Determination of Chemical Form of Antimony in Contaminated Soil around a Smelter Using X-ray Absorption Fine Structure

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Only limited information is available about the behavior of antimony (Sb) in contaminated soils. However, understanding the behavior of Sb in contaminated soils is important, because the toxicity or solubility of this element depends on its chemical state. In this study, we investigated the levels of Sb and the chemical forms of Sb in the soil around a smelter using X-ray absorption fine structure (XAFS) spectra. The highest Sb concentration in the contaminated soil was 2900 mg/kg dry soil. According to Sb-K edge X-ray absorption near edge (XANE) spectra, the Sb in the soil was in the form of Sb(V) compounds. The similarity of extended XAFS (EXAFS) spectra suggests that Sb speciation was independent of the sampling site, which indicates that Sb or Sb_2O_3 emitted from the smelter was converted into Sb(V) compounds in the soil.

Introduction

Although antimony (Sb) is widely used in flame-retardants, lead storage batteries, solders, and paints, Sb and its compounds are considered pollutants of priority interest in developed countries. In Japan, the water quality monitoring regulations for Sb in drinking and surface water established a limit of 15 μg/L in 2003. In the USA and the European Union, the standards are much more strict, at 6 and 5 μg/L, respectively.[1] Consequently, environmental pollution by Sb has attracted much attention. Sb contamination of soil has been reported in some countries,[2-11] and research has examined the mobility of Sb in the soil and the transfer of Sb to plants.[7,9,11] The toxicity or solubility of Sb depends on its chemical state. Sb(III) is about ten times more toxic than Sb(V),[12] because Sb(V) is easier to excrete than Sb(III).[13] Accordingly, it is important to know the chemical form as well as the content of Sb in environmental matrices. Some research on determining Sb species in soil using solvent extraction has been conducted.[7,9] Generally speaking, solvent extraction methods have some limitations in metal speciation, including 1) the incomplete dissolution of the target phases; 2) the removal of non-target species; 3) the incomplete removal of a dissolved species due to re-adsorption on remaining soil components or re-precipitation with the added reagent; and 4) a change in the valence of redox-sensitive elements.[14]

Consequently, it is necessary to speciate Sb in contaminated soil directly. However, there are few reports on the direct speciation of chemical form of Sb in contaminated soil using X-ray based methods. Ordinary methods like lab-scale XRD or XPS cannot detect information about the structure of a chemical shift of Sb due to the trace amount in contaminated soil.

In this study, we determined the level of environmental contamination by Sb around a smelter in a field survey and attempted to speciate the chemical form of Sb in the soil directly using X-ray absorption fine structure (XAFS) spectra in SPring-8, which can produce light that is about one billion times more brilliant than conventional X-ray sources.

Experimental Design

Location and samples

The smelter was located in Shiga Prefecture, Japan. In this facility, Sb metal and Sb oxides were smelted from Sb ores between 1967 and 1981. At present, only the oxidation of Sb to Sb_2O_3 is conducted.

Soil samples were collected at several locations around the smelter using a core sampler or a hand auger operated in the vertical depth direction. The locations were a field (sites F1 – 4), riverbank (BN1 – 6), riverbed (RB1 and 2), bamboo grove (BB1 and 2), grassland (G1 – 7), ridge (RD), shrine site (S), flood plain (FP1 – 5), paddy (PD1 and 2) and vacant lot (V1 – 4). The sampling points around the smelter are shown in Fig. 1. The levels of Sb at 34 sites were measured at different depths of

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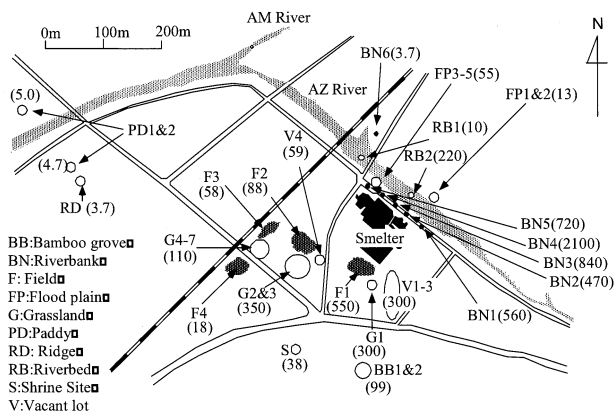E-mail: takaoka@epsehost.env.kyoto-u.ac.jp

Fig. 1   The distribution map of antimony concentrations in the surface layer of each soil.   The value in parentheses is the Sb concentration in the surface soil in mg/kg.
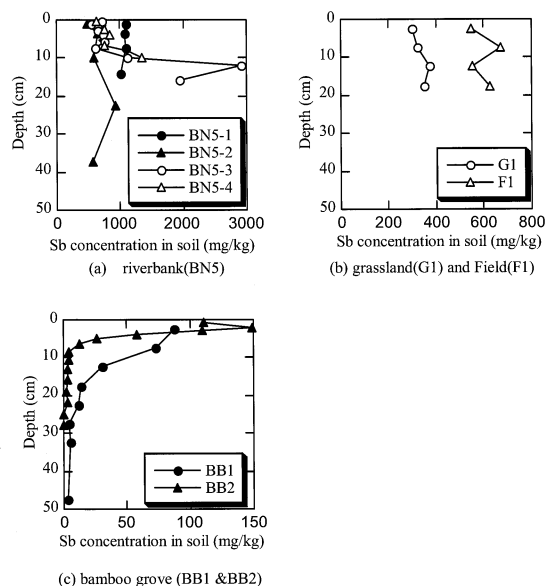

Fig. 2   Antimony vertical distributions in BN5 (riverbank), G1 (grass land), F1 (field) and BB1 and 2 (bamboo grove) area.

soil. In this study, the surface layer constitutes the top 1 cm of soil. Sampling was conducted four times at BN5, the location nearest the smelter. In addition, soil from the riverbed was collected after AZ river had dried up during summer season.

Determining of Sb concentrations

   Sb concentrations in soil samples were determined using instrumental neutron activation analysis (INAA) at the Kyoto University Research Reactor (KUR). After oven-drying at 60°C for 48 h, the soil samples were irradiated for 1 h at the Pn-2 irradiation point in KUR at an output of 5 MW.[15] The neutron density was about 2.75×10^{13} n s^{-1} cm^{-2}. After the samples were cooled for about 4 weeks, the intensity of gamma rays from ^{124}Sb (half life: 60.2 days; energy, 1691 keV) was measured using a Ge solid-state detector (EG&G Ortec: GEM30185-P). The measurement time was 7200 s/sample. The Sb concentration was calibrated using the BCR-CRM176 standard (City Waste Incineration Ash, Commission of the European Communities; certified value of Sb = 412 mg/kg).

XAFS measurements

   Sb-K edge X-ray absorption experiments were carried out on a beamline BL01B1 at SPring-8 (Hyogo, Japan) with a ring energy of 8 GeV and a stored current from 60 to 100 mA.[16] The main optics were the standard SPring-8 bending magnet system, which contains two mirrors and a fixed-exit double crystal monochromator. Higher harmonics were reduced by reflection on the two mirrors. The X-ray absorption spectra of reference materials and soil samples were recorded in transmission mode using ionization chambers and in fluorescent mode using a Lytle detector, respectively.   The incident beam was monochromatized using a Si(311) two-crystal monochromator. X-ray absorption values were recorded every 1.0 and 4.0 eV in the X-ray absorption near edge structure (XANES) and the extended XAFS (EXAFS) regions, respectively.

   Data reduction was performed using a FACOM M1800 computer at the Kyoto University Data Processing Center and a REX2000 (Rigaku Co. Ltd.). The normalization method has been reported in detail elsewhere.[17]

   XAFS measurements were conducted for five soil samples that had relatively high concentrations: BN5 – 3 (surface and 20 cm depth), F1 (surface and 5 – 10 cm), and G2 (surface). Four Sb compounds were used as reference materials: Sb, Sb$_2$O$_3$ (Wako Pure Chemical Industries), Sb$_2$O$_5$ (Soekawa Chemicals), and SbOCl (Nacalai Tesque).

Results and Discussion

Sb concentrations in the soil

   Figure 1 shows the distribution of Sb concentrations in the soil surface layer (values are in parentheses).   High concentrations of Sb were detected in a wide area around the smelter. In the surface layer, Sb concentrations ranged from 3.7 to 2100 mg/kg, with large variation at each sampling location. Asami *et al.* reported that Sb concentrations in non-polluted soils in Japan range from 0.13 to 0.91 mg/kg, as determined by acid digestion with 6 M HCl and atomic absorption spectroscopy.[2] The Sb concentration measured by INAA at control points in a forest 30 km from the city center of Kyoto, Japan, was lower than 2 mg/kg.[18] In this study, the lowest concentrations were obtained in soils from the paddy (PD1 and 2), ridge (RD), and riverbank (BN6), which were located west or north of the smelter. However, these concentrations were still more than twice as high as the reported background levels in Japan. In particular, the soil within a short distance from the facility was extremely contaminated. In the riverbank (BN1 – 5), the closest sampling site, the Sb concentration in the surface layer was 470 – 2100 mg/kg. Figure 2 (a) shows the vertical distribution of Sb in the BN5 soil. Sampling was repeated four times in this area, and the Sb concentrations in all four samples exceeded 500 mg/kg. Moreover, the Sb concentration did not decrease with increasing depth. The highest Sb concentration (2900 mg/kg) was detected in the soil at a depth of 20 cm in the riverbank (BN5) and was more than 1000 times higher than the background level (2 mg/kg).[18]   The soil from riverbank contained slightly more gravel compared to the soil from the other sites.   However, there was no difference among the riverbank sites (BN1 – 5). Highly contaminated sites south of the smelter included a field (F1), grassland (G1 – 3), and vacant lot (V1 – 3). No difference in soil properties between highly and lower contaminated sites was observed in each location. Figure 2 (b) shows the vertical distribution of Sb at G1 and F1. At these sites, we observed no marked reduction in the Sb concentrations between the soil at the surface and at a depth of 20 cm.
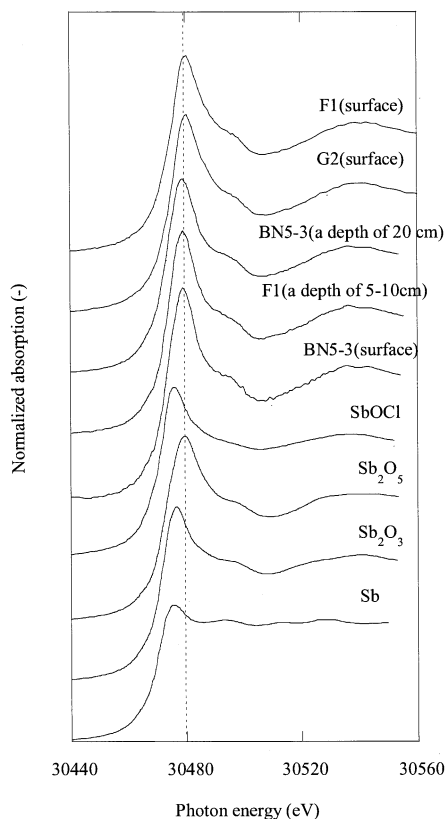
Fig. 3   Sb K-edge XANES spectra of five soil samples and reference materials: soil samples, in fluorescence mode; reference materials, in transmission mode.

Even in the soils that had not been recently disturbed, such as the shrine site and the bamboo grove (S and BB1, 2), the Sb concentrations in the surface layer were high, although they decreased exponentially with depth (Fig. 2 (c)). In almost all of the soil samples, except from highly contaminated soils, the Sb concentrations in the soil decreased to background levels at depths of 1 – 2 m.

From these results, we conclude that main source of pollution is air transportation from the smelter stack. In this region, the prevailing winds come from the north or northwest. This is in agreement with our observations that the Sb concentrations in the soil were low to the north and west and high to the south. Moreover, we observed no marked reductions in the Sb concentrations in the soil near the smelter. The soil at the closer sites (BN1 – 5, V1 – 3, G1 – 3) may have been polluted by Sb-contaminated soils or by slag from the smelter. In area F1, the Sb concentrations did not decrease in a vertical direction. Soil mixing during cultivation may have had an effect of uniformity on the soil in a vertical direction, because this area has been used for farming.

In some of the depth profiles from highly contaminated soils, the Sb concentration was slightly higher at depths of 10 – 20 cm than in the surface soil. Conversely, in less contaminated soils, the Sb concentrations decreased with increasing depth. These results suggest that Sb is transferred in a vertical direction.

A large difference between the riverbed samples (RB1 and 2) can be seen in Fig. 1. The Sb concentration at RB2 was much higher than at RB1. An effluent port from the smelter was located between points RB1 and RB2. This implies that wastewater containing Sb was released from this port into the AZ river and that Sb is still being released from the smelter.

Chemical state of Sb in the soil

Figure 3 shows the Sb K-edge XANES spectra of five soil samples and four reference materials. The Sb concentrations in each soil sample, BN5 – 3 (from the surface and a depth of 20 cm), F1 (surface and 5 – 10 cm), and G2 (surface, were 550 and 2900, 550 and 670, and 390 mg/kg, respectively. Each XANES spectrum of a soil sample had a similar shape. The first peak positions of the soil samples were between 30479.1 and 30480.1 eV. This suggests that the local structure around Sb was quite similar in all of the soil samples. The edge position in energy is a more reliable criterion, and the chemical shift of the XANES spectrum is the standard method for evaluating the oxidation state. In this research, the first inflection point was regarded as the absorption edge. The absorption edges of Sb(0), Sb_2O_3(III), SbOCl(III), and Sb_2O_5(V) are 30470.3, 30472.0, 30472.1, and 30474.3 eV, respectively, whereas those of the soil samples ranged from 30473.9 to 30475.0 eV, indicating that all of the soils contained Sb(V) species.

Furthermore, the normalized height of the white line is 1.60 for Sb_2O_3 and about 1.68 for Sb_2O_5. The heights of the white lines of Sb compounds in the soil samples ranged from 1.64 to 1.74, which also suggested that the dominant state was Sb(V) species. The white line of BN5 – 3 (20 cm depth) was slightly lower than that of the other samples. Anaerobic conditions at a depth of 20 cm may influence the chemical state of Sb.

Figures 4 and 5 show k^3-weighted EXAFS spectra and their Fourier transformations for five soil samples and reference materials, respectively. The amplitudes and phases of all the soil sample spectra are quite similar. Some oscillations in only one soil sample BN5 – 3 (20 cm depth) were observed beyond 12 Å^{-1}, although all spectra are noisier at higher k values. The similarity of the EXAFS spectra of the soil suggests that Sb speciation is independent of the sampling site. It is possible to use principal component analysis (PCA) to determine a statistically meaningful number of components in the sample.[14,19] PCA was conducted using commercial Excel add-on software (Esumi Co. Ltd., Japan). According to PCA of the five k^3-weighted EXAFS spectra, the first and second principal components accounted for 89.3% and 4.7% of the variance, respectively, which suggests that only one chemical form was present in the soil samples, although the number of principal components was small due to the lack of data.

The k^3-weighted Fourier transformation was conducted against the EXAFS spectra of the soils in the k range of 3.0 – 12.0 Å^{-1} to obtain the radial structure function (RSF). All RSFs were also quite similar, and one prominent peak was observed near 1.6 Å due to oxygen coordinating the Sb atom. The RSFs of Sb_2O_5 and Sb_2O_3 showed a peak at about 3.2 Å in the second shell, but that peak was not observed in the soil samples clearly. Although noise at higher k value may influence the peak at about 3.2 Å in the soil samples, it was estimated that the Sb compound did not form a regular structure like Sb_2O_5.

Many studies have reported the dominance of Sb(V) under aerobic conditions in the environment using redox speciation methods with solvents,[1] although we did not examine metal speciation using a solvent. Our XAFS result is in agreement with these reports. Our findings that Sb is transferred vertically and that Sb(V)–Sb(V) bonding disappears (as indicated by the RSF of Sb in the soil samples) suggest that antimonate ion was formed in the soil. Although Sb_2O_5 and Sb_2O_3 are barely soluble in water, they generate antimonate anions upon dissolution.[20] According to Belzile *et al*.[21] and Filella *et al*.,[20] bacteria or amorphous iron and manganese oxyhydroxides in the soil play a role in the oxidation of Sb(OH)$^{3-}$ to Sb(OH)$^{6-}$ in pore water. Therefore, the following pathway may be involved

Fig. 4 k^3-Weighted EXAFS spectra for five soil samples and refernce materials.
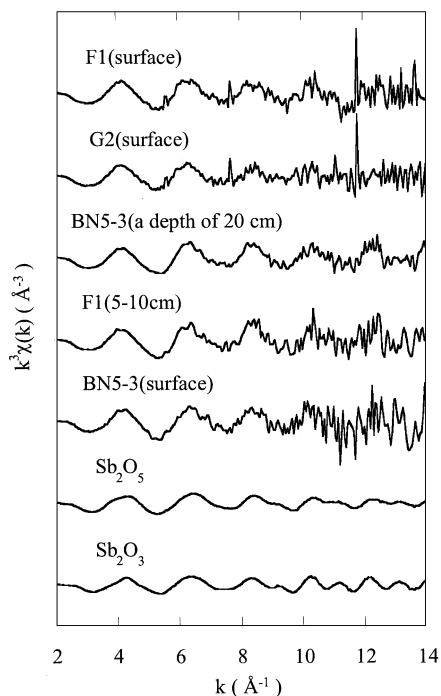

Fig. 5   Fourier transforms of k^3-weighted EXAFS spectra for five soil samples and reference materials.

in the oxidation of Sb_2O_3 to Sb(V) compounds in the soil: Sb_2O_3 in the soil dissolves to form $Sb(OH)^{3-}$ in pore water, where the $Sb(OH)^{3-}$ is oxidized to $Sb(OH)^{6-}$. The $Sb(OH)^{6-}$ is adsorbed on humic substances or amorphous iron and manganese oxyhydroxides. At present, the smelter is only used for the oxidation of Sb to Sb_2O_3. Therefore, the Sb or Sb_2O_3 emitted from the smelter is converted into Sb(V) compounds in the soil. Moreover, the change from Sb(III) to Sb(V) results in a natural reduction in the Sb toxicity in the soil.

Conclusions

In this study, we obtained the following results. In the surface layer of soil, Sb concentrations ranged from 1 to 2100 mg/kg and varied markedly with sampling location. Sb was detected over a wide area, indicating that the main source of pollution is air transportation from the smelter stack. The analysis of riverbed samples indicated that Sb is also released from an effluent port into the river.

The XANES spectra of the soil samples were all similar, and according to the Sb-K edge XANES spectra, the Sb in the soil consisted of Sb(V) compounds. The white line of BN5 – 3 (at a depth of 20 cm) was slightly lower than in the other samples. The anaerobic conditions at a depth of 20 cm may influence the chemical state of Sb. All RSFs were also quite similar, and one prominent peak was observed near 1.6 Å due to oxygen coordinating the Sb atoms. The RSF of Sb_2O_5 shows a peak at about 3.2 Å, but this peak was not observed in the soil samples clearly. We found that Sb(V) compounds do not form orderly structures like Sb_2O_5.

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