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Oxidation of antimony (III) in soil by manganese (IV) oxide using X-ray absorption fine structure

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ABSTRACT

The oxidation of antimony (III) in soils was studied using X-ray absorption fine structure (XAFS) spectra. An andosol soil sample and artificial soil samples (SiO_2 blended with iron (III) hydroxide and manganese (IV) oxide) were used herein. After adding antimony (III) oxide to all soil samples, the oxidation process was observed by recording the XAFS spectra of Sb K-edge, Fe K-edge, and Mn K-edge. The results indicated that manganese (IV) oxide played an important role in the oxidation of Sb(III); however iron (III) hydroxide was not directly related to the reaction. During a 2-hr continuous Sb K-edge X-ray absorption near edge structure (XANES) measurement with an interval of 1 min of one of the artificial soil samples ($\text{SiO}_2 + \text{MnO}_2 + \text{Sb}_2\text{O}_3$), a pseudo-first-order reaction was determined with an average estimated rate of $0.52 \pm 0.04 \text{ hr}^{-1}$. Compared to the lower oxidation rate of andosol, it is suggested that because of the low concentration of Mn(IV) in natural soils, the oxidation process of Sb(III) might be relatively slow and require more time to convert Sb(III) to Sb(V).

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Introduction

Antimony is consumed in a variety of industrial products, including flame-retardants, batteries, airplane bearings, and alloys, with a total of over 100,000 tons used annually worldwide (Onishi, 1978; Carlin, 2000). It has been identified as an environmental pollutant because of its sizeable emission (Tian et al., 2014) and toxicological properties such as those causing cancer (Foy et al., 1978; Gebel, 1997). There are numerous reports of Sb pollution, particularly in shooting-range areas as well as mining and smelting areas (Scheinost et al., 2006; Guo et al., 2014a). Okkenhaug et al. (2011) found that total Sb concentrations in soils from an active Sb mining area were considerably high (527–11,798 mg/kg) and dominated by Sb(V). In the soils from shooting-range areas, Sb concentrations of up to 5900 mg/kg have been found (Fahrenhorst and Renger, 1990; Basunia and Landsberger, 2001; Knechtenhofer et al., 2003; Johnson et al.,

2005), which is more than 11,000 times greater than an estimated global average Sb concentration in soil of 0.5 mg/kg (Reimann and Caritat, 1998). In addition, studies on Sb speciation indicate that the toxicity of Sb species is similar to that of arsenic species. Both belong to group 15 of the periodic table, and Sb(III) is much more poisonous than Sb(V) (Gurmani et al., 1994).

Antimony exists mainly as Sb(III) and Sb(V) in environmental samples. In oxic water systems, antimony is mainly present as Sb(V). In addition, antimony is sometimes present with a low amount of Sb(III) (Filella et al., 2002). For soil systems, some studies have indicated that Sb_2O_3 emitted from smelting operations remained in that form after being deposited onto surface soils (Ainsworth et al., 1991; Hammel et al., 2000). However, it is generally believed that Sb(V) is the predominant species present in soils. Mitsunobu et al. (2006) found that antimony was exclusively present in the oxidized form, i.e., Sb(V), over a wide redox range (standard hydrogen electrode (E_{H}))

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ranges from 360 to -140 mV; pH = 8) in Ichinokawa soil-water system. Oorts et al. (2008) also found that more than 70% of antimony added as Sb_2O_3 to soils was converted to Sb(V) within two days. According to previous studies, antimony present in the environment can be changed from Sb(III) to Sb(V). Belzile et al. (2001) confirmed that amorphous Fe and Mn oxyhydroxides present in natural waters and sediments can play a detoxifying role by adsorbing and oxidizing the more toxic Sb(III) content to Sb(V). Furthermore, Bai et al. (2017) conducted batch experiments to determine the oxidation and adsorption characteristics of Sb species in aquatic environments. They found that Sb species were mainly oxidized by biogenic Mn(IV) oxide and adsorbed by FeOOH. However, few studies have investigated the oxidation process of Sb(III) in soil and the oxidation mechanism is yet to be clarified.

This study aimed to simulate Sb contamination in soil and investigate the oxidation reaction of Sb(III) using Sb K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses before and after oxidation. The XANES spectra of Fe and Mn were also used to determine whether iron (III) hydroxide or manganese (IV) oxide caused the reaction to occur.

1. Materials and methods

1.1. Soil samples and reagents

Japan has active volcanoes, and andosols cover 16.4% of the total land surface and 46.5% of arable upland fields (Ministry of Agriculture, Fishery and Forestry, 1991). These volcanic soils are initially acidic and have high contents of Al and Fe (Shindo and Honma, 2001). Herein, we used andosol collected from a park in Tokyo (depth = 0–20 cm). It was freeze dried and passed through a 2-mm mesh sieve. The concentrations of Fe and Mn in the soil samples were 10,600 and 860 mg/kg, respectively. There were no obvious Sb pollution sources near the sample site, and Sb was not detected in the soil before the Sb oxidation reaction experiment.

To simplify the reaction system, iron (III) hydroxide (α -FeOOH) and manganese (IV) oxide (MnO_2) powders, which are commercially available pure, powdered reagents from Rare Metallic Co., Ltd., Japan, were added to the SiO_2 (alpha-quartz) powder and mechanically mixed for 10 min to prepare the artificial soil samples. The concentrations of Fe and Mn added to the artificial soil samples were 5 and 1 wt.%, respectively.

High concentrations of Sb in contaminated soil have been reported by several researchers (Fahrenhorst and Renger, 1990; Basunia and Landsberger, 2001; Knechtenhofer et al., 2003; Johnson et al., 2005; Okkenhaug et al., 2011); therefore, 1000 mg/kg of Sb(III), considered as an environmentally realistic concentration for this study, was added to the soil samples. Sb_2O_3 and SiO_2 were obtained from Wako Pure Chemical Industries Ltd., Japan.

1.2. Oxidation experiment

An Sb(III) oxidation reaction was performed by directly adding the Sb_2O_3 powder to the andosol and artificial soil samples, followed by mixing for 10 min. The water content was adjusted to 30%, and the soil samples were sealed in polystyrene bags for

X-ray absorption fine structure (XAFS) measurements. Measurements were immediately performed after the addition of Sb (reaction time (RT) = 0 day), representing the beginning of the oxidation reaction, and continued for several days (RT = 1, 3, 5, and 14 days). Evidence has shown that 70% of antimony added as Sb_2O_3 to soils was present as Sb(V) within two days (Oorts et al., 2008). Therefore, in this study, the experiment duration was 5 days and the samples were measured again after two weeks for final confirmation. In addition, a 2-hr continuous Sb K-edge XAFS measurement with an interval of 1 min of the artificial soil samples was conducted to observe and understand the process and the mechanism of the oxidation reaction of Sb(III) in the soil.

1.3. XAFS measurement

Sb K-edge XAFS spectra were collected in fluorescence mode using a Lytle detector at the beamline (AR-NW10A, Photon Factory Advanced Ring, Tsukuba, Japan). Fe and Mn K-edge XAFS measurements were also performed in fluorescence mode using the Lytle detector at the beamline (BL-12C, Photon Factory, Tsukuba, Japan). Both the XANES and EXAFS regions were recorded for Sb, and XANES regions were recorded for Fe and Mn. An Si(311) monochromator was used for the Sb XAFS measurement and calibrated relative to the Sb K-edge of metallic antimony (30,491 eV). For Fe and Mn XANES measurements, an Si(111) monochromator was used and beam energy was calibrated using Cu foil. XANES and EXAFS analyses were conducted using the REX2000 software package (version 2.5.5, Rigaku Corp., Japan). Fe and Mn reference spectra were collected using several Fe and Mn compounds with various oxidation states. The Sb(III)/Sb(V) ratios in the soil samples were calculated using the REX2000 software package via linear combination fitting (LCF) employing two reference spectra of Sb_2O_3 and $\text{K}[\text{Sb}(\text{OH})_6]$. The theoretical phase shift and amplitude functions employed in the fitting procedure were extracted using the FEFF 7.0 software package (Zabinsky et al., 1995; Ankudinov and Rehr, 1997).

2. Results and discussion

Sb_2O_3 is a stable compound and is not easily oxidized by oxygen in air. Before sealing the soil samples in polystyrene bags after the addition of Sb_2O_3 and H_2O , most of the air was squeezed out of the bags. Therefore, the oxidation of Sb could have been caused only by the compounds or elements in the soils.

2.1. Sb speciation in andosol

Sb K-edge XANES spectra of andosol are shown in Fig. 1. The XANES spectra of the reference compounds Sb_2O_3 and $\text{K}[\text{Sb}(\text{OH})_6]$ indicated that Sb(III) had a lower absorption edge energy of 30,493.7 eV and a relatively less pronounced white line in comparison with Sb(V). The results of the first measurement (RT = 0 day) were nearly same as those of the Sb_2O_3 spectra. However, the sample spectra became much closer to the $\text{K}[\text{Sb}(\text{OH})_6]$ spectra after two weeks of reaction time. Based on the speciation fitting result estimated by REX2000 for the spectra of 14 days, approximately 71.2% of Sb was in pentavalent form. Because of the high concentration of the Sb(III) content

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