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Antarctic winter mercury and ozone depletion events over sea ice

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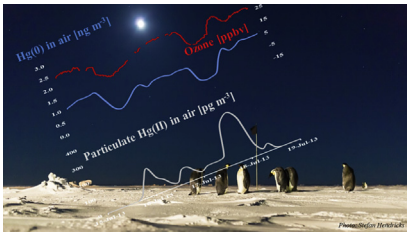
HIGHLIGHTS

- Atmospheric mercury and ozone depletions were detected during Antarctic winter.
- Winter depletion events were detected exclusively over sea ice areas.
- Higher formation of particulate mercury during winter depletions.

GRAPHICAL ABSTRACT



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ABSTRACT

During atmospheric mercury and ozone depletion events in the springtime in polar regions gaseous elemental mercury and ozone undergo rapid declines. Mercury is quickly transformed into oxidation products, which are subsequently removed by deposition. Here we show that such events also occur during Antarctic winter over sea ice areas, leading to additional deposition of mercury. Over four months in the Weddell Sea we measured gaseous elemental, oxidized, and particulate-bound mercury, as well as ozone in the troposphere and total and elemental mercury concentrations in snow, demonstrating a series of depletion and deposition events between July and September.

The winter depletions in July were characterized by stronger correlations between mercury and ozone and larger formation of particulate-bound mercury in air compared to later spring events. It appears that light at large solar zenith angles is sufficient to initiate the photolytic formation of halogen radicals. We also propose a dark mechanism that could explain observed events in air masses coming from dark regions. Br_2 that could be the main actor in dark conditions was possibly formed in high concentrations in the marine boundary layer in the dark. These high concentrations may also have caused the formation of high concentrations of $CHBr_3$ and CH_2I_2 in the top layers of the Antarctic sea ice observed during winter.

These new findings show that the extent of depletion events is larger than previously believed and that winter depletions result in additional deposition of mercury that could be transferred to marine and terrestrial ecosystems.

1. Introduction

Mercury, a toxic pollutant, exists in the atmosphere

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predominantly as a stable monoatomic gas which can be transported to polar regions and can be oxidized and deposited, and thereby threaten polar ecosystems. The deposition of mercury is driven by chemical transformations between different mercury species with different physical and chemical characteristics. Models have shown that dry deposition of gaseous elemental mercury (GEM) is significant, especially onto plants (Zhang et al., 2012). Oxidized forms of mercury, however, is deposited faster onto nearby surfaces (Skov et al., 2004; Brooks et al., 2011). Oxidation of mercury to Hg(II) has been reported to occur at mid-latitudes due to reaction with halogen radicals formed from halogens released from sea surfaces (Obrist et al., 2011).

These reactions occur in large scale during springtime in polar regions, leading to large deposition of oxidized atmospheric mercury. Springtime atmospheric mercury depletion events (AMDEs) were first observed in the Arctic in 1995 (Schroeder et al., 1998) and since then have been regularly observed in both polar regions (Ebinghaus et al., 2002; Brooks et al., 2008; Steffen, 2008). AMDEs, oceanic transport, riverine inputs and dry and wet deposition contribute to the net accumulation of mercury in the Arctic marine and terrestrial ecosystems (Outridge et al., 2008). Considering only the Arctic, it is estimated that AMDEs alone are responsible for the deposition of up to 100 tons of mercury per year north of the polar circle (Durnford and Dastoor (2011). AMDEs have therefore been discussed as playing a significant role for the total deposition of mercury in polar regions (Steffen, 2008; Skov et al., 2004). Following the conversion into more toxic organo-metallic forms, mercury bioaccumulates and biomagnifies in polar marine food webs.

The corresponding lower tropospheric ozone depletion events (ODEs) were first described in 1988 and are connected to sunlight-induced production of bromine radicals reacting with ozone. These events occur within the surface boundary layer, but can reach up to an altitude of 2 km over sea ice-covered areas of the polar oceans during springtime (Barrie et al., 1988). It has been suggested that the frequency of ODEs has increased since the 1960s in the Arctic (Tarasick and Bottenheim, 2002; Shepler et al., 2005), but so far no significant trends have been observed for AMDEs, likely due to the short time scale of measurements (Berg et al., 2013).

ODEs and AMDEs have previously been observed during spring (from August to October) at several coastal stations around the Weddell Sea, but have so far not been recorded in July (Ebinghaus et al., 2002; Dommergue et al., 2010; Pfaffhuber et al., 2012; Jones et al., 2013; Temme et al., 2003). Mercury depletions have been detected at Cape Point, not only during spring but during all seasons, having no concurrent ozone depletions. The events occurred only during periods of low wind speeds (<5 m s^{-1}) and are believed to have a small geographical scale (~100 km), without being connected to polar spring halogen chemistry (Brunke et al., 2010).

Here we present measurements showing that mercury and ozone depletions occur over sea ice areas in Antarctica earlier than previously observed. These results will give new insights into the cycling and fate of mercury in polar regions.

2. Material and methods

2.1. Antarctic expeditions

The measurements were performed over the Weddell Sea, Antarctica onboard icebreaker R/V Polarstern during two scientific expeditions (ANTXXIX/6&7, Fig. 1). The winter expedition ANTXXIX/6 started in Cape Town on 8 June 2013, and ended in Punta Arenas on 12 August 2013. The spring expedition (ANTXXIX/7) lasted from 14 August to 16 October 2013, starting in Punta Arenas

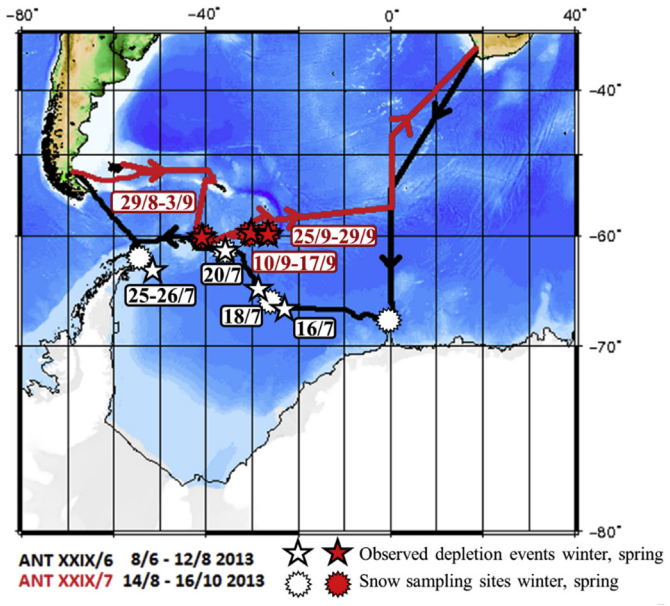

Fig. 1. Cruise routes and depletion events.

and ending in Cape Town. Snow samples were collected during both expeditions and analyzed for elemental and total mercury concentrations. Circle stars in Fig. 1 mark snow sampling sites.

Routes of the cruises ANTXXIX/6 (black) and 7 (red). Stars show locations where depletion events were observed and circle stars mark snow sampling areas.

2.2. Onboard atmospheric measurements

Fractionation of mercury species in air was performed using a fully automated mercury speciation system (Tekran 1130/1135 and Tekran 2537A CVAFS mercury detector). This device continuously measured the concentrations of gaseous elemental mercury (GEM) (5 min resolution), gaseous oxidized mercury (GOM) and oxidized mercury associated with particles (HgP) (2 h resolution). GOM is defined here as the fraction of oxidized mercury collected with a potassium chloride (KCl) coated annular quartz denuder. Mercury on particles smaller than 2.5 μm (defined here as HgP) was collected with a column with embedded quartz chips and a quartz re-generable filter (Gustin et al., 2013).

More information about the instrumentation, detection limits, limitations, SOP protocols and maintenance is supplied in SI Appendix, Supplementary methods S1.

Ozone was continuously measured by UV photometry using a commercial instrument (Thermo Scientific model 49i) in a similar set-up used during previous cruises (Jacobi et al., 2006). The air intake was installed close to the mercury speciation system. The data collected at 15 s intervals are reported here as 10 min averages, with a detection limit of 1 ppb. Zero and potential shift of the device was regularly controlled using the internal ozone generator.

BrO detection was undertaken using a Mode-Locked Cavity Enhanced Absorption Spectroscopy instrument. Further details about the instrument and its performance are given in SI Appendix, Supplementary methods S5.

2.3. Sampling and analyzes of snow and sea ice

Surface snow samples were collected using an acid-cleaned plastic shovel. The snow was sampled by scraping the top layer of