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Records of anthropogenic antimony in the glacial snow from the southeastern Tibetan Plateau

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ABSTRACT

Antimony (Sb) is a ubiquitous element in the environment that is potentially toxic at very low concentrations. In this study, surface snow/ice and snowpit samples were collected from four glaciers in the southeastern Tibetan Plateau in June 2015. The concentrations of Sb and other elements were measured in these samples. The results showed that the average concentration of Sb was approximately 2.58 pg g^{-1} with a range of 1.64–9.20 pg g^{-1}. The average Sb concentration in the study area was comparable to that recorded in a Mt. Everest ice core and higher than that in Arctic and Antarctic snow/ice but much lower than that in Tien Shan and Alps ice cores. Sb presented different variations with other toxic elements (Pb and Cr) and a crustal element (Al) in the three snowpits, which indicated the impact of a different source or post-deposition processes. The enrichment factor of Sb was larger than 10, suggesting that anthropogenic sources provided important contributions to Sb deposition in the glaciers. The Sb in the glacial snow was mainly loaded in the fourth component in principal component analysis, exhibiting discrepancies with crustal elements (Fe and Ca) and other toxic metals (Pb). Backward trajectories revealed that the air mass arriving at the southeastern Tibetan Plateau mostly originated from the Bay of Bengal and the South Asia in June. Thus, pollutants from the South Asia could play an important role in Sb deposition in the studied region. The released Sb from glacier meltwater in the Tibetan Plateau and surrounding areas might pose a risk to the livelihoods and well-being of those in downstream regions.

1. Introduction

Antimony (Sb) is a ubiquitous element in the environment that has been used by humans since the Early Bronze Age (Filella et al., 2009; Smichowski, 2008). It is present in the Earth's crust at concentrations below 1 mg kg^{-1} (Wedepohl, 1995). In addition to the natural sources (e.g., volcanoes, rock weathering, and soil runoff) responsible for Sb emissions in the environment, modern uses of Sb include it being a catalyst in the manufacturing of PET (polyethylene terephthalate), a component of brake linings (as Sb_2S_3), a cable covering, in ammunitions and bearing and a flame retardant in adhesives, papers, rubber and textiles (Pacyna and Pacyna, 2001; Smichowski, 2008). The release of such Sb-containing compounds into the environment can lead to considerable interconversion of Sb compounds by chemical and biological action (Filella et al., 2009; Krachler et al., 2005; Smichowski, 2008).

Antimony is potentially toxic at very low concentrations and has no known biological function (Filella et al., 2009). Elemental Sb is more toxic than its salts, and inorganic species of Sb are more toxic than organic ones. Sb(III) compounds are approximately 10 times more toxic than Sb(V) species. The U.S. Environmental Protection Agency and the German Research Community have listed Sb as a priority pollutant, but it has not been classified for carcinogenicity (USEPA, 1999). There have been remarkably few quantitative studies on the biogeochemical behavior and ultimate fate of Sb in the environment compared to other potentially toxic metals,

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such as Pb, Hg, and As, worldwide (Bolanz, 2014). There are still major gaps in our knowledge on natural sources of Sb and its variability at different temporal and spatial scales. Within this context, glaciers are commonly exploited as valuable environmental archives of atmospheric Sb deposition (Krachler et al., 2005).

Investigation of Sb in snow and ice cores has widely become an area of scientific interest under climate change. In the Alps, measured Sb concentrations ranged from 0.2 to 109 pg g^{-1} based on various sections of a 140 m snow/ice core drilled from Mont Blanc. Concentrations in recent snow were found to be significantly higher (×5) than that those in ice dated from before the middle of 19th century, indicating a contribution from oil and coal combustion (Van de Velde et al., 1999). In Arctic Canada, Sb concentrations ranged from 0.07 to 108 pg g^{-1} with a median of 0.98 pg g^{-1} based on a 63.72 m ice core and a 5 m deep snowpit in Devon Island; the Sb signal peaked during the 1950–1960 AD time period, indicating contamination from industrialization, the economic boom following WWII, and the recent introduction of flue gas filter technologies and emission reduction efforts (Krachler et al., 2008, 2005). The modern Sb EFc (referenced to scandium) was ~25 and may have resulted from Asian production of Sb sulfides, such as stibnite (Sb_2S_3), and as a by-product of Pb and Cu smelting. In central East Antarctica, Sb had shown significant enrichment due to either anthropogenic activities or volcanic eruptions over the past 50 years; the observed decrease after 2000 CE suggested that government regulations for pollution control was effective in reducing air pollution at both the global and regional levels (Hong et al., 2012).

The Tibetan Plateau (TP) and surrounding mountains represent one of the most concentrated glacier regions on Earth (Yao et al., 2012a). The region is also referred as the "Asian Water Tower" due to its many prominent Asian rivers (Immerzeel et al., 2010). These glaciers has been largely experiencing shrinkage, which affects the water source of large rivers and the one billion people living downstream (Immerzeel et al., 2010; Yao et al., 2012b). Consequently, Sb and other toxic metals cycles in this region are more susceptible to impacting human activities and potentially pose health risk to a large human population. Limited studies have hampered our knowledge about the seasonal-spatial variations and sources of Sb in snowpit and ice core records from the TP. In the high-altitude Himalayan glaciers, Sb from 1205 to 2002 CE was determined from a Mount Everest ice core. Compared to the pre-1900 period, increasing concentrations and EFc were observed after the 1970s, with the highest enrichment factors (EFs) for Sn (2.6) and the lowest for As (1.4) in the 1995–2002 CE time period (Hong et al., 2009). The increases in Sb and other elements can be attributed to increased anthropogenic emissions from stationary fossil fuel combustion and nonferrous metals production, e.g., in India. For the Yuzhu peak glacier, the Sb recorded in a snowpit had an average concentration of 8 pg g^{-1} (Li et al., 2011). In a Tien Shan ice core, slight enhancements of Sb was observed since the 1950s (Liu et al., 2011). However, in the vast area of the TP, studies of Sb in snow and ice remained sparse compared to the other elements, such as Hg, As and Pb (Burn-Nunes et al., 2014; Huang et al., 2012; Kang et al., 2007; Zhang et al., 2012). Further studies were required to investigate the distribution and to delineate the sources of Sb in snow and ice in the TP.

In this study, surface snow/ice and snowpit samples were retrieved from the Dongga, Renlongba, Demula, and Azha glaciers located in the southeastern TP in June 2015 (Fig. 1). These samples were analyzed to further understand the distribution of Sb and its sources in the southeastern TP. This study will enrich the snow and ice Sb dataset in the high-altitude glacier regions in the TP and enhance our understanding of the atmospheric deposition and transportation of Sb in the region. Furthermore, this study will promote the interpretation of historical records of atmospheric Sb deposition through ice cores from the TP.

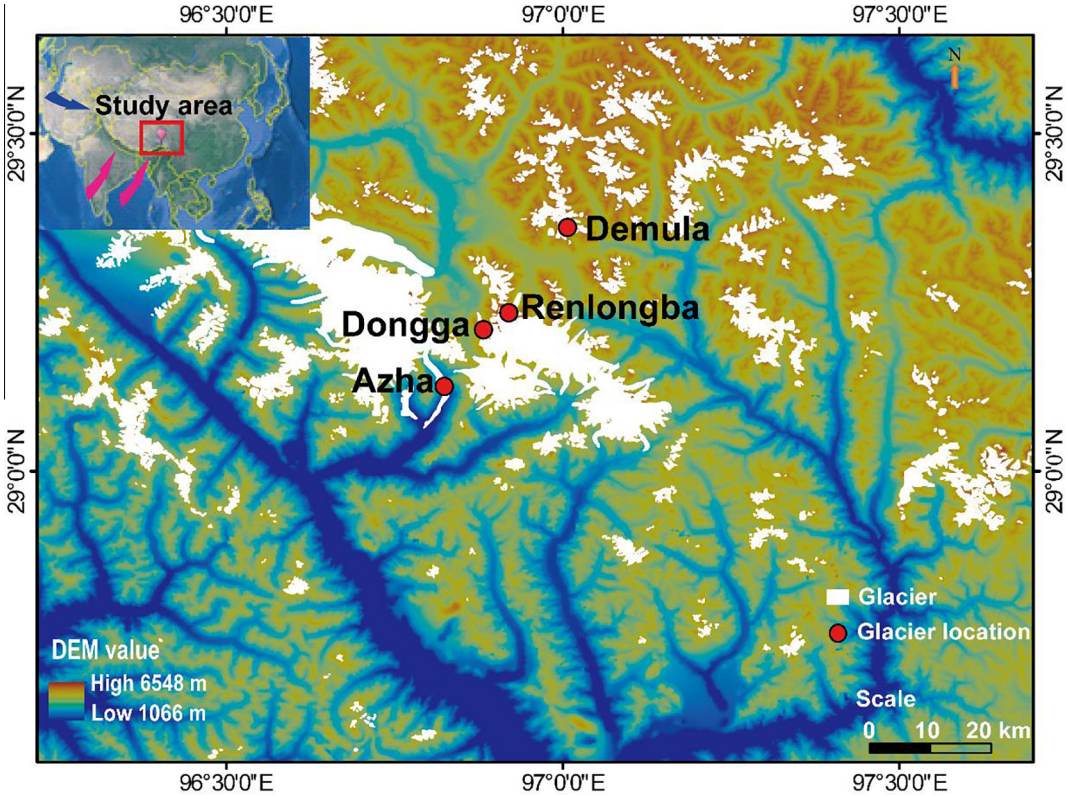

Fig. 1. Location map showing the sampling glaciers in the southeastern Tibetan Plateau. The red dots represent the location of the four investigated glaciers, and the size represents the average concentrations of Sb in the separate glacier.

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