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**Dynamic recycling of
gaseous elemental
mercury**

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Dynamic recycling of gaseous elemental mercury in the boundary layer of the Antarctic Plateau

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Abstract

Gaseous elemental mercury (Hg(0)) was investigated in the troposphere and in the interstitial air extracted from the snow at Dome Concordia station (alt. 3320 m) on the Antarctic Plateau during January 2009. Measurements showed evidence of a very dynamic and daily cycling of Hg(0) inside the mixing layer with a range of values from 0.2 ngm⁻³ up to 2.3 ngm⁻³. During low solar irradiation periods, fast Hg(0) oxidation processes in a confined layer were observed leading to an enrichment of the upper snow layers in divalent Hg. Unexpectedly high Hg(0) concentrations for such a remote place were measured under higher solar irradiation due to the reemission of Hg(0) by the snowpack via photochemical reactions. Hg(0) concentrations showed a negative correlation with ozone mixing ratios, which contrasts with atmospheric mercury depletion events observed during the Arctic spring. It remains unclear whether halogens are involved in Hg(0) oxidation. We suggest that snow surfaces may play a role in promoting the heterogeneous oxidation of Hg(0). The cycling of other oxidants should be investigated together with Hg in order to clarify the complex reactivity on the Antarctic Plateau.

1 Introduction

Gaseous elemental mercury (Hg(0)) is the most abundant form of mercury (Hg) in the troposphere with a background concentration of approximately 1.5 ngm⁻³ in the Northern Hemisphere and 1.1 ngm⁻³ in the Southern Hemisphere (Sprovieri et al., 2010). Hg(0) is also thought to have a tropospheric residence time of about 1 yr, which means that it can be globally transported far from its emission sources (Selin et al., 2007). Oxidized Hg compounds, such as the operationally defined reactive gaseous Hg (RGM) and Hg associated with airborne particulate matter (HgP) are normally found at much lower concentrations (in the pgm⁻³ range) in the troposphere. The atmospheric lifetime of Hg(0) dramatically decreases to a few hours during fast oxidation processes

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involving bromine radicals as observed in various coastal locations in the Arctic (Steffen et al., 2008 and reference therein) and in Antarctica (Ebinghaus et al., 2002; Sprovieri et al., 2002; Brooks et al., 2008b) during springtime.

To date, research activities dealing with Hg in polar regions have focused primarily on the Northern Hemisphere troposphere, whereas the atmospheric cycling of Hg in the Antarctic, including the impact of the Antarctic continent on the global geochemical cycle of Hg, have not been explored in great detail (Dommergue et al., 2010). Antarctica, which is seven times larger than Greenland, has been considered a chemically-inactive and cold sink, where atmospheric species, including Hg, are buried in the ice-cap. However, recent studies have shown that the inner plateau is a highly oxidizing area (Eisele et al., 2008) and that some compounds, such as nitrogen in the form of nitrate, may undergo multiple cycles between the snow surface and the overlying atmosphere (Davis et al., 2008). In particular, the behavior of atmospheric Hg on the high altitude Antarctic Plateau (several millions of km² with an elevation above 2 km) is an open and vast field of research. To date, only one atmospheric study has been carried out with modern on-line instruments on the Antarctic Plateau at South Pole (90° S) (Brooks et al., 2008a). The authors report an unusual Hg cycle with high levels of oxidized Hg species and high Hg deposition on snow surfaces. The detailed mechanisms and the compounds involved in this reactivity remain uncertain. It highlights the fact that investigating the air/snow interface is essential for our comprehension of Hg cycling.

After two decades of intensive research on atmospheric Hg in the Arctic, we are now facing a new research challenge in Antarctica. The reactivity of Hg on the Antarctic Plateau has to be further explored in order to provide new data for understanding the global atmospheric Hg reactivity and to improve reactivity and deposition models (Selin et al., 2007). It is also important to understand the role of the snow on the overlying atmosphere. Atmospheric measurements on the Antarctic ice cap will also be useful to improve our interpretation of ice core data (Vandal et al., 1993; Jitaru et al., 2009).

To further develop our understanding of the physico-chemical processes involving Hg over this large area of the planet, we report results from the summer 2009 atmospheric

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campaign at Dome Concordia (DC) station (75° S, 123° E). Measurements of Hg(0) both in the snowpack interstitial air (SIA) and in the overlying atmosphere were conducted.

2 Measurements

2.1 Tropospheric measurements

This study was conducted at Dome Concordia station (75° 06' S, 123° 20' E, 3320 m above sea level) from 22 January to 30 January 2009. Dome Concordia station (DC) is located 1100 km away from the nearest coast of East Antarctica as shown in Fig. 1. During this study, there was 24 h of sunlight. Local time (UTC + 8) is used for convenience throughout the paper.

To minimize contamination from the station, Hg(0) measurements were performed in an atmospherically clean area located upstream the dominant winds, 800 m south of the station. We sampled ambient air 20 cm and 200 cm above the snow surface through a clean PTFE line. We used a Tekran 2537A analyzer for the continuous monitoring of Hg(0). Hg(0) in the pre-filtered air stream (soda lime trap and 0.2 μm PTFE filter) was alternatively collected on two gold cartridges at a flow rate of 1.0 l min⁻¹. Hg(0) was thermally desorbed and detected by cold vapor atomic fluorescence spectrometry at 253.7 nm. The dual cartridge system makes continuous measurements with a collection time which was set to 5.0 min. The analyzer was calibrated every 24 h using an internal automatic permeation source injection. We also performed external calibrations by injection of a known amount of Hg vapors before and after the field campaign. With this configuration mode, we achieved a detection limit of about 0.1 ng m⁻³.

During the same period, we also measured continuously the concentration of Hg(0) in snow interstitial air (SIA) at depths of 40 cm, 80 cm, 120 cm and 160 cm below the snow surface. GAMAS probes (Gaseous Mercury in Interstitial Air in Snow, Dommergue et al., 2003a) were connected to the Tekran 2537 analyzer. A heated 6-port

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solenoid valve (2 inlets in the atmosphere, 4 inside the snowpack) performed an alternate sampling of each inlet every 10 min. Blanks of the probes and of the sampling system were performed using Hg-free air supplied by an activated charcoal cartridge. As discussed in detail elsewhere (Dommergue et al., 2003b), the continuous sampling of interstitial air is subject to some artifacts. We tried to minimize them using the lowest possible flow rate (1 l min^{-1}) and a short sampling time at each depth (10 min). The nature of the snowpack itself generates uncertainties on the origin of the sampled air. As a consequence, our measurements give us some information on the existence of physico-chemical processes inside the snowpack but they are not accurate enough to identify the exact spatial origin of Hg(0).

Ozone (O_3) measurements were continuously performed with a UV absorption monitor (Thermo Electron Corporation model 49I, Franklin, MA). The steel inlet of the sampling line was located at 5 m above the ground level in the chemically clean area. The data collected at 30 s intervals are reported as 30 min averages.

Meteorological data including continuous measurements of vertical gradients of wind and temperatures were available at the American Tower. Continuous measurements were performed at 6 heights (3.5, 10.6, 18, 25.3, 32.7 and 41.9 m) and are reported as 30 min averages (Genthon et al., 2010, 2012).

2.2 Snow sampling and analysis

Snow samples were collected daily at DC and on the logistic trail between DC and the coastal site of Dumont d'Urville station ($60^\circ 40' \text{ S}$, $140^\circ 01' \text{ E}$, 40 m a.s.l., Fig. 1) from 2 February to 11 February. The samples were immediately stored in the dark at -20° C until analyzed. We used acid cleaned PTFE 250 ml bottles and clean sampling procedures. Field blanks and transportation blanks were also taken. Total Hg (THg) in snow samples was measured with a Tekran Model 2600 using USEPA method 1631 revision E. Samples were oxidized with 0.5 % v/v BrCl to preserve divalent Hg in solution and to digest strongly bound Hg(II) complexes. Excess BrCl was neutralized with pre-purified hydroxylamine hydrochloride. The sample was automatically injected together

with SnCl_2 , into a reaction vessel, reducing Hg(II) to Hg(0) . Hg(0) was carried in an argon stream to two online gold traps. After thermal desorption, Hg(0) was detected by atomic fluorescence spectrometry. The Tekran Model 2600 was calibrated daily with the NIST SRM-1641d Hg standard. The limit of detection, calculated as 10 times the standard deviation of a set of 10 analytical blanks was 0.3 ng l^{-1} and relative accuracy was determined to be $\pm 8\%$ using a certified reference material (ORMS-4, National Research Council Canada). All samples were analyzed in triplicate.

Field blanks obtained at DC contained unexpectedly high levels of THg. We were forced to discard the whole set of data. Quality controls showed no contamination for snow samples collected on the logistic trail however.

3 Results and discussion

3.1 First observations of a diurnal cycling of Hg(0) in the boundary layer of the Antarctic Plateau

As presented in Fig. 2, Hg(0) concentrations in the lower troposphere of DC varied from 0.2 ng m^{-3} to 2.3 ng m^{-3} (mean of $0.85 \pm 0.46 \text{ ng m}^{-3}$). Our data are in the range of values retrieved during the same season at coastal Antarctic sites such as Neumayer Station ($\sim 1 \text{ ng m}^{-3}$ for Total Gaseous Mercury, Ebinghaus et al., 2002), Terra Nova Bay ($0.9 \pm 0.3 \text{ ng m}^{-3}$, Sprovieri et al., 2002), McMurdo ($1.20 \pm 1.08 \text{ ng m}^{-3}$, Brooks et al., 2008b) or at the Norwegian Antarctic Research Station, Troll ($0.93 \pm 0.19 \text{ ng m}^{-3}$, Pfaffhuber et al., 2012). During the single study ever published carried out with modern instruments on the Antarctic Plateau, Brooks et al. (2008a) reported Hg(0) values of $0.54 \pm 0.19 \text{ ng m}^{-3}$ at South Pole station in November–December. While both Antarctic Plateau sites showed comparable low values, our study additionally revealed that Hg(0) exhibited significant and daily cycling. As presented in Fig. 3, Hg(0) concentrations were usually minimal around 00:00 LT and well below 0.93 ng m^{-3} which is supposed to be the Antarctic background (Pfaffhuber et al., 2012). Atmospheric Hg(0) reached

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maximal concentrations around noon with high values for such a remote place. High day-to-day fluctuations were also observed. For example, the average Hg(0) concentration was $1.25 \pm 0.45 \text{ ng m}^{-3}$ on 23–24 January, and $0.29 \pm 0.15 \text{ ng m}^{-3}$ on 28 January.

The interpretation of atmospheric Hg(0) measurements at DC is very complex considering the lack of detailed knowledge of both atmospheric composition and the various physico-chemical phenomena that are likely involved. Among possible mechanisms that drive the dynamics of Hg(0) variations at a daily scale, the impact of local meteorological conditions such as the vertical mixing, the role of the snowpack as a source of Hg(0) and the possible atmospheric loss of Hg(0) by oxidation processes deserve further discussion.

3.2 Influence of local meteorological conditions on Hg(0) measurements

The Antarctic Plateau is characterized by strong surface temperature variations and by the development of a very shallow nighttime boundary layer that can significantly impact the vertical mixing of chemical species (Schwerdtfeger, 1984; Garratt, 1994). When the solar irradiation is low at night, the snow surface is colder than the overlying atmosphere. This thermal stratification associated with horizontal wind speed stratification prevents any vertical mixing. Conversely, the surface temperature rises as the solar irradiation increases. Turbulence starts to develop from the surface leading to fast vertical mixing. As a consequence, the mixing layer, that is the first vertical layer above the surface in which mixing is efficient, is characterized by daily oscillations (e.g. Legrand et al., 2009). An assessment of the height and dynamics of the mixing layer can be inferred using a regional climatic model over the Antarctic continent. The MAR model simulations (Gallee and Schayes, 1994; Gallee, 1995) are validated through observations from weather stations at DC (Gallee and Gorodetskaya, 2010). Using MAR simulations, we calculated that the mixing layer could be very thin at night (around 20 m) as shown in Fig. 4c. Night time vertical mixing was limited to the first 20 m of the low troposphere, which was confined and isolated from the overlying atmospheric layers. Our Hg(0) measurements around midnight thus provided information on the Hg(0)

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behavior at the air-snow interface. During day hours, the vertical mixing is greater and the mixing layer could increase up to a height of 250 m resulting in an efficient air mixing from the snow surface to higher altitudes in the troposphere. As shown in Fig. 4c, the mixing layer oscillations were also subject to high day-to-day fluctuations and their interpretation is complex and well beyond the scope of this study. Among the parameters influencing the mixing layer height, wind is an important factor that also governs snow-to-air exchanges through wind pumping (Sokratov and Sato, 2001).

To further understand these physical phenomena, measurements of the vertical temperature profiles are useful since turbulence redistributes temperature in the mixing layer. As presented in Fig. 4a, the absence of temperature gradients indicates the existence of an active vertical mixing of the chemical species in the first 41.9 m of the troposphere at least. These conditions coincided with increasing Hg(0) concentrations. When a vertical gradient of temperature was measured, it indicates the occurrence of stratified conditions and the absence of vertical mixing for Hg(0), the lowest temperatures being at the air-snow interface. These conditions were usually observed during night hours and correspond to an abrupt decrease of atmospheric Hg(0) concentrations. The night hours between 23 and 24 January were the only ones that showed no wind and no temperature stratification due to the occurrence of higher temperatures during that night. However, such conditions are still those of a stable atmosphere with limited vertical mixing. During that night, the typical Hg(0) decrease was not observed and the concentrations remained roughly constant around 1.2 ng m^{-3} .

Hg(0) measurements combined with the analysis of the local meteorology suggest that we recorded a loss of Hg(0) in a shallow mixing layer during low solar irradiation hours. As the solar irradiation increased during the day, we observed mixing with the overlying atmospheric layer combined with Hg(0) emissions from the snow-pack. In their study at South Pole, Brooks et al. (2008a) assumed low Hg(0) values ($<0.2 \text{ ng m}^{-3}$) above the mixing layer. Although high altitude vertical profiles of Hg(0) should be done to further explore this assumption, we suggest that the Hg(0) concentrations in the overlying layers (excluding some potential subsidence events that are

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discussed below) could be in the range of the Antarctic background as proposed in Pfaffhuber et al. (2012).

3.3 Snow as an intense photochemical source of Hg(0)

The evolution in time of Hg(0) concentrations in the snow interstitial air (SIA) is presented in Fig. 5. During the campaign, we observed a decrease in the mean Hg(0) concentration in the SIA with depth. Depths of 40 cm and 80 cm exhibited higher concentrations than ambient ones while Hg(0) concentrations deeper in the snow (120 and 160 cm) were below ambient air values. At South Pole, Brooks et al. (2008a) reported Hg(0) concentrations peaking at 3 ng m^{-3} at a depth of 3 cm, indicating that the upper snow layer produced Hg(0). SIA measurements clearly showed diel variation with minimum concentrations at night and maximum concentrations during day hours. SIA measurement patterns mirrored ambient value oscillations with maxima of 5.0 and 4.5 ng m^{-3} on 24 and 25 January, respectively. The amplitude of variations appeared to be smaller in the SIA than in the ambient air as we sampled deeper in the snowpack.

Our THg measurements confirm that surface snow in the Antarctic Plateau contains significant amounts of divalent Hg with concentrations up to a couple of hundred ng l^{-1} . THg concentrations between DC and Dumont d'Urville were in the range $4.2\text{--}194.4 \text{ ng l}^{-1}$ (mean value 47.0 ng l^{-1}). The closest sample from DC (collected 131 km away) showed a THg concentration of $60.3 \pm 8.1 \text{ ng l}^{-1}$ ($n = 3$). These levels were higher than background values as encountered in Antarctic ice cores (Planchon et al., 2004) and in agreement with the surface snow average of 198 ng l^{-1} at South Pole (Brooks et al., 2008a). Although we did not excavate snow pits to report THg vertical profiles, Brooks et al., (2008a) observed a very fast decrease in THg concentrations with respect to depth with concentrations falling to around 10 ng l^{-1} below 25 cm deep. That SIA concentrations in the upper layer of the snowpack exceed ambient air concentration and that significant amounts of divalent Hg(II) are present in the top snow layer point to the snow as a significant source of Hg(0) input to the atmosphere.

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Examining physical processes first, there is a striking positive correlation between atmospheric Hg(0) and air temperature (see Fig. 4). It could be due to the adsorption equilibrium of Hg(0) on snow crystals: as temperature rises, Hg(0) is released to the gas phase. However, the adsorption of Hg(0) on the snow surface is very weak with a partition coefficient (i.e. the ratio between adsorbed molecules per cm² and the concentration in the gas phase expressed in molecules cm⁻³) K_{linC} in the 10⁻⁴ cm range at 240 K (Bartels-Rausch et al., 2008). This means that 300 atoms of Hg only would be adsorbed per cm² of ice given an average atmospheric Hg(0) concentration of 1 ng m⁻³. If we assume that the first 10 cm of the snowpack are in equilibrium with the atmospheric boundary layer and consider a snow specific surface area of 30 m² kg⁻¹ and a snow density of 300 kg m⁻³ (Gallet et al., 2011), we calculate that the upper 10 cm of the snowpack only contained about 10⁻⁴ ng of adsorbed Hg per square meter of ground surface. This very low value is not sufficient to explain Hg(0) variations of about 1 to 2 ng m⁻³ observed above the snowpack. Adsorption and desorption processes of Hg(0) on snow grains cannot therefore account for the Hg(0) variations at DC.

Photoreduction of previously deposited Hg(II) is a more plausible hypothesis in order to explain Hg(0) emissions from snow. It has been observed both in the field and in laboratory experiments with snow from diverse origins (for a review, refer to Durnford and Dastoor, 2011). Now, how can Hg(0) production in the snow lead to levels more than twice as high as supposed background levels? A rapid calculation using a snow density of 300 kg m⁻³ shows that a loss of 6 ng l⁻¹ of Hg(II) from the top 10 cm of the snowpack would lead to a homogeneous concentration increase of 0.9 ng m⁻³ in a mixing layer of 200 m high. Assuming an emission duration of 12 h, the resulting Hg(0) flux from the snowpack would be 15 ng m⁻² h⁻¹. By comparison, an Hg(0) flux of 10 ng m⁻² h⁻¹ over a 16 h time period was measured in mid November 2003 from Antarctic snow at South Pole (Brooks et al., 2008a) when solar radiation was lower than in our study. Therefore, the increase in Hg(0) concentration in ambient air is explained by the photoreduction of Hg(II) species in the active photic zone of the snowpack. This is consistent with the elevated concentrations measured in the SIA and compatible with previously observed

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Hg(0) fluxes at the air/snowpack interface of Antarctic regions. The amplitude of Hg(0) emissions may also be driven by atmospheric conditions. Boundary layer dynamics, turbulence and wind pumping affect these emissions and their transport in the atmosphere. For instance, wind speed influences the mixing layer stability. It also affects the ventilation processes of the snowpack, that are more efficient than diffusion in order to transport Hg(0). Overlying wind speed increase can dramatically increase the transport of gas through the interstitial air of snow (Albert and Shultz, 2002) and can affect mercury emissions (Steffen et al., 2002). A lower wind speed as observed on 24 January probably allowed for a build-up of Hg(0) and a less efficient dispersion.

3.4 Night-time depletion of atmospheric Hg(0)

Model simulations and meteorological temperature gradients demonstrated the existence of a shallow mixing layer during night hours that coincides with an average decrease of Hg(0) after 4 p.m. (Fig. 3). We hypothesize that the Hg(0) decrease is due to oxidation processes leading to Hg(II) increases in snow. We did not measure RGM at DC, but Brooks et al. (2008a) observed the deposition of RGM at South Pole Station with an estimated flux of $-10.8 \text{ ng m}^{-2} \text{ h}^{-1}$. In this study, the authors suggested that Hg(0) was oxidized by bromine species in the upper layer of the free troposphere and that subsequently oxidized mercury species were deposited onto the snow surface. They showed that mercury oxidation begins to peak from the end of December with maximum values at the end of January when extremely high oxidized Hg concentrations were measured in the near-surface air (RGM + HgP $\sim 100\text{--}1000 \text{ pg m}^{-3}$).

3.4.1 Is halogen oxidation in the gas phase an option?

Our first hypothesis is that the loss of Hg(0) in the atmosphere results from oxidation by halogens in the gas phase. The very fast Hg(0) decrease that we observed can be roughly compared to Atmospheric Mercury Depletion Events (AMDE) occurring in coastal Arctic and Antarctic places. Due to the short lifetime of Hg(0) in the presence

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of Br or BrO, bromine species were suspected to be efficient oxidants for Hg(0) (Ariya et al., 2004). A strong positive linear correlation between Hg(0) and O₃ was observed at coastal arctic sites during the episodic springtime mercury depletion events (Schroeder et al., 1998; Steffen et al., 2008), suggesting similar reaction pathways involving reactive halogens (Lindberg et al., 2002). According to theoretical studies (Khalizov et al., 2003; Goodsite et al., 2004; Maron et al., 2008), Hg + Br might be a first reaction leading to unstable oxidized Hg products. In order to stabilize the oxidation products into divalent Hg species, a second step is necessary. The first reaction has been experimentally verified but there is no experimental evidence of the second one (Donohoue et al., 2006). Experimental findings in coastal Antarctica are however ambiguous. A dramatic decrease of atmospheric Hg(0) was observed in all the records at coastal sites during the spring or the summer suggesting similarities with AMDE. However, both a positive correlation and a negative correlation or the absence of correlation between Hg(0) and ozone were also observed (Ebinghaus et al., 2002; Sprovieri et al., 2002; Temme et al., 2003; Pfaffhuber et al., 2012). As shown in Fig. 4 where 30 min averaged O₃ mixing ratios at DC are reported, a negative correlation between Hg(0) and O₃ was observed during our field campaign without any dramatic depletion of O₃ at any time. At a daily scale, the O₃ level reached its maximum around midnight when Hg(0) was minimum. The highest levels for O₃ (between 26 and 31 ppbv) were observed on 22, 25 and 28 January around midnight, when Hg(0) was depleted below 0.3 ng m⁻³.

If Hg(0) was oxidized by halogen (such as Br) radicals, it might also lead to O₃ destruction. The O₃ loss could be compensated for by ozone production by elevated levels of nitrogen oxides (>200 pptv). As shown by Davis et al. (2008), the photodenitrification of surface snow is responsible for high NO_x levels (a few hundreds of pptv) at South Pole during the summer. A consequence of these high NO_x summer levels is a significant photochemical production of O₃ that is detected in ozone mixing ratios (Crawford et al., 2001). At DC, NO_x are in the same range of concentrations (Frey, 2011) and significantly influence the ozone cycling (Legrand et al., 2009). These antagonist mechanisms for O₃ could result in a net production during the night hours

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inside the mixing layer. The oxidation reaction for Hg(0) could be a two-step mechanism (Goodsite et al., 2004) with a first step leading to an unstable HgBr. HgBr would further react to reach a more stable state of energy through a reaction with Br, OH, or O₃ to form Hg(II) products that are subsequently incorporated into snow. Given the temperature dependencies of the reactions, lower temperatures at night could decrease the lifetime of Hg(0).

While halogen chemistry is univoqually observed in the marine boundary layer where marine salts provide a local source of halogens, their presence in significant quantities far from the coast in the Antarctic Plateau still remains uncertain. At DC, winter storms can transport marine species including halogens to the Plateau (Jourdain et al., 2008) and sea spray significantly contributes to aerosol ion mass at DC, especially in the winter (Udisti et al., 2012). These authors reported that changes in large-scale atmospheric circulation favor the advection of marine air masses contributing to sea-spray events at DC. Although the source of sea spray is mainly due to bubble bursting over ocean open waters (Mason, 1954), some rare events may originate from frost flower formation on sea-ice (Rankin et al., 2000). We investigated the possible transport of air masses from marine origin by computing back-trajectories using HYSPLIT (Draxler and Rolph, 2003) but we could not find any evidence of transport of marine air masses during our field campaign at DC.

This absence of evidence does not necessarily imply that halogen chemistry does not take place. Measurable levels of BrO (typically between 1 and 3 pptv) were recently observed in the atmosphere over the Greenland ice sheet 400 km from the ocean and in air masses not originating from the sea (Stutz et al., 2011). It was suggested that snowpack photochemistry could be a possible source of BrO to the atmosphere (Dibb et al., 2010; Stutz et al., 2011). However the sources of bromide remained unclear and could be the falling snow and the transport of some bromine species from the free troposphere or marine regions. Measurements of some gaseous oxidized Hg species (RGM) and BrO over a 4-day period were significantly correlated at Summit (Brooks et al., 2011). The conversion of Hg(0) to RGM was not sufficiently unequivocal in their

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data set however. There are currently no measurements of Br- in the snow nor of reactive bromine species in the atmosphere of DC or other Central Antarctic places to support that the snowpack could be the initial source of halogen species. Field measurements of Br/BrO mixing ratios need to be performed to support this hypothesis.

5 Recent findings and the singularity of the Antarctic atmosphere led us to examine additional hypotheses. Recently, a study showed that air masses in the upper troposphere originating from the stratosphere were enriched in oxidized Hg (Lyman and Jaffe, 2012). A previous study of the lower stratosphere showed the existence of some amounts of Hg ions containing particles (Murphy et al., 1998, 2006). A maximum of Hg(II) may exist near the tropopause along with bromine containing particles. Bromine alone would not explain the production of Hg(II) through Hg(0) oxidation and some other halogens must be involved (Holmes et al., 2010; Lyman and Jaffe, 2012). During winter time, the Antarctic atmosphere does not have a tropopause as at lower latitudes, which facilitates stratosphere to troposphere exchanges as shown by cosmogenic tracers indicating influx of stratospheric air into the troposphere (Wagenbach et al., 1998). 15 These stratospheric inputs were discovered at DC in the winter (July–September) by studying the isotopic composition ($\Delta^{17}\text{O}$) of atmospheric particulate nitrate (Frey et al., 2009) and cannot be ruled out later in the season since the photolytic recycling of nitrate above snow alters the isotopic signature of the stratosphere. Stratospheric sedimentation of Hg(II)-halogen particles would explain an initial source of Hg(II) in snow as found in the snow samples. The fate of such particles once deposited in snow is uncertain, but the photolytic reaction of Hg(II)-halogen species could potentially lead not only to the emission of photo-reduced Hg(0) but also of reactive halogens in the gas phase. Experimental evidence of such processes has never been observed so far, and 25 the lack of halogen measurements in the Antarctic Plateau makes it difficult to assess the possible role of halogens at DC.

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3.4.2 The potential role of heterogeneous reactions

According to Brooks et al. (2008a), the Hg oxidation rate peak period (January–February) roughly corresponds to the annual photochemical peak cycles of nitrogen oxides, OH and HO₂. During this period, OH concentrations can reach several 10⁶ molecules cm⁻³ (Davis et al., 2008). NO_x are also abundant and influence the ozone cycling (Legrand et al., 2009). The present knowledge of gas phase kinetics cannot support other gas phase oxidation pathways that fit with our Hg observations. We are inclined to think that heterogeneous chemistry is a second possibility that has to be seriously investigated to explain the observed daily Hg(0) depletion.

A recent review of Hg atmospheric chemistry reminds us wisely that gas phase reactions drive to some extent the lifetime of gaseous mercury (Subir et al., 2011, 2012). Heterogeneous reactions are also important environmental processes that occur in clouds and in the presence of particles. We should mention that snow surfaces are known to play an important role on the tropospheric chemistry as well (Dominé and Shepson, 2002). It is thus unrealistic to apply our knowledge of gas-phase kinetics only to the understanding of atmospheric processes that were observed in Antarctica. Because the mixing layer was very shallow at night, the influence of snowpack chemistry on measured atmospheric concentration is overwhelmed and may indicate that the removal of atmospheric Hg(0) involves snow mediated processes such as heterogeneous chemistry. Oxidation products such as Hg(II) species could strongly interact with snow surfaces leading to more efficient oxidation pathways. Among other unclear processes, the very low levels of Hg(0) in the lower interstitial air of the snowpack (Fig. 5) raise the question of the fate of Hg(0) in the firn and suggest a possible dark oxidation of Hg(0). The same pattern was observed in other snowpacks in the Arctic (Maron et al., 2008). Similar decreasing concentrations in the deeper interstitial air were also observed for ozone at Alert in Canada (Albert et al., 2002) or at Summit in Greenland (Peterson and Honrath, 2001; Helmig et al., 2009). So far, no mechanisms have been validated for O₃ and Hg.

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Clegg and Abbatt (2001) experimentally measured the kinetics of SO₂ oxidation by H₂O₂ on ice surfaces. The reaction was found to be fast enough to determine the lifetime of SO₂ in clouds, making the gas phase oxidation by OH a minor process. A recent study showed that a freezing acidic solution containing nitrite (250 μM) or hydrogen peroxide (2.2 μM) can oxidize dissolved elemental mercury in the dark (O'Concubhair et al., 2012). Although it is not clear if it occurs during freezing, it suggests that similar processes could occur at DC in the snow at night, which fits well with the observed decrease in Hg(0) concentrations. Many oxidants could be involved such as nitrous acid (HONO) or hydrogen peroxide (O'Concubhair et al., 2012). Nitrous acid was recently shown to peak in the atmosphere at DC in the evening (Kerbrat et al., 2012). The HONO photochemical source remains unclear. Hydrogen peroxide was noticeably present in South Pole snow (~10 μM) that is considered to be a strong H₂O₂ source in the summer (Hutterli et al., 2004). Nitric acid could be a potential reactant too as its probable cycling between snow and atmosphere is an important process of the NO_x chemistry (Huey et al., 2004).

Detailed kinetic studies of multiphasic Hg(0) oxidation using ice/snow surfaces are not available yet. We believe that our observations should motivate further studies to identify processes involved in the cycling of Hg in the Antarctic Plateau. Although the photoreduction of Hg(II) species in snow and the release of Hg(0) from the snowpack are well documented, there are still serious shortcomings in how we can explain the fast oxidation processes observed above and probably inside the snowpack.

4 Conclusions

This second study of the Hg cycle on an Antarctic inland site highlights both the spatial variability and the complexity of chemical pathways involved in Hg reactivity. At DC, Hg(0) was negatively correlated with O₃ mixing ratios and followed high diel and day-to-day fluctuations. Dramatic losses of Hg(0) were daily observed in the boundary layer suggesting fast oxidation processes. This oxidation was exacerbated during low

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irradiation periods in a confined mixing layer and led to the increase of Hg(II) levels in surface snow. Based on our current knowledge of gas phase chemistry, oxidation by halogen species (such as bromine) is still an open possibility. Bromine could be provided by the transport of marine air masses or an advection from the high troposphere.

5 The coincidental observation of oxidation occurring during lower irradiation and in a shallow boundary layer suggests that snow surfaces are likely to play an important role in Hg reactivity. Due to the dynamic cycling of oxidant and nitrogen compounds in the summer on the Antarctic Plateau, we believe that heterogeneous chemistry of Hg(0) with compounds such as HONO, H₂O₂ or HNO₃ is a hypothesis that has to be
10 seriously examined.

Both atmospheric and interstitial air measurements confirmed an intense production of Hg(0) from the photoreduction of previously deposited Hg(II) species in snow. When the solar radiation generated active vertical turbulence during daytime, the mixing layer height increased rapidly together with Hg(0) levels that could reach very high concentrations for such a remote place. Therefore, repetitive recycling of Hg species exists
15 in the boundary layer of DC during summertime that combines Hg(0) oxidation and subsequent reemission of Hg(II) products via photochemical reactions.

Considering the large surface and the Hg amounts stored on the Antarctic continent, these phenomena could play an important role at a regional scale. However, quantifying
20 their impact is complex because the seasonality of Hg chemistry in the Antarctic has not been studied yet. The winter cycle of Hg(0) on the Antarctic Plateau will be explored in the close future but we speculate that Hg(0) reactivity could be far less pronounced due to the absence of light during long periods.

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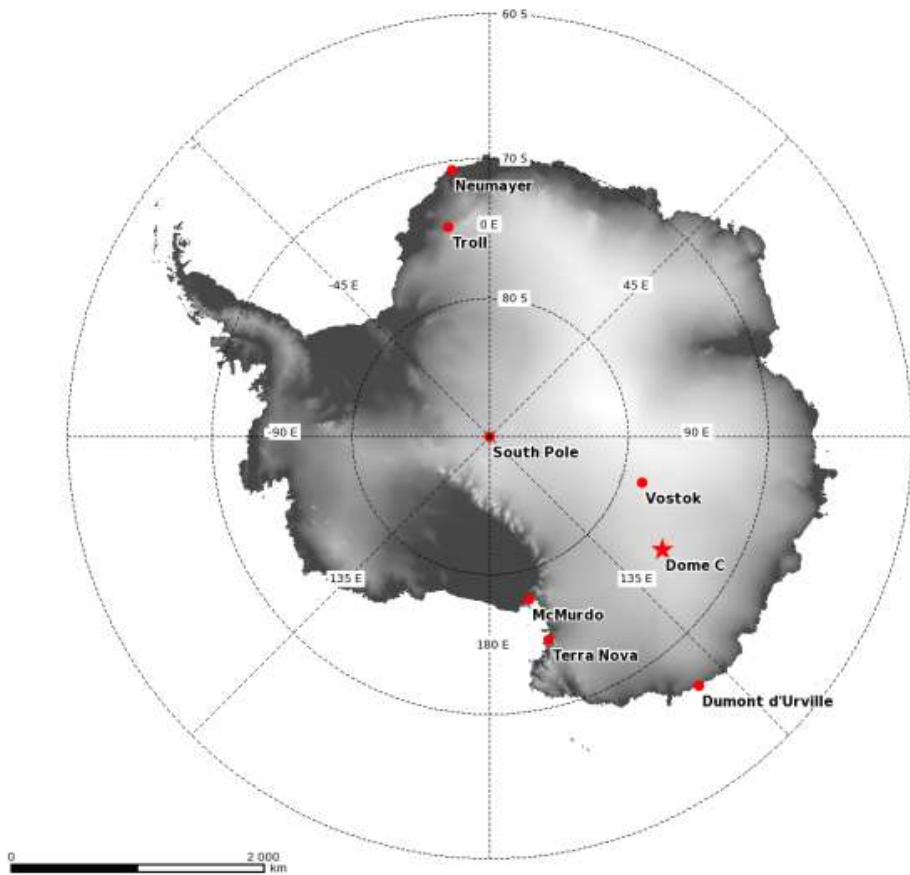


Fig. 1. Antarctic map with the localization of major scientific stations where atmospheric Hg concentrations have been measured.

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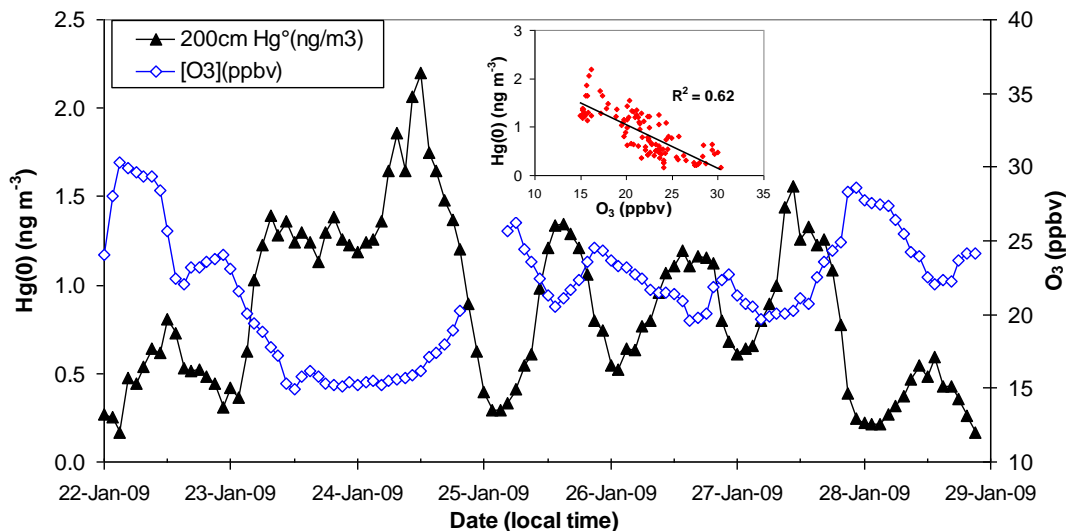


Fig. 2. Hg(0) concentrations (black line) and ozone concentrations (blue line) measured at 200 cm and 500 cm, respectively above the snow surface at DC in 2009. The negative linear correlation between ozone and Hg(0) is shown as an inset graph.

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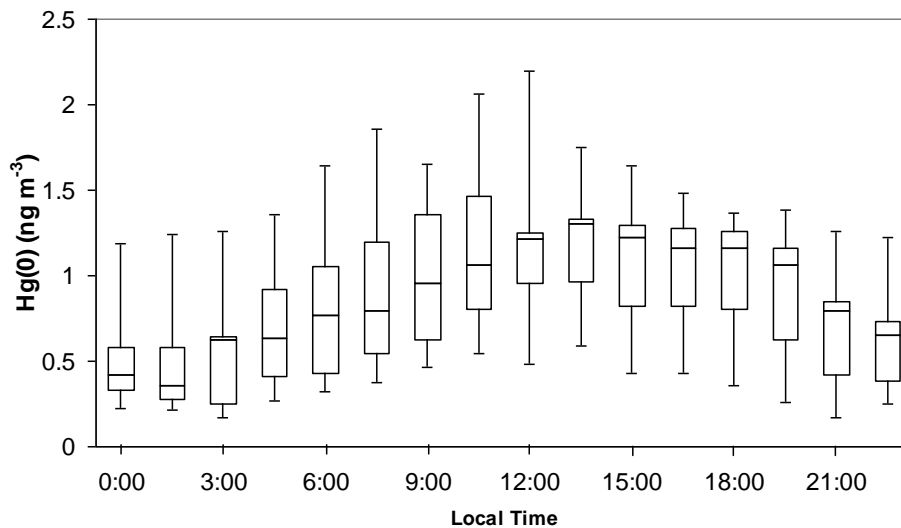


Fig. 3. Box and whisker plot of the average daily cycle for atmospheric Hg(0) concentrations at DC in 90 min bins. Boxes extend from 25 % to 75 % quartiles; the middle line represents the median value. The whiskers extend from min to max values.

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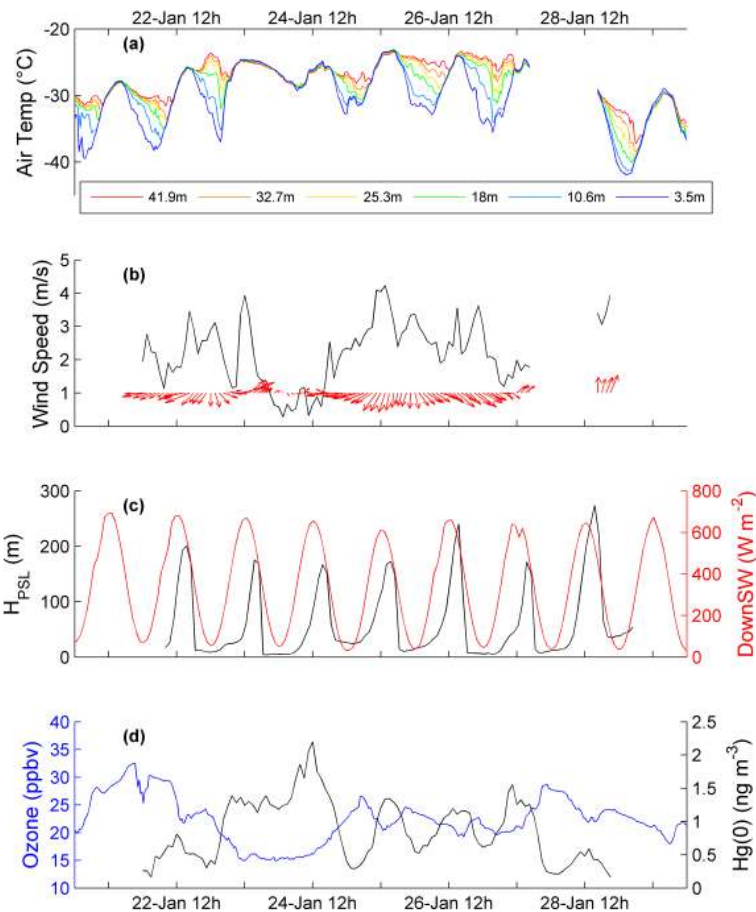


Fig. 4. Time series of (a) air temperature measured at different heights, (b) wind speed (black line) and direction (red arrows), (c) boundary layer height (black line) as calculated by MAR and downward shortwave radiation (red line), (d) ozone and Hg(0) concentrations.

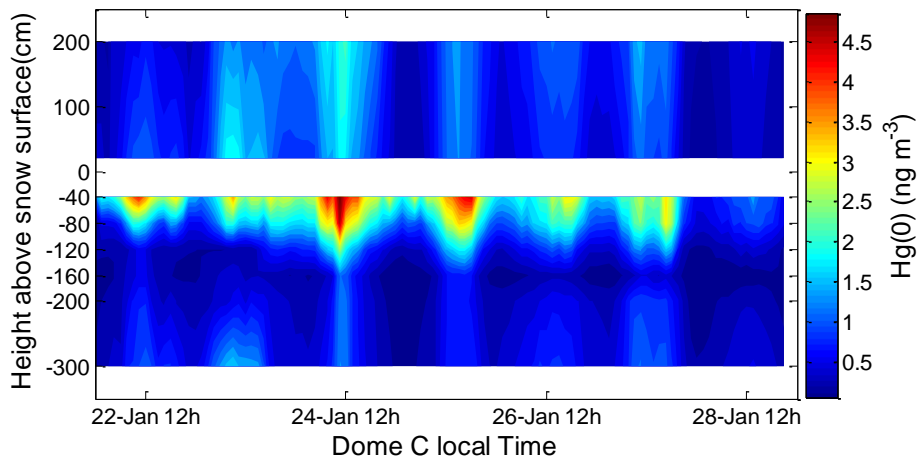


Fig. 5. Time series of Hg(0) concentrations measured above and below the snow.

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