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Net deposition of mercury to the Antarctic Plateau enhanced by sea salt

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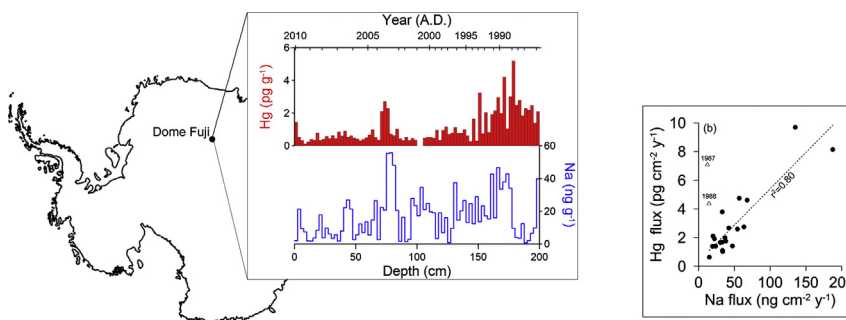
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HIGHLIGHTS

- Sub-annual variations in Hg deposition were reconstructed from Dome Fuji snowpack.
- Cold vapor ICP-SFMS was applied to resolve a difference of sub-pg Hg g⁻¹.
- Increased concentrations of Hg and Na⁺ were near-synchronous.
- A significant correlation was found between their annual deposition fluxes.
- Sea salt can control the net Hg deposition to the Antarctic Plateau.

GRAPHICAL ABSTRACT



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ABSTRACT

Photochemically driven mercury (Hg) exchange between the atmosphere and the Antarctic Plateau snowpack has been observed. An imbalance in bidirectional flux causes a fraction of Hg to remain in the snowpack perennially, but the factors that control the amount of Hg sequestered on the Antarctic Plateau are not fully understood. We analyzed sub-annual variations in total Hg (Hg_T) deposition to Dome Fuji over the period of 1986–2010 using cold vapor inductively coupled plasma mass spectrometry and compared concentrations with those of sea salt components (Na⁺ and Cl⁻). Hg_T ranged from 0.12 to 5.19 pg g⁻¹ (n = 78) and was relatively high when the Na⁺ concentrations were high in the same or underlying snow layers. A significant correlation (r = 0.7) was found between the annual deposition fluxes of Hg_T and Na⁺. Despite different origins and behavior of Hg and sea salt, the near-synchronous increases in the concentrations and correlation between the fluxes suggest that sea salt can intervene in the air-snow Hg exchange and promote the net deposition of Hg in the Antarctic Plateau.

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1. Introduction

The Antarctic Plateau snowpack has been used for reconstructing past variations in global atmospheric background levels of trace metals (Boutron, 1995; Hong et al., 2012; Soyol-Erdene et al., 2011). In general,

trace metal concentrations in Antarctic Plateau snow are considered dependent on their atmospheric loads, but recent studies have revealed that mercury (Hg) concentrations are primarily controlled by photochemical redox reactions (Angot et al., 2016; Brooks et al., 2008a). This is firstly because gaseous elemental Hg (Hg⁰), the predominant form of Hg in the Antarctic atmosphere, weakly interacts with snow (Bartels-Rausch et al., 2008; Ferrari et al., 2004). The oxidized form (Hg^{II}) is highly reactive and easily adsorbed by snow. Thus, the oxidation of atmospheric Hg⁰ to Hg^{II} leads to Hg deposition and can increase

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Hg concentrations in surface snow up to hundreds of pg g^{-1} (Brooks et al., 2008a; Dommergue et al., 2010). Such surficial enrichment of Hg is usually transient, because most of the deposited Hg^{II} is photochemically reduced back to Hg^0 and returned to the atmosphere (Han et al., 2014). Only a fraction of Hg remains in snow over the course of the air–snow Hg exchange. As a footprint of the Hg exchange, this fraction is essential for investigating the factors affecting the bidirectional Hg flux (Sherman et al., 2010). Moreover, this fraction is destined for perennial sequestration in deep snow and ice (Brooks et al., 2008a; Jitaru et al., 2009). These temporary and perennial Hg fluxes can be important components of the global Hg cycle due to the vast extent (>5 million km^2) of the Antarctic Plateau (Brooks et al., 2008a).

In the Antarctic Plateau, a few studies have reported high total Hg concentrations (Hg_T) in surface snow driven by the oxidation of atmospheric Hg^0 during the summer. Brooks et al. (2008a) observed high Hg_T in the top layer of a snow pit (198 pg g^{-1}) and drifting snow (84 pg g^{-1}) at the South Pole. Comparable values were reported from near Dome C (4.2–194 pg g^{-1} ; Dommergue et al., 2012). Although the elevations were less at Dome A (0.2–8.3 pg g^{-1} ; Li et al., 2014) and Dome Fuji (<0.4 –10.8 pg g^{-1} ; Han et al., 2011), Hg_T concentrations in the surface snow were still higher than those in snow pits (0– <4 m in depth); this is consistent with the summertime enhancement of Hg deposition (Han et al., 2014; Li et al., 2014). The difference of the surficial Hg_T among the sites may indicate a spatio-temporal heterogeneity of Hg dynamics over the vast Antarctic Plateau, spatial variation in snow accumulation, inconsistent sampling thickness for surface snow and different analytical methods (Han et al., 2014).

How the surface snow becomes enriched with Hg during the summer is still uncertain. A central question has been what oxidizes atmospheric Hg^0 to Hg^{II} and consequently promotes Hg deposition. In coastal/sea ice regions, marine halogens derived from nearby sea ice have been identified as major oxidants leading to Hg^0 oxidation, rapid deposition of Hg^{II} , and atmospheric Hg depletion (Brooks et al., 2008b; Nerentorp Mastromonaco et al., 2016). Marine halogens have been proposed to play the same role in the Antarctic Plateau (Brooks et al., 2008a). However, minimal amounts of marine halogens can reach the remote inland (Hara et al., 2004; Suzuki et al., 2002) and even less during the summer when photochemistry is active (Hara et al., 2004). Even if marine halogens are the major oxidants in the Antarctic Plateau, the potential relationship between the halogen and Hg concentrations in snow is liable to disappear due to the post-depositional behavior of Hg (Dommergue et al., 2012; Han et al., 2014). For example, the slow snow accumulation at Dome Fuji (~ 8 cm y^{-1}) allows ample time for the photochemical reduction and re-emission of the deposited Hg, when an effective sunlight penetration depth of >10 cm under dry snow conditions is considered (King and Simpson, 2001). Influences of non-halogen radicals (e.g., OH, NO_2 or HO_2 ; Angot et al., 2016) on the Hg^0 oxidation can be another obstacle to revealing the relationship between the halogen and Hg concentrations in snow.

Despite re-emission, a fraction of Hg is perennially sequestered in the snowpack. The Hg sequestration rate varies with atmospheric and snow conditions that regulate the bidirectional Hg flux (Durnford and Dastoor, 2011). Accordingly, reconstruction of the temporal variation in Hg sequestration can contribute to understanding past environmental conditions. For instance, the Hg sequestration rate was substantially higher under the dusty conditions of the glacial period (121 $\text{pg cm}^{-2} \text{yr}^{-1}$; Jitaru et al., 2009) compared to the present (<3 $\text{pg cm}^{-2} \text{yr}^{-1}$; Han et al., 2014); the higher sequestration rate was attributed to dust particles behaving as a scavenger of atmospheric Hg^{II} and a stabilizer of particle-bound Hg^{II} against re-emission (Jitaru et al., 2009).

Measuring the low concentrations of Hg_T in the Antarctic Plateau snow requires a precise analytical technique. Previously, ICP-SFMS (inductively coupled plasma sector field spectrometry) performed comparably to the conventional cold vapor (CV) generation method (e.g., CV atomic fluorescence spectrometry) (Planchon et al., 2004). Less sample consumption is an advantage of using ICP-SFMS, which is especially

important when sample volume is limited (Han et al., 2011; Jitaru et al., 2009). However, signal-to-background ratio and instrumental sensitivity were insufficient to resolve a difference of sub- pg g^{-1} for Antarctic snow samples (Han et al., 2014). Therefore, we adopted CV-ICP-SFMS for more precise determination of the Hg contents in Antarctic Plateau snow. Using the CV system improved the signal-to-background ratio by up to a factor of 10.

CV-ICP-SFMS was applied to a Dome Fuji snow pit, with samples collected every 2.5 cm from the surface down to a depth of 2 m. Because the sampling interval (2.5 cm) was equivalent to approximately one-third of the annual snow accumulation at Dome Fuji ($< \sim 10$ cm as snow; Kameda et al., 2008), the temporal variation in the snow composition could be investigated on a sub-annual scale. We compared Hg_T with the Na^+ and Cl^- concentrations and $\delta^{18}\text{O}$ to examine the interrelations between them and evaluated the temporal variation in Hg deposition. We expect this study to contribute to the understanding of the dynamics of Hg in the Antarctic Plateau and its role in the global Hg cycle.

Recently, research based on year-round monitoring of atmospheric Hg has been reported from Antarctic inland sites (Angot et al., 2016; Pfaffhuber et al., 2012). Those studies observed significant variations of atmospheric Hg^0 on diurnal to seasonal time scales resulting from active photochemical interactions between the atmosphere and the snowpack. Our results can give a clue to the connection between the short-term variations in atmospheric Hg and the resulting variations in snowpack Hg concentrations on sub-annual to multi-year scales.

2. Materials and methods

2.1. Sample description

A snow pit was excavated at a site (77.39°S, 39.62°E, 3790 m) near Dome Fuji in East Antarctica on January 21, 2010, during the 51st Japanese Antarctic Research Expedition (Fig. 1). Snow samples were collected from the surface down to a depth of 2 m by inserting a Teflon cylinder (I.D. 2.5 cm) horizontally into the pit wall. The snow from each layer was separated into two containers: a 125 mL PFA bottle for the analyses of Hg and Ba, and a 1 L LDPE bottle for the analyses of stable oxygen isotopes ($\delta^{18}\text{O}$) and major ions (Na^+ , Cl^- and SO_4^{2-}). The sample bottles were double-sealed in acid-cleaned LDPE bags and were kept frozen in the dark until further processing. Two PFA bottles for the depth interval of 100–105 cm were lost during transport. All sampling

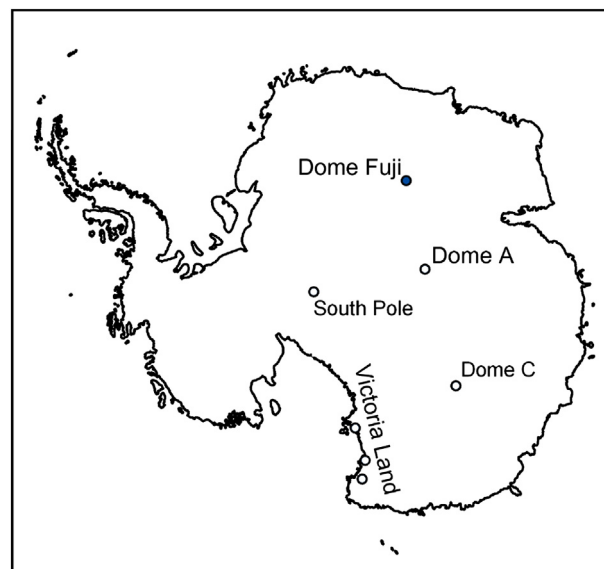


Fig. 1. The sampling location for the 2 m deep Dome Fuji snow pit (closed circle). The sites for the studies cited in the text are also indicated (open circle).

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