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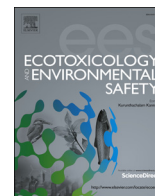
Antimony release from contaminated mine soils and its migration in four typical soils using lysimeter experiments

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ABSTRACT

Antimony (Sb) can pose great risks to the environment in mining and smelting areas. The migration of Sb in contaminated mine soil was studied using lysimeter experiments. The exchangeable concentration of soil Sb decreased with artificial leaching. The concentrations of Sb retained in the subsoil layers (5–25 cm deep) were the highest for Isohumosol and Ferrosol and the lowest for Sandy soil. The Sb concentrations in soil solutions decreased with soil depth, and were adequately simulated using a logarithmic function. The Sb migration pattern in Sandy soil was markedly different from the patterns in the other soils which suggested that Sb may be transported in soil colloids. Environmental factors such as water content, soil temperature, and oxidation–reduction potential of the soil had different effects on Sb migration in Sandy soil and Primosol. The high Fe and Mn contents in Ferrosol and Isohumosol significantly decreased the mobility of Sb in these soils. The Na and Sb concentrations in soils used in the experiments positively correlated with each other ($P < 0.01$). The Sb concentrations in soil solutions, the Sb chemical fraction patterns, and the Sb/Na ratios decreased in the order Sandy soil > Primosol > Isohumosol > Ferrosol, and we concluded that the Sb mobility in the soils also decreased in that order.

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1. Introduction

Antimony (Sb) and its alloys have been widely used in semiconductor devices, batteries, munitions, brakes, and fire prevention materials (Okkenhaug et al., 2016; Wilson et al., 2010). The evidence suggests that human are strongly influencing the environmental geochemistry of Sb (Sharifi et al., 2016). Antimony concentrations in soil in areas where smelting is performed may reach 59.8 g kg^{-1}, which is much higher than the maximum permissible concentration (35 mg kg^{-1}) in soil recommended by the World Health Organization (WHO, 1996). High concentrations of Sb have been found to cause chronic toxic and carcinogenic effects in humans (Hammel et al., 2000). There are more Sb reserves in China than in any other country, and China produced about 80% of all Sb around the world in 2014 (U.S. Geological Survey, 2015). Serious Sb pollution has been found in several Chinese provinces (6946–16,389 mg kg^{-1}), especially around the largest Sb mine in the world, in Xikuangshan, Hunan Province (Li et al., 2014; Fu et al., 2016).

The mobilization of Sb in a soil depends on the soil characteristics and environmental factors. Synthetic metal hydroxides have been used as adsorbents of Sb in most studies in which the mobility of Sb has been investigated. Metal (hydr)oxides have been shown to adsorb Sb and affect the migration of Sb in soils (Wilson et al., 2010; Huang et al., 2012). Leleyter and Probst (1999) found that 40–75% of the Sb in soil was adsorbed to iron hydroxides. Strong evidence for preferential binding of Sb to iron oxides as inner-sphere surface complexes has been provided using extended X-ray adsorption fine structure measurements (Ilgen and Trainor, 2011; Guo et al., 2014). Vithanage et al. (2013) found direct evidence for strong interactions between Sb and Fe–O in red earth soils. A significant proportion of the Sb in soil has also been found to be retained by organic matter (Sh et al., 2012). The potential for Sb to migrate through soil at small-arms firing ranges has been found to increase as the soil pH increases and the oxidation–reduction potential (E_h) of the soil decreases (Martin et al., 2013). The E_h was recognized as an important factor controlling the Sb mobility in an acidic floodplain soil reported by Frohne et al. (2011). The solubility of Sb has been found to decrease as the clay and organic matter contents in soil increase (Tighe et al., 2013). Antimony has been found to be poorly mobile in soil, and Sb

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concentrations in soil leachates of less than 0.45 µg L^{-1} have been found (Hou et al., 2013). The migration of Sb through soil has been measured qualitatively in most previous studies, and there is a paucity of quantitative data on the distributions of Sb in different media.

Lysimeter experiments are able to simulate field conditions more closely than the commonly used column tests. Lysimeter experiments can provide quantitative information on the mass balance of a material of interest and allow environmental factors to be monitored that cannot usually be monitored in field experiments. The arsenic (As), chromium (Cr), molybdenum (Mo), vanadium(V), cadmium (Cd), copper(Cu), nickel(Ni), zinc(Zn), cobalt(Co), and their controlling factors in soils were studied using lysimeters (Shaheen et al., 2014a, 2014b). However, only limited studies had to quantitatively investigate the migration of Sb in contaminated soil using lysimeters. We measured the migration of exogenous Sb through uncontaminated soil in an earlier study (Hou et al., 2013). Too little exogenous Sb was present in that study to allow us to observe Sb migration through the sublayer profile, but different Sb fraction and migration patterns were found in experiments using exogenous Sb and naturally aged Sb-contaminated soil.

In the study presented here, we added Sb-contaminated soil to the surfaces of uncontaminated soils to simulate the release of Sb from naturally aged Sb-contaminated soil, to allow us to follow Sb migration through the soil. The Sb-contaminated soil that was used had been contaminated by Sb smelting and the soil had aged for many years. The effects of environmental factors (such as the water content and oxidation–reduction potential of the soil and the ion concentration in the soil) on Sb migration through the soil were also investigated. The main objectives were to determine (1) the solubility of Sb present in four "naturally" contaminated soils and the Sb chemical fractions in those soils, (2) the release of Sb from contaminated soil and the Sb distributions between the soil and soil solution in each soil, and (3) which factors affected Sb migration in each soil. The results of the study will help us describe the Sb migration process and provide value insight into remediation of Sb-contaminated soil.

2. Materials and methods

2.1. Sb-contaminated soil

The Sb-contaminated soil that was used was a clay loam soil collected from the Xikuangshan mining area (27°45′28″N, 111°29′08″E), Hunan Province, China, in April 2013. Surface soil samples (from 0 to 20 cm deep) were collected from near a mineral waste dump. The properties of the soil are shown in Table S1. The Sb concentration in the soil was 1081 mg kg^{-1}. The Sb-contaminated soil contained Na at a high concentration because Na is used in the smelting process. The contaminated soil was air dried, passed through a 2-mm sieve, and homogenized by mixing. 40 kg of this soil was placed on top of each lysimeter, forming a layer 5 cm deep. The contaminated soil on each lysimeter was allowed to equilibrate for approximately one month under natural conditions (outside the room) before the leaching experiments were conducted.

2.2. Lysimeters

Four lysimeters (L1–L4) were used. Each lysimeter contained the contaminated soil (0–5 cm depth) and one of four representative Chinese soils (5–140 cm depth). The representative soils were: Ferrosol (L1) from Qiyang, Hunan Province (111°52′32″E, 26°45′12″N) (Ferrosol for the Chinese soil classification and ultisols for the US soil taxonomy) (Brady and Weil, 1996; Shi et al., 2004); Primosol (L2) from Changping, Beijing, (115°50′17″E, 40°02′18″N) (Primosol for Chinese soil classification and Inceptisols for the US soil taxonomy); Isohumosol (L3) from Hailun, Heilongjiang Province (126°38′00″E, 47°26′00″N) (Isohumosol for Chinese soil classification and Mollisols for the US soil taxonomy); and Sandy soil (L4) from Chaoyang, Beijing (116°26′26″E, 40°03′28″N) (Sandy soil for Chinese soil classification and Shifting Sand for the US soil taxonomy). These soils were collected and added to the lysimeters in 2008 following the method described by Hou et al. (2013). The properties of the soils and the methods used to determine them are shown in Table S1.

A porous ceramic cup, to collect soil solution, was fixed at each of the depths 10, 15, 25, 35, 55, 85, and 115 cm below the soil surface. A circular opening 5 cm in diameter in the center of the bottom of each container was connected to a sump tank to allow leachate to be collected. The lysimeters were allowed to drain freely, so leachate drained out whenever a soil was saturated.

2.3. Leaching

Artificial rainfall (Table S2) was prepared for each lysimeter to match the typical composition and acidity of precipitation in the area the main soil used in that lysimeter had been collected from (Hou et al., 2013). A leaching experiment was conducted from 10 June to 11 November 2013. L1, L2, L3, and L4 received 942 mm, 448 mm, 335 mm, and 448 mm, respectively, artificial rainfall (as a spray) over the course of the experiment. Natural precipitation (302 mm) fell during the experiment.

The lysimeters were left open to the environment to ensure they were at or close to their field capacities. The soil solution and leachate from each lysimeter was sampled every two weeks, and the samples were digested and analyzed to avoid the colloid bind Sb (Hu et al., 2008). The E_h, water potential, volumetric moisture content in the soil, and temperature in each lysimeter were recorded by a data logger every 30 min, and the data were aggregated to give daily means.

2.4. Soil sampling and analysis

After the leaching experiment was complete, samples of the contaminated soil (0–5 cm depth) and soil from 5 to 25-cm deep were collected using a soil corer (5 cm diameter). Soil sample from 5 to 25-cm deep was divided into 2-cm slices. Each sample was freeze dried and passed through a 2-mm sieve. The total Sb concentration in each sample was determined after digesting the sample in acid (Hou et al., 2005). Each analysis was conducted in triplicate, and the relative standard deviation for the total Sb concentration in each sample was < 10%. The Sb concentrations in the extracts were determined using an inductively couple plasma-mass spectrometry instrument (7500c; Agilent Technologies, Santa Clara, CA, USA), the limit of determination was 0.15 µg L^{-1}. A soil reference material (GBW07309 from China) was analyzed to determine the reliability of the method. The Sb concentration that was found (0.94 ± 0.03 mg kg^{-1}) agreed well with the reference concentration (0.93 ± 0.32 mg kg^{-1}). The sequential extraction procedure described by Hou et al. (2005) was used to extract the Sb in each soil sample as eight operationally defined chemical fractions, the exchangeable, carbonate bound, metal–organic complex bound (Me-org), easily reducible metal oxide bound (Re-MeOx), H_2O_2 extractable organic material bound (H_2O_2-Org), amorphous metal oxide bound (Am-MnOx), crystalline Fe oxide bound (Cr-FeOx), and residual fractions.