MERCURY POLLUTION IN THE ARCTIC AND ANTARCTIC REGIONS

Francesca Sprovieri and Nicola Pirrone

CNR-Institute for Atmospheric Pollution, Division of Rende, 87036 Rende, Italy

INTRODUCTION

There is increasing evidence that the Arctic region, once considered a remote environment, is greatly impacted by global pollution. While there are virtually no anthropogenic pollution sources within the Arctic itself, it is, in fact, impacted by emissions from many of the world's largest industrial regions, resulting in surprisingly high pollution levels, especially during winter and spring, when "Arctic Haze"(the first indication of global pollution impact) forms. The occurrence of contaminants in the Arctic is influenced by the nature and rate of emissions from sources, the processes by which these compounds are transported to the Arctic, removal processes, and the direct atmospheric exchange with snow-pack, lake ice, sea ice, and the surface ocean. To assess mercury airborne transport and deposition in the Northern Hemisphere long-term measurements performed at stations of the EMEP monitoring network (Berg and Hjellbrekke, 1998) and the North American NADP/MDN monitoring network (*NADP/MDN*, 2002) were used in addition to the data of short-term measurements performed during episodic measurement campaigns. Numerous measurements have shown that the global background concentration of mercury in surface air ranges from 1 to 2 ng m^{-3}, though local mercury concentrations in industrial regions can be several times higher. The highest concentrations (above 2.2 ng m^{-3}) are typical of Europe, South-eastern Asia and the eastern part of North America, which are also the main emission regions and, therefore, characterized by the highest depositions. However, even in the remote parts of the Atlantic and Pacific oceans, as well as in the Arctic, mercury in surface air does not fall below 1.4 ng m^{-3}. Trajectory cluster analysis and a PSCF model (Potential Source Contribution Function) have been used by Cheng and Schroeder (2001) to investigate the relationship between sources and receptors for Hg concentrations observed at Alert, in the Canadian high Arctic, during 1995 and, therefore, to identify major anthropogenic Hg emission source regions in the northern hemisphere that contribute significantly to the Hg^0 concentrations measured at Alert throughout 1995. The analysis of 10-day back trajectories have shown that atmospheric transport of Hg to Alert is dominated by air masses from Eurasia which cross the Arctic Ocean. . In particular, long-range transport of Hg^0 only occurred in the cold seasons (Autumn and Winter), while summertime flows tend to circulate in the Arctic Ocean and do not travel very far (Cheng and Schroeder, 2001). Atmospheric transport, therefore, is shorter in the summer than in the winter season showing the seasonal variability of the flow patterns. The contribution of specific regions of the Northern Hemisphere to the mercury pollution of the Arctic environment is shown in Figure 1. The most significant contribution is made by Asian (33%) and European (22%) sources (Ryboshapko, 2003).

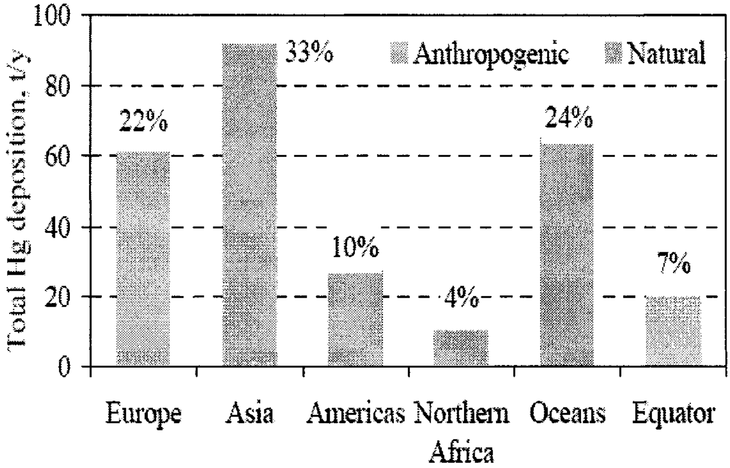

Figure 1 Global mercury impact to the Arctic
Source: Ryboshapko, 2003

The total mercury deposition to the Arctic is assessed at about 270 t/y. Of this amount, about 50% is contributed by anthropogenic emission sources. Several studies suggest that there has been a recent increase in Hg levels in Arctic biota, lake sediments, arctic food supplies (Lockhart et al., 1998) as well as in native people of circumpolar countries (AMAP, 1997; AMAP, 1998), despite a 20-yr decrease in global atmospheric Hg emissions since 1989 (Pirrone, et al., 1996; Pacyna, et al., 2001). If global emissions clearly decreased, another explanation for the marked Hg deposition increase in the Arctic must be sought.

CLIMATE AND METEOROLOGY

The Antarctic continent is in many ways quite different from its northern counterpart. Antarctica is a high, ice-covered land mass surrounded by the southern extensions of the Atlantic, Pacific, and Indian Oceans (Figure 2).

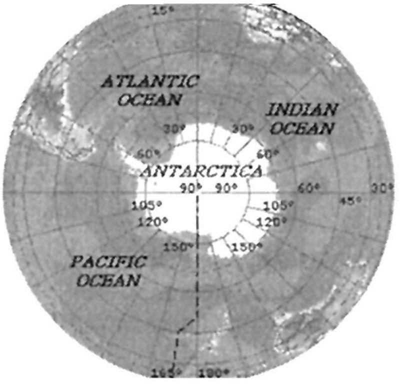

Figure 2. The Antarctic Continent.

On the other hand, the vast region of the Arctic consists of the ice-covered Arctic Ocean surrounded by many islands and the continental mass lands of northern North America, northern Europe and northern Asia (Figure 3).

As a result of these differences, the climates of the two regions are very different. The overwhelming characteristic of polar regions, in terms of both intensity and duration, is the cold. The long winter night ensures very low temperatures. The polar regions thus, show large seasonal variations in incoming solar radiation, from none during the winter months to 24 hours of sunlight at mid-summer receiving, on an annual basis, less solar radiation than other parts of the world. However, the radiation levels vary greatly depending on the season and in their respective mid-summers the daily totals are greater than at other places on earth.

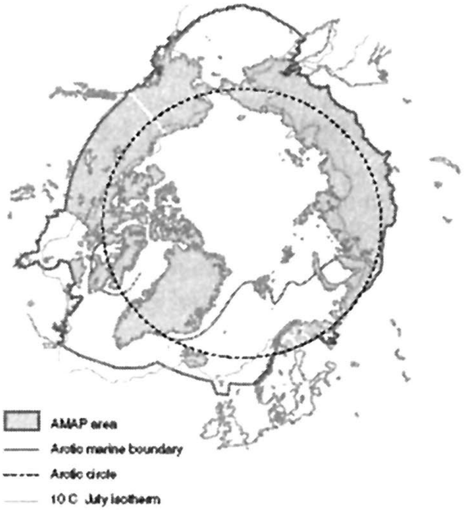

Figure 3. The Arctic Region as defined by Temperature, the Arctic marine boundary AMAP and assessment area.

Source: AMAP 1998.

Large part of the solar radiation that reaches the Earth is reflected by extensive cloud, snow and ice cover. The high albedo of polar regions, from the persistent snow and ice and the large loss of long-wave radiation due to the exceptional clarity and dryness of the atmosphere, is a key factor in the surface energy budget and ensures a net loss of radiation in all or most of the months of the year. This radiation imbalance produces low temperatures and results in a redistribution of heat from southern latitudes via air and ocean currents (Varjo and Tietze 1987). The loss is, in fact, compensated through transport of sensible and latent heat from lower latitudes, usually within cyclones, and by heat carried within ocean currents. Because of the lack of transport of warm current to the Southern Ocean and the pressure of strong westerlies, which blocks heat supply over the Antarctic, the Antarctic is colder than the Arctic. Summer temperatures in most of the Antarctic continent remain well below freezing. In the Arctic, however, rapid and strong snowmelt produces a large influx of fresh water to the rivers and Arctic Ocean in the spring and summer and supports a burst of life during a brief and intense summer. Important circulation systems of the world's oceans are driven by sinking cold water at the periphery of polar regions. On the basis of temperature, the Arctic is defined as the area north of the 10°C July isotherm, i.e., north of the region which has a mean July isotherm, i.e., north of the region which has a mean July temperature of 10°C (Figure-3) (Linell and Tedrow 1981, Woo and Gregor 1992). Based on oceanographic characteristics, the marine boundary of the Arctic is situated along the convergence of cool, less saline surface waters from the Arctic Ocean and warmer, saltier waters from oceans to the south. The frequency and the position of the persistent high-low-pressure systems not only play an

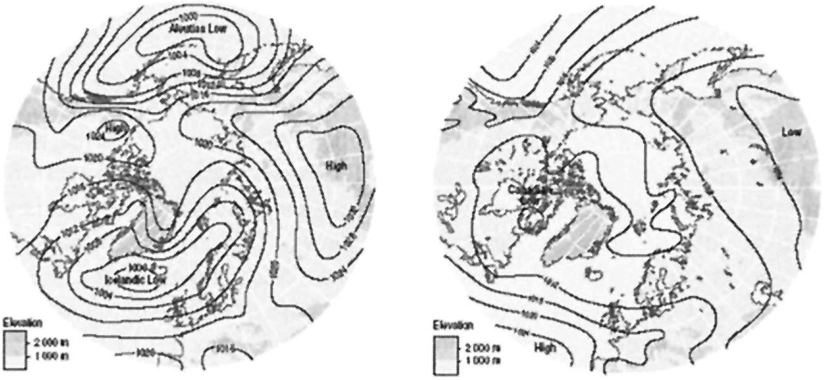

Figure 4. Mean atmospheric sea-level pressure (mb) in the Arctic during the winter and spring seasonal.

Source: AMAP, 1998.

important role in the existence of the regional and local climates in the polar regions, but also link the Arctic and Antarctic climatic system to the world climatic system influencing also the atmospheric air mass circulation which deliver contaminants to the poles. During the winter and spring seasons, the lower tropospheric circulation of the northern polar region is dominated by high pressure over the continents and low pressure over the northern Pacific and Atlantic Oceans (Figure 4). In particular, the intense Siberian high pressure cell tends to force air on its western side northward into the Arctic. The high pressure ridge over North America generally drives air out of the Arctic southward, resulting in the transport of air over Siberia into the High Arctic, and south over North America.

Consequently, contaminants which are introduced into the atmosphere in Siberia or Eastern Europe (in either vapour form or bound to small particles which have a low deposition velocity) are frequently transported into the Arctic region. Moreover, anticyclones are characterized by relatively low wind speed, and thus stagnant conditions. Near the surface, the relative lack of cloud cover and low incident solar radiation during Arctic winter can produce extended periods of surface radiation inversions. These factors reduce the effectiveness of vertical mixing and removal at the surface, resulting in the accumulation of contaminants in the lower Arctic atmosphere. Some air is also exchanged with the south when low pressure vortices along the Arctic front mix warm southern air with cold northern air in a large-scale turbulent eddy. In summer, the continental high pressure cells disappear, and the oceanic low pressure cells weaken, particularly in the north Pacific. Northward transport from mid-latitudes decreases accordingly. In contrast to the winter period, in the summer, south-to-north transport from Eurasia is, therefore, much weaker as the Siberian high dissipates. The mean air circulation pattern in the lower part of the atmosphere yields to a more circular clockwise flow around the North Polar Region. Marked variation in cloud cover and precipitation accompanies this seasonal variation.

ATMOSPHERIC MERCURY DEPLETION EVENTS (AMDES)

A surprising discovery that provided a great impetus for Arctic atmospheric chemistry research in several nations interested in preventing pollution of polar regions, was the observing of an unusual phenomenon called Atmospheric Mercury Depletion Events (AMDEs) in the atmospheric boundary layer of the Arctic and sub-arctic regions. Figure 5 shows several sampling Arctic and sub-arctic locations where intensive mercury measurement campaigns were performed in order to study the spatial extent of the AMDEs and above all, to understand the atmospheric mechanism behind these springtime phenomena. During the 3-month period following polar sunrise, it has been identified for the first time at Alert in the Canadian High Arctic (Schroeder et al. 1998; 2003), an atmospheric mechanism by which gaseous elemental mercury (Hg^0) may be converted to reactive and water-soluble forms (Reactive Gaseous Mercury (RGM) and/or Particulate Mercury (Hg-p)) that deposit quickly thus increasing the mercury fluxes and deposition processes in the fragile ecosystems of the Arctic and/or Antarctica.

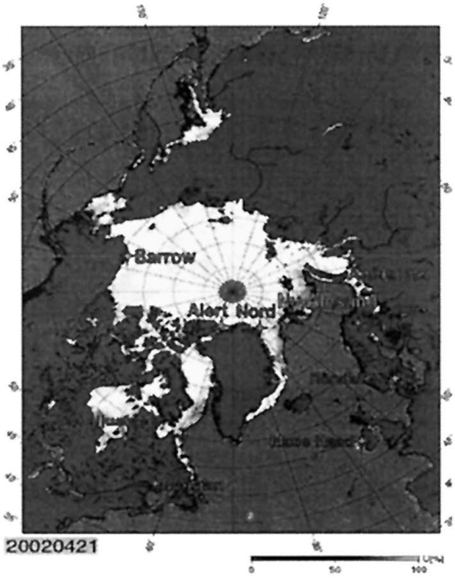

Figure 5. Mercury sampling locations in the Arctic and sub-Arctic region.

Source: Berg et al., 2003.

Springtime AMDEs first noted in the Arctic and observed each spring, have also been observed in Antarctica (Ebinghaus et al., 2002). The recent increase in Hg accumulation in the Arctic is, therefore, a direct consequence of the AMDEs. Figure 6 illustrates the net effect of AMDEs on the annual deposition of mercury in the Arctic. The contribution of AMDEs (occurring over several weeks) to the annual mercury deposition may be as high as 50% in coastal Arctic regions. AMDEs occur at the same time as tropospheric ozone depletion events suggesting

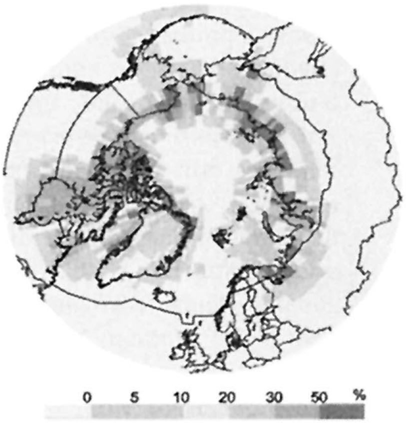

Figure 6. The contribution of MDEs to annual mercury deposition in the Arctic.

Source: AMAP, 1998.

that both species were removed by similar unknown homogeneous and/or heterogeneous chemical reactions. The AMDEs are in fact, strongly correlated with ground-level ozone depletion events (Schroeder et al., 1998) which had been discovered 10 years earlier (Barrie et al., 1988). These events cannot be explained by changing meteorology alone but occur when the atmosphere is in a chemically "perturbed" condition. The results of a number of studies suggest that catalytic destruction involving the $BrO_{(g)}$ radical is responsible for the O_3 depletion. Ozone depletions are caused by photochemically-initiated autocatalytic reactions involving reactive halogen species (such as Br and BrO) derived from sea-salt aerosols in areas of active open water (opened series of open leads and polynyas where the wave activity and sea-salt aerosol generation is very high). Hence, it is very likely that mercury depletion events, having temporal ground level concentrations similar to those of ozone, occur in polar areas through similar mechanisms. Given, thus, the correlation between O_3 and $Hg^0_{(g)}$, and the simultaneous increase in Hg associated with particulate matter (Schroeder et al., 1998; Lu et al., 2001) and RGM (Lindberg et al., 2001) it is thought that BrO, or another Br containing radical formed in the period around the polar sunrise, is responsible for the sudden increase in the oxidation rate of $Hg^0_{(g)}$ and the formation of less volatile and more soluble $Hg^{(II)}$ compounds which are deposited or condense onto pre-existing particulate matter (Lu et al., 2001; Lindberg et al., 2001; Berg et al., 2003a,b; Steffen and Schroeder, 2002; Poissant and Pilote, 2001, Ebinghaus et al., 2002). Although, the kinetic data on the reactions of mercury with atomic halogens is actually scarce, the interaction with halogen radicals seems to be the only plausible process accounting for the fast mercury depletion in the Arctic and/or Antarctic troposphere. The systematic seasonality of AMDEs leads to the supposition that the depletions of O_3 and Hg^0 require both sunlight conditions and a frozen aerosol or snow surface. The frozen surfaces on the Arctic Ocean are, in fact, enriched by concentrations of halide ions (Br-, Cl^-), sunlight conditions probably trigger the release of halogen containing compounds to the atmosphere. Other reactive halogen species present in the Arctic could be thermodynamically able to oxidize Hg^0 to form RGM in the gaseous phase, including Cl_2, Br_2, BrCl, HOCl and HOBr. However, molecular Cl_2, Br_2, and BrCl are not likely to produce in-situ RGM formation observed in the Arctic during springtime since they can be rapidly photolyzed by solar radiations (Fan, S.-M. Et al., 1992). HOCl and HOBr are more resistant under sunlight conditions but they do not exhibit a strong diurnal cycle in the remote marine boundary layer (Mozurkewich, 1995), therefore, they may not account for the reactive mercury species production during polar sunrise. Two RGM species have been considered as products: mercury oxide (HgO) and mercury halides ($HgBr_2$/$HgCl_2$). Based on published studies of reactive halogens in the Arctic (Foster, et al., 2001), $HgBr_2$ should be favored considering also that the KCl-Annular denuders may preferentially collect $HgBr_2/HgCl_2$ over HgO (Landis et al., 2003). During AMDEs elevated RGM (and/or Hg-p) also coincided with periods characterized by increased levels of column BrO. One potential indicator of the overall spatial extent of these events is illustrated by the monthly GOME maps of BrO distribution. These and related maps (Lu et al., 2001) clearly confirm that MDEs and associated RGM (Hg-p) production should be concentrated in coastal zones and might not be expected in other locations (e.g., continental areas).

Photolyzable bromine which builds up under the ice, escapes through constantly changing patterns of open leads and polynyas. These dynamic open water areas are also sources of sea-salt aerosols, water vapour, and heat from the comparatively warm ocean waters. All these products are concentrated in the near surface air due to the lack of vertical convection, (caused by limited solar input, the high-albedo of the snow/ice surfaces, and a positive temperature inversion). The bromine source regions are, thus, concentrated in the dynamic areas of annual sea ice, and the advection of Br compounds to inland and ice-shelf regions is controlled by prevailing winds and is effectively influenced by topography. Oxidation of Hg^0 and enhanced deposition of RGM (Hg-p) would not be expected in areas without advection of Br compounds. Under these conditions, several arctic experiments have shown that RGM reached high levels exceeding those measured near industrial point sources (Sheu et al., 2001). Garbarino et al. (2002) shown that mercury concentrations in snow over sea ice were highest in the predominately downwind direction of the open water leads and polynyas surrounding Point Barrow (e.g., to the west), an area that often shows enhanced BrO. When these surface emissions of photolyzable bromine encounter air-mass containing Hg^0 emissions from southern latitudes under sunlight conditions, mercury depletion/deposition events will occur.

The springtime mercury deposition rates in the Arctic could therefore be related to a function of the spatial coverage of annual sea ice, the air-mass transport of mercury emissions to this region, and local air-mass circulation. These phenomena are, in turn, controlled by average spring and summertime temperatures. The atmospheric oxidation of elemental mercury (Hg^0) to Hg(II) after polar sunrise is also evident from the increase in concentrations of mercury observed in surface snow from the polar night to the Arctic spring (Lu et al., 2001; Lindberg et al., 2002). The Arctic environment may, therefore, act as a global sink for atmospheric mercury. More recently, with the improvement of RGM and Hg-p sampling techniques, investigations of the atmospheric mercury chemistry have been performed at different maritime circumpolar stations to examine and to better understand the mercury depletion mechanism through integrated experiments involving mercury concentrations also in the snow/ice surfaces.

SAMPLING LOCATION AND SPATIAL EXTEND OF THE MERCURY DEPLETION EVENTS IN THE ARCTIC REGION

Several field experiments have been performed at different Arctic locations (see Table 1) in order to better understand the chemical processes that may act to enhance the capture of Hg from the global atmosphere and its deleterious impact on Arctic ecosystems.

High-temporal-resolution Hg measurements performed at Alert, Nunavut, Canada (82.5N, 62.3W), showed for the first time in 1995, an unsuspected atmospheric process during the 3-month period following polar sunrise (mid-March to mid-June at Alert); atmospheric mercury concentrations showed extraordinary fluctuations from background concentrations to undetectable levels (<0.1ng m^{-3}) (Schroeder et al., 1998).

Table 1. Atmospheric mercury species measurements performed at different Arctic locations from 1995 to 2003.

Measurement Sites	Coordinates	Period	Measurement type	Techniques	References
Alert (Canada)	82°5'N 62°3'W	1995-2002	Hg^0; TPM	Tekran 2537A; AE-TPM Traps; CRPU-(Cold Regions Pyrolysis Unit)	Schoroeder et al., 1998; Lu et al., 2001; Steffen et al., 2002
Barrow (Alaska)	71°19'N 156°37'W	1999-2003	Hg^0; RGM; Hg-p	Tekran 2537A; Tekran 1130 and KCl-Coated Annular Denuders; Tekran 1135;	Lindberg et al., 2002
Nord (Greenland)	81°30'N 16°40' W	1998-2002	Hg^0	Tekran 2537A;	Skov et al., 2004
Ny-Alesund (Svalbard Islands)	78°54' N 11°53' E	2000-2003	TGM; Hg^0; RGM; Hg-p; TPM	Tekran 2537A; Tekran 1130 and KCl-Coated Annular Denuders; Tekran 1135; AE-TPM Traps ;	Berg et al., 2001;2003; Sommar et al., 2004; Sprovieri et al., submitted
Amderma (Russia)	69°43'N 61°37'E	2000-2001	Hg^0	Tekran 2537A;	AMAP, 2002

Three periods were clearly distinguished due to different Hg behaviour observed during the year: (i) fall/winter period, with background Hg^0 concentrations (1.5 – 1.6 ng m^{-3}); (ii) springtime, with highly variable Hg^0 levels often to well below the detection limit and (iii) summertime, with higher Hg^0 concentrations probably due to the warm season in which temperatures and/or sunlight conditions induced volatile Hg^0 emission and/or re-emission from water and land surfaces to the atmosphere (Schroeder et al., 1998).

Moreover, Hg^0 depleted as O_3 showing a very strong correlation with ground level ozone concentrations. The discovery of the AMDEs, have enhanced research interest in this region thus several and intensive measurement expeditions were performed from the 1995 to 2001 (Steffen and Schroeder, 2002). In their Alert study, Steffen and Schroeder (2002) found that Hg concentrations associated with particles increased at the same time of the Hg^0 concentrations decreased. This was the first indication that atmospheric chemical reactions were converting Hg^0 to inorganic Hg(II) species, less volatile than the Hg^0 and more likely to associate to particles. The Spring 1998 campaigns confirmed the strong anti-correlation between Hg^0 and Hg-p (Lu et al., 2001) observed at Alert.

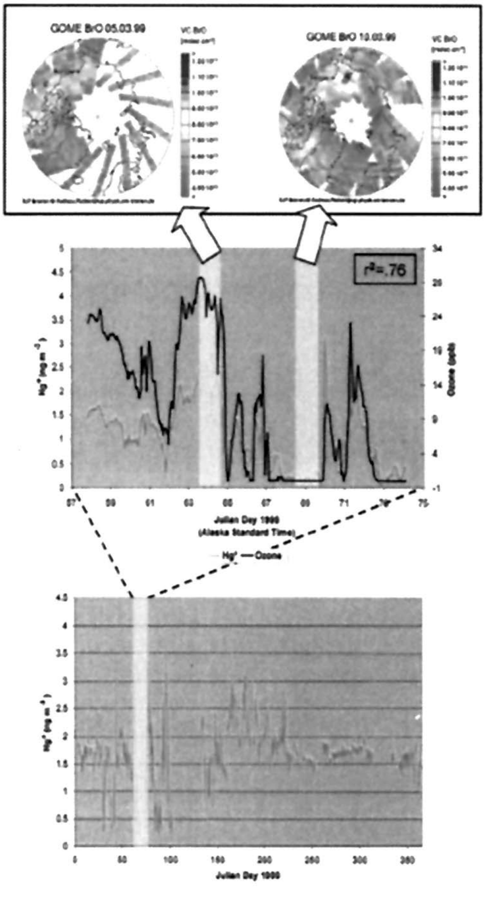

Figure 7. Hg° concentrations at Barrow during 1999.

Source: Lindberg et al. 2002.

Intensive measurement campaigns performed at Pt. Barrow, Alaska (Lindberg et al., 2001; Lindberg et al., 2002) from 1999 to 2003 showed for the first time, that during depletion events, significant concentrations of RGM were reported. All of the data were collected at the NOAA-Climate monitoring and Diagnostic Laboratory (CMDL) in Barrow, AK. The sampling site is located at Point Barrow and is surrounded by water to the north, east, and west. Barrow is geographically the northern-most point in Alaska, located at 71°19.'N, 156°37'W about 1600 km south of Alert. The 1999 data (Figure 7) provide the first confirmation of AMDEs at this more southerly Arctic site with the RGM production during AMDEs at significant levels when Hg^0 is being depleted. Although others have suggested that the depleted Hg^0 at Alert accumulates in the aerosol-phase Hg (Schroeder et al., 1998), Barrow data clearly indicate an important change in gaseous speciation during AMDEs, producing levels of RGM unprecedented at remote and rural sites (Lindberg et al., 1998; Ebinghaus et al., 1999; Munthe et al., 2001). The depletion events observed begin within a few days of polar sunrise (late January) and persist until snowmelt (early June), suggesting a role of both sunlight and frozen surfaces.

Gaseous and aerosol Br also exhibit strong seasonal cycles at Barrow and, like RGM, peak annually between January and June. During this period, aerosol Br increases nearly 20-fold over typical concentrations and can exceed 100 ng m^{-3}. Hypotheses for the sources of this Br include aerosol enrichment by bubble bursting from the sea-surface microlayer, and/or other aerosol-related reactions.

The most probable mechanism involves heterogeneous reactions at the interface of hygroscopic sea-salt aerosol many of which are initiated in the surface microlayer of snowflakes or the snowpack (Barrie et al., 1997). Particulate Hg (Hg-p) samples collected at Barrow (Landis et al., 2001) indicate that RGM is clearly the primary species being formed during this AMDE period and that the two species behave differently. For example, during a period with 3-5 hours of darkness, particulate Hg and RGM were anti-correlated, with Hg-p peaking just prior to sunrise when RGM was at its daily minimum but decreasing rapidly upon sunrise (Landis et al., 2001).

The authors suggest that different reaction pathways or reactants may be responsible for creating Hg-p as compared to RGM and that the Hg-p produced at night is photosensitive. One candidate reaction would involve aerosol-bound BrCl that would readily oxidize any sorbed Hg^0 but that is rapidly decomposed under sunlight (Fan et al., 1992). However, upon the advent of 24-h were now positively correlated (Landis et al., 2001). The authors speculate that the Hg-p detected after 24-h sun reflects RGM sorbed onto the existing aerosol. These observations may help explain why the air at Alert appears to be characterized by a larger Hg-p/RGM ratio than at Barrow (Lu et al., 2001). The surface reactivity of airborne RGM suggests that it would readily partition to the aerosol phase upon formation. Hence, Hg-p/RGM ratios may be useful indicators of the age (time since oxidation of

Hg^0), and hence transport distance, of depleted air masses. Barrow data suggested that at least some RGM is being formed in situ at ground level, while Hg^0 in the air sampled at Alert may have undergone significant depletion/oxidation events over the sea ice prior to being sampled at the Alert station.

Atmospheric mercury depletion events have also been studied at Station North, Northeast Greenland, 81°36'N, 16°40'W, during the Arctic Spring (Skov et al., 2004). GEM and O_3 were measured starting from 1998 and 1999, respectively, until August 2002. Weekly average concentrations of atmospheric bromine were also determined from samples collected on particle filters. Figure-8 shows the results of ozone and Hg^0 measurements together with concentrations of fBr. Ozone and Hg^0 were rather stable from September/October until the end of February/beginning of March. Then, a highly perturbed period appeared where both ozone and Hg^0 were depleted to zero from, respectively, about 40 ppbv and 1.5 ng m^{-3}. At the same time fBr increases and reaches a maximum of about 10 ng m^{-3}. Ozone and Hg^0 have been observed to deplete simultaneously and to be highly correlated during atmospheric AMDEs (Schroeder et al., 1998). After the depletion period, some very high concentrations of Hg^0 appeared with values above 2 ng m^{-3} in 2000, up to 1.9 ng/m3 in 2001 and at a maximum of 5.7 ng m^{-3} in 2002. High values after AMDEs are also observed at Alert (Schroeder et al., 1998), Barrow (Lindberg et al., 2002), and Svalbard (Berg et al., 2001), and they are attributed to to reemission of mercury to the atmosphere. In the spring 2001-2002 Canadian and Russian scientists collaboratively measured Hg^0 concentrations for the first time in the Russian high Arctic at Amderma (69°43'N, 61°37'E) and were observed AMDEs in the period from the end of March until the middle. These results confirm that the springtime depletion of mercury after polar sunrise is a mechanism endemic to Polar Regions and that Hg^0 is chemically converted to more reactive mercury species during the AMDEs. Atmospheric mercury measurements were carried out on routine basis at Ny-Alesund (78.9°N, 11.9°E) (Spitzbergen, Svalbard Islands) from February 2000 to the end of May 2003. Additionally, intensive measurement campaigns were performed in the presence of 24 hours daylight after polar sunrise, from about the middle of April to middle of May during the years 2000-2003 (Berg et al., 2003; Sommar et al., 2004; Sprovieri et al., submitted). Ny-Ålesund is situated at the southern shore of Kongsfjorden on the West Coast of Spitzbergen in the Norwegian high Arctic at about 15 km from the northernmost Barents Sea. An offshoot of the waning Gulf Current (West Spitzbergen current) causes ice-free conditions along the west coast of Spitzbergen during the entire year. Measurements were performed at the Global Atmospheric Watch monitoring observatory operated by the Norwegian Institute for Air Research (NILU) at Zeppelin

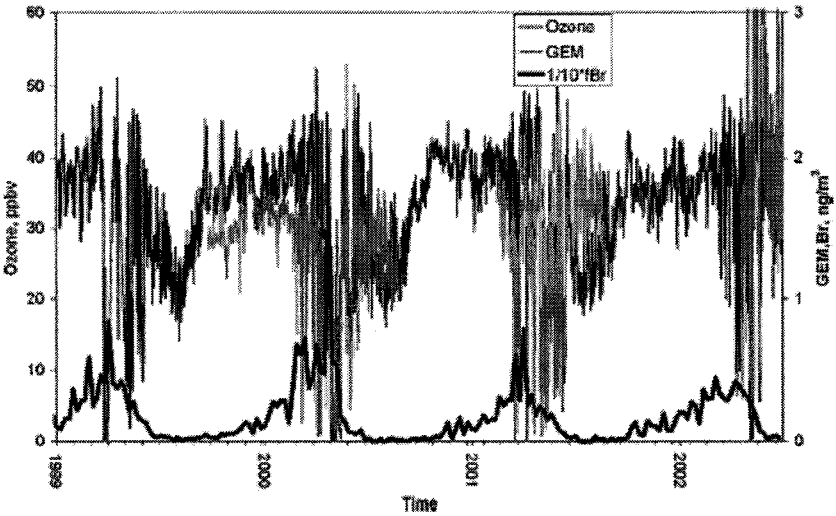

Figure 8. Hourly O3 mixing ratios and weekly concentrations of fBr measured from 1999 to 2002 at Station North, Greenland. GEM was measured each Spring from 2000 to 2002.

Source: Skov et al. 2004.

Mountain (474-m a.s.l). The theory of RGM and PM formation during depletion of elemental Hg in the Arctic, has been strengthened by the results from the intensive measurement campaigns performed each spring from 2000 to 2003. Hg^0concentrations at Zeppelin were within the range <0.1 - 3 ng m^{-3}. The annual averages for 2000, 2001 and 2002 were 1.47, 1.56 and 1.59 ng m^{-3}, respectively.

Episodic depletions of Hg^0, closely resembling ozone depletions in Arctic surface level air, were frequently observed during an intensive atmospheric mercury campaign performed at Ny-Alesund, (Svalbard Islands, Spitzbergen) from April 18th to May 12th 2003, during the arctic springtime (Sprovieri et al., submitted). Hg^0 concentrations dropped from around 1.5ng m^{-3} to undetectable levels (< 0.1 g m^{-3}) and were strongly correlated with surface O_3 depletion. GEM, RGM and Hg-p concentrations were measured using a method extensively tested by Landis et al. (2002), which can provide automated measurements of speciated atmospheric mercury concentration levels. GEM, RGM and Hg-p concentrations were simultaneously quantified by an automatic integrated system (a Tekran automated unit, Model 1130 and a Tekran 1135 particulate unit, coupled to an automated gas-phase mercury analyser, Tekran 2537A). Three GEM depletion events were clearly observed during the springtime campaign at Zeppelin Station (474-m a.s.l.). Regarding the first and major depletion event, depicted from 21th to 22th of April, Hg^0 levels dropped very fast within 24 hours and the concentrations changed from about 1.7 ng m^{-3} to below the detection limit. This depletion, instead of other two minor events, is characterized by several dips and spikes in the Hg^0 trend with concentrations always below 0.9 ng m^{-3} which could be interpreted as minor depletion episodes. During the following minor depletion episodes Hg^0 dropped below 0.25 and 0.5 ng m^{-3} respectively.During the ODEs, Hg^0 exhibits a strong correlation with O_3 ($r^2 = 0.8$) suggesting a possible link with the chemical reactions which destroy tropospheric ozone, as first suggested by Schroeder et al. (1998). Dramatically increased levels of Hg-p and RGM were measured as Hg^0 concentrations dropped to undetectable levels at Ny-Alesund, as well as at several Arctic sites. The RGM data show that during springtime AMDEs, RGM appears at significant levels only when Hg^0 is being depleted, clearly indicating an important change in *gaseous* speciation during AMDEs. RGM concentration-time series were in the range between 2.5 pg m^{-3} to 228.1 pg m^{-3} and Hg-p concentration-time series were in the range between 0.26 pg m^{-3} to 98.6 pg m^{-3}, peaking just during the first and major depletion event. The data obtained at Ny-Alesund in particular, indicate that RGM is clearly the primary species formed during the AMDE period and that behaved differently from Hg-p.

Particulate mercury samples collected at Barrow (Lindberg et al., 2002) also showed RGM as the primary species during the AMDE period with a different behaviour of both mercury species. Lindberg et al. (2002), however, observed that Hg-p peaks during not 24-hour sunlight but just prior to sunrise. Hg-p data at Ny-Alesund were obtained during 24-hour sunlight conditions suggesting that different reaction pathways or reactants may be, probably, responsible for creating Hg-p as compared to RGM during the first and major AMDE. In addition, the general low Hg-p/RGM ratio observed during 24-hr sunlight conditions at Barrow led to speculate that the Hg-p detected after 24-h sun could reflect RGM sorbed onto the existing aerosol. BrO distribution from GOME satellite data and back-trajectories (by HYSPLIT Model) have been compared with mercury species concentrations obtained at Ny-Alesund during the 2003 experiment. The results show evidence, in a preliminary analysis, that the most probable mechanism, driving the Hg^0 depletion and the simultaneous RGM production, is not solely action of atmospheric halogen chemistry at Ny-Alesund but also that an important role is played by the transport of air masses already depleted from mercury prior to arrive at the sampling site at Zeppelin.

THE MERCURY DEPLETION EVENTS IN THE ANTARCTIC REGION

The first extended baseline data for the concentration and speciation of atmospheric mercury (TGM and dimethylmercury, DMM) in Antarctica were reported by De Mora et al. (1993). Annual average TGM values were 0.52, 0.60 and 0.52 over three consecutive years, and DMM values were less than 10% of the TGM values, and often below the detection limit. The seawater and atmospheric concentration of DMM have also been measured in the Antarctic Ocean by Pongratz and Heumann (1999) who found the

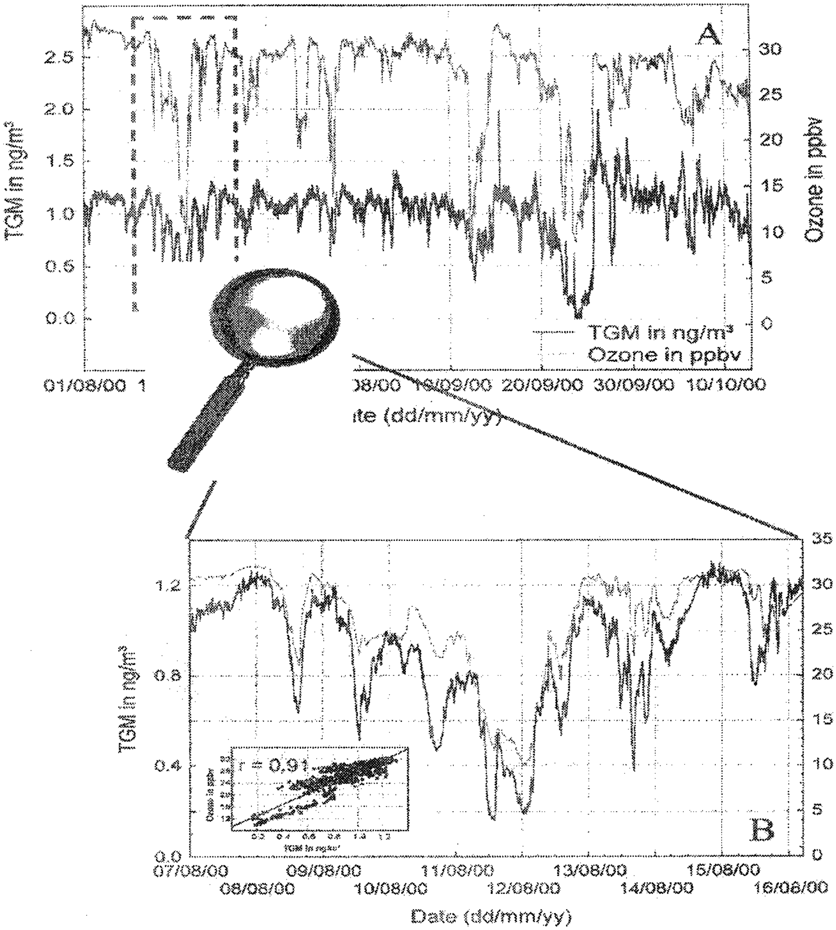

Figure 9. O3 and TGM concentrations during the MDEs observed at Neumayer, Antartica from August to October 2000.

Source: Ebinghaus et al. 2002.

mean atmospheric concentration to be 6 pg m^{-3}. However, Hg speciation and the variation of Hg species in the Antarctic region are currently not known.

The measurements reported by Ebinghaus et al. (2002) comprise the first annual time series of ground-level TGM (Total Gaseous Mercury) concentrations in the Antarctic to investigate the occurrence of possible AMDEs in south polar regions. The study also provides high-resolution data that can be compared with existing data sets of AMDEs in the Arctic revealing similarities and differences in the temporal and quantitative sequence of AMDEs after polar sunrise. The TGM series measured in Antarctica at the German Research Station at Neumayer (70°39'S, 8°15'W) by Ebinghaus et al. (2002) showed several Hg depletion events during Antarctic springtime (between August and November) 2000 (Figure 9), with minimum daily average concentrations of about 0.1 ng m^{-3}; TGM and O3 were strongly positively correlated as seen in the Arctic boundary layer after polar sunrise. At Neumayer (relative to the beginning of spring in both hemispheres) the ozone depletion events are less frequent, and are shorter (Lehrer, 1999). Friess (2001) documented that the numerous strong and sudden enhancements of BrO detected during August and September 1999 and 2000 at Neumayer are caused by BrO located in the lower troposphere, released by well-known autocatalytic processes on acidified sea-salt surfaces.

The TGM data can be characterized by three different time periods: (i) Between January and February 2000 and December 2000-February 2001, in which TGM concentrations were highly variable. During this time period, TGM and ozone concentrations are frequently negatively correlated; (ii) the period between March and July 2000, which shows TGM concentrations at constant level of background (about 1.146 ng m^{-3}) while ozone concentrations constantly increased. (iii) the period between August and November 2000, in which several simultaneous depletion events of surface-level TGM and ozone were detected with minimum daily average TGM concentrations of about 0.1 ng m^{-3}. Ebinghaus et al. (2002) also found that these Hg depletion events coincided with enhanced column densities of BrO over the sea ice around the Antarctic continent after polar sunrise (September) as shown from measurements performed using the satellite borne GOME instrument. Air masses at ground level coming from the sea ice surface, accompanied by BrO enhancements, could be a necessary prerequisite for the MDEs at Neumayer. Most of the sea ice where enhanced BrO concentrations are found is located north of Neumayer station at lower latitudes. Therefore, the sea ice is a possible place where the photochemical reaction of ozone and Br atoms and/or the following reaction of BrO radicals and Hg^0 can take place in the Antarctic during the springtime.

After an intensive measurement campaign carried out at Terra Nova Bay, between November 1999 and January 2000, during which opposite trends between TGM concentrations and the quantity of Hg associated with particulate matter was observed (Sprovieri and Pirrone, 2000), the desirability of more detailed measurements of atmospheric Hg species in Antarctica was clear, in order to understand Hg cycling in polar environment. Atmospheric mercury measurements were performed at the Italian Antarctic Station, in Terra Nova Bay (74°41'S, 164°70'E) from the middle of November 2000 to the middle of January 2001. Terra Nova Bay is a small gulf inlet of the Ross Sea on the western coast of the Antarctic continent; the atmospheric measurement site is at Icaro Camp situated at 3.5 km from the main Italian Antarctic Station (IAS), on a hilltop 90 m a.s.l. The results obtained provide simultaneous measurements of both Hg^0 and RGM performed in Antarctica. Hg^0 concentrations were in the range of 0.29 ng m^{-3} to 2.3 ng m^{-3} with a mean value of 0.9±0.3 ng m^{-3}. The average Hg^0 concentration was substantially lower than values obtained elsewhere. In the Northern Hemisphere mercury fluxes to the atmosphere derived from emission estimates for major natural and anthropogenic sources and ambient concentration measurements are higher than those evaluated for the Southern Hemisphere. This adds weight to the widely accepted hypothesis that the background Hg concentrations between the two hemispheres are different. Figure-10 shows Hg^0 and O_3 ambient concentrations for the measurement period. The data is comparable to that of Ebinghaus et al. (2002) for the periods January and February 2000, and December 2000 to January 2001, which were characterized by variable TGM concentrations (Ebinghaus et al., 2002) measured TGM as there were no denuders on their instrument to remove RGM) and during which TGM and O3 were often negatively correlated.

RGM concentrations during the measurement period were surprisingly high and comparable with those at sites directly influenced by significant anthropogenic Hg sources (in the range of 10.53 pg m^{-3} to 334.2 pg m^{-3} with a mean value of 116.3 ± 77.8 pg m^{-3}). Recent studies performed in the Arctic (Lindberg et al., 2001) also report very high RGM concentrations between polar dawn and snowmelt, suggesting that there are specific mechanisms and/or characteristics of polar environments that at certain times, and apparently in the presence of surface snow are extremely favourable to the production of RGM. Comparable RGM results have been reported by Temme et al. (2003) during an intensive measurement campaign performed at the German Research Station (Neumayer) during Antarctic summertime. They found RGM values ranged between 5 pg m^{-3} and maximum levels of more than 300 pg m^{-3} from December 2000 to February 2001. The high concentrations of RGM measured at Terra Nova Bay are somewhat surprising above all because the period in which the measurements were performed was not one in which simultaneous ozone and mercury depletion events occurred, when it has been shown that RGM production increases significantly (Lindberg et al., 2002). The only possible source of RGM is, in these particular conditions, the gas phase oxidation of Hg^0.

According with Temme et al. (2003), the very high RGM concentrations at Terra Nova Bay as well as Neumayer should be influenced by local production of oxidized gaseous mercury species over the Antarctic continent or shelf ice during polar summer. Recent investigations in the Arctic, have

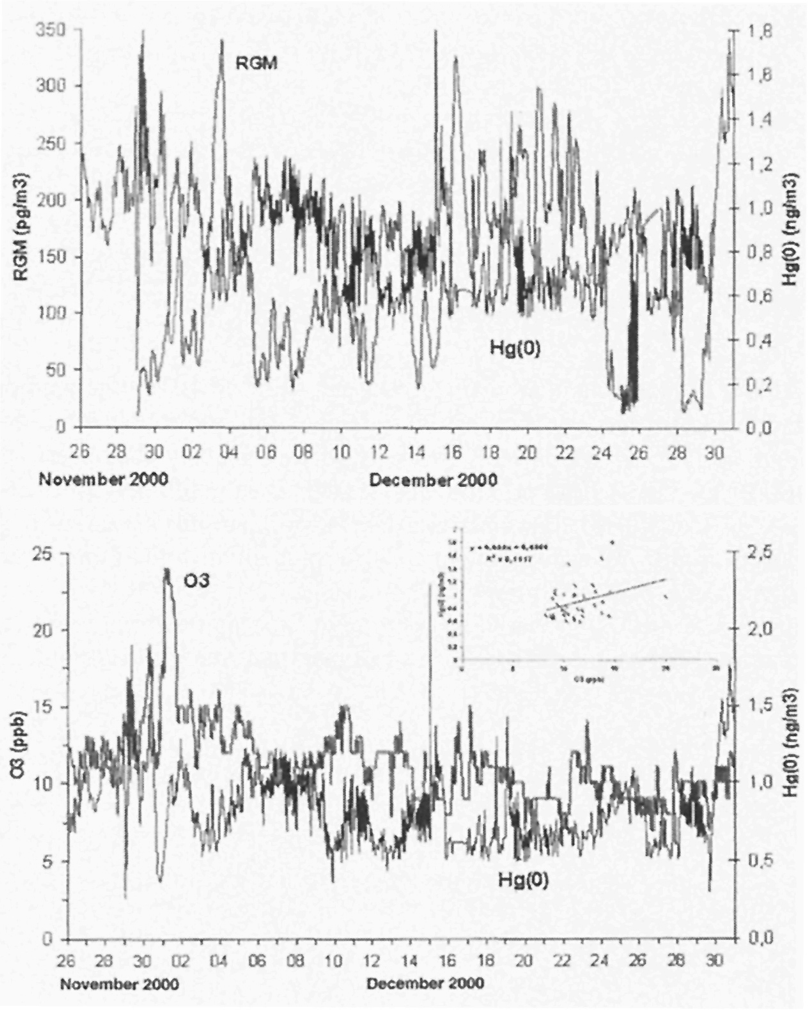

Figure 10. Two-hourly mean GEM and RGM concentrations at Terra Nova Bay, Antarctica from November to December 2000.

Source: Sprovieri et al. (2002).

highlighted that there are gas phase oxidation processes occurring which are as unknown, probably involving bromine-containing radicals. However, although in the Arctic the highest RGM concentrations were found during MDEs elevated concentrations were found at Barrow until snowmelt. Snowmelt is much more limited even at coastal Antarctic sites than it is at Arctic sites such as Barrow, which suggests that the snow-pack is directly involved in maintaining high RGM concentrations. Further studies are necessary to explain the reaction mechanism and the kinetics of the MDEs and the RGM production identified during measurement campaigns in the Antarctic during springtime depletion period (Ebinghaus et al., 2002; Temme et al., 2003) and for the no depletion period (Sprovieri et al., 2002). It is also important to combine the results observed with trajectory calculations in combination with sea ice maps in order to investigate the origin of the depleted air masses and the actual places where the chemical reactions involving ozone, reactive bromine species, and elemental mercury take places.

MERCURY DEPOSITION TO THE SNOW AND ICE SURFACES IN THE POLAR REGIONS AND AIR-SNOW-ICE EXCHANGE PROCESS

The mechanism of the conversion of Hg^0 into RGM (and/or Hg-p) is not well understood neither are the roles of the snow pack and the host of chemicals existing therein. For this reason various conversion and air–snow interaction studies were undertaken during measurement campaigns from the 1997-1998. The first observations of the seasonal variation of Hg content in snow on the Arctic Ocean are reported by Lu et al. (2001). Fresh snow samples were taken in the spring snow-pack of the Eastern Canadian Arctic, Hudson Bay, and Greenland. In the Canadian Island Archipelago, and at coastal sites on Hudson Bay, concentrations were generally much higher (25 - 160 ng L^{-1}) and enhanced Hg levels in snow were clearly reflected in the 4-fold increase from the dark winter months (Nov. 1997 to Jan. 1998: 7.8 ng L−1) to the sunlit spring months (Feb. to May, 1998: 34 ng L−1). These snow data are consistent with observed tropospheric O_3 and Hg^0 depletion events, and satellite observations of atmospheric BrO concentrations in the northern hemisphere (Richter et al., 1998). These observations constitute direct evidence of a link between sunlight-assisted Hg^0 oxidation, greatly enhanced atmospheric Hg(II) wet and/or dry deposition, and elevated mercury concentrations in Arctic snow and snow-pack during springtime. Similar results were obtained in subsequent years and, during springtime

2000 at Alert, a 20-fold increase in Hg concentration in the snow samples from before an AMDE to after an AMDE was observed (Steffen et al., 2002). Using, the technique of the CRPU- Cold Regions Pyrolysis Unit, it was found that during AMDEs, when Hg^0 concentrations decrease, a significant amount of mercury (in forms not identify by the instrument) remain in the air. Hence it was deduced that the remaining component not recovered throughout pyrolysis, was removed from the air, presumably having been deposited to the frozen surface (Steffen et al., 2002). This finding substantiates the argument that the converted Hg^0 during AMDEs is deposited onto the snow. In support of this hypothesis, closer to the surface at Alert, vertical concentration gradients of mercury were measured in the interstitial air within the snow-pack and in the air above the snow at 190 and 120 cm height. Profiles were measured during both the dark and light periods and before and during AMDEs. These profile data showed no significant difference in Hg^0 concentrations between near surface and those at 1.9 and 1.2m heights during dark and 24-hours daylight conditions before an AMDE; in contrast, while a depletion event occurred, the Hg^0 concentration in the air column above 10 cm remained invariant with height but close to the surface a noticeable increase in the Hg^0 concentration was observed. Concurrent ozone profiles exhibited a sharp decrease at the surface level. These data suggested that the snow pack was a source of Hg^0 but a sink for ozone. Hg^0 behaves in a manner that is different from ozone as the two substances approach and interact with the frozen surface. The nature of this interaction is complex and is not yet fully understood at this time. Other profile studies between the interstitial air and air above the snow pack show a positive gradient suggesting that Hg^0 is emitted from the snow pack. The interstitial air in the snow pack was, in fact, alternately measured and, in particular, these measurements showed that the concentration of Hg^0 in the interstitial air in the snow pack was almost continually higher than in ambient air, especially when an AMDE occurred. This shows that Hg^0 was almost continually released from the snow pack indicating that the snow was a source of mercury. During and after the AMDEs, pulses of Hg^0 were observed to be emitted from the snow pack. It is thought that some of the oxidised species of mercury that are previously deposited during the AMDEs, under sunlight conditions, are reduced back to Hg^0 through chemical photo-reduction processes and are then released from the snow pack to the air above the snow surface. Flux measurements obtained during the following years at several arctic locations (Alert, Ny-Alesund) suggested a slightly increased flux of Hg^0 following an AMDE, confirming the complex atmospheric mercury chemistry in the Arctic. During Barrow expeditions (2000-2001) Lindberg et al. (2002) observed an increase of Hg^0 from <1 to >90 ng/L over this period. The 1998 data from a ship frozen in the Beaufort Sea 550 km north of Barrow have shown similar trends in surface snow (Welch et al., 1999). During snowmelt at Barrow under the 24-h daylight mercury exhibited surprisingly dynamic behaviour: MDEs ended abruptly, airborne Hg^0 spiked and airborne RGM decreased to detection limit (1 pg m^{-3}), while total Hg concentrations in snow decreased drastically, by 92%. Since a possible source of this airborne Hg^0 spike probably derived from the interaction between the snow pack and the air immediately above it leading to Hg^0 evasion from the snow-pack (Schroeder et al., 1998). Hg2+(aq) is readily photo-reduced to Hg^0 and evaded from surface waters (Lindberg et al., 2000) The flux of snow-pack Hg to air and water is thus clearly influenced by the melting process. To investigate the behaviour of Hg in snow Lalonde et al. (2002) studied Hg^0 and total Hg concentrations at different snow-pack depths above a frozen lake (Sainte-Foy, QC Canada). Results indicate that deposited Hg is highly labile in snow-pack samples, decreasing, on average, by 60% within 24 h after deposition in the first snow stratum while total Hg levels at depth were lower than near the surface, and remain constant over time. It was hypothesized that Hg depletion in snow could be caused by a rapid snow-air Hg exchange resulting from Hg(II) photo-induced reduction to volatile Hg^0. Hence, since once deposited, Hg could be rapidly reduced and re-emitted and the massive Hg deposition events observed in springtime in polar regions may probably have less impact than previously anticipated in research studies. Ferrari et al. (2004) studied Hg concentrations pattern in the interstitial air of snow during night and day conditions at Station Nord, Greenland, during March, 2002. The sampling period was shortly after polar sunrise and before any ozone and mercury depletion events. Results obtained indicated mercury oxidation and reduction processes in the top layers of the snow-pack. Recently it was proposed that homogeneous and/ or heterogeneous processes between Hg^0 and Br /BrO radicals were leading to the deposition of oxidised Hg from the interstitial air of snow onto the snow grains (Ferrari et al., 2004). The snow-pack can also be a source of Hg^0 to the atmosphere through Hg(II) reduction by HO_2 and/or photo-dissociation of some Hg(II) complexes (Dommergue et al., 2003a). The snow samples were taken at different depths. Hg^0 concentrations at 60 and 100 cm depth do not exhibit the same pattern as those at 20 and 40 cm. No night and day profile was observed for these deeper depths indicating that the production was affecting mainly the top layers of the snow-pack. Levels of Hg^0 in the atmosphere were relatively constant at Station Nord in Greenland shortly after polar sunrise, whereas the concentrations in interstitial air of snow varied much more with a depletion during the day and a production at night. The observed production must then be driven by internal chemical processes, and not by change in atmospheric conditions. Depletion of Hg^0 in the interstitial air of snow is probably the result of homogeneous and/or heterogeneous chemistry with halogenated species (especially Br and BrO) leading to the formation of Hg(II) and its adsorption on the snow surfaces. The Artic snow pack is known to produce active bromine and chlorine species in the interaction process between sea-salts, ozone and acid species in the snow (Fan and Jacob, 1992; Tang and Mc Connel, 1996). The production of reactive species is even possible during low irradiation periods. Moreover, reaction between Hg^0 and Br radicals is fast (Ariya et al., 2002). Thus, similarly to the depletions of atmospheric Hg^0 and ozone in polar regions during springtime, Hg^0 depletion in the interstitial air of the snow could be the result of fast oxidation processes involving halogenated radicals. Therefore, during the day, under sunlight conditions with solar irradiation strong enough to produce Br-radicals, mercury, in its oxidized form Hg(II), accumulate in the snow-pack and the oxidation processes in the snow-pack is, therefore, more active than reduction. After the sunset, with solar radiation weaker, oxidation is less active and allows the reduction to be predominant. Hg^0 production occurring in the snow-pack during the night requires the presence of a potential reductant of Hg(II). However, research studies recently performed (Dommergue et al., 2003a) have shown a production of Hg^0 in the air of the snow in Kuujjuarapik (Canada) during the day, directly correlated with solar radiation suggesting that Hg^0 production is driven by a photo-chemically induced reduction and proposing, as a potential reductant, hydroperoxyl radicals (HO_2) (Lin and Pehkonen, 1999). The major source of HO_2 is assumed to be the photolysis of formaldehyde (HCHO) both in the troposphere and in the snow-pack interstitial air (Sumner and Shepson, 1999). The mechanism by which Hg^0 is emitted from the snow during night time is at present unknown, however this reduction process could be explained if a night time source of HO_2 exists in the air of the snow pack. Hg fluxes to the atmosphere calculated at Nord-Greenland (0.06-0.4 ng m^{-2} h^{-1}) were weaker compared to those observed by Schroeder (2003) at different Arctic sites (1-8 ng m^{-2} h^{-1}). However, Steffen et al. (2002) have shown that without any mercury depletion event, gaseous mercury concentration was homogeneous from the snow surface to a height of a few meters above the snow. Enhanced concentrations of Hg in surface snow are clearly evident throughout the AMDE period also at Ny-Alesund. Results from snow samples performed during several spring campaigns have shown Hg concentrations variable from a background of about 2 ng L^{-1} during the polar night to about 40 ng L^{-1} in the Arctic spring. After Hg^0 events, Hg concentrations increased from background values to 100 ng L^{-1}. The ratio between deposition and reemission is an important parameter that determines the impact of mercury depletion in the Arctic environment. More research is needed to improve our understanding of this exceptional aspect of environmental mercury cycling.

CONCLUSIONS

The substantial different geographical distribution of landmasses around both poles influences the Hg^0 annual mean observed in the Arctic (1.59 ng m^{-3} to 1.60 ng m^{-3}) and Antarctica (1.04 ng m^{-3}). The Antarctic region is remote from human activities on the other continents being far from landmasses; in contrast, the Arctic region is surrounded by northern North America, northern Europe and northern Asia, therefore, it undergoes to the anthropogenic influences came from the continents themselves. However, several emission Hg data sets have shown that during the last 20-years there is been in the Northern Hemisphere a decrease in global atmospheric Hg emission of about 30% despite the recent increase in Hg levels observed in Arctic biota, lake sediments, arctic food as well as in native people of circumpolar countries as recently carried out by different studies. A potential explanation for the opposite trends observed concerning the Hg increase in polar biota and the Hg decrease in global emissions, could be the AMDEs, probably a relatively recent atmospheric mechanism by which Hg^0 (Hg^0) may be converted to reactive and water-soluble forms (RGM and/or Hg-p) that deposit quickly thus increasing the mercury fluxes and deposition processes in the fragile ecosystems of the Arctic and/or Antarctica. Enhanced concentrations of Hg in surface snow are clearly evident during the AMDEs that lead, therefore, to enhanced Hg inputs into polar ecosystems (about 300 Tonnes in the Arctic and from 50 to 100 tonnes in the Antarctica). The observations seen in the polar regions, thus constitute direct evidence of a link between sunlight assisted Hg^o oxidation, greatly enhanced atmospheric Hg(II) wet and/or dry deposition, and elevated Hg concentrations in the polar snow-pack in spring. Several studies on the Hg fate carried out in the polar regions suggested that a significant fraction of deposited Hg is bioavailable (up to 40%), about 25% can be re-emitted to the atmosphere and the fraction in meltwater is more than 50%.

It has been thought, in fact, that the AMDEs are, probably, a recent phenomena due to the climate global changes in the polar regions and, in general, to the global warming of the planet over the last 30 – 40 years. This last leading to a decreasing trend in multi-year ice coverage, earlier timing of snowmelt, increasing ocean temperature and increasing atmospheric circulation can impact the dynamics of the AMDEs. These climate changes have, in fact, increased atmospheric transport of photo-oxidants and production of reactive halogens (Br/Cl) in the polar regions enhancing Hg oxidation reactions. The decreasing, in addition, in total column ozone amounts over the polar areas and the subsequent increasing of the incident solar UV-B which influence the production of reactive halogen species could lead to increase of the Hg^0 oxidation processes and Hg accumulation in polar ecosystems.

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