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 given mercury (Hg) 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) thus stimulating a significant amount of research including measurements of gaseous elemental mercury (Hg°) reaction rate constant with atmospheric oxidants, experimental and modelling studies in order to understand the cycling of Hg 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 Event” (AMDE), during which Hg° through a series of photochemically-initiated reactions involving halogens, may be converted to a reactive form that may accumulate in polar ecosystems. The discovery of the AMDE, 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 Hg 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 Hg may be recycled. Therefore, the contribution of this unique reactivity occurring in polar atmospheres to the global budget of atmospheric Hg 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

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 polar environmental surfaces more rapidly than anywhere else due to a phenomenon called Atmospheric Mercury Depletion Events (AMDEs) sparked considerable interest in the research community. Since then, hundreds of papers were published on that topic, as well as a few review papers mainly focusing on northern regions (Hedgecock et al., 2008; Poissant et al., 2008; Steffen et al., 2008; Dommergue et al., 2009; Nguyen et al., 2009). 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 hemisphere. Yet, 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 or 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 a long-range transport of man-made emissions of mercury (Hg). In Antarctica, gross mercury input is probably controlled by the South Hemisphere emissions. While Northern Hemisphere HG° 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). Therefore studying the cycling of Hg in Polar Regions is first necessary to understand and follow the extent of the contamination within these ecosystems. While mercury concentrations in biota of some arctic areas are known to have increased with time (Dietz et al., 2009) and to be rather high, there is not clear evidence of increased mercury bioaccumulation in continental Antarctica (Bargagli, 2001). However, recent studies showed that higher deposition rates could exist due to an active reactivity of Hg with halogen on coastal areas (Bargagli et al., 2007).

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 play an important role in the reactivity of the overlying atmosphere. They are a source of halogen recycling and deposition and burial substrate. 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 probable explanation is that the oxidation of gaseous mercury by sea-salt-derived halogens occurred in the cold atmosphere.

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 turned to be 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 perspective 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° 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° and RGM.

2.2 Atmospheric measurements in cold regions

Polar mercury speciation, mercury fluxes measurements, and snow pack 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 residency times are proper for the speciation of mercury into the 3 components, (2) prevent unintended mercury absorption in the sampling stream, 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 residency time over the KCl coated annular denuder. At the foggy coastal sites item (2) requires that dry air must be used to flush the system, otherwise the iodated carbon canisters (used to trap 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 unintended contaminates are not introduced.

Under very cold conditions the heated sample lines should be kept fully external to the climate controlled 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 stream 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. Snow pack sampling must take care to use a sun shield to prevent photoreduction during pit excavation and sampling.

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 yet these typically have populations of fewer than 100 people. The overwhelming majority of anthropogenic Hg loading to the environment and biota derives from global rather than local input.

Antarctica is characterized by a vast, cold, dry, high-altitude polar plateau, 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. Far from anthropogenic emissions, and isolated by the circumpolar vortex, only the longest-lived of the global atmospheric contaminants, such as Hg°, make their way to the Antarctica polar plateau.

3.1.1 A picture of available data

Few field mercury experiments have been performed in Antarctica compared to those carried out in the Arctic. Mercury measurements performed at different location of the Antarctic region are reported in Table 1 and in Figure 1. Hg° levels are far below the concentrations observed in the Arctic due to the remoteness from anthropogenic sources and probably to the influence of a reactivity, which is not well evaluated. 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 location 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) 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., 2002; Temme et al., 2003), the US Station McMurdo (Brooks et al., 2008b). Two sites on the Antarctic Plateau has also been explored at the US South Pole Station (Arimoto et al., 2004; Brooks et al., 2008a) and at the French-Italian Concordia Base (Courteaud et al.).

3.1.2 Atmospheric reactivity at coastal sites

Similar to the Arctic, atmospheric mercury and ozone (O_3) depletion events are most noticeable along coastlines where polynyas and coastal, or flaw, leads provide frequently freezing sea ice surfaces as a source of atmospheric bromine. In fact mercury processes in Antarctica probably begin with marine bromine emissions. 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. The related atmospheric bromine compound, BrO, can be detected with satellite (Richter et al., 1998) indicating regions and magnitudes of bromine emissions (see Figure 2).

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 south Polar Regions were obtained by Ebinghaus et al. (2002) at the German Research Station at Neumayer. AMDEs were observed during Antarctic springtime 2000 with minimum daily average concentrations of about 0.1 ng.m^{-3}. 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. TGM and O_3 were positively correlated 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 during Antarctic sunrise means that the depletion of Hg^0 also depends on photochemically-produced oxidants and thus on the rates of Br atom production and loss. Friess (2001) detected enhancements of BrO in the lower troposphere, during the same period, using DOAS. Ebinghaus et al. (2002) also found that AMDEs coincided with enhanced column densities of BrO from measurements by the satellite-borne GOME instrument over the sea ice around the Antarctic continent after polar sunrise (Figure 2 as an example). 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.

It in fact, seems reasonable to suppose that BrO or another halogen-containing radical or compound is responsible for an increase in Hg^0 oxidation and the formation of less volatile Hg(II) compounds (Boudries and Bottenheim, 2000). Among RHS thermodynamically favorable in oxidizing 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° to Hg(II) 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 addition, it should be noted that RGM and PHg consists of various oxidized compounds that are actually only operationally defined therefore the efficiency of the collection methods could be different among Hg(II) species sampled. 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, Antarctica. 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° 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° oxidation and deposition is difficult to determine, as their marine sources and reactivity with Hg° appear 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 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° depletion events during summertime. In fact, either no correlation or a significant negative correlation was rather observed between Hg° and O_3 (Sprovieri et al., 2002; Temme et al., 2003). The Hg° 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. The authors proposed a gas-phase oxidation of Hg^0 by potential oxidants (i.e. $OH^\bullet$, $HO_2^\bullet$, $NO_3^\bullet$) associated with high levels of NO. These oxidants result from photo-denitrification processes in the snow-pack (Zhou et al., 2001) 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.

3.1.3 Reactivity on the Polar Plateau

On the Antarctic Polar Plateau where the snowpack is perennial and the bromine process decoupled by distance from the original 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.

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 the summer solstice with maximum values ~February 1 when 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° transport and bromine snow pack recycling that may drive the atmospheric chemical production of oxidized mercury species. This delay could be due to the requirement of "seed" reactive halogens to drive the recycling of halogens from the surface snow (Simpson et al., 2007; Piot and von Glasow, 2008). Another recent study showed at Concordia (Courteaud et al.) that Hg° ground levels were both affected by the snowpack recycling and the variations of the boundary layer height. Contrarily to South Pole station, the daily diurnal cycle of the UV irradiance at Concordia significantly modulates the Hg° levels with a significant local Hg° production (through photochemical processes occurring at the snow surface) when a thin boundary layer (<50 m) is maintained. Later, the high solar radiations lead to a strong increase of the boundary layer height. Hg° levels are then diluted in a strongly Hg°-depleted air. The deposition of oxidized mercury is massive leading to hundreds of $ng.L^{-1}$ of Hg(II) on the surface snow and in deeper layers of the snowpack.

The observations on the Polar Plateau showed atmospheric oxidized mercury depositing to the snow pack, subsequent photoreduction, and emissions of Hg° 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 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 is driven by the surrounding sea ice as a vast bromine source, Southern Hemisphere Hg emissions, the sun, and the cold Spring/Summer temperatures. However mechanisms of reactivity are not fully understood. A major global obstruction to the formation of atmospheric Hg(II) is believed to be the fast thermal decomposition of the Hg(I) radical, HgBr (Holmes et al., 2006). This fast thermal decomposition rate dominates chemistry above 0°C, but the rate decreases by half with every 6°C drop in temperature below 0°C (Goodsite et al., 2004; Holmes et al., 2006). The mercury in the air over the Polar Plateau (the coldest place on Earth), unlike any other location, is predominately Hg(II) in Spring and Summer (Brooks et al., 2008a). While Arctic and Antarctic coastal sites experience episodic mercury depletion events which occur predominantly in the late winter and early spring, the polar plateau experiences nearly-constant mercury events, peaking in the summer. Holmes et al. (2006) shows that subsiding air from any part of the troposphere could bring to the surface gaseous Hg(II), formed by reactions with Br, together with elevated ozone. However the discovery of Hg reactivity on the Antarctic Plateau is a fairly new topic, and these studies open a vast area of research for the future.

3.2 Tropospheric reactivity in the Antarctic vs the Arctic

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 Arctic. Although in the Arctic the highest RGM concentrations were found during AMDEs, elevated concentrations were found at Barrow 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. 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 Eurasian 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.

4 Conclusions

The observations seen in the Antarctic region, thus 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. Significant differences are observed on coastal areas and on the Antarctic Plateau, which is largely unexplored. We believe that the Antarctic continent will reveal important discoveries in a close future on the Hg reactivity and its importance on the global cycle of Hg.

The discovery of the AMDE was initially considered to result in an important net input of atmospheric Hg into the polar surfaces (Ariya et al., 2004). 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 Hg may be recycled. Therefore, the contribution of this unique reactivity occurring in polar atmospheres to the global budget of atmospheric Hg and the role played by snow and ice surfaces of these regions need of more deep investigations including experimental monitoring and modelling studies. In addition, the ratio between deposition onto snow pack and reemission is an important parameter that determines the impact of AMDEs in the Antarctic environment. 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.

Long-term measurements of Hg° and other atmospheric Hg species in the Antarctic are very limited and need to be increased. A great deal of attention must be paid to inland sites (i.e. on the Polar Plateau). Measurements in Antarctica can yield critical information to better understand the processes involved in the cycling of Hg in the polar atmosphere and thus the deposition of this pollutant to this pristine environment. Long-term measurements of Hg in the polar atmosphere must be put into place so that the effects of these changes to Hg distribution in this environment can be monitored and scrutinized.

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References

Arimoto, R., Schloesslin, C., Davis, D., Hogan, A., Grube, P., Fitzgerald, W., and Lamborg, C.: Lead and mercury in aerosol particles collected over the South Pole during ISCAT-2000, Atmos. Environ., 38, 5485-5491, 2004.

Ariya, P. A., Dastoor, A. P., Amyot, M., Schroeder, W. H., Barrie, L., Anlauf, K., Raofie, F., Ryzhkov, A., Davignon, D., Lalonde, J., and Steffen, A.: The Arctic: a sink for mercury, Tellus B, 56, 397-403, 2004.

Bargagli, R.: Trace metals in Antarctic organisms and the development of circumpolar biomonitoring networks, in: Reviews of Environmental Contamination and Toxicology, Vol 171, Reviews of Environmental Contamination and Toxicology, Springer-Verlag, New York, 53-110, 2001.

Bargagli, R., Monaci, F., and Bucci, C.: Environmental biogeochemistry of mercury in Antarctic ecosystems, Soil Biol. Biochem., 39, 352-360, 2007.

Boudries, H., and Bottenheim, J. W.: Cl and Br atom concentrations during a surface boundary layer ozone depletion event in the Canadian high Arctic, Geophys. Res. Lett., 27, 517-520, 2000.

Brooks, S., Arimoto, R., Lindberg, S., and Southworth, G.: Antarctic polar plateau snow surface conversion of deposited oxidized mercury to gaseous elemental mercury with fractional long-term burial, Atmos. Environ., 42, 2877-2884, 2008a.

Brooks, S., Lindberg, S., Southworth, G., and Arimoto, R.: Springtime atmospheric mercury speciation in the McMurdo, Antarctica coastal region, Atmos. Environ., 42, 2885-2893, DOI 10.1016/j.atmosenv.2007.06.038, 2008b.

Calvert, J. G., and Lindberg, S. E.: A modeling study of the mechanism of the halogen-ozone-mercury homogeneous reactions in the troposphere during the polar spring, Atmos. Environ., 37, 4467-4481, 2003.

Castro, L., Dommergue, A., Ferrari, C., and Maron, L.: A DFT study of the reactions of O3 with Hg° or Br, Atmos. Environ., 43, 5708-5711, 2009.

Courteaud, J., Dommergue, A., and Ferrari, C.: Reactivity and speciation of mercury in Concordia Station perennial snow pack, East Antarctica   In preparation,

De Mora, S. J., Patterson, J. E., and Bibby, D. M.: Baseline atmospheric mercury studies at Ross Island, Antarctica, Antarct. Sci., 5, 323- 326, 1993.

Dietz, R., Outridge, P. M., and Hobson, K. A.: Anthropogenic contributions to mercury levels in present-day Arctic animals--A review, Sci. Total Environ., 407, 6120-6131, 2009.

Dommergue, A., Ferrari, C. P., Amyot, M., Brooks, S., Sprovieri, F., and Steffen, A.: Spatial coverage and temporal trends of atmospheric mercury measurements in polar regions, in: Mercury fate and transport in the global atmosphere: emissions, measurements and models, edited by: Pirrone, N., and Mason, R. P., Springer, 720, 2009.

Ebinghaus, R., Kock, H. H., Temme, C., Einax, J. W., Löwe, A. G., Richter, A., Burrows, J. P., and Schroeder, W. H.: Antarctic Springtime Depletion of Atmospheric Mercury, Environ. Sci. Technol., 36, 1238 –1244, 2002.

Eisele, F., Davis, D. D., Helmig, D., Oltmans, S. J., Neff, W., Huey, G., Tanner, D., Chen, G., Crawford, J., Arimoto, R., Buhr, M., Mauldin, L., Hutterli, M., Dibb, J., Blake, D., Brooks, S. B., Johnson, B., Roberts, J. M., Wang, Y., Tan, D., and Flocke, F.: Antarctic Tropospheric Chemistry Investigation (ANTCI) 2003 overview, Atmos. Environ., 42, 2749-2761, 2008.

Faïn, X., Ferrari, C. P., Dommergue, A., Albert, M. R., Battle, M., Severinghaus, J., Arnaud, L., Barnola, J.-M., Cairns, W., Barbante, C., and Boutron, C.: Polar firn air reveals large-scale impact of anthropogenic mercury emissions during the 1970s, Proc. Natl. Acad. Sci. U. S. A., 10.1073/pnas.0905117106, 10.1073/pnas.0905117106, 2009.

Fan, S. M., and Jacob, D. J.: Surface ozone depletion in arctic spring sustained by bromine reactions on aerosols, Nature, 359, 522–524, 1992.

Friess, U.: Spectroscopic Measurements of Atmospheric Trace Gases at Neumayer-Station, Antarctica, Ph.D. Thesis, University of Heidelberg, Heidelberg, Germany, 2001.

Goodsite, M. E., Plane, J. M. C., and Skov, H.: A theoretical study of the oxidation of Hg-0 to HgBr2 in the troposphere, Environ. Sci. Technol., 38, 1772-1776, 2004.

Hedgecock, I. M., Pirrone, N., and Sprovieri, F.: Chasing quicksilver northward: mercury chemistry in the Arctic troposphere, Environ. Chem., 5, 131-134, 10.1071/en08001, 2008.

Holmes, C. D., Jacob, D. J., and Yang, X.: Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere, Geophys. Res. Lett., 33, 2006.

Hynes, A. J., Donohoue, D. L., Goodsite, M. E., and Hedgecock, I. M.: Our current understanding of major chemical and physical processes affecting Hg dynamics in the atmosphere and at the air-water/terrestrial interfaces, in: Mercury fate and transport in the global atmosphere: emissions, measurements and models edited by: Pirrone, N., and Mason, R. P., Springer, 427-457, 2009.

Jitaru, P., Gabrielli, P., Marteel, A., Plane, J. M. C., Planchon, F. A. M., Gauchard, P. A., Ferrari, C. P., Boutron, C. F., Adams, F. C., Hong, S., Cescon, P., and Barbante, C.: Atmospheric depletion of mercury over Antarctica during glacial periods, Nature Geosci., 2, 505-508, 10.1038/ngeo549, 2009.

Lehrer, E.: Polar Tropospheric Ozone Loss, Ph.D. Thesis, University of Heidelberg, Heidelberg, Germany, 1999.

Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X. B., Fitzgerald, W., Pirrone, N., Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, Ambio, 36, 19-32, 2007.

Lindberg, S. E., Brooks, S., Lin, C. J., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M., and Richter, A.: Dynamic Oxidation of Gaseous Mercury in the Arctic Troposphere at Polar Sunrise, Environ. Sci. Technol., 36, 1245–1256, 2002.

Maron, L., Dommergue, A., Ferrari, C. P., Delacour-Larose, M., and Faïn, X.: How elementary mercury react in presence of halogen radicals and/or halogen anions: A DFT investigation, Chem.-Eur. J., 14, 8322-8329, 2008.

Nguyen, H. T., Kim, K.-H., Shon, Z.-H., and Hong, S.: A Review of Atmospheric Mercury in the Polar Environment, Crit. Rev. Environ. Sci. Tech., 39, 552 - 584, 2009.

Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., and Wilson, S.: Global anthropogenic mercury emission inventory for 2000, Atmos. Environ., 40, 4048-4063, 2006.

Piot, M., and von Glasow, R.: The potential importance of frost flowers, recycling on snow, and open leads for ozone depletion events, Atmos. Chem. Phys., 8, 2437-2467, 2008.

Poissant, L., Zhang, H. H., Canario, J., and Constant, P.: Critical review of mercury fates and contamination in the arctic tundra ecosystem, Sci. Total Environ., 400, 173-211, DOI 10.1016/j.scitotenv.2008.06.050, 2008.

Richter, A., Wittrock, F., Eisinger, M., and Burrows, J. P.: GOME observations of tropospheric BrO in northern hemispheric spring and summer 1997, Geophys. Res. Lett., 25, 2683-2686, 1998.

Saiz-Lopez, A., Mahajan, A. S., Salmon, R. A., Bauguitte, S. J. B., Jones, A. E., Roscoe, H. K., and Plane, J. M. C.: Boundary layer halogens in coastal Antarctica, Science, 317, 348-351, 10.1126/science.1141408, 2007.

Saiz-Lopez, A., Plane, J. M. C., Mahajan, A. S., Anderson, P. S., Bauguitte, S. J. B., Jones, A. E., Roscoe, H. K., Salmon, R. A., Bloss, W. J., Lee, J. D., and Heard, D. E.: On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O3, HOx, NOx and the Hg lifetime, Atmos. Chem. Phys., 8, 887-900, 2008.

Schroeder, W. H., Anlauf, K. G., Barrie, L. A., Lu, J. Y., Steffen, A., Schneeberger, D. R., and Berg, T.: Arctic springtime depletion of mercury, Nature, 394, 331–332, 1998.

Selin, N. E., Jacob, D. J., Park, R. J., Yantosca, R. M., Strode, S., Jaegle, L., and Jaffe, D.: Chemical cycling and deposition of atmospheric mercury: Global constraints from observations, J. Geophys. Res., 112, D02308, doi:02310.01029/02006JD007450, 2007.

Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H. W., Kaleschke, L., Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, Atmos. Chem. Phys., 7, 4375-4418, 2007.

Sprovieri, F., and Pirrone, N.: A preliminary assessment of mercury levels in the Antarctic and Arctic troposphere, J. Aerosol Sci., 31, 757-758, 2000.

Sprovieri, F., Pirrone, N., Hedgecock, I. M., Landis, M. S., and Stevens, R. K.: Intensive atmospheric mercury measurements at Terra Nova Bay in Antarctica during November and December 2000, J. Geophys. Res.-Atmos., 107, 2002.

Steffen, A., Douglas, T., Amyot, M., Ariya, P., Aspmo, K., Berg, T., Bottenheim, J., Brooks, S., Cobbett, F., Dastoor, A., Dommergue, A., Ebinghaus, R., Ferrari, C., Gardfeldt, K., Goodsite, M. E., Lean, D., Poulain, A. J., Scherz, C., Skov, H., Sommar, J., and Temme, C.: A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow, Atmos. Chem. Phys., 8, 1445-1482, 2008.

Temme, C., Einax, J. W., Ebinghaus, R., and Schroeder, W. H.: Measurements of Atmospheric Mercury Species at a Coastal Site in the Antarctic and over the South Atlantic Ocean during Polar Summer, Environ. Sci. Technol., 37, 22–31, 2003.

Vogt, R., Crutzen, P. J., and Sander, R.: A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, Nature, 383, 327-330, 1996.

Zhou, X. L., Beine, H. J., Honrath, R. E., Fuentes, J. D., Simpson, W., Shepson, P. B., and Bottenheim, J. W.: Snowpack photochemical production of HONO: a major source of OH in the Arctic boundary layer in springtime, Geophys. Res. Lett., 28, 4087-4090, 2001.

Table 1 - Summary of atmospheric mercury measurements performed at different Antarctic locations from 1985 to 2009. NA: data not available; BDL: concentrations below detection limit (The manufacturer reports a detection limit for 5min samples of 0.10 ng.m^{-3})

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., 2002; Temme et al., 2003)
70°39’S 08°15’W			Hg°	0.99 ± 0.27	0.16	1.89	
			RGM	NA	5.10^{-3}	~ 300.10^{-3}	
			TPM	NA	15.10^{-3}	120.10^{-3}	
Terra Nova Bay	1999-2001	Tekran 2537A; 1130 and KCl-Coated Annular Denuders; Gold-mini Traps;AE-TPM Traps	TGM	0.81 ± 0.1	0.5	0.9	(Sprovieri and Pirrone, 2000; Sprovieri et al., 2002)
74°41’S, 164°07’E			Hg°	0.9 ± 0.3	0.29	2.3	
			RGM	(116±78).10^{-3}	~11.10^{-3}	334.10^{-3}	
			TPM	(12± 6).10^{-3}	~4.10^{-3}	20.10^{-3}	
South Pole	Nov-Dec	Tekran 2537A; 1130, 1135	Hg°	0.54± 0.19	0.24	0.82	(Brooks et al., 2008a)

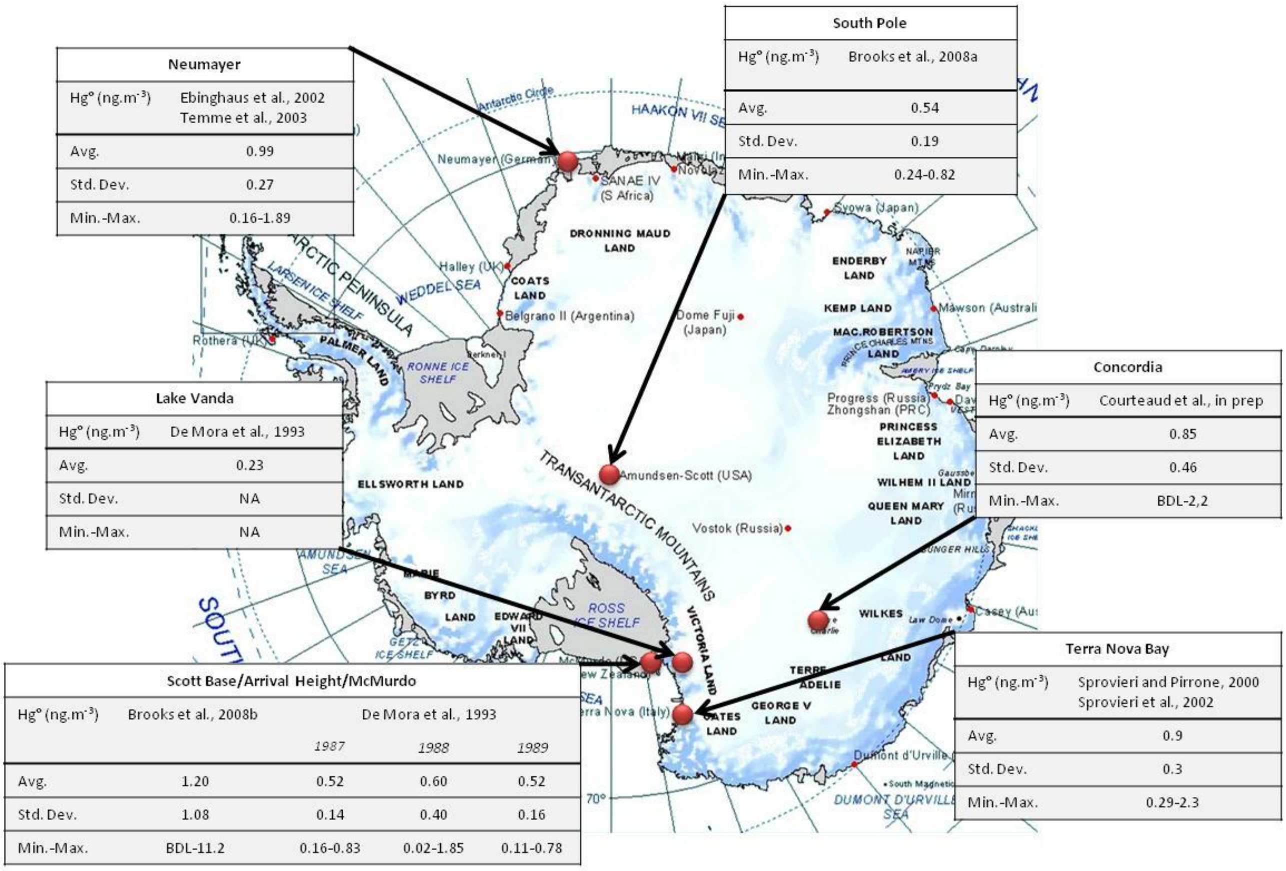
90°00’S	2003;Nov 2005		RGM	$(344\pm151).10^{-3}$	95.10^{-3}	705.10^{-3}	
			PHg	$(224 \pm 119).\ 10^{-3}$	71.10^{-3}	660.10^{-3}	
	Nov 2000-Dec 2001	Filters	TPM	$(166 \pm 147).\ 10^{-3}$	11.10^{-3}	827.10^{-3}	(Arimoto et al., 2004)
McMurdo	Oct-Nov 2003	Tekran 2537A; 1130, 1135	Hg°	1.20 ± 1.08	BDL	11.16	(Brooks et al., 2008b)
77°13’S 166°45’E			RGM	$(116 \pm 45).10^{-3}$	29.10^{-3}	275.10^{-3}	
			PHg	$(49 \pm36).10^{-3}$	5.10^{-3}	182.10^{-3}	
Concordia	Jan 2009	Tekran 2537A	Hg°	0.85±0.46	BDL	2.2	(Courteaud et al.)
75°06′S 123°20′E							

Figure captions

Figure 1. Measurement sites for gaseous atmospheric mercury (Hg°) in Antarctica.

Figure 2. Monthly average map of total BrO retrieved from measurements of the GOME-2 instrument in October 2007 on the Antarctic Continent. 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° 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

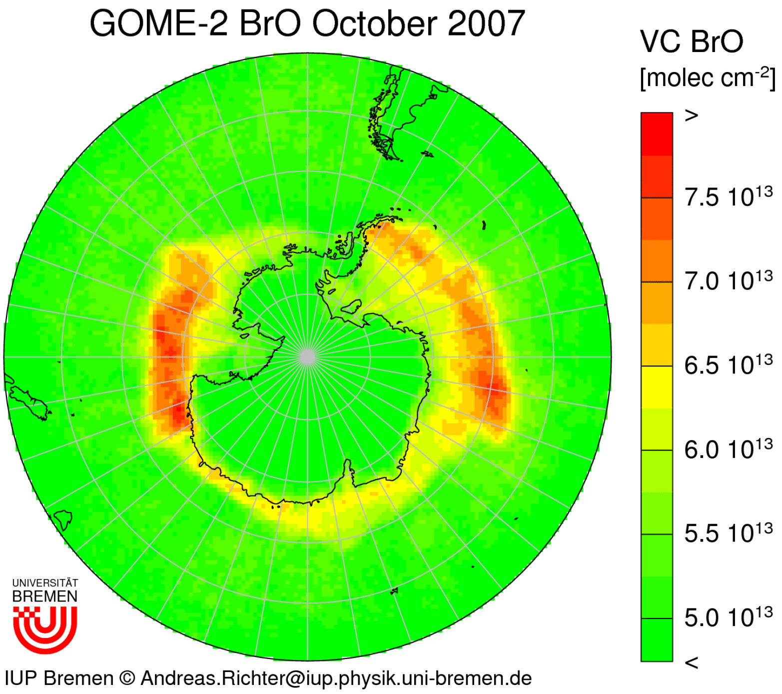
Hg° (ng.m^{-3})	Courteaud et al., in prep
Avg.	0.85
Std. Dev.	0.46
Min.-Max.	BDL-2,2

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


GOME-2 BrO October 2007
VC BrO
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7.5 10^13
7.0 10^13
6.5 10^13
6.0 10^13
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5.0 10^13
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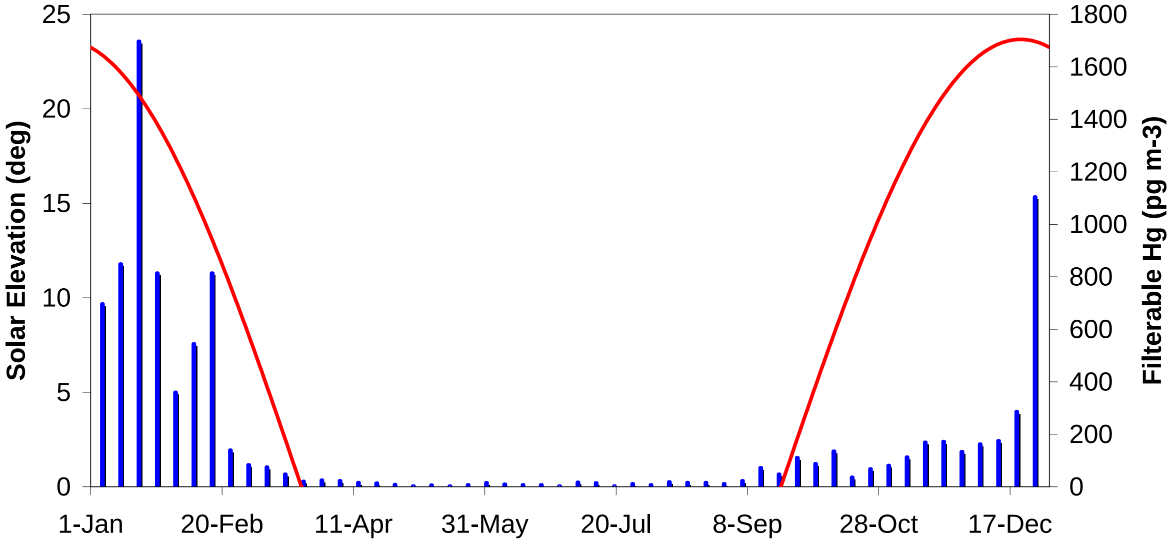
BREMEN
IUP Bremen © Andreas.Richter@iup.physik.uni-bremen.de


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