Changes in the Atmospheric Fluxes of Arsenic, Antimony, Thallium, and Bismuth to the Antarctic Snow during the Past 50 Years

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Abstract

Arsenic, Sb, Tl and Bi are highly toxic elements and found in trace amounts in the earth's crust. Various investigations documented that the atmospheric load and geochemical cycles of these rare elements in the Northern Hemisphere where industrial activities are intensive, have been controlled by changing emissions from various natural and industrial processes in modern times. In order to understand the atmospheric behavior of As, Sb, Tl, and Bi in the most remote areas in the Southern Hemisphere, we have determined these elements in a continuous series of 80 snow samples from a 4-m snow pit, covering 50 years from 1957 to 2007, at Dome Fuji in East Antarctica. They were measured by ultrasensitive inductively coupled sector field mass spectrometry (ICP-SFMS) under a Class 10 ultraclean condition. Concentrations of As, Sb, Tl, and Bi are extremely low, with mean values of 11.3 pg g^{-1} for As, 0.29 pg g^{-1} for Sb, 0.07 pg g^{-1} for Tl, and 0.12 pg g^{-1} for Bi, respectively. Our snow profiles show that a large fraction of Sb, Tl, and Bi can be attributed to anthropogenic sources, while more than a half of the total Tl originated from natural sources, especially from volcanic emissions including the Mt. Erebus volcano plume in East Antarctica. Our data suggest that Tl is a unique signature for identifying volcanic aerosol from both quiescently degassing and eruptive volcanoes.

Key words: Toxic elements, East Antarctica, Dome Fuji, snow pit, volcanic contribution

Introduction

Toxic trace elements are released from various natural and high temperature industrial processes and disperse through the atmosphere over long distances, which may cause an environmental and human health risk on a large scale. Today, the global anthropogenic emissions of different trace elements are larger than or comparable to natural emissions (Pacyna and Pacyna, 2001). Volcanoes act as an important contributor to the atmospheric injection of volatile trace elements (Hinkley et al., 1999). Among such volatile elements, As, Sb, Tl, and Bi are of great concern, because they are highly toxic elements and both quiescent and eruptive volcanoes can control their atmospheric load and atmospheric flux.

Investigations of the occurrence of trace elements in successive snow and ice layers allow us to properly assess the relative influence of natural and anthropogenic emissions on the atmospheric cycles of trace elements. While Antarctic snow and ice provide valuable insights into the changing rates and sources of atmospheric deposition of As, Sb, Tl, and Bi on a large scale, however, there are no complete and long-term records of these elements at least covering several decades. This is mainly because of difficulties in measuring As, Sb, Tl, and Bi due to extremely low concentrations in

Antarctic snow and ice.

Here, we present preliminary data on the occurrence of Antarctic atmospheric As, Sb, Tl, and Bi as recorded in the snow layers collected in East Antarctica. This covers a 50 year time period from 1957 to 2007.

Materials and Methods

In December 2007, a continuous series of 80 snow samples from a 4-m deep snow pit was collected at Dome Fuji Station, Dronning Maud land, East Antarctica (77°18′01″S, 39°47′12″E, 3785 m above sea level) during the Japanese-Swedish IPY Antarctic Expedition. The sampling site is characterized by a very low accumulation rate of 2.5 cm w.e.a^{-1} (Kameda et al., 1997). Because of extremely low concentration level of trace elements in Antarctic snow, ultra-clean procedures and great precaution were taken during the whole sampling steps to prevent the possibility of snow contamination in the field (Hur et al., 2007).

All sample handling and analytical operations were performed under a Class 10 laminar airflow bench or booth in clean laboratories (Class 1000) located at KOPRI. Concentrations of As, Sb, Tl, Bi, Ba, and Rb were determined using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) (Element2, Thermo Fisher Scientific, Bremen, Germany) equipped with an Apex high-sensitivity inlet system (Apex IR, Elemental Scientific Incorporated, Omaha, Nebraska, United States) (Hong et al., 2009). Repeatability of measurements ranged from 5% to 35% depending on the element and the concentrations. The accuracy of the method was further verified by analyzing a certified reference material (SLRS-5, riverine water). Cations (Na^+, K^+) and anions (F^-, SO_4^{2-}) were determined using a Dionex 320 ion chromatograph equipped with CS 12/As 11 columns.

Results and Discussion

The dating of the snow samples is primarily important to interpret the data. Since annual snow accumulation rate is very low (2.5 cm w.e.a^{-1}) at the sampling site, it is difficult to make a year-by-year dating of snow layers at depths by using vertical profiles of δO^{18} and chemical species such as methane sulfonic acid (MSA) and NO_3^- which all show very strong seasonal changes in concentration (Minikin et al., 1998; Wagenbach et al., 1998). Therefore, the dating was established by large volcanic events, which are characterized by a sharp spike in non-sea-salt SO_4^{2-} (nss-SO_4^{2-}) at a relatively short depth interval. In our nss-SO_4^{2-} profile, two large volcanic events were identified at 110 cm and 335 cm (Fig. 1). The nss-SO_4^{2-} spike at 110 cm corresponds to the Pinatubo signature, which gives the age of 1992/1993, 1.5 years after the Pinatubo eruption in June 1991. The nss-SO_4^{2-} spike at 335 cm corresponds to the age of 1963/1964, about 1 year after the Agung eruption in February 1963. Using these volcanic layers as a reference and the mean snow density (318 kg m^{-3}) (Iizuka et al., 2004), we calculated an annual mean snow accumulation rate of 2.5 cm w.e.a^{-1}, which is the same value as given by Kameda et al (1997). Stratigraphic dating for the whole snow depth reveals that our snow pit samples cover a 50 year time period from 1957 to 2007.

Concentrations of As, Sb, Tl, and Bi measured in 80 snow samples are found to be very low for all elements. Median concentrations ranged from 0.06 pg g^{-1} for Tl to 9.3 pg g^{-1} for As. As shown in Fig. 1, there are large variations in the concentrations and large differences in the amplitude of the variations from one element to another.

As an approach to evaluate the relative contribution from natural versus anthropogenic sources, we have calculated crustal enrichment factor (EFc). EFc is defined as the concentration ratio of a given element to that of Ba (which is a good proxy of mineral dust) in the snow, normalized to the same concentration ratio characteristic of the upper continental crust (Wedepohl, 1995). Mean EFc values are 822 for As, 1.5 for Rb, 109 for Sb, 12 for Tl, and 142 for Bi, respectively. This indicates that Rb is mostly in crustal origin and the contribution from mineral dust is potentially important for Tl. Conversely, very high EFc values for As, Sb, and Bi indicate that the contribution from mineral dust is negligible for these elements.

Contribution from sea-salt spray was evaluated for each element from Na concentrations measured in the snow and the element/Na ratios in surface ocean water. In previous studies, these ratios were often combined with tentative enrichment for elements in sea-derived aerosols relative to seawater (see, e.g., Hur et al., 2007). The contribution from sea-salt spray both with and without such tentative enrichments was found to be negligible for Sb and Bi and to account for a small part (~5%) of the

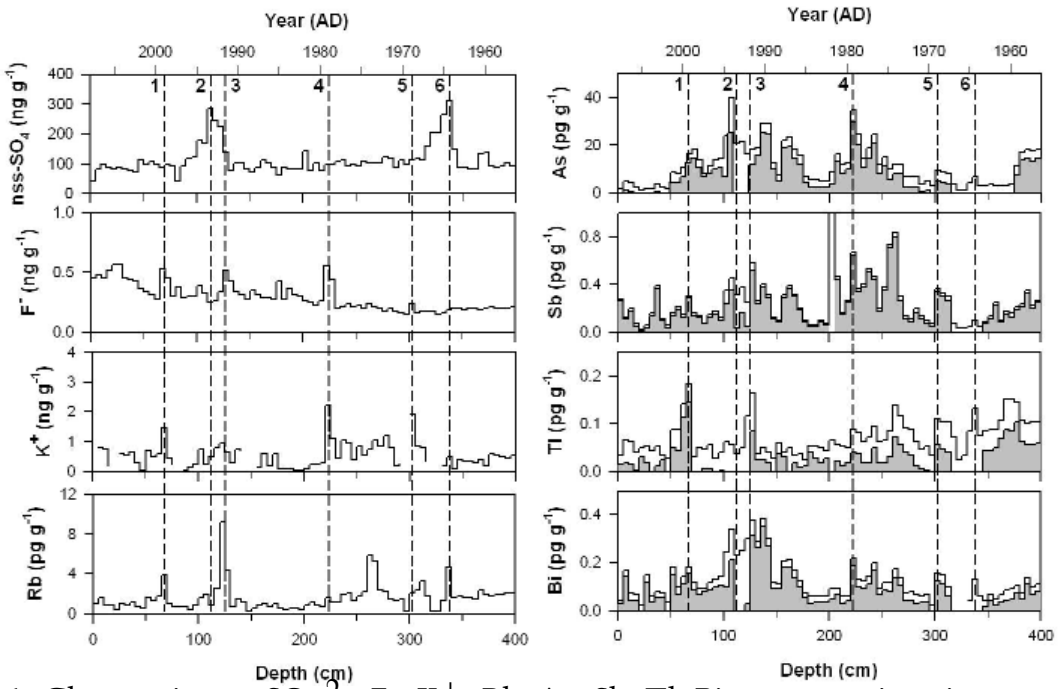

Figure 1. Changes in nss-SO_4^{2-}, F^-, K^+, Rb, As, Sb, Tl, Bi concentrations in a continuous series of 80 snow samples from a 4-m snow pit collected at Dome Fuji Station, East Antarctica. Shaded areas refer to the concentrations after subtracting the estimated natural contributions. Dashed lines represent the position of the snow layers characterized by a sharp increase in nss-SO_4^{2-}, F^-, K^+ , and Rb concentrations.

measured As and Tl concentrations.

We now consider the contribution from volcanic emissions, which is expected to be large for As, Sb, Tl, and Bi, because volcanic emissions can account for significant part of the global emissions of these elements to the atmosphere (Nriagu, 1989; Hinkley et al., 1999). In previous studies, the contribution from volcanoes was evaluated from volcanic fraction of the nss-SO_4^{2-} concentrations in each sample and mean values of element/S ratios of volcanic emissions given by published sets of data from individual volcanoes (see, e.g. Hur et al., 2007). However, such estimation must be very tentative, because of the large dispersion in the published element/S ratios in volcanic emissions. We here employed element/S ratios estimated from the Mt. Agung and the Pinatubo fallout at 335 and 110 cm depths by using the excess nss-SO_4^{2-} concentration above the background level (96±18 ng g^{-1}), assuming that anthropogenic sources are not significant during the corresponding time period. As seen in Fig. 1 (dashed line 6), the concentration of As and Sb are not observed to increase in the snow layer corresponding to Mt. Agung eruption, while there are small peaks for Tl and Bi. This suggests that the Agung impact on the deposition of volatile trace elements to the Antarctic snow was not strong. For the Pinatubo eruption signal (dashed line 2), As, Sb, and Bi show relatively elevated concentrations. For Tl, concentrations are found to have high values in the snow layer of dashed line 3 in Fig. 1. This snow layer is likely to correspond to the Cerro Hudson eruption (Legrand and Wagenbach, 1999), because peaks of tracers of volcanic gas (F-) and ash (Rb) are coincident with Tl peak. Compared to the Pinatubo located at the 15^oN latitude, the proximity (at the 45.5^oS latitude) of the Cerro Hudson volcano to Antarctica appears to result in the input of large quantities of volcanic ash in the Cerro Hudson snow layer. Based on the excess nss-SO_4^{2-}, As, Sb, Tl, and Bi above the background levels in the Pinatubo and Cerro Hudson snow layers, median element/S ratios of volcanic emissions were estimated to be $7.8*10^{-4}$ for As, $0.05*10^{-4}$ for Sb, $0.08*10^{-4}$ for Tl, and $0.07*10^{-4}$ for Bi, respectively. It should be noted that these estimates must be used as upper limits, because of possible input of anthropogenic sources during the corresponding time period. Using median element/S ratios of volcanic emissions from the Pinatubo and Cerro Hudson eruptions, the contribution from volcanoes was evaluated.

After subtracting the contributions from different natural sources from the measured concentrations, it appears that a large fraction of As, Sb, and Bi cannot be explained by natural sources as shown in Fig. 1. The results indicate that an increasing trend of As, Sb, and Bi fluxes at Dome Fuji since ~1970 can be attributed to the contribution from anthropogenic sources. Atmospheric deposition rates peaked in ~1980 and 1990 for As, in the mid-1970s for Sb, and in 1990 for Bi. For Tl, the natural contributions appear to account for more than a half of the total Tl found in the profile. Note that prominent Tl concentration peaks occurred at 65 and 300 cm depths (dashed lines 1 and 5), along with F^- (slight increase at 300 cm depth) and K^+ peaks. Despite no peak of nss-SO_4^{2-} at the same depth intervals, we propose that these Tl peaks could be attributed to volcanic gas plume emitted from the Mt. Erebus volcano, an active volcano on Ross Island Antarctica (Zreda-Gostynskq et al., 1997). By comparison, a similar Tl peak is not observed at 220 cm depth, accompanying elevated F^- and K^+ concentrations. This suggests that the emission rates of volatile elements have had different in the Erebus plume. Altogether, our data indicate that Tl is a unique signature for identifying volcanic aerosol emitted from both quiescently degassing and eruptive volcanoes.

Conclusion

Our Antarctic snow profiles, covering 50 years from 1957 to 2007, show that anthropogenic contributions dominated the atmospheric fluxes of As, Sb and Bi to the snow at Dome Fuji in East Antarctica, while more than a half of Tl deposition was attributed to natural contributions, especially from volcanic emissions. Our data indentified sporadic Tl peaks related to volcanic emissions from the Mt. Erebus in East Antarctica. It represents Tl as a unique signature for volcanic aerosol derived from both quiescently degassing and eruptive volcanoes.

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