmann Messtechnik GmbH) (Hönninger and Platt, 2002; Frieß et al., 2004, 2006, 2011; Wagner et al., 2004) with a spectral resolution of 0.7 nm. Scattered sun light was collected by rotating telescope from a series of elevation angles: 2°, 5°, 10° and 20° and 90° (zenith orientation). Differential slant column densities (DSCDs) are directly measured from the instrument and represent the integrated concentrations of the absorbers along the scattered light path relative to the absorbers in measured reference spectrum selected from zenith observations. The vertical column density (VCD) is the vertically integrated trace gas concentration and is independent from the line of sight and the observed light path. DSCD and VCD are linked through an air mass factor AMF = DSCD/VCD which reflects the radiative transfer within the atmosphere and is determined through radiative transfer models (RTMs). Various aerosol scenarios were simulated using the radiative transfer model McArtim (Deutchmann, 2009) at 361 nm. Aerosol extinction values between 0.02 and 1 km^{-1} were used in the simulations with different profiles (with variable thickness) closely confined in a narrow layer over the surface and extending up to 2500 m in the atmosphere from the surface.

3 Results and discussion

3.1 Mercury measurements over the sea ice

The atmospheric mercury species measured during this campaign include gaseous elemental mercury (GEM), reactive gas phase mercury (RGM) and particulate mercury (PHg). Figure 2 shows the time series of GEM, RGM and PHg measured on the sea ice from 14 to 26 March 2009. Table 1 shows the descriptive statistics of this data set with a comparison to the tundra site. A GEM concentration of less than 0.77 ng m^{-3} was calculated as the upper limit indicating that an AMDE is occurring. This value is two standard deviations below the September–December mean GEM concentration for Barrow (from 2007 to 2009) (Steffen et al., 2012a). In this study, the GEM concentrations are below this threshold for 63 % of the total number of hourly averages, with a mean concentration of 0.59 ± 0.40 ng m^{-3}. The considerable variation that is associated with AMDEs is shown by the standard deviation for all the Hg parameters reported. Annual average GEM concentrations for Barrow (2007–2009) are 1.15 ng m^{-3} and are lower than the northern hemispheric average ($\sim$ 1.70 ng m^{-3}) (Slemr et al., 2003; Steffen et al., 2005). The PHg concentrations measured during this study are high, in comparison to temperate regions (Steffen et al., 2012b), with a mean concentration of 393 ± 237 pg m^{-3} and a maximum of 900 pg m^{-3}. RGM concentrations are lower than PHg, with a mean concentration of 30 ± 24 pg m^{-3} and a maximum value of 105 pg m^{-3}. These RGM concentrations are lower than others reported from Barrow (Lindberg et al., 2002) and we attribute the differences to spatial, seasonal and inter-annual variability. Figure 2 also shows the negative relationship between GEM concentration and PHg/RGM concentration during the measured time period which is commonly associated with AMDE chemistry.

Table 1. Mercury concentration data descriptive statistics from measurements over the sea ice and tundra.

	GEM Ice ($\mathrm{ng\,m}^{-3}$)	PHg Ice ($\mathrm{pg\,m}^{-3}$)	RGM Ice ($\mathrm{pg\,m}^{-3}$)	GEM Tundra ($\mathrm{ng\,m}^{-3}$)
Mean	0.59	393.49	30.10	0.79
Median	0.53	332.76	25.04	0.75
Std. Dev	0.40	236.74	23.69	0.56
Max	1.51	900.11	105.40	2.92
Min	0.01	47.09	3.52	0.00
R^2 vs O_3	0.76	0.61	0.10	0.52

On 14 March, the instruments were installed on the sea ice and subsequently moved on 19 March (22:00 UTC) and 23 March (21:00 UTC) to OOTI sites 1–3, respectively, to assess different surfaces and proximity to open leads (Fig. 1a). The surfaces of the three sites ranged from a few-day-old frost flower field with some surface snow (new ice pan), an ice pan with surface snow and an ice pan with 1–2-day-old frost flowers in which we cut an open hole through the ice which quickly froze over. Frost flowers are formed from water vapour above the sea ice into intricate ice crystal clusters (Simpson et al., 2007; Douglas et al., 2012a) that have the appearance of flowers on the surface. Brine enriched in sea salts are wicked up through the ice into these crystals. These three surfaces all represent highly saline surface young (nilas) sea ice with some frost flowers. Figure 3 shows the Moderate Resolution Imaging Spectroradiometer (MODIS) satellite images of our sample locations. Bands 1, 2, and 7

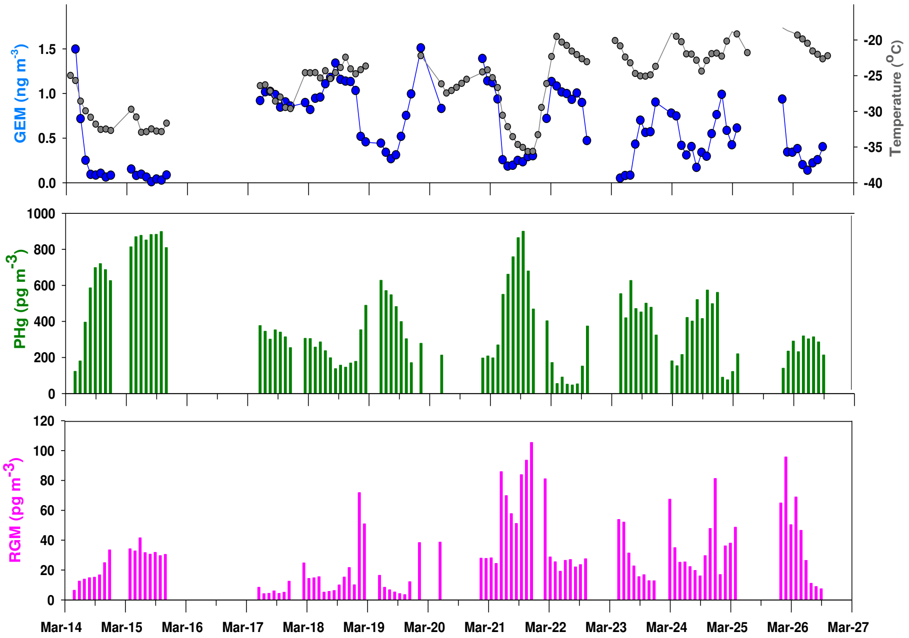

Fig. 2. Hourly speciation and air temperature data from over the ice. Gaseous elemental mercury (GEM, top) is reported in ng m^{-3}, and reactive gaseous mercury (RGM, bottom) and particulate mercury (PHg, middle) are reported in pg m^{-3}. Air temperature is reported in °C. The gaps in data indicate when the system was moved to a new site or when the power failed.

from the MODIS Aqua satellite are used to identify sea ice on 14–25 March when the sky was mostly clear. The satellite images, however, show that all locations are represented predominantly by first-year sea ice (blue) and some younger sea ice (darker blue) in refrozen areas where the ice cover was fractured by ice divergence. Since the surfaces of the sites are not vastly different in salinity and had little snow cover, for this paper we assume the surfaces are similar. From the satellite images, the interesting feature is the behaviour of the sea ice around the lead and this will be discussed later.

It is thought that the chemistry that leads to AMDEs occurs in the gas phase by oxidation of GEM to RGM. Once produced, RGM can partition/adsorb to particles in the air as PHg (Rutter and Schauer, 2007; Amos et al., 2012) or deposit to the surface. It has been theorized that the ratio of RGM to PHg reflects the transport distance of an air mass from where a depletion occurred and a low RGM : PHg indicates that the depletion occurred further away (Lindberg et al., 2002). Thus, if depletion events are initiated and occur over the Arctic Ocean, it might be reasonable to expect higher RGM than PHg concentrations when collecting measurements on the sea ice. However, the concentrations of PHg measured in this study are almost ten times higher than RGM over the sea ice. This was also observed in March 2008 from an icebreaker on the Beaufort Sea where the average concentration ratio of PHg : RGM was approximately 10.6 : 1 (Latonas, 2010). This result either dispels the theory that the ratio can indicate lifetime or shows that this study was not undertaken where depletion events occurred. Over the sea ice, the particle load in the air is likely the contributing factor in these elevated PHg concentrations. RGM can partition onto sea salt particles and other available surfaces (Rutter and Schauer, 2007). Both RGM and PHg have a higher dry deposition velocity (0.5 to 6 cm s^{-1} and 0.02 to 2 cm s^{-1}, respectively) than GEM (0.1 to 0.4 cm s^{-1}) (Zhang et al., 2009) that allows for faster deposition. Amos et al. (2012) showed, in their model simulation, stronger deposition of oxidized Hg at higher latitudes. They also concluded that high PHg fractions are yielded in colder air masses with high aerosol burdens. This current study supports these modelled results qualitatively, with higher PHg : RGM ratios at lower temperatures (not shown), but, due to a lack of PM$_{2.5}$ concentration data in this study, the partitioning could not be compared quantitatively.

3.2 Particle load and mercury on the sea ice

Using mini-MAX-DOAS, the position and thickness of the aerosol layer close to the study site can be modelled to confirm the presence or absence of aerosols as well as the position and thickness of the layer in the atmosphere. The sizes of the aerosols measured with the MAX-DOAS are not limited to the size of particles measured by the mercury instrument (< 2.5 µm). The modelled results indicate that small aerosol load, with an extinction of 0.08 km^{-1}, is confined in a layer 100 m thick over the surface on 14 and 25 March. This confirms that there is a measured concentration of particles present in the lower surface air at the OOTI site. These

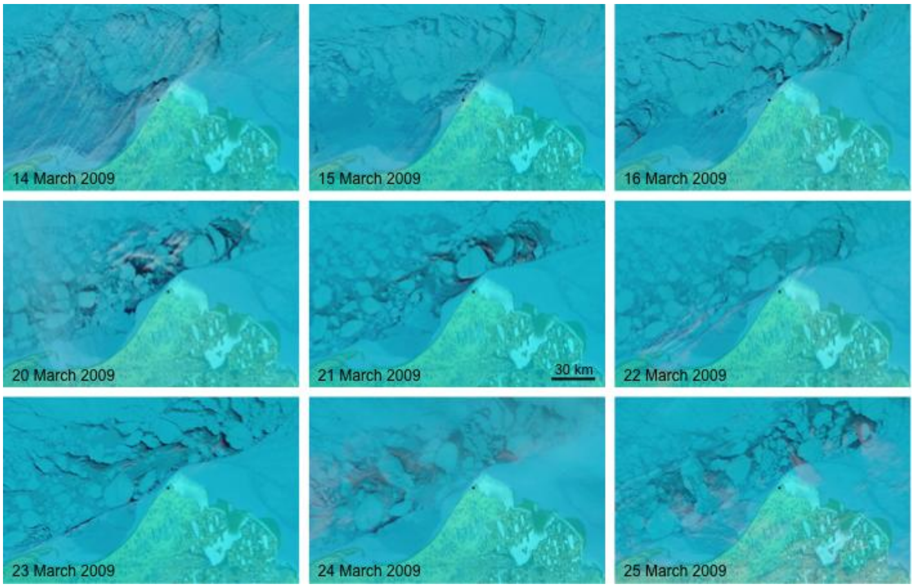

Fig. 3. MODIS satellite images of the sea ice conditions for 14–25 March 2009: 14–16 March, 20–22 March and 23–15 March are when samples were collected over the sea ice at sites 1, 2 and 3, respectively. 14–16 March represents Event 1; 20, 21 and 24 March represent Event 2, and 25 March represents Event 3. The black dot indicates the sampling location. The colours represent as follows: very light blue (lake ice or ice lagoon); light blue (first-year or older sea ice); darker blue (thinner and younger sea ice) and black (open water or thin new/nilas ice).

results further suggest that, on the afternoon of 25 March, an increased aerosol load (extinction coefficient of 0.3 km^{-1}) is homogeneously distributed within 350 m from the surface and emerged following a shift of the wind direction from 225° to 25° and an increase in wind speed. This shift correlates to a shift in the PHg and RGM distribution.

Natural sea salt, aged sea salt and other mixed particles are ubiquitous over the sea ice. In Ny-Ålesund, these particles fall into the $> 0.5\,\mu m$ size fraction range (Weinbruch et al., 2012). Other particle types commonly measured around the Arctic Ocean include sea salt sulphate, Arctic haze particles such as non-sea-salt sulphate and soot/black carbon. Sea salt sulphate aerodynamic diameters have been measured in the North Atlantic greater than 0.95 µm but are lower in the springtime to a size less than 0.49 µm (Seguin et al., 2011). Non-sea-salt sulphate diameter ranges between 0.49 and 0.95 µm (Seguin et al., 2011). Another type of suspended particle reported around the Arctic Ocean is diamond dust (Douglas et al., 2008; Domine et al., 2011). These small needle-like crystals form in the air on clear, cold days and have a relatively large surface area on which reactions can occur. They are reported to have a length between 1 and 1000 µm (Ohtake et al., 1982; Walden et al., 2003; Intrieri and Shupe, 2004). Douglas et al. (2008) reported high total Hg concentrations of 92–1370 $ng\,L^{-1}$ in these crystals and concluded that they are likely a source of elevated Hg measured on the surface. The size of diamond dust is, for the most part, greater than the inlet cut-off of the mercury instrument (2.5 µm). However, as the ice crystals hit the impactor on the instrument, there is potential for them to shatter and be measured by the instrument (Leaitch, personal communication to A. Stefffen, 2012). The contribution from diamond dust to the total particle load is likely minor but cannot be ruled out as a contributor to PHg levels because the Hg concentration in them is so high. PHg reported here is likely capturing the particles described above at this location over the sea ice. Interestingly, in 2005, RGM measurements collected in Barrow inland from the sea ice (approximately 0.5 km) around the same time of year exceeded 800 $pg\,m^{-3}$ at times, which may suggest significantly higher RGM concentrations inland than over the sea ice (Douglas et al., 2008). Unfortunately, PHg concentrations were not measured during that study to compare with the current one.

It is likely that low temperatures and the availability of sea salt and sulphate aerosols, as well as ice crystals around the sea ice, enable the RGM formed in the atmosphere to adsorb onto particles and result in the predominance of PHg measured over the sea ice. This finding is significant as the majority of mass balance calculations investigating the impact of AMDEs over the whole Arctic have relied on data collected inland or at coastal sites where sea salts may not be as predominant as over the ocean. Thus, current mass balance calculations may not accurately reflect the concentration of PHg over the sea ice.

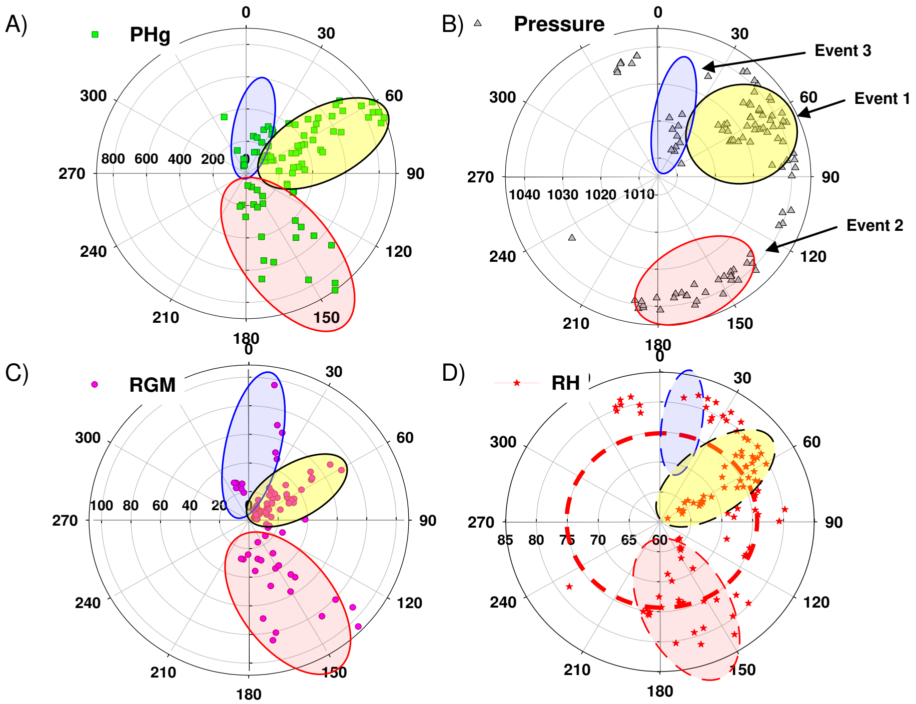

Fig. 4. Wind roses of **(A)** PHg concentration data (pg m^{-3}), **(B)** air pressure (mB), **(C)** RGM concentration data (pg m^{-3}) and **(D)** percent relative humidity (%) for the data from 14 to 27 March 2009 from over the sea ice. Yellow, red and blue circles represent events 1, 2 and 3, respectively.

3.3 Mercury, meteorology and sea ice

In order to understand what could influence atmospheric mercury speciation concentration data over the sea ice, several atmospheric factors are investigated. Not surprisingly, a strong relationship between RGM and solar radiation is found which indicates that RGM is derived through photochemical reactions. PHg concentrations do not peak with solar radiation but lag behind by a few hours, suggesting that this fraction of Hg is not directly formed by photochemical processes. The highest peaks in PHg (Fig. 2: 15 and 21 March) are found when the air temperature is at the lowest ($< -30\,°\mathrm{C}$), the wind speeds are low (between 1 and 2 m s^{-1}), relative humidity (RH) is below the average and the solar radiation is in a low period. The meteorological conditions reported on these days are ones in which ice crystals (diamond dust) can form in the air and provide a surface onto which newly formed RGM can adhere. Low temperatures also favour the partitioning of semi-volatile RGM compounds to the particle phase (Amos et al., 2012). Direct observations of diamond dust events were made on 21 and 22 March 2009 (Domine et al., 2011), raising the interesting hypothesis that RGM partitioning onto these crystals is the cause for the peak in PHg. The RGM and PHg data on these days differ from the other times in that they both peak during low solar radiation. The authors suggest that at the beginning of this time period RGM increases but that, as diamond dust crystals begin to form, some of this RGM adsorbs to these crystals and is detected as PHg. Such a shift would explain the atypical near-concurrent PHg and RGM peaks at this time.

Figure 4 shows the concentration of RGM and PHg, pressure and relative humidity in relation to wind direction. While these measurements were all made at locations surrounded by sea ice, the air coming from 330° to 75° is considered "from over the ocean only", while from 130° to 210° the air has originated from the "tundra" before travelling for a short distance over sea ice (see also Fig. 1a). The air pressure data (Fig. 4b) are first plotted with wind direction, and the clear groupings of air pressure and wind direction were used to define three air system events (the circles in the figure). The Hg data are grouped as "events 1, 2 and 3" according to these air systems. Table 2 summarizes the data shown in Fig. 4 and shows the mean and range of values for wind direction, air pressure, % RH, PHg and RGM concentration. Table 2 also includes r^2 values from linear regressions between PHg and RGM with ozone and BrO for the entire period and for each of the three events. The dates of these events are as follows: Event 1: 14–19 March; Event 2: 20, 21, 24 and 25 March; and Event 3: 25–26 March. The results in Fig. 4 show that when the air is from around 60° (Event 1 yellow circle – sea ice) PHg is above the total mean concentration and RGM is below. When the air is coming from 150° (Event 2 red circle – tundra), RGM is above its

Table 2. Summary information for data collected over the sea ice for the total study period and events 1, 2 and 3.

	Units	Total	Event 1 (yellow)	Event 2 (red)	Event 3 (blue)
Dates		14-26 March	14–19 March	20, 21, 24 March	25–26 March
Wind direction Centre (range)	Degree	210–330 (30–90)	60 (120–180)	150 (0–30)	15
Air pressure Mean (range)	mbar	1035 (1012–1042)	1035 (1026–1041)	1038 (1035–1042)	1019 (1012–1035)
PHg concentration Mean (range)	pg m^{-3}	393.5 (47.1–900.1)	449.8 (123.1–898.9)	367.4 (47.1–900.1)	255.5 (140.2–319.6)
RGM concentration Mean (range)	pg m^{-3}	30.1 (3.5–105.4)	18.3 (3.5–71.8)	39.4 (12.8–105.4)	42.9 (7.4–95.7)
% relative humidity mean (range)	percent	74.8 (61.3–82.3)	71.5 (61.7–78.7)	75.9 (64.2–82.3)	80.7 (78.2–81.9)
R^2 with Ozone PHg/RGM	n/a	0.61/0.10	0.82/0.01	0.63/0.19	0.58/0.29
R^2 with BrO GEM/PHg/ RGM	n/a	0.48/0.1/0.36	0.58/0.08/0.74	0.04/0.14/0.01	0.03/0.03/0.37
Number of data points	n/a	96–101	37–44	42–50	10–12

total mean and PHg is just below its total mean (but includes the high PHg peak discussed above). When the air is coming from 15° (Event 3 blue circle – sea ice), RGM is above its total mean and PHg is well below. Events 1 and 3 show discernable characteristics, while Event 2 does not (air originating from over the tundra).

The average RH during events 1, 2 and 3 are below 75 %, around 75 % and above 75 %, respectively, as seen in Table 2. These results show that there may be a relationship between the concentration of either PHg or RGM and RH. The deliquescence point of NaCl is at 75 % RH (Chen and Lee, 2001), which could indicate that these particles would have absorbed water, grown to where they could be more readily removed from the air at this point, are too large to be sampled (> 2.5 µm) or have reached a point where RGM is less likely to partition onto the sea salt and remain in the air. Air temperature can also play a role in the frequency of AMDEs (Cole and Steffen, 2010). In this study, air temperatures are investigated with PHg and RGM over the sea ice. PHg is positively correlated (linearly) with air temperature ($r^2 = 0.53$), but RGM shows no linear relationship with temperature.

The distances between the sample locations and the nearest refrozen ice/open water or nilas ice are estimated using MODIS satellite images. These estimates are summarized in Table 3 and are separated into events 1, 2 and 3 to assess whether there are links between the proximity of certain sea ice and mercury concentrations. During Event 1, a strong depletion of GEM and elevation in PHg are reported when the sampling site was located close to refrozen sea ice (1.2–1.8 km). At this time, the air measured is directly from the direction of this refrozen lead and is concurrent with the low GEM and high PHg concentrations. At the beginning of Event 2, the refrozen sea ice is further away from the sampling site (4–5 km) but an open lead is within 8 km. The proximity of the open lead may explain the increase in the % RH if the air mass with moisture from the lead came near the study site; however the wind direction during this event is predominately from the south, and thus the chemistry is not likely impacted from this lead. On March 25, during Event 3, open leads are closer at 12.5 km to the measurement and GEM is again depleted. These results suggest that both open leads and recently frozen sea ice are associated with GEM loss and with differences between RGM and PHg concentration levels.

3.4 Mercury, ozone and halogens over the sea ice

The relationship between GEM and ozone (O_3) has been well documented during AMDEs in the Arctic springtime (Schroeder et al., 1998; Ebinghaus et al., 2002; Berg et al., 2003a; Poissant and Pilote, 2003; Skov et al., 2004). The correlation suggests that common chemistry is responsible for the depletion of both. Linear regressions are performed on GEM, PHg and RGM with O_3 for the whole study period and for each event (Tables 1 and 2). GEM and O_3 show a strong linear relationship over the sea ice ($r^2 = 0.76$). While there is a reasonable linear relationship between PHg and O_3 over the study period ($r^2 = 0.61$), the strongest relationship was reported during Event 1 ($r^2 = 0.82$). There is little re-

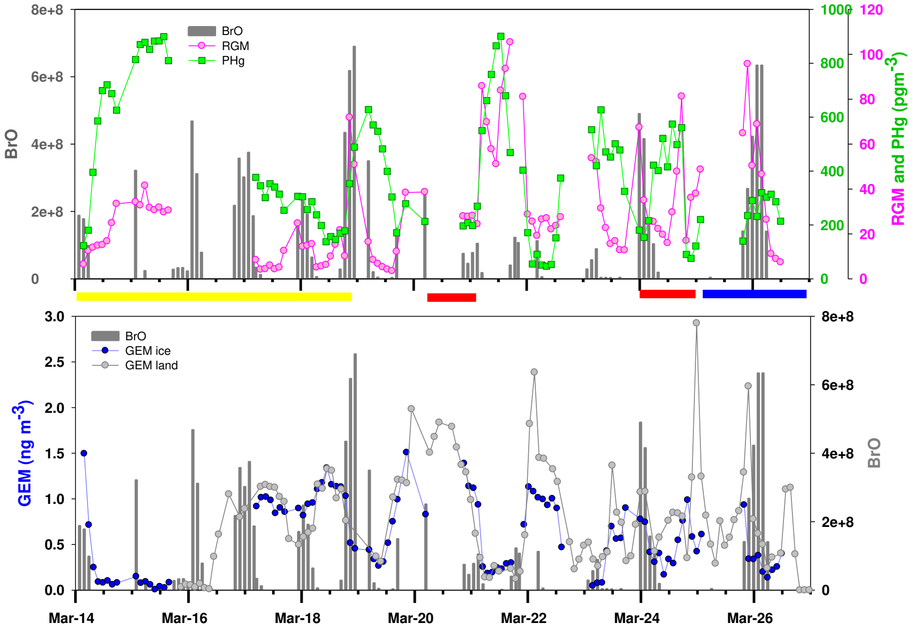

Fig. 5. BrO and PHg/RGM measurements over the sea ice and BrO and GEM measurements over both tundra and sea ice. Events 1, 2 and 3 are marked as yellow, red and blue, respectively.

Table 3. Estimated distances from the sampling locations on the sea ice to the nearest refrozen sea ice and nearest open water or nilas according to date and event.

Date	Distance to nearest refrozen sea ice (km)	Distance to nearest open water or nilas (km)	Corresponding event
14 March	1.4	11.0	1
15 March	1.2	7.0	1
16 March	1.8	9.0	1
20 March	4.4	5.4	2
21 March	5.0	8.5	2
22 March	5.8	45.0	
23 March	6.7	29.6	
24 March	6.8	18.8	2
25 March	6.3	12.5	3

lationship between O_3 and RGM in this data; however, the lifetime of RGM is short, and thus a strong relationship is not expected (Simpson et al., 2007).

Measurements of BrO are also collected during this study and Fig. 5 shows the time series of RGM, PHg, GEM and BrO. Table 2 shows the correlations of the mercury species with BrO (for the ice data). It can be seen in Fig. 5 that BrO is elevated at the beginning of a depletion event when GEM decreases and RGM/PHg increase and, as the event continues, BrO subsequently decreases. The results in Table 2 show that there is little to no linear relationship between BrO and PHg but a reasonable correlation between BrO and RGM for the periods when the air originates from over the ocean (Event 1 and especially Event 3). RGM and BrO are both products of bromine atom chemistry, which suggests that this chemistry is at play. The atmospheric conditions for Events 1 and 3 are as follows: Event 1 has high PHg, RH below 75 %, air temperature below −25 °C, a positive correlation between RGM and BrO and a negative correlation between PHg and O_3. These conditions can promote Br formation that, in turn, leads to RGM production where, under cold temperatures, the particles in the air provide the surface onto which RGM can adsorb and lead to elevated PHg concentrations. Event 3 has low PHg, RH above 75 %, air temperature above −25 °C, and again a positive correlation between RGM and BrO, and a negative correlation between PHg and O_3. The absence of a BrO–RGM correlation in Event 2 may result from the high-diamond-dust and high-PHg event that occurred on 21–22 March. As well, the lifetimes of BrO and RGM are quite different, which makes a direct analysis of these chemicals challenging (BrO has a reported lifetime of 2 minutes and RGM, depending on the species, approximately 3.7 days (Corbitt et al., 2011)). However, given their high correlation during events 1 and 3, the lifetime of RGM may be closer to that of BrO under some Arctic conditions. If true, this suggests that the assumption that RGM is predominant over PHg in air masses experiencing active AMDE chemistry may not be accurate in very cold or particle-rich air masses.

3.5 Atmospheric mercury differences between sea ice and inland tundra

The difference between GEM concentrations over the sea ice and inland over the snow-covered tundra is also investigated. A summary of the GEM concentrations for the two

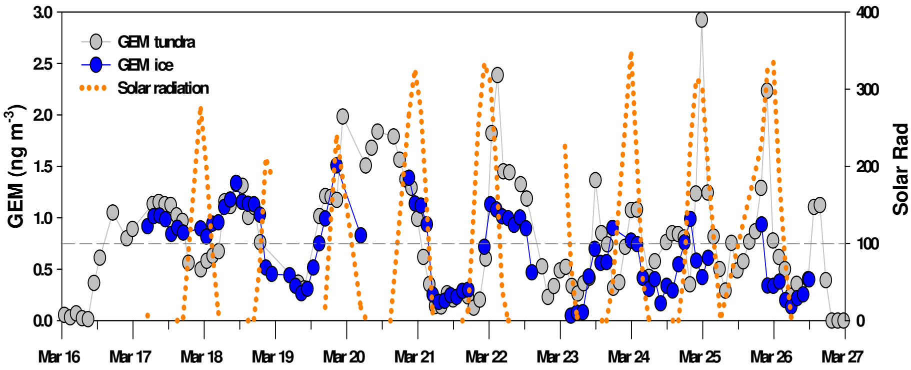

Fig. 6. GEM measurements over tundra inland (grey circles), over the sea ice (blue circles), solar radiation (orange) and the defined threshold for mercury depletions (0.77 ng m^{-3}) (dashed grey line).

locations is shown in Table 1. The mean GEM concentration, with 95 % confidence interval, over the tundra is significantly higher (0.79 ± 0.11 ng m^{-3}) than that recorded over the sea ice (0.59 ± 0.08 ng m^{-3}). The minimum concentration at both locations is the same, but the maximum over the tundra is higher than over the ice (2.92 and 1.51 ng m^{-3}, respectively). A linear correlation between O_3 and GEM is made for both sites and the results are shown in Table 1. These results show that there is a stronger linear relationship of O_3 and GEM over the sea ice than inland, as reflected by r^2 values of 0.76 and 0.52, respectively. This and the higher inland mean GEM concentration can be explained by inspecting the GEM concentrations from each site together. Figure 6 shows the time series from GEM measurements inland over the tundra (grey circles) and from over the sea ice (blue circles), the solar radiation (orange dots) and the defined depletion concentration threshold (dashed grey line). This plot shows that both sites experience depletion events around the same time and to the same level throughout most of the study. The striking difference between these two data sets is the strong peaks of GEM at the tundra site following the end of a depletion event which are not concurrently observed over the ocean. GEM (and O_3) concentrations generally do return to background after depletion through mixing (generally from aloft). However, it has also been shown that some GEM is emitted from the snowpack following depletion events (Steffen et al., 2002; Poulain et al., 2004; Kirk et al., 2006), likely due to photoreduction processes of oxidized mercury (Lalonde et al., 2002; Poulain et al., 2004; Durnford and Dastoor, 2011). The strong peaks of GEM at the tundra site at the end of an AMDE indicates that the amount of GEM returning to the air is much higher (nearly double in concentration) than that over sea ice. These results suggest that emission of GEM from the tundra snowpack occurs with a different magnitude than the emission recorded over the sea ice. The instruments were run beside each other for several days: a correlation of 0.9 was found for GEM, and thus the differences are not a result of instrument bias. It is also observed that after a spike in GEM concentrations at both locations the GEM is again oxidized and depleted from the air. This cycle continued throughout the study.

We hypothesize that the much smaller size of the GEM spikes over the sea ice is due to the presence of large quantities of NaCl in the snow over the ocean surface. It was suggested by Poulain et al. (2004) and Lehnherr and St. Louis (2009) that the photoreduction of oxidized Hg is suppressed by the presence of chloride. To investigate this further, snow samples from over the sea ice and around the land tundra site were collected and analysed for major ions and total Hg. The samples were collected randomly (for the purpose of this investigation) over the study period and thus were averaged for overall concentrations rather than reported daily. The overall results show that the average concentration of mercury in the surface snow over land (16 samples) and sea ice (13 samples) are 66 ± 30 (range 25–136) ng L^{-1} and 75 ± 47 (range 34–212) ng L^{-1}, respectively. These results indicate that there is somewhat more Hg in snow over the ice than over the tundra; however, there is high variability in this data. While a Mann–Whitney U test showed that these concentrations are not statistically different (95 % confidence), they do follow the pattern of previously reported results where concentrations of mercury in the snow are lower further inland from the coast (Douglas et al., 2008). However, the major ion data show that the chloride are six times higher in the snow over the sea ice than the tundra while bromide concentrations are twice as high in snow over the sea ice than the tundra. Higher concentration of chloride in the snow over the sea ice supports the hypothesis that the lower emission of GEM over the sea ice (in comparison with the tundra) is caused by a suppression of the photoreduction of RGM/PHg by chloride. The important corollary is that the sea ice snow can retain substantially more mercury than surface snow inland. The conclusion that the sea ice snow retains more mercury than tundra snow is a significant finding that needs to be factored into the current models investigating the cycling of mercury in the Arctic Ocean region.

4 Conclusions

In March 2009, measurements of GEM, RGM and PHg were collected near new sea ice and open leads and fractures in the Chukchi/Beaufort Sea near Barrow, Alaska, as part of the OASIS and OASIS-Canada International Polar Year programmes. These results represent the first published atmospheric mercury speciation measurements collected and reported on the sea ice. Concurrent observations of ozone, bromine oxide and a suite of meteorological parameters are also reported to explore their role of the atmosphere in the cycling of mercury over the sea ice. High levels of PHg associated with low air temperatures and RH below 75 % over the sea ice. The average PHg concentration was substantially higher than RGM over the sea ice. Sea salts and ice crystals around the sea ice provide surfaces to which RGM, created through AMDEs, could adsorb. Three distinct events occurred during the study that reflected different air masses and allowed study of the conditions and mercury speciation. Higher PHg concentrations than RGM are observed when measuring close to a refrozen lead. It was shown that, when O_3 and BrO chemistry was active, there were linear relationships between GEM, PHg and O_3 and between RGM and BrO, demonstrating the complexity of the atmospheric chemistry associated with AMDEs.

GEM was measured simultaneously at sites over the tundra and the nearby sea ice. A comparison of these results shows a significant difference in the magnitude of the emission of GEM once AMDEs ceased at the two locations. Higher chloride concentrations in the snow over the sea ice are the most likely explanation for the lower GEM emission over the sea ice due to the suppression of photoreduction processes of RGM/PHg to GEM in the presence of chloride. We conclude that the sea ice snow retains substantially more mercury than surface snow inland. This result needs to be factored into modelling efforts predicting the impacts of sea ice changes on the mercury cycle over the Arctic Ocean.

The sea ice on the Arctic Ocean is rapidly moving toward a greater fraction of thinner, more dynamic first-year ice with the following characteristics: more open leads, enhanced sea salt particle formation, more new ice formation, more frost flowers, and more brine wicking to the ice surface (Douglas et al., 2012a). As a consequence, the future Arctic Ocean sea ice and snowpack regime are expected to be increasingly halogen- and sea-salt-rich. This could have major implications for the deposition and ultimate fate of mercury in the Arctic for two reasons. Firstly, these properties of first-year ice are believed to support the activation of sea salt bromide (Nghiem et al., 2012), and therefore this scenario would likely result in increased atomic bromine concentrations and hence more widespread AMDEs in the Arctic atmosphere. Secondly, the more sea salt available on the surface of the Arctic Ocean (and potentially inland), the more deposited mercury may be retained. Thus, the present (and future) Arctic Ocean is likely a larger sink for atmospherically deposited mercury than has been previously been realized from field and modelling activities. Any potential for snow enriched in sea salts to move from the sea ice to the land in coastal environments will have higher mercury retention and thus a stronger impact of AMDEs on the coastal ecosystems.

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