Speciation and stable isotope variations of antimony in size fractionated aerosol collected from a tunnel and an urban air in Japan

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Antimony (Sb) is widely contained in artificial materials such as flame retardant, brake pad, paint, pigment, and catalyst. Recently, Sb has become a problem as an emerging pollutant in developed country. Antimony is highly volatile element. Tian et al. (2014) estimated that 58% of Sb in atmosphere is derived from anthropogenic activities such as fuel combustion, non-ferrous metal production, pig iron, waste incineration and brake wear. However, chemical processes during emission from each source has not been well investigated. In this study, We tried to discuss sources and chemical processes of Sb during emission to the atmosphere from size fractionated aerosol samples collected from a tunnel and an urban atmosphere.

The aerosol samples were collected both in Yasumiyama Tunnel, Hiroshima (sample YT), and on a roof of science building, the University of Tokyo (sample TS). Concentration of trace elements of the aerosol samples was determined by inductively coupled mass spectrometry (ICP-MS) after acid digestion using mixed acids (HNO_3/HCl/HF). Antimony K-edge X-ray absorption fine structure (XAFS) analysis was conducted at the synchrotron beam line BL37XU (micro-beam) and BL01B1 (bulk analysis), SPring-8, Japan. Antimony isotopic compositions were measured using multicollector ICP-MS (MC-ICP-MS). The Sb standard solution which we used as the isotope ratio reference material was purchased from SPEX CertiPrep (1000 mg/L)., The desolvator (Aridus-II) was utilized in sample introduction system to enhance the sensitivity of Sb. Compared with general introduction using spray chamber, the sensitivity was increased by ca. 200 times.

The enrichment factors (EF) of Sb (EF_{Sb}: $(Sb/Al)_{aerosol}/(Sb/Al)_{crust}$) in YT and TS were $>10^5$ and $>10^3$, respectively, suggesting larger impacts of anthropogenic emission particularly in the tunnel site. The dominant source of Sb in YT is plausibly a brake pad since a tunnel is semi-closed system. This is supported by higher EF_{Sb} in secondary particles than primary particles.

The X-ray absorption near edge structure (XANES) showed that primary and secondary particles in YT were mainly Sb(V). In TS, both Sb(III) and Sb(V) were detected from primary particles, while Sb(V) was predominant in secondary particles. Varica et al. (2013) indicated as results of XAFS analysis that the Sb in a brake pad is originally Sb(III), while 50% of Sb on the surface of a wheel is converted to Sb(V). The presence of Sb(V) with the large fraction in the primary particle of YT suggested that the Sb(III) in brake pad was mostly converted to Sb(V) due to braking. Although the predominant source of Sb in TS is difficult to constrain solely from the speciation results, Sb used for industrial purpose is generally Sb_2O_3. Higher presence of Sb(V) in secondary particles suggested they were formed by oxidation of Sb during emission process. This is possibly attributed to the higher volatility of Sb(V) compounds than that of Sb(III).

Antimony stable isotope ratio (δ^{123}Sb) was varied from 0.1 to 0.7‰ in YT while almost constant in TS (~0.7‰). The δ^{123}Sb in secondary particle is slightly higher than primary ones in YT, suggesting that volatile Sb(V) becomes heavier than original brake pad. However, reproducibility of isotope analysis is still low to support this data statistically.

Considering all the data, anthropogenic impact seems high in the aerosol of urban air sample, and oxidation of Sb in industrial material possibly contributes to release of Sb into the atmosphere.

Keywords: aerosol, antimony, stable isotope ratio, speciation

