Overview of mercury measurements in the Antarctic troposphere

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Abstract

Polar ecosystems are considered to be the last pristine environments of the earth relatively uninfluenced by human activities. Antarctica in particular, compared to the Arctic is considered to be even less affected by any kind of anthropogenic influences. Once contaminants reach the Polar Regions, their lifetime in the troposphere depends on local removal processes. Atmospheric mercury, in particular, has unique characteristics that include long-range transport to Polar Regions and the transformation to more toxic and water-soluble compounds that may potentially become bioavailable. These chemical-physical properties have placed mercury on the priority list of an increasing number of International, European and National conventions, and agreements, aimed at the protection of the ecosystems including human health (i.e. GEO, UNEP, AMAP, UN-ECE, HELCOM, OSPAR). This interest, in turn, stimulates a significant amount of research including measurements of gaseous elemental mercury reaction rate constant with atmospheric oxidants, experimental and modelling studies in order to understand the cycling of mercury in Polar Regions, and its impact to these ecosystems. Special attention in terms of contamination of Polar Regions is paid to the consequences of the springtime phenomena, referred to as “Atmospheric Mercury Depletion Events” (AMDEs), during which elemental mercury through a series of photochemically-initiated reactions involving halogens, may be converted to a reactive form that may accumulate in polar coastal, or sea ice, ecosystems. The discovery of the AMDEs, first noted in the Arctic, has also been observed at both poles and was initially considered to result in an important net input of atmospheric mercury into the polar surfaces. However, recent studies point out that complex processes take place after deposition that may result in less significant net-inputs from the atmosphere since a fraction, sometimes significant, of deposited mercury may be recycled. Therefore, the contribution of this unique reactivity occurring in polar atmospheres to the global budget of atmospheric mercury, and the role played by snow and ice surfaces of these regions, are important issues. This paper presents a review of atmospheric mercury studies conducted in the Antarctic troposphere, both at coastal locations and on the Antarctic Plateau since 1985. Our current understanding of atmospheric reactivity in this region is also presented.

1 Introduction

Antarctica is often considered as a giant cold trap where many long-lived species or atmospheric oxidation products are deposited and buried in the ice fields (Eisele et al., 2008). This vast continent of 14 million km^2, almost entirely covered by ice, revealed surprising findings on the biogeochemical cycle of major elements such as sulfur and nitrogen (Eisele et al., 2008 and references therein). Antarctica is a place of choice for atmospheric studies, because it has no real primary sources, except volcanoes, and is uninhabited except for a few scientific stations. However, due to a combination of logistical issues, harsh meteorological conditions, studies are *de facto* scarce. Polar Regions, like other regions of the planet, are impacted by long-range transport of man-made emissions of mercury (Hg). In Antarctica, gross mercury input is probably controlled by the Southern Hemisphere emissions. While Northern Hemisphere Hg(0) concentrations have likely been decreasing (Faïn et al., 2009) following the decrease of Northern Hemisphere emissions over the last decades, Southern Hemisphere emissions increased from 1990 to 1995, and have stayed roughly constant since 1995. From 1990 to 1995 Africa emissions increased from 200 to 400 tons/year, Australia from 50 to 100 tons/year, and South America from 55 to 80 tons/year (Pacyna et al., 2006; Lindberg et al., 2007).

The discovery made in Alert (Canada) in 1995 (Schroeder et al., 1998), which revealed that elemental gaseous mercury (Hg(0)) is oxidized and deposited onto arctic snow surfaces more rapidly than anywhere else due to a phenomenon called Atmospheric Mercury Depletion Events (AMDEs), has sparked considerable interest in the research community. While the tropospheric reactivity of mercury (Hg) in the Arctic is more and more documented only a few attempts were made to study the Hg cycle in the Southern Polar Regions. Following Schroeder et al. (1998) study, AMDEs were observed in Coastal Antarctica after polar sunrise at Neumayer and Terra Nova Bay (Ebinghaus et al., 2002b; Sprovieri et al., 2002).

The study of the Hg cycling in Antarctica is first necessary to understand and follow the extent of the contamination within these ecosystems. Mercury concentrations in biota of some Arctic areas are known to have increased with time (Dietz et al., 2009) and to be rather high. In Antarctica, available data on Hg concentrations in water, sediments, phytoplankton, macroalgae, krill and several species of benthic invertebrates compiled by Bargagli et al. (2008) indicate that there is no enhanced bioavailability of Hg in the Southern Ocean food web. However, recent studies showed an enhanced Hg bioaccumulation in terrestrial ecosystem collected samples close to Terra Nova Bay (Bargagli et al., 2005), suggesting that local deposition events of Hg may impact these ecosystems.

Second, the role of the Antarctic continent and its influence on the global geochemical cycle of mercury is unclear today, and is certainly under evaluated by current models (Selin et al., 2007). Ice and snow cover are known to play an important role in the reactivity of the overlying atmosphere (Dominé and Shepson, 2002). For example, there is new evidence suggesting that nitrogen, in the form of nitrate, may undergo multiple recycling within a given photochemical season (Davis et al., 2008).

Finally, the 3 km of ice that lies below the surface of the Antarctic continent is also used as an archive to retrieve the content of ancient atmospheres over hundreds of thousands of years (Jitaru et al., 2009). It was shown that Hg deposition in surface snows was greater during the coldest climatic stages, coincident with the highest atmospheric dust loads. A possible explanation is that the oxidation of gaseous mercury by sea-salt-derived halogens occurred in the cold atmosphere. An understanding of atmospheric chemistry of Hg is therefore relevant because it provides one of the critical inputs for evaluating the air-to-snow ‘‘transfer function’’ for a chemical specie.

This article presents a current state of Hg measurements in the Antarctic troposphere. Most of the research activities are today located in the Northern Hemisphere with long-term data for only a few sites. The Antarctic regions have not been extensively monitored yet, and only sporadic measurements have been made. However, an effort has been first made to study the processes of AMDEs on coastal sites. More recently, the Antarctic Plateau has become a new focus of attention. All these efforts show that we currently underestimate the role of this continent on the global cycle of mercury, and that it offers broad perspectives in terms of new findings on Hg cycling.

2 Methodology

2.1 Definitions

Gaseous elemental mercury, Reactive Gaseous Mercury (RGM) and Particle associated mercury (PHg) are the most commonly measured and monitored fractions. Considering these three atmospheric species, Hg(0) is maybe the only component that is easily and accurately measured in the field. RGM and PHg are operationally defined and thus measurements from different sites may be complex to inter-compare. In some cases, Total Gaseous mercury (TGM) may be provided. It generally refers to the sum of Hg(0) and RGM.

2.2 Instrumentation

A summary of the instrumentation and of the experimental set-up is provided in Table 1. All recent (i.e. after 2000) Hg(0) measurements presented here were performed using a commercially available unit Tekran 2537A. This automated instrument allows for continuous measurement of Hg(0) in ambient air with a high sensitivity using gold trap amalgamation, thermal desorption and detection by Atomic Fluorescence Spectroscopy (AFS). The Tekran 2537A performs automated recalibrations for Hg(0) using an internal permeation source, which provides approximately 1 pg/s of Hg(0) at 50 °C into a zero airstream. This permeation sources is periodically recalibrated by manual injections of Hg(0) vapor using a microsyringe. Intercomparison campaigns have shown good agreement using different Tekran 2537 units (Aspmo et al., 2005). In Polar Regions, some researchers report ambient air collected with this method as TGM which includes both the Hg(0) and RGM species (Ebinghaus et al., 2002b). However, if a filter (soda lime trap for instance) is placed at the inlet of the sample line, it is most likely that RGM is removed and thus only Hg(0) is collected (Steffen et al., 2002; Steffen et al., 2008). Using these instruments a detection limit of 0.1 ng.m^{-3} can be achieved.

Older Hg(0) or TGM measurements (De Mora et al., 1993) were achieved by drawing air through collectors containing silvered sand. The tubes were sealed and analyzed within a few days of collection by photoacoustic spectroscopy. Unfortunately, the measurement technique used by De Mora et al. (1993) has, to our knowledge, not been compared with modern instrumentation. Therefore data obtained using this technique should be cautiously considered even though the range of concentration that was obtained is coherent with recent measurements obtained using automated sensors. Intercomparison campaigns using automated and manual trap methods have however shown comparable results (Ebinghaus et al., 1999; Munthe et al., 2001) to the Tekran 2537.

RGM concentration are measured with a Tekran 1130 mercury speciation unit, which gives the Tekran 2537A mercury vapor analyzer the ability to concurrently monitor both Hg(0) and RGM. A KCl-coated quartz annular denuder captures reactive gaseous mercury while allowing elemental mercury to pass through. The denuder is heated to 500°C in a stream of Hg free air. The thermally-released Hg is passed over a pyrolysis chamber (~800°C). The RGM is thermally decomposed to Hg(0) and is transferred to the Tekran 2537A. RGM is usually detected in the low pg.m^{-3} concentration range. A direct primary calibration method for RGM does not yet exist. In addition, KCl denuders are known to collect $HgCl_2$ and/or $HgBr_2$ (Steffen et al., 2008), and the chemical speciation of RGM has yet to be determined. Therefore RGM values should be carefully considered.

PHg values were obtained by different methods. Measurements at Neumayer (Ebinghaus et al., 2002b; Temme et al., 2003) were done using an AESminiSamplR developed by the Meteorological Service of Canada (Lu et al., 1998). This miniaturized device consists of a quartz tube with a 6-mm quartz fiber filter disk, served as both particulate trap and pyrolyzer for airborne particulate mercury species. At Terra Nova Bay (Sprovieri and Pirrone, 2000; Sprovieri et al., 2002), PHg concentrations were obtained by collecting airborne particles on micro-quartz fibre filters mounted in a quartz tube for 48h at a flow-rate of 4.5 LPM and analyzed by AFS. Brooks et al. (2008a; 2008b) used the Tekran 1135, a commercially-available unit. The Tekran 1135 is used together with the Model 1130 Speciation Unit and the Model 2537 Mercury Analyzer. RGM is captured in the 1130 unit (see description above) and the fine fraction particulate bound mercury species are then trapped onto a unique quartz regenerable filter. Arimoto et al. (2004) samples were collected with high-volume sampling on Whatman filters (Whatman Ltd., Maidstone, UK). Filters were digested following the protocol outlined in Landing et al. (1998) and analyzed by inductively coupled plasma mass spectrometry (ICPMS). Similar to RGM, PHg measurements have to be carefully considered because of the lack of intercomparability. Intercomparison exercises realized using different automated and manual techniques (Munthe et al., 2001; Aspmo et al., 2005) have shown the need of substantial improvement in the characterization of oxidized mercury species, and a direct primary calibration method for PHg. The fraction of particulate mercury as determined by automated instrument might differ significantly from the fraction measured using filter collection.

2.3 Atmospheric measurements in cold regions

Mercury speciation sampling methods are similar to methods conducted around the world with exceptions made for the extreme cold, the blowing snow layer, the high altitude of the polar ice caps, and the high magnitude of mercury fluxes in and out of the surface snow.

Care must be taken to (1) ensure that flow volumes and residence times are appropriate for the speciation of mercury into the 3 components, (2) prevent unintended mercury absorption in the sampling lines, and (3) ensure near 100% collection efficiency onto the pre-concentrating gold cartridges. Atop the high-altitude polar plateau item (1) requires matching the volume flow to a 0.1 second residence time over the KCl-coated annular denuder. At foggy coastal sites item (2) requires that dry air must be used to flush the system, otherwise the iodated carbon canisters (used to remove all mercury from the flush air) can potential introduce iodine into the flush stream, where it can unintentional oxidize gaseous elemental mercury. In all locations item (3) requires a high purity inert carrier gas, and a sampling location (such as a clean air sector) where contamination is minimized.

Under very cold conditions the heated sample lines should be kept fully external from the air-conditioned area, otherwise the temperature change between interior and exterior portions will induce hot/cold zones and mercury absorption/desorption at the tubing walls. The exterior front-end cases and the exterior sampling lines should have robust insulation and heating systems that will not significantly vary the set temperatures regardless of weather conditions. The inlet position must be placed sufficiently above the blowing snow layer, but remain within the lowest 10% of the atmospheric boundary layer, which may be as shallow as a few 10's of meters.

3 Results and Discussion

3.1 Atmospheric Mercury in the Antarctic

Antarctica and the Southern Ocean are located in a remote region, with no indigenous human population and no industrial activity. Human activity is minimal and localized. Human presence in the region largely consists of scientific investigations and logistical operations in support of these investigations. The greatest human impact can be expected where research is carried out at long-term stations, with populations typically less than 100 people. Far from anthropogenic emissions, and isolated by the circumpolar vortex, only the longest-lived of the global atmospheric contaminants, such as Hg(0), make their way to the Antarctica Plateau. The overwhelming majority of anthropogenic Hg loading to the environment and biota derives from global, rather than local, inputs. Antarctica is characterized by a vast, cold, dry, high-altitude polar plateau (>2400m), and a coastal region where the seasonal freezing and melting of sea ice surrounding the continent is the Earth's largest seasonal energy exchange event. This vast freezing of sea ice liberates sea salt bromine (Br), chlorine (Cl), and iodine (I). The Polar Plateau chemistry is dominated, during the annual sunlit period, by an oxidizing canopy of OH, O_3, and HO_2 (Eisele et al., 2008).

3.1.1 A summary of available Hg species measurements

Few field experiments dedicated to mercury have been performed in Antarctica compared to those carried out in the Arctic. Mercury measurements performed at different locations within the Antarctic region are reported in Table 2 and shown in Figure 1. The first baseline data for the concentration and speciation of atmospheric mercury in Antarctica were reported by De Mora et al. (1993). Mercury measurements were carried out at three sampling locations in the vicinity of McMurdo throughout 1985 and 1989. In particular, a preliminary study was carried out on the frozen surface of Lake Vanda (77°33'S, 161°37'E) in the Wright Valley during December 1985. While obviously limited, the data were interesting and suggested that TGM concentrations in Antarctica were substantially lower than those observed elsewhere (0.23 $ng.m^{-3}$). Therefore, further studies were conducted throughout 1987 and 1988 at Scott

Base (77°51’S 166°46’E) and during 1989 at Arrival Heights (77°11’S, 166°40’E), also on Ross Island. The mean TGM for 1987 was 0.52 ± 0.14 ng.m^{-3}, whereas the corresponding 1988 value was 0.60 ± 0.40 ng.m^{-3}. At the third site, mean TGM value was 0.52 ± 0.16 ng.m^{-3}. Recent advances in mercury measurements included a gain in sensitivity and automated high- frequency continuous measurements. It gave the opportunity to extend the monitoring of atmospheric mercury reactivity, which has been made in several coastal locations at the Italian Antarctic Station in Terra Nova Bay (Sprovieri and Pirrone, 2000; Sprovieri et al., 2002), the German Research Station Neumayer (Ebinghaus et al., 2002b; Temme et al., 2003), the US Station McMurdo (Brooks et al., 2008b). Two sites on the Antarctic Plateau have also been explored at the US South Pole Station (Arimoto et al., 2004; Brooks et al., 2008a) and more recently at the French-Italian Concordia Base (Courteaud et al., 2010).

3.1.2 Atmospheric reactivity at Antarctic coastal sites

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 Antarctic ecosystems, high-temporal-resolution Hg measurements were performed. The first annual time series of ground-level TGM concentrations in the Antarctic to investigate the occurrence of possible AMDEs in Southern Polar Regions were obtained by Ebinghaus et al. (2002b) at the German Research Station at Neumayer. In that study AMDEs were observed during Antarctic springtime 2000 with minimum daily average concentrations of about 0.1 ng.m^{-3}. Similar springtime mercury dynamics was also observed at two other coastal locations at Terra Nova Bay (Sprovieri et al., 2002) and McMurdo (Brooks et al., 2008b). The high-resolution data were compared with existing data sets of AMDEs in the Arctic and revealed similarities between the temporal and quantitative sequence of AMDEs after polar sunrise. During early springtime (August-October), TGM and ozone (O_3) were positively correlated (Ebinghaus et al., 2002b) as in the Arctic boundary layer (Schroeder et al., 1998), even if the ozone depletion events at Neumayer are less frequent, and shorter (Lehrer, 1999). The positive correlation between Hg(0) and O_3 concentrations near the coasts during Antarctic sunrise means that the depletion of Hg(0) also depends on photochemically-produced oxidants. Friess (2001) detected enhancements of atmospheric bromine compound, BrO in the lower troposphere, during the same period, using Differential Optical Absorption Spectroscopy (DOAS). Ebinghaus et al. (2002b) also found that AMDEs at Neumayer station coincided with enhanced column densities of BrO for this area, derived from measurements by the satellite-borne GOME (Richter et al., 1998) indicating regions and magnitudes of bromine emissions. As illustrated in Figure 2, the BrO in the near-surface air (lowest 1 km) is superimposed on the satellite column measurements, where the stratospheric and upper tropospheric concentrations are assumed to be relatively uniform. Thus the ~30% enhancements from the background BrO to the highest column concentrations represents significant BrO concentrations in the lowest 1 km of the atmospheric column. Air masses at ground level coming from the sea ice surface, accompanied by BrO enhancements, could be a necessary condition for the AMDEs in Coastal Antarctica. Atmospheric mercury and ozone depletion events are noticeable along the sea ice edges where polynyas and flaw leads (waterway opening between pack ice and fast ice) provide frequently freezing sea ice surfaces as a source of atmospheric bromine. Freezing sea water under very cold temperatures traps bromine sea salts within the forming ice matrix. Within hours, brine is squeezed out of the solidifying ice resulting in briny frost flowers, which both dramatically increase the ice surface area, and transport the concentrated bromine ions to the air interface. Based on the available data, we are inclined to hypothesize that in Antarctic coastal areas the enhanced oxidation of Hg(0) is similar to that which has been observed in the Arctic and speculate here that it similar involves BrO or other halogen-containing radical or compounds. Among reactive halogen species thermodynamically favoured to oxidize Hg(0) to form RGM and/or PHg in the gaseous phase, Cl_2, Br_2, and BrCl appear to be most probable (Fan and Jacob, 1992; Vogt et al., 1996; Richter et al., 1998). Molecular Cl_2, Br_2, and BrCl are, however, not likely to produce *in situ* RGM formation because they rapidly undergo photolysis in sunlight conditions (Vogt et al., 1996; Richter et al., 1998). Therefore, springtime photochemical dissociation of the molecular forms of the halogens (Br_2 and/or Cl_2) results in the corresponding atomic species production, Br/Cl, which may also directly oxidize Hg(0) to Hg(I) to produce unidentified species such as HgX* (Lindberg et al., 2002; Calvert and Lindberg, 2003; Goodsite et al., 2004; Maron et al., 2008; Castro et al., 2009) which may then be further oxidized to Hg(II) (Hynes et al., 2009). In the case of iodine, Saiz-Lopez et al. (2008) measured bromine oxide, BrO, and iodine oxide, IO, simultaneously within the atmospheric boundary layer near the coastal site of Halley Station. Both species were present throughout the annual sunlit period and exhibit similar seasonal cycles and concentrations. Their measurement of the springtime peak of iodine oxide (20 pptv) remains the highest concentration recorded anywhere in the ambient atmosphere. The combination of high levels of bromine and iodine could significantly enhance ozone and Hg(0) depletion within the boundary layer (Saiz-Lopez et al., 2007; Saiz-Lopez et al., 2008). The relative influences of the halogens, Br, Cl, and I, on Hg(0) oxidation and deposition are difficult to determine, as their marine sources and reactivity with Hg(0) appear to be similar.

Both at the Italian Antarctic Station in Terra Nova Bay - where opposite trends between TGM concentrations and the quantity of Hg associated with particulate matter was previously observed (Sprovieri and Pirrone, 2000) - and at the German Research Station at Neumayer, high RGM concentrations (i.e. > 300 pg.m^{-3}) were recorded comparable to those directly observed by anthropogenic Hg sources (Sprovieri et al., 2002; Temme et al., 2003). Interestingly, these high levels were measured in the absence of simultaneous ozone and Hg(0) depletion events during summertime. In fact, either no correlation or a significant negative correlation was rather observed between Hg(0) and O_3 (Sprovieri et al., 2002; Temme et al., 2003). The Hg(0) depletions recorded in January show no significant correlation to any additional parameters that were measured (Temme et al., 2003). The very high RGM concentrations at both coastal sites could be influenced by the local production of oxidized gaseous mercury species over the Antarctic continent or by shelf ice during polar summer. This suggests that the oxidation of Hg(0) to RGM, and a concurrent production of O_3, has already occurred before the air parcels were advected to the sampling site. Temme et al. (2003) proposed a gas-phase oxidation of Hg(0) by potential oxidants (i.e. $OH^{\bullet}$, $HO_2^{\bullet}$) associated with high levels of NO. These oxidants result from photo-denitrification processes in the snow-pack (Jones et al., 2008) which may maintain the high RGM concentrations that were observed. Therefore, additional atmospheric measurements of potential precursor compounds and isentropic trajectory calculations are required to potentially ascertain the reaction mechanism and origin of the air masses reaching the measurements locations where these high RGM levels are observed during the Antarctic summer.

On coastal sites high levels of oxidized Hg species up to 300 pg.m^{-3} have been observed. These species are deposited onto coastal snowpacks leading to high total Hg concentrations around 40-430 ng.L^{-1} in the surface snow (Brooks et al., 2008b) and around 10-40 ng.L^{-1} onto adjacent glaciers of the McMurdo Dry Valleys (Witherow and Lyons, 2008). The post depositional fate of these compounds is not fully explored however a fraction is reemitted following their photoreduction as evidenced by some atmospheric Hg(0) peaks measured at McMurdo (Brooks et al., 2008b).

3.1.3 Reactivity on the Antarctic Plateau

On the Antarctic Plateau where the snowpack is perennial and distant from halogen emissions from freezing sea ice sources, oxidized mercury species were first reported by Arimoto et al. (2004) from high volume filter results at the South Pole station clean air sector. They report elevated PHg levels up to 150 pg.m^{-3} from November to January. More recently Brooks et al. (2008a) combined mercury measurements in snow and air, with vertical mercury flux measurements at the South Pole. It shows that filterable Hg concentrations (RGM + PHg) are totally absent during the dark fall and winter seasons (Figure 3), implying that sunlight is a requirement to produce these oxidized mercury species. Moreover, polar sunrise (~September 21 at the South Pole) heralds negligible mercury oxidation. Mercury oxidation rates only begin to peak around mid-summer with maximum values ~February 1 when extremely high oxidized mercury concentrations were measured in the near-surface air (e.g., RGM + PHg; 100-1000 pg.m^{-3}). It indicates a delay between the re-emerging sunlight and the Hg(0) transport, and the oxidizing canopy that likely drives the atmospheric chemical production of oxidized mercury species. This peak Hg oxidation period (January–February) roughly corresponds to the annual photochemical peak cycles of nitrogen oxides, OH and HO_2 (Mauldin III et al., 2004; Davis et al., 2008). Another recent study at Concordia (Courteaud et al., 2010) showed that Hg(0) ground levels were both affected by the snowpack recycling and the variations of the boundary layer height. Contrarily to South Pole station, the diurnal radiation cycle at Concordia significantly modulates the sensible heat flux during the course of the day leading to an increase of the boundary layer height during the afternoon (Legrand et al., 2009). A significant local Hg(0) production (through photochemical processes occurring at the snow surface) was measured when a thin boundary layer (<50 m) was maintained. Later, the strong increase of the boundary layer height may lead to a significant decrease of Hg(0) levels diluted by strongly Hg(0)-depleted air.

The deposition of oxidized mercury is massive leading to hundreds of ng.L^{-1} of Hg(II) in the surface snow and in deeper layers of the snowpack measured at both Concordia and South Pole.

The observations on the Polar Plateau showed atmospheric oxidized mercury depositing to the snow pack, subsequent photoreduction, and emissions of Hg(0) from the surface. Given the dry conditions of the Antarctic Polar Plateau (burial/snowfall rate is ~10 cm/year) only ~10%

of the deposited mercury is deeply buried (sequestered), resulting in some 60 metric tons Hg annually based on concentrations and flux rates presented in Brooks et al. (2008a). This dynamic mercury cycle on the Polar Plateau appears to be driven by Southern Hemisphere Hg emissions, photochemistry, and the related oxidizing canopy enshrouding the entire high plateau. However mechanisms of reactivity are not fully understood.

3.2 Tropospheric reactivity in the Antarctic vs. the Arctic

Slemr et al. (2003) estimated a Southern Hemisphere background Hg(0) concentration of 1.2 ng.m^{-3}, lower than background concentrations measured in the Northern Hemisphere around 1.7 ng.m^{-3} (Ebinghaus et al., 2002a). In the Arctic, a mean Hg(0) value around 1.5-1.6 ng.m^{-3} is observed at monitoring sites such as Alert, Canada (Steffen et al., 2005). Though there is an obvious need of long-term monitoring data at coastal sites in Antarctica, a mean annual value around 1.0 ng.m^{-3} might be inferred from current Hg(0) measurements. The higher Hg(0) concentrations observed in the Arctic when compared to the Antarctica clearly indicate the different chemical composition of the troposphere as a result of the location of the measurements areas. In fact, the Arctic is surrounded by populated continents from which pollution is released and transported to the north. In contrast, the Antarctic is entirely surrounded by the Southern Ocean and is far from any anthropogenic emissions. In particular, fluxes of mercury to the atmosphere, mainly from anthropogenic and continental sources in the Northern Hemisphere (particularly from Eurasia and North America in late winter and spring), are greater than those in the Southern Hemisphere, and higher atmospheric concentrations are found in the North than the South. Finally, the reactivity of Hg(0) (in particular oxidation processes) might be more intense in the Antarctic than in the Arctic, however the reactivity is not well evaluated and intensive atmospheric campaigns focused on atmospheric Hg and other oxidants should be carried out.

Similar to the Arctic, atmospheric mercury and ozone depletion events are most noticeable along the sea ice edges. Both spatial and temporal coverage of Hg measurements in the Antarctic are very limited. The behaviour of mercury species may be associated with a number of reactive chemicals and reactions that take place in the atmosphere after polar sunrise. The tropospheric chemistry of the polar areas is distinctly different than in the other parts of the earth due to natural differences of meteorological and solar radiation conditions.

During the winter months, in total lack of solar radiation, temperature and humidity conditions are very low, so the vertical mixing of the lower stratified Antarctic troposphere is hindered. The direct consequence is that the abundance of photochemically labile compounds will rise, while the level of photochemical products will be low. During spring and summer, solar radiation is present 24 hours a day and under sunlight conditions, the elevated concentrations of reactants present in the Antarctic atmosphere can initiate a sequence of atmospheric chemical transformations often different than other latitudes. It can be anticipated that in the polar troposphere, free radical precursors that build up in the darkness of the polar winter begin to photodissociate and the resulting gas phase radicals may play a fundamental role in the elemental gas phase mercury decrease seen in Antarctica and in the Arctic. Although in the Arctic the highest RGM concentrations were found during AMDEs, elevated concentrations were found at Barrow (Alaska) extending to the end of the annual snowmelt (Lindberg et al., 2002). Snowmelt is more limited in the Antarctic, even at coastal sites, than it is in the Arctic, which suggests that the snowpack is directly involved in maintaining high RGM concentrations.

While Arctic and Antarctic coastal sites experience episodic mercury depletion events which occur predominantly in the late winter and early spring, the elevated altitude Polar Plateau experiences nearly-constant oxidized mercury enhancements over the sunlit period, peaking in the summer. These unexplained events have not been recorded over the Northern Hemisphere ice cap at Summit (3600 m) in Greenland) (Faïn et al., 2008).

4 Conclusions

In general, the observations made in the Antarctic region constitute direct evidence of a link between sunlight-assisted Hg(0) oxidation, greatly enhanced atmospheric Hg(II) wet and/or dry deposition, and elevated Hg concentrations in the polar snow-pack. Antarctic coastal sites experience episodic mercury depletion events which occur predominantly in the late winter and early spring. However significant differences are observed on coastal areas and on the Antarctic Plateau, which is largely unexplored. This dynamic mercury cycle on the Polar Plateau appears to be driven by the Southern Hemisphere Hg emissions, photochemistry, and the related oxidizing canopy enshrouding the entire high plateau. However mechanisms of reactivity are not fully understood. The mercury in the air over the Polar Plateau (the coldest place on Earth), unlike any other known location, is predominately Hg(II) in summer. The discovery of Hg reactivity on the Antarctic Plateau, and total mercury concentrations of ~200 ng.L^{-1} in the snowpack is a fairly new topic, and these studies open a vast area of research for the future. The fast reactivity of Hg(0) and the periodic occurrence of oxidized species of Hg in the Antarctic troposphere from late winter to summer may result in an important net input of atmospheric Hg into the polar surfaces. However, complex processes take place after deposition that may result in less significant net-inputs from the atmosphere since a fraction, sometimes significant, of deposited Hg may be recycled. The ratio between deposition onto snow pack and reemission is an important parameter that determines the net impact of AMDEs in the Antarctic environment.

The goal of this review is to provide a current view of the Hg chemistry in the Antarctic troposphere. It highlights the fact that Hg science in Antarctica is very limited, and that this continent is particularly unexplored regarding Hg. Therefore, the contribution of this unique reactivity occurring in the Antarctic troposphere to the global budget of atmospheric Hg and the role played by snow and ice surfaces of these regions need further investigations, including experimental monitoring and modelling studies. The dynamic species transformations of atmospheric mercury during Antarctic spring and summer illustrate the complexity of photochemical reactions in Polar Regions and have revealed the limitations in our understanding of the chemical cycling of mercury, and other atmospheric constituents/contaminants in remote regions with seasonally variable sea-ice coverage. In order to gain a better understanding of Hg cycling in Antarctica, we propose the following future research directions:

- Long-term measurements of Hg(0) and other atmospheric Hg species in the Antarctic which are very limited and need to be increased. They must be put also into place at several coastal locations so that the effects of the changes to Hg distribution in this environment can be monitored and scrutinized.
- Measurements of deposition rates of Hg species in coastal environments, their post depositional fate, and their transfer to the ecosystems in order to assess the potential threat to these pristine ecosystems.
- Measurements on the Polar Plateau, where a unique reactivity and recycling of Hg species is observed. The measurements should combine long-term atmospheric measurements of Hg species together with atmospheric oxidants. The cycling of deposition/reemission might influence significantly the interpretation of ice cores.

Therefore measurements should also include Hg determination in surface snow and in deeper snow layers at various locations of the Plateau in order to assess the net input of atmospheric Hg to the snow surfaces. The nature of diffusion of mercury species in surfaces and interfaces (i.e., snow/ice) should also be characterized.

- A significant improvement of our understanding of atmospheric chemistry and kinetics. Current understandings are based on limited laboratory and theoretical studies. Some of the reactions, involving Hg(0) and hydroxyl and halogen radicals for instance, are not clearly defined and reaction products are not well understood. Therefore, research activities on heterogeneous mercury reactions (theoretical, kinetic and dynamic studies) should be included as well as proper incorporation in atmospheric modeling.
- A 1-D photochemical model of the surface snow and air column which includes Hg and the oxidizing canopy of the polar plateau.

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Table 1 A summary of some analytical parameters for atmospheric Hg species measurements

Instrument	**Hg Species**	**Typical Duration;flow rate**	**Detection limit**	**Precision**	**Reference**
Tekran 2537A	Hg(0)/TGM	5 min.; 1.5 L.min^{-1}	<0.1 ng.m^{-3}	2%	Tekran Corp.
Silver gilded sand traps	TGM	24-48 hours; 1 L.min^{-1}	0.05 ng.m^{-3}	4%	(De Mora et al., 1993)
Tekran 1130 Front end	RGM	2 hours; 10 L.min^{-1}	3.1 pg.m^{-3}	15%	(Landis et al., 2002)
Tekran 1135 Front end	PHg	2 hours; 10 L.min^{-1}	~3 pg.m^{-3}	~15%	Our estimates
AES-Mini-Traps-quartz	PHg	48 hours; 3.5-4.5 L.min^{-1}	~2 pg.m^{-3}	~20%	(Lu et al., 1998; Temme et al., 2003)
Whatman filters	PHg	24 hours; ~1.1 m^{3}.min^{-1}	Not reported	~20%	(Arimoto et al., 2004)
Micro-Quartz fibre filters	PHg	48 hr; 4.5 L.min^{-1}	~2 pg.m^{-3}	~20%	(Sprovieri and Pirrone, 2000)

Table 2 - Summary of atmospheric mercury measurements performed at different Antarctic locations from 1985 to 2009. NA: data not available; BDL: concentrations below detection limit

Measurement sites	**Period**	**Methods**	**Species**	**Statistical Parameters in $ng.m^{-3}$**			**References**
				Mean ± Std dev.	Min.	Max.	
Lake Vanda 77°33’S 161°37’E	Dec 1985	Manual-silvered/gilded sand collectors	TGM	0.23 ± NA	NA	NA	(De Mora et al., 1993)
Scott Base	1987	Manual-silvered/gilded sand collectors	TGM	0.52 ± 0.14	0.16	0.83	(De Mora et al., 1993)
77°51’S 166°46’E	1988		TGM	0.60 ± 0.40	0.02	1.85	
Arrival Heights 77°11’S 166°40’E	1989	Manual-silvered/gilded sand collectors	TGM	0.52 ± 0.16	0.11	0.78	(De Mora et al., 1993)
Neumayer	2000-2001	Tekran 2537A; 1130 and KCl-Coated Annular Denuders; AESmini-Traps	TGM	1.08 ± 0.29	0.27	2.34	(Ebinghaus et al., 2002b; Temme et al., 2003)
70°39’S 08°15’W			Hg(0)	0.99 ± 0.27	0.16	1.89	
			RGM	NA	5.10^{-3}	~ 300.10^{-3}	
			PHg	NA	15.10^{-3}	120.10^{-3}	
Terra Nova Bay	1999-2001	Tekran 2537A; 1130 and KCl-Coated Annular Denuders; Gold-mini Traps Filter collection	TGM	0.81 ± 0.1	0.5	0.9	(Sprovieri and Pirrone, 2000; Sprovieri et al., 2002)
74°41’S, 164°07’E			Hg(0)	0.9 ± 0.3	0.29	2.3	
			RGM	$(116\pm78).10^{-3}$	~11.10^{-3}	334.10^{-3}	
			PHg	$(12\pm 6).10^{-3}$	~4.10^{-3}	20.10^{-3}	
South Pole	Nov-Dec	Tekran 2537A; 1130, 1135	Hg(0)	0.54± 0.19	0.24	0.82	(Brooks et al., 2008a)

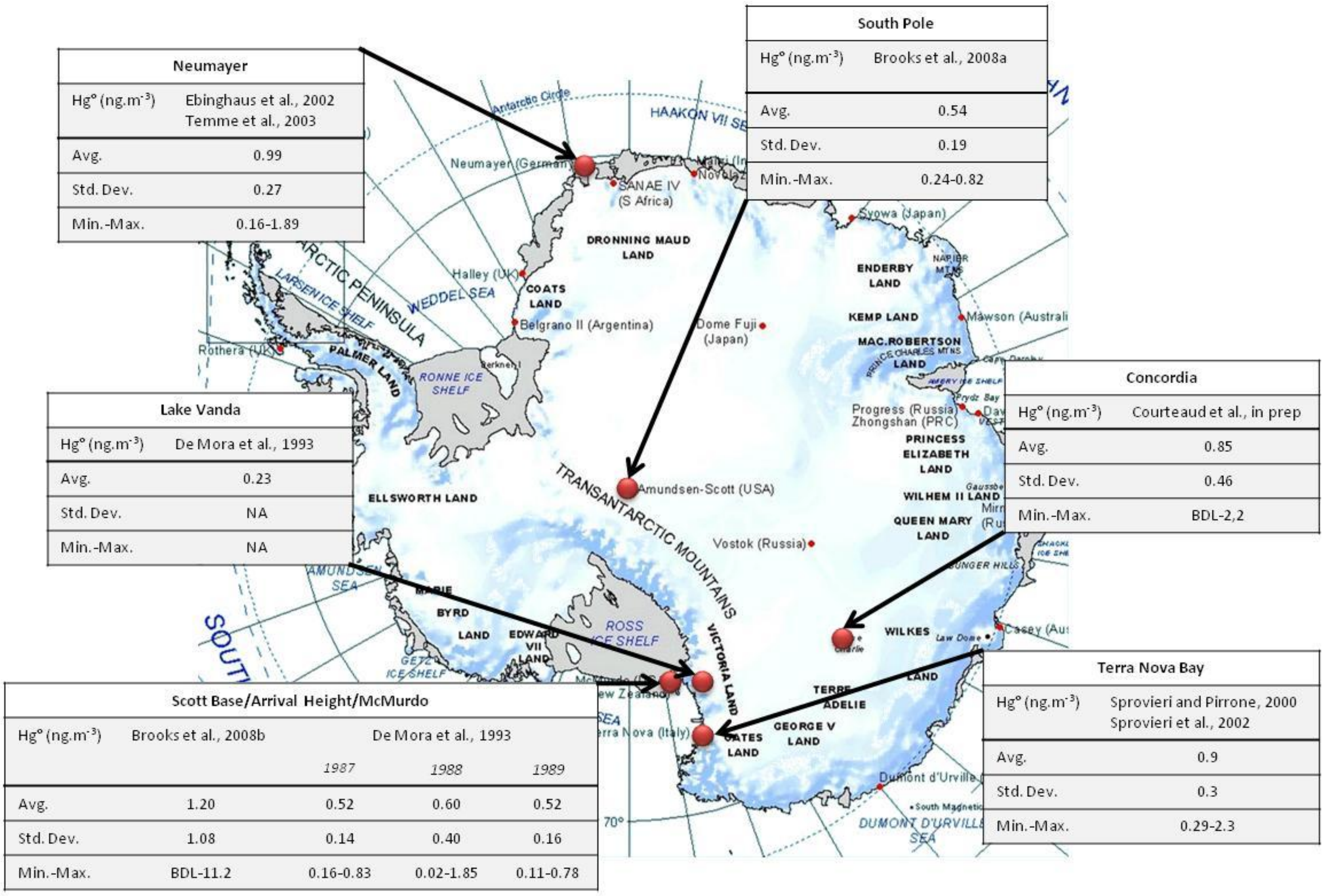
90°00’S	2003;Nov 2005		RGM	(344±151).10^{-3}	95.10^{-3}	705.10^{-3}	
			PHg	(224 ± 119). 10^{-3}	71.10^{-3}	660.10^{-3}	
	Nov 2000-Dec 2001	Filter collection	PHg	(166 ± 147). 10^{-3}	11.10^{-3}	827.10^{-3}	(Arimoto et al., 2004)
McMurdo	Oct-Nov 2003	Tekran 2537A; 1130, 1135	Hg(0)	1.20 ± 1.08	BDL	11.16	(Brooks et al., 2008b)
77°13’S 166°45’E			RGM	(116 ± 45).10^{-3}	29.10^{-3}	275.10^{-3}	
			PHg	(49 ±36).10^{-3}	5.10^{-3}	182.10^{-3}	
Concordia	Jan 2009	Tekran 2537A	Hg(0)	0.85±0.46	BDL	2.2	(Courteaud et al., 2010)
75°06′S 123°20′E							

Figure captions

Figure 1. Measurement sites for gaseous atmospheric mercury in Antarctica.

Figure 2. An example of higher BrO concentrations (in red) observed each year around the Antarctic continent during springtime. This monthly average map shows total BrO retrieved from measurements of the GOME-2 instrument in October 2007. The columns include both the stratospheric contribution (about 5.10E^{13} molec.cm^{-2}) and the tropospheric BrO amounts. (Richter et al., 1998)

Figure 3. Weekly averages of total filterable (the sum of RGM and PHg) mercury concentrations (bars) collected as Hg on high volume filters, and the annual solar elevation angles (line) at South Pole Station. High volume filters allow Hg(0) is pass but collect PHg and a significant portion of the RGM (after (Brooks et al., 2008a)).



Neumayer

Hg° (ng.m^{-3})	Ebinghaus et al., 2002 Temme et al., 2003
Avg.	0.99
Std. Dev.	0.27
Min.-Max.	0.16-1.89

South Pole

Hg° (ng.m^{-3})	Brooks et al., 2008a
Avg.	0.54
Std. Dev.	0.19
Min.-Max.	0.24-0.82

Lake Vanda

Hg° (ng.m^{-3})	De Mora et al., 1993
Avg.	0.23
Std. Dev.	NA
Min.-Max.	NA

Concordia

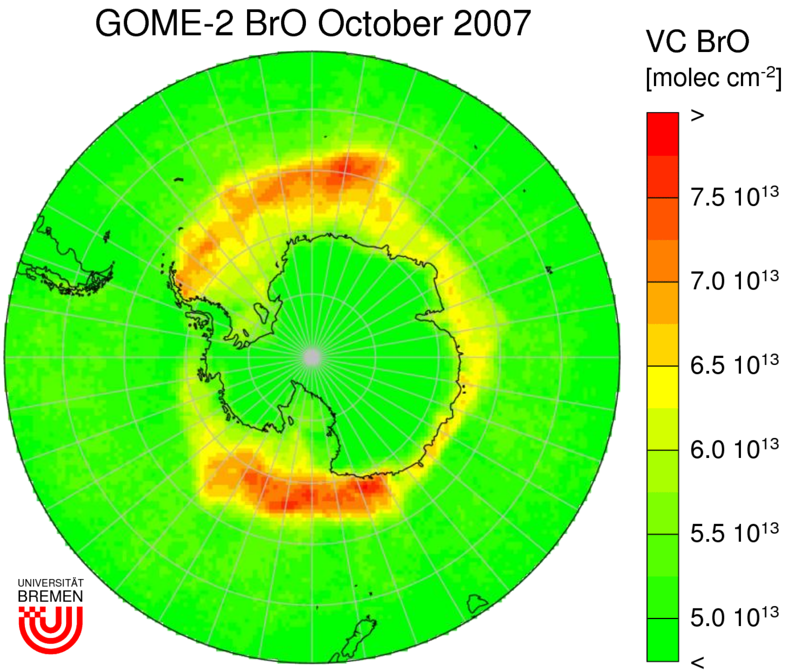
Hg° (ng.m^{-3})	Courteaud et al., in prep
Avg.	0.85
Std. Dev.	0.46
Min.-Max.	BDL-2,2

Scott Base/Arrival Height/McMurdo

Hg° (ng.m^{-3})	Brooks et al., 2008b	De Mora et al., 1993		
		1987	*1988*	*1989*
Avg.	1.20	0.52	0.60	0.52
Std. Dev.	1.08	0.14	0.40	0.16
Min.-Max.	BDL-11.2	0.16-0.83	0.02-1.85	0.11-0.78

Terra Nova Bay

Hg° (ng.m^{-3})	Sprovieri and Pirrone, 2000 Sprovieri et al., 2002
Avg.	0.9
Std. Dev.	0.3
Min.-Max.	0.29-2.3



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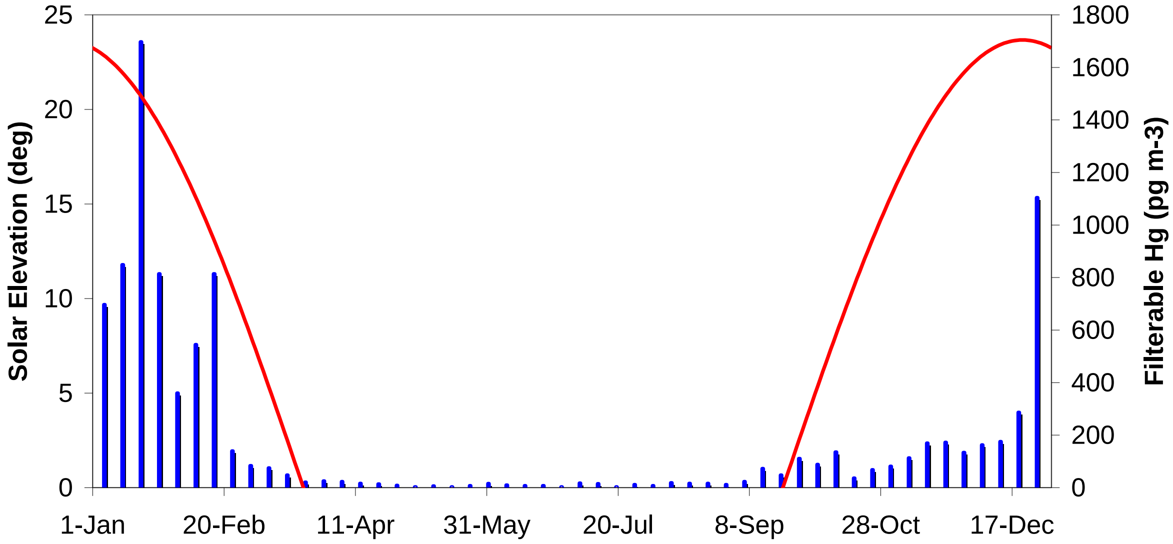
Solar Elevation (deg)
Filterable Hg (pg m-3)
25
20
15
10
5
0
1800
1600
1400
1200
1000
800
600
400
200
0
1-Jan
20-Feb
11-Apr
31-May
20-Jul
8-Sep
28-Oct
17-Dec