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Gaseous elemental mercury in the marine boundary layer and air-sea flux in the Southern Ocean in austral summer

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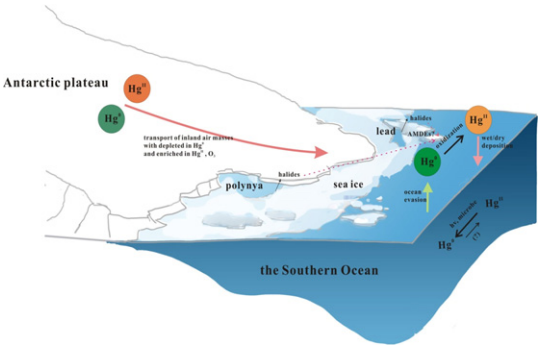
HIGHLIGHTS

- Atmospheric mercury depletion may occur in austral summer over the Southern Ocean.
- GEM-depleted air form the Antarctic Plateau may transport to MBL.
- Elevated GEM concentrations in the MBL and DGM are linked with sea ice change.
- The Southern Ocean is a net source for gaseous element mercury in the summer.

GRAPHICAL ABSTRACT



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ABSTRACT

Gaseous elemental mercury (GEM) in the marine boundary layer (MBL), and dissolved gaseous mercury (DGM) in surface seawater of the Southern Ocean were measured in the austral summer from December 13, 2014 to February 1, 2015. GEM concentrations in the MBL ranged from 0.4 to 1.9 ng m^{-3} (mean ± standard deviation: 0.9 ± 0.2 ng m^{-3}), whereas DGM concentrations in surface seawater ranged from 7.0 to 75.9 pg L^{-1} (mean ± standard deviation: 23.7 ± 13.2 pg L^{-1}). The occasionally observed low GEM in the MBL suggested either the occurrence of atmospheric mercury depletion in summer, or the transport of GEM-depleted air from the Antarctic Plateau. Elevated GEM concentrations in the MBL and DGM concentrations in surface seawater were consistently observed in the ice-covered region of the Ross Sea implying the influence of the sea ice environment. Diminishing sea ice could cause more mercury evasion from the ocean to the air. Using the thin film gas exchange model, the air-sea fluxes of gaseous mercury in non-ice-covered area during the study period were estimated to range from 0.0 to 6.5 ng m^{-2} h^{-1} with a mean value of 1.5 ± 1.8 ng m^{-2} h^{-1}, revealing GEM (re-)emission from the East Southern Ocean in summer.

1. Introduction

Mercury (Hg) is a global contaminant due to its unique chemical properties, capacity for bioaccumulation, and toxicity (Ariya et al., 2015). Mercury is released to the air by both natural (e.g., volcanoes, weathering, forest fires) and anthropogenic (e.g., combustion of fossil fuels, mining and metallurgy, waste disposal) sources (Lindberg et al., 2007). Three types of mercury are identified in the atmosphere based on their physical and chemical properties: gaseous element mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). GEM is the dominant form of mercury in the air; its long

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residence time (between 6 month and 2 years) is primarily responsible for the global transport of mercury (Pirrone and Mason, 2009). GOM and PBM typically account for a small fraction of the total mercury in the air, both have much shorter residence times (within a few weeks) as they are effectively removed from the atmosphere by wet and dry deposition (Lindberg et al., 2007).

Atmospheric mobilization and exchange at the air-water interface are important processes in biogeochemical cycling of mercury at the Earth's surface. Atmospheric deposition is the principal pathways for mercury to the surface open ocean (Mason et al., 1994), which would supply mercury for the subsequent reactions such as methylation to methylmercury that biomagnifies up the aquatic food chain. Divalent mercury (Hg^{II}) in seawater could also be reduced, photolytically (Lanzillotta et al., 2002) or biologically (Lanzillotta et al., 2004), with the resulting Hg^0 evading back to the atmosphere. Therefore, the transformation of mercury and its compounds in marine waters is crucial to the understanding of the way in which mercury released to the atmosphere is eventually taken up by biota, thereby becoming a health risk to ecosystems and human beings (Strode et al., 2007).

Simultaneous measurements of dissolved gaseous mercury (DGM) in seawater and GEM in air, combined with measurements of the sea and air temperature and wind speed, can be used to estimate the elemental mercury fluxes across the air-sea interface. The magnitude of these fluxes is one of the indispensable parameters in compartmental and atmospheric mercury models; however, data on these fluxes are limited both spatially and temporally (Strode et al., 2007). Although some measurements have been carried out in the Equatorial Pacific Ocean (Kim and Fitzgerald, 1986), the Atlantic Ocean (Andersson et al., 2011; Kuss et al., 2011), the Arctic Ocean (Andersson et al., 2008b), the Mediterranean Sea (Gårdfeldt et al., 2003), the Baltic Sea (Kuss and Schneider, 2007; Wängberg et al., 2001), and the South China Sea (Fu et al., 2010), few data are available for the Southern Ocean. Mastromonaco et al. (2016b) recently reported continuous measurements of GEM in air and DGM in surface seawater in the seas of western Antarctica, which showed spatial and seasonal variations. DGM concentrations in the open sea during spring (12 ± 7 pg L^{-1}) were higher than that during summer (7 ± 7 pg L^{-1}), concurring with a net evasion (1.1 ± 1.6 ng m^{-2} h^{-1}) of elemental mercury during spring and deposition (-1.2 ± 1.3 ng m^{-2} h^{-1}) during summer (Mastromonaco et al., 2016b).

The Southern Ocean is far away from major anthropogenic mercury emissions, but a very sensitive area for mercury bioaccumulation. Enhanced mercury concentrations in the seas near the Antarctic (Cossa et al., 2011; Mastromonaco et al., 2017), and even contamination in Antarctic biota (Bargagli, 2008; Bargagli et al., 2005; Brasso et al., 2012; Carravieri et al., 2013; Carravieri et al., 2014) have been observed. Over polar oceans, atmospheric mercury depletion events (AMDEs) occur during springtime when GEM is photochemically oxidized to reactive mercury, which is then readily deposited into the surface environment (Steffen et al., 2008). It has been shown that the oxidized mercury deposited in the Arctic during AMDEs can be photoreduced and re-emitted back to the atmosphere in summer (Aspmo et al., 2006). AMDEs are known to occur over the Southern Ocean (Dommergue et al., 2010; Ebinghaus et al., 2002; Mastromonaco et al., 2016c), but the fate of the AMDE-deposited mercury in the Southern Ocean is much less studied. Furthermore, evidence is merging that the sea ice environment can play an important role in the distribution, transport and transformation of mercury in the Antarctic or Arctic (Andersson et al., 2008b; Beattie et al., 2014; Chaulk et al., 2011; Cossa et al., 2011; Douglas et al., 2008; Mastromonaco et al., 2016a; Mastromonaco et al., 2017; Mastromonaco et al., 2016c; Wang et al., 2017). As such, the presence and dynamics of sea ice and snow is expected to greatly affect the mercury exchange between the air and the ocean.

As part of the 31th Chinese National Antarctic Research Expedition (CHINARE) aboard R/V Xuelong, here we report the measurements of the GEM in the marine boundary layer (MBL) and DGM in the surface seawater in the Southern Ocean. These data, along with the ancillary meteorological data allowed us to estimate air-sea fluxes of mercury exchange in the remote East Southern Ocean in austral summer.

2. Experimental setup

2.1. Site locations

With a total area of 20.3×10^6 km^2, the Southern Ocean is comprised of the southernmost seas of the Pacific, Indian, and Atlantic Ocean, completely encircling the continent of Antarctica and extending to 60°S. Sea-surface temperatures vary from about −2 to 10 °C. Cyclonic storms travel eastward around the continent and frequently become intense because of the temperature contrast between ice and the open ocean. Seasonal, floating sea ice surrounds the Antarctic continent, covers ~15% of Southern Ocean in February and ~85% in September (Gordon, 1981). In austral summer, sea ice stays mostly offshore, especially in the Weddle Sea and Ross Sea.

The sampling campaign was conducted aboard R/V Xuelong that navigated in the Southern Ocean (70°E–180°E, southernmost seas of the Indian to Pacific Ocean) from December 13, 2014 to February 1, 2015 in austral summer. The campaign started along the Antarctic coast from Prydz Bay to Ross Sea, then to Christchurch, New Zealand, for replenishment, and returned to Prydz Bay (see Fig. 1).

2.2. Sampling techniques and analysis

Real-time GEM concentrations in the ambient air were continuously measured during the cruise, using an automatic mercury analyzer (Model 2537X, Tekran Inc., Toronto, Canada). Details about the method can be found in our earlier studies in the Arctic (Yu et al., 2014) and Antarctic (Wang et al., 2016b; Xia et al., 2010). It should be noted that some GOM may also be measured by Tekran 2537 if it is able to pass through the inlet tubing and the PTFE filter (Gustin et al., 2015; Slemr et al., 2015; Temme et al., 2003); however, extensive examination of observations from various sites including the Troll Antarctica Research Station suggests the contribution of GOM in the Tekran-based GEM measurement is insignificant when compared with other uncertainties (Slemr et al., 2015; Sprovieri et al., 2016). The Tekran-based GEM measurement has also been used widely around the world, allowing intercomparisons globally (Aspmo et al., 2005; Sprovieri et al., 2016). Meteorological, hydrologic and GPS data were obtained from the ship's monitoring system; these included wind direction, wind speed (SPD), air pressure (P), relative humidity (RH), atmospheric temperature (AT), sea surface temperature (SST), salinity, ship direction and ship speed, all averaged over 5 min. O_3 and CO mixing ratios in the air were measured continuously using an O_3 analyzer (EC9810, Ecotech Pty Ltd., Australia) and a CO analyzer (EC9830, Ecotech Pty Ltd., Australia), respectively, as detailed earlier (He et al., 2016; Yu et al., 2015). Both the O_3 and CO analyzer were calibrated before departure by a reference instrument with a generator to give known O_3 concentration gas and by a standard mixture of CO in gas, respectively. The O_3 analyzer was operated with a manual zero calibration for 40 to 50 min every 10 days, and the CO analyzer ran automatic zero calibration for about 15 min every 3 h (Yu et al., 2015). The air intakes for the monitoring instruments were located at the front of the icebreaker (about 15 m above the sea surface), opposite from the ship's power system to minimize the impact of the smoke plume from the chimney. We further discarded any data point obtained when the icebreaker's speed was ≤2 knot or when the wind was coming from the stern (relative wind direction to the heading of Xuelong between 120° and 240°).

The HYSPLIT transport and dispersion model (Wang et al., 2009) from NOAA-ARL (Air Resources Laboratory) (http://www.arl.noaa.gov/ready/hysplit4.html) was used to identify the source of air masses from selected points. Sea ice concentrations were acquired from the