X-ray Absorption Study on the Dominance of Sb(V) as Secondary Antimony Species in Soil

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Determination of the oxidation state of Sb by X-ray absorption near-edge structure spectroscopy was conducted to soil samples in natural mine tailing and laboratory experiments. It was found that Sb was in oxidized form, Sb(V), rather than Sb(III) in soil under reductive condition in laboratory experiments ($Eh = -222$ mV, pH 5.2) and in natural mine tailing samples ($Eh = -17$ mV, pH 7.7). These results suggested that Sb exists dominantly as Sb(V) in soil under wide range of natural redox conditions.

Antimony is a toxic trace element widely distributed in the lithosphere and mainly associated with As as sulfides or oxides. Antimony can be introduced in aquatic environment through natural processes such as rock weathering and volcanic activity.[1] In general, natural abundance of Sb in soil is normally low (<1 mg/kg),[2] but Sb at elevated concentrations can be found near Sb deposits and in contaminated area by human activities. Since Sb(III) compounds are more toxic than Sb(V), Sb analysis in environmental samples require the discrimination between Sb(III) and Sb(V) to assess the toxic hazard.[3] Many past studies for Sb speciation are limited to water samples using HPLC and voltammetry methods. However, speciation of Sb in solid phase such as soil and sediment is also essential to understand fully the Sb behavior in environment.

In this study, we employed X-ray absorption near-edge structure (XANES) to distinguish Sb(III) and Sb(V) in solid phase directly and applied it to soil samples in laboratory experiments and natural samples, while we also determined the Sb(III)/Sb(V) ratio in soil water by conventional HPLC-ICP-MS. Takaoka et al. reported Sb speciation in contaminated soil (only solid phase) using X-ray absorption fine structure spectroscopy.[4] However, to understand further the reaction and dynamics for Sb in soil–water systems, the speciation of Sb both in solid and liquid phases is needed.

The laboratory experiment was conducted based on a method in literature.[5,6] The soil used was fine textured Gray lawland soil from paddy field in National Institute of Agro-Environmental Science (Tsukuba, Japan), which was air-dried, homogenized, and sieved (2 mm) before use. Major element compositions of the soil were reported in Takahashi et al.,[6] while Sb abundance was 796 μg/kg. For the laboratory experiments, 10.0 g of the soil was put into 50 mL styrene tube with Milli-Q water and 0.10 g D(+)-glucose (Wako, Japan) was added to promote reductive condition in the system. Then, 1.0 mg of Sb(V) was added to the system as a solution prepared by dissolution of $Na[Sb(OH)_6]$ (Wako, Japan). To observe the oxidation state of Sb under various redox conditions, the total amount of water in the soil was varied during incubation, noted as the degree of water saturation (W_S). The W_S value was defined as the volume ratio of water and soil (density of dried soil: 2.64 g/cm^3) in the system, where $W_S = 0\%$ is the moisture content in the soil at 110 °C.[5] These samples were incubated at 25 °C for 9 days. The Eh and pH were measured by a Pt electrode (Fujiwara Sci., EHS–120) and a glass electrode (Horiba, D–51), respectively. When the incubation period finished, the soil water was extracted by a soil water sampler (Fujiwara Sci., FV–448) for HPLC-ICP-MS analysis after Milli-Q water was added for every sample to keep the water–soil ratio constant, while the soil was employed for XANES measurement.[4] We can ignore Sb abundance in soil water remaining in the soil samples due to its low abundance (<1% of total Sb) in the analyzed samples.

Natural soil samples containing Sb were collected around Ichinokawa mine pithead, Ehime, Japan, which was formerly one of the largest Sb (stibnite: Sb_2S_3) mine.[7] Soil samples were collected at different depths in a wetland tailing site to observe oxidation state of Sb under various redox condition. The abundance of Sb in surface and subsurface (5 cm in depth) soil samples are 7180 and 1940 mg/kg, respectively. Wet soil samples were passed through a 500-μm stainless steel sieve. Soil samples in the laboratory experiments and the natural samples were packed in air-tight polyethylene bag and stored at −20 °C to avoid the change of oxidation state before XANES analysis.[8]

Antimony K-edge XANES spectra were obtained at the beamline BL01B1 in SPring-8 (Hyogo, Japan) with a Si(311) double-crystal monochrometer and two mirrors. The measurements were carried out at room temperature under ambient air conditions. The energy calibration was conducted with Sb_2O_3, where the maximum intensity of the first peak was fixed at 30.491 keV. The fluorescence yield was measured using a 19-element Ge semiconductor detector. The Sb(III)/Sb(V) ratio in the soil water was determined by HPLC connected to ICP-MS (VG PQ-3).[9] An anion exchange column (TSKgel super IC-AP, Toso) was used at 40 °C. The mobile phase was 20 mM EDTA solution (Wako, Japan) at pH 4.7.

Figure 1 shows Eh and pH values in the laboratory experiments and natural samples. In the laboratory experiments, the Eh values showed that the redox condition became reductive at larger W_S, since the increase in water amount diminishes oxygen supply into soil. In natural samples, Eh decreased in the subsurface soil (depth: 5 cm). Figure 2 shows the normalized Sb K-edge XANES spectra of standard materials, laboratory experiment samples, and natural samples. It is obvious that the absorption edge shifts to higher energy when the oxidation state of Sb is larger. This suggests that the position of the XANES peak can be used to distinguish between Sb(III) and Sb(V). In laboratory experiment samples, the absorption edges at various W_S ($W_S = 140$ and 220%) were similar to that of $Sb(OH)_6^-$ solution. Other fine structures including a broad peak at 30.55 keV were almost identical between laboratory experiment samples and $Sb(OH)_6^-$ in solution (Figure 2). These results suggested that the oxidation state of Sb was only Sb(V) in soil in laboratory experiments and that Sb adsorbed on the soil has similar local structure to $Sb(OH)_6^-$. In a similar soil–water system, As existed as a mixture of As(III) and As(V) (Eh = 154 mV, pH 5.6) in soil,[6,10] whereas Sb was completely in oxidized form, Sb(V), even in very reductive condition (W_S: 220%, Eh = −222 mV). Therefore, it is suggested that Sb(III) is oxidized much more readily than As(III) which belongs to the same group in the periodic table. On the other hand, Eh–pH diagram for Sb in Sb–S–O–H system shows that the major species of Sb is $Sb(OH)_3$ or Sb_2S_3 in the Eh–pH region in this study.[11] This difference may be caused by the fact that many environmental factors such as biological activity or kinetic effect cannot be included in the simplified thermodynamic calculation.[12] Belzile et al. reported that Sb(III) was strongly adsorbed onto amorphous Fe and Mn oxyhydroxides and rapidly oxidized to Sb(V).[13] In this study, however, as the reductive condition progressed, considerable amount of Sb(III) was found in the soil water (Figure 3), while Sb(III) in the soil was less than 5% estimated by the simulation of the XANES. These results suggest that (1) if the adsorption reaction of Sb is in equilibrium, Sb(V) has a higher affinity to this soil than Sb(III) at the Eh–pH region of this study, or (2) the reduction rate of Sb(V) to Sb(III) in solid phase is very slow compared with the experimental period. The increase of total dissolved Sb with increasing W_S (Figure 3) probably results from the dissolution of Fe and Mn oxyhydroxides containing a large amount of Sb, as was found for As.[6]

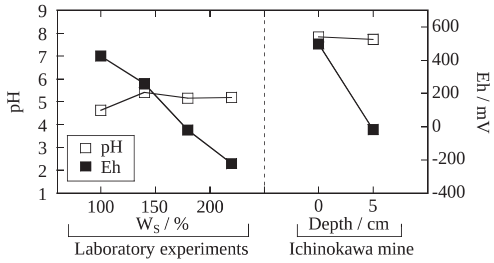

Figure 1. Eh and pH values in soil water of the laboratory experiments and natural samples around Ichinokawa mine.

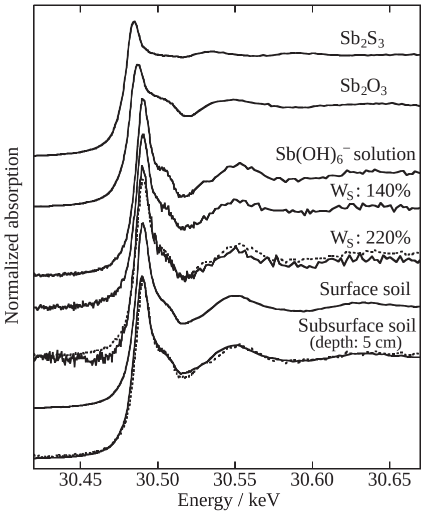

Figure 2. Antimony K-edge XANES spectra of the standard materials (Sb_2S_3, Sb_2O_3, and $Sb(OH)_6^-$ solution), laboratory experiment samples, and natural soil samples around Ichinokawa mine. The spectrum of $Sb(OH)_6^-$ was overlapped with other spectra by dotted curves for comparison.

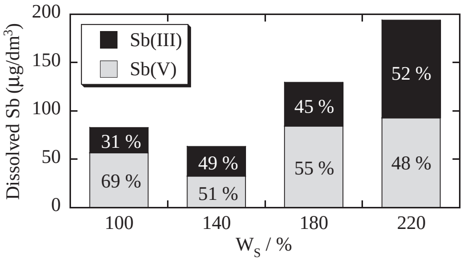

Figure 3. Concentration of Sb(III) and Sb(V) in soil water at different degrees of water saturation (W_S) in the laboratory experiments. The numerical values in each bar graph stand for the percentage of Sb(III) and Sb(V) in the soil water.

The XANES spectra of natural soil samples around Ichinokawa mine suggests that Sb is in Sb(V) in surface and subsurface (Figure 2). This trend is consistent with the results of laboratory experiments. Since the primary source of tailing sediment is stibnite (Sb_2S_3), it is suggested that Sb was oxidized to Sb(V) secondarily after leaching to aqueous phase.

In this study, it was shown that Sb(V) is stable oxidation state over wide Eh range under natural redox condition and that Sb is oxidized easily compared with As, which has been supposed to show similar behavior to Sb in environment. Coupled application of XANES and HPLC method is useful to understand the Sb behavior in aquatic environment.

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