Solubility, toxicity and sorption of antimony from smelter release

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ABSTRACT

Antimony (Sb) occurs in the environment both naturally and anthropogenically. Numerous activities cause its anthropogenic accumulation and the release is mainly into the terrestrial environment. Therefore, it is crucial to investigate the fate of Sb in soils at the smelting sites where its deposition is often very high and the land needs to be cleaned up. However, little is known regarding the sorption behavior of environmentally found Sb oxidized states in the soils with different characteristics and compositions. The present study examined solubility and toxicity of Sb from the soils polluted due to the smelting operations. An inhibition of seed growth was used as an indicator of the toxic effect of Sb. Batch adsorption experiments were conducted over the pH range of 3–7 and in different equilibrium concentrations of Sb (III) as a form of the smelter release. The water soluble proportion of Sb was low (0.70–1.63%) compared to its deposition in the surface soils; however, extracted amounts caused a slightly reduced germination rate of wheat seeds with a lighter weight. Nevertheless, the soil soluble Sb concentration did not produce severe toxicity symptoms in the growth of roots and sprouts of the germinated seeds. The effects of Sb (III) and (V) forms were slightly different at the level of 5 mg·L^{-1}. In Sb (III) solution the smaller elongation of both sprouts and roots was observed as compared to the control samples while in Sb (V) solution only sprout lengths were shorter. Distribution coefficient (K_d) of Sb in soil water system was estimated to be 56 mL·g^{-1} at pH values of 3 and 10–17 mL·g^{-1} at pH of 6–7. Thus, neutral pH increases Sb mobility and its translocation to the plants that should be accounted of in agricultural production and remediation activities.

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1. Introduction

Antimony is considered a non-essential element and is toxic to most living organisms at elevated concentrations. Anthropogenic sources such as mining operations and smelting plants are major contributors to Sb deposition in the environment. Chinese vein-type ore deposits of Sb account for 55% of the world's resources of Sb (Wu, 1993) and the country has been dominant globally in its production over the last 10 decades (Antimony Mining in China, 2010). As a consequence, the water and soil as well as fauna and flora within Sb mining and smelting areas are significantly contaminated by this metalloid (Fu et al., 2011; He, 2007; Tserenpil and Liu, 2011; Wang et al., 2010). Hence, studies dedicated to how to diminish its accumulation are required and results need to be put into action.

Background Sb levels in soils vary in the different regions (Filella et al., 2002); for instance, in European soils it ranges between 0.1 and 1.9 mg·kg^{-1} (Salminen, 2005), in American soils <1–8.8 mg·kg^{-1} (Smith and Huyck, 1999) and in Chinese soils it varies from 0.8 to 3.0 mg·kg^{-1} (Qi and Cao, 1991). The antimony smelters have caused high accumulations, for instance 705 mg·kg^{-1} measured at one mining and smelting district (Ettler et al., 2007), 2159 mg·kg^{-1} in Xikuangshan mine, China (Wang et al., 2010), 2900 mg·kg^{-1} around a smelter in Japan (Takaoka et al., 2005) and very high levels up to 80,200 mg·kg^{-1} in another old smelting site (Wilson et al., 2004); also 2060 mg kg^{-1} was measured in a lead smelting site (Ettler et al., 2010) and 10 mg·g^{-1} was found at a copper smelting area (Crecelius et al., 1975).

An anthropogenic input of metals tends to exist as the fractions of exchangeable, weakly absorbed, hydrous-oxide bound or organic bound rather than in the residual fraction (Ratuzny et al., 2009). But anthropogenic Sb is often present as an insoluble and immobile species in the soil environment. Therefore, its absorption by plants is considered to be low (Flynn et al., 2003; Hammel et al., 2000). However, some plant species such as *Achillea ageratum*, *Plantago lanceolata* and *Silene vulgaris* (Baroni et al., 2000), *Dittrichia viscosa* (Murciego et al., 2007), and macrofungi (Borovicka et al., 2006) were found to be strong accumulators of Sb. The phytoextraction process based on a plant's ability to accumulate specific metal contaminants is an attempt to bring some degree of remediation to polluted soils by eliminating accumulation levels. For highly insoluble metal pollutants such as Pb, Zn and Cd, chemically enhanced phyto-extraction processes have been used with success (Luo et al., 2005). However, it is risky because soluble forms of metals may leach to the ground water.

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Plant uptake of a metal is directly related to the metal's solubility and mobility; for example, Sb concentrations in plants are proportional to soluble Sb in the soil (Tschan et al., 2009). Antimony adsorption on soil matrixes is potentially important in management of Sb pollution as sorption is one of the main barriers to its dispersion by water or availability for plant uptake. The data on Sb sorption in the original soils are considerably less as compared to those reported for the particular soil phases. Antimony association with soil phases, such as clay minerals, Fe and Al hydrous oxides and organic matter, is strong and highly dependent on the mineral's origin, pH medium and their oxidizing ability (Gal et al., 2006; Thanabalasingam and Pickering, 1990; Tighe et al., 2005). Antimony (V) has been used to study the sorption capacity and kinetics of both organic rich acidic soil (Tighe et al., 2005) and calcareous soil (Martinez-Llado et al., 2011) (the latter presenting relatively high pH value and low iron content). A few other surveys can be found on Sb sorption on soils (King, 1988). However, only one comparable reference by Nakamaru et al. (2006) was found on Sb (III) sorption in soil where ^{124}Sb radiotracer was used.

The primary aims of the present work were to examine the toxicity of dissolved Sb levels from the smelter polluted soils and to examine Sb (III) partitioning between soil solids and solutions. These two aspects have been studied concurrently to determine the condition when a higher amount of Sb is available for plant uptakes in terms of Sb sorption in a particular pH media.

2. Materials and methods

2.1. Samples and site description

Soil samples were taken in the proximity of an abandoned Sb smelter in Guangxi Zhuang, China that had been in operation for 12 years since 1996. The land within the vicinity of the smelter has been used for agricultural cultivation both before and after abandonment of smelting activity; however, cultivation was stopped at some locations because of a drastic decrease in plant growth. In this study, the smelter contaminated soils were taken from fallow farmland (site 1) that had not been cultivated for the last 5 years and from uncultivated (site 2) and currently cultivated (sites 3 and 4) areas. The soil texture was mainly silty loam or silty clay loam, pH values were 4.6–6.9 and total organic carbon concentration ranges from 1.6 to 2.1% (Tserenpil and Liu, 2011). The area has a subtropical climate and an abundant rainfall with an average annual precipitation of 1250 to 1750 mm.

2.2. Methods

2.2.1. Soil water extraction and wheat germination experiment

Water extraction was employed by shaking 30 g (in dry base) of native surface soils with 300 mL deionized water (18.2 MΩ·cm) for 24 h. Phase separation was accomplished by centrifugation at a speed of 10,000 rpm. The soil water extracts (SWEs) were then filtered using 0.45 μm membranes before the following analysis. pH value was measured with a Sartorius Professional pH Meter PP-50, dissolved organic carbon (DOC) by high TOCII, Elementar Analysensysteme GmbH (Germany) and Sb concentration was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Platform ICP, Micromass Instruments Corporation, Manchester, UK). The SWEs were stored in a refrigerator at 4 °C until their use in the toxicity study.

The resultant SWEs were used in toxicity experiments representing a seed growing habitat (that paralleled field conditions); and an inhibition of seed germination rates and root and sprout elongation were used as indicators of the toxic effect of Sb. The toxicity study was conducted during wheat seed germination because the beginning stage of plant growth is deemed the most sensitive to metal (Bajji et al., 2002). Winter wheat MaiFeng 1 and MaiFeng 2 used for this experiment are local species in Guizhou province (along the northern border with Guangxi

Zhang Province where the studied samples were taken). MaiFeng 1 and MaiFeng 2 differed in their masses and were 6.833 g and 6.203 g for 100 grains, respectively. To ascertain the toxicity effect of Sb (III) and (V) on the wheat seeds, Sb was supplied as $C_4H_4KO_7Sb$ (analytical reagent grade, Tianjin, China) and H_6KO_6Sb (analytical reagent, Fluka, Czech Republic), respectively. Spiked concentrations of 5 mg·L^{-1} of both Sb (III) and (V) solutions were prepared by dissolving appropriate Sb salts in deionized water immediately before their use.

Cultures were immersed in SWEs, 5 mg·L^{-1} aqueous solutions of Sb (III), Sb (V) and in the deionized water (as a control) for 21 h after sterilization with 15% of H_2O_2 followed by thorough rinsing with deionized water. The germination was continued for 4 days at 25 °C with day time light exposure. All trials were conducted in triplicate placing 20 seeds in each Petri dish. The dishes were sealed with Parafilm to prevent water loss and during the germination period dishes were not restored either with water or SWEs. The germination process was observed daily and the total number of sprouted seeds was tabulated (Table 2). In Table 2, data recorded are presenting the same values for three parallel dishes or data represent two analogous values with the third distinct excluded. After 4 days the lengths of the longest roots and sprouts on seedlings were recorded. EXCEL 2007 and Origin 6.0 professional were used for statistical analysis to calculate average value and standard deviation for each set of trials and to illustrate figures. For Fig. 1, the standard deviation was estimated for n = 32–40 and data for Table 1 were mostly acquired from duplicate analysis, only for several cases it was n = 3.

2.2.2. Adsorption experiment

Laboratory batch experiments were carried out to study the adsorption of Sb (III) by the soil for 24 h equilibrium. A reduced form of Sb was used in this work since Sb_2O_3 is considered to be smelter
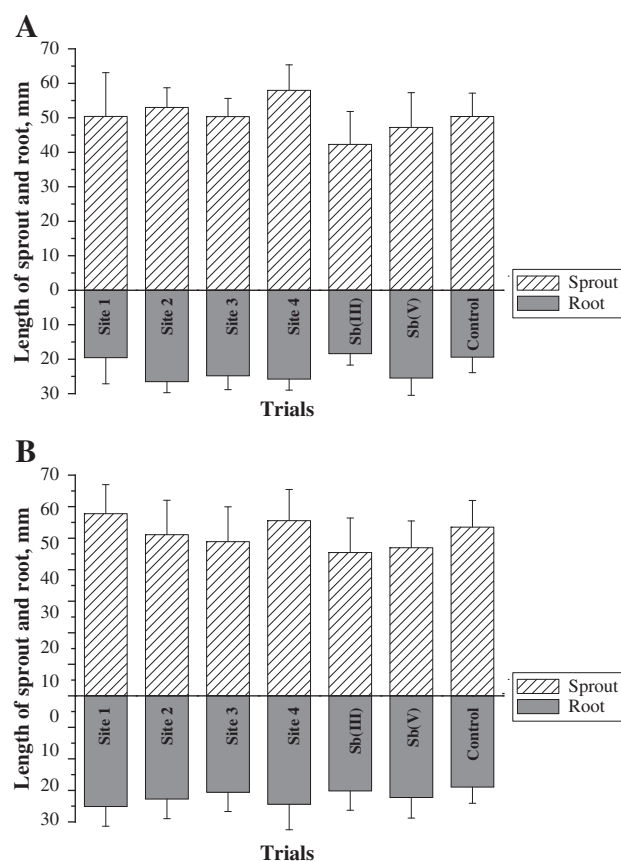

Fig. 1. The growth of roots and sprouts of germinated seeds treated by the soil water extracts and 5 mg·L^{-1} of Sb solutions compared to control: A) MaiFeng 1; (B) MaiFeng 2.

Table 1
Characteristics of the soil water extracts from the smelting site soils.

Parameters	Soil water extracts				
	Site 1 (0–5 cm)	Site 1 (30–40 cm)	Site 2 (0–50 cm)	Site 3 (0–10 cm)	Site 4 (0–10 cm)
pH	4.99	5.75	5.78	6.68	6.12
DOC[a], mg·L^{-1}	149.8 ± 0.9 (n = 3)	91.5 ± 1.3	51.5 ± 1.5 (n = 3)	26.2 ± 0.5	42.2 ± 1.2
Water extractable Sb, mg·kg^{-1}	5.28 ± 0.36	0.11 ± 0.02	31.61 ± 0.81	6.75 ± 0.78	6.50 ± 0.97
Sb concentration in soil[b], mg·kg^{-1}	760	2.5	3328	413	497

[a] Dissolved organic carbon (DOC).
[b] Data in Tserenpil and Liu (2011).

release. In addition, a subsurface soil sample (at site 1) was taken because this profile was less affected by the agricultural and smelting activities (Tserenpil and Liu, 2011). 100 mL of Sb (III) stock was prepared by dissolving 2.1596 g of C$_4$H$_4$KO$_7$Sb·0.5H$_2$O, from which work solutions were prepared by serial dilution. The sorption experiments were conducted in two variants (1) pH dependent and (2) dependent on Sb concentration. In all the adsorption trials, 1 g of oven dried (40 °C) ground soil sample and 20 mL of 0.02 M NaNO$_3$ (suspension final pH was 6.42) were used. In the concentration dependent adsorption experiments, three initial concentrations of Sb at levels of 1.66 mg·L^{-1}, 5.32 mg·L^{-1} and 10.73 mg·L^{-1} were used. The pH of the stock solutions was adjusted to 6.42, so it was the same as the soil/NaNO$_3$ suspension. It was then added to the individual trials, and the mixtures shaken until equilibrium was achieved.

In another series of tests, pH values of the suspensions were adjusted to 3, 4, 5, 6 and 7 using HNO$_3$ or NaOH solutions. The Sb concentration of 1.66 mg·L^{-1} (0.14·10^{-4} M) was used for each different pH. For both variants after 24 h equilibrium, supernatants were centrifuged and filtered by using 0.45 μm membrane before analysis. Antimony concentrations in the solutions were measured by ICP-MS. The Sb distribution coefficients between soil and solution were calculated based on Sb concentration in the solution before and after the sorption process, using the following formula:

$$K_d = \frac{\Delta C \cdot V}{C_{sol} \cdot m}$$

K_d the distribution coefficient of Sb on soil, mL·g^{-1}
ΔC difference of Sb concentration in initial and equilibrium solutions, mg·mL^{-1}
C_{sol} concentration of Sb in the equilibrium solution, mg·mL^{-1}
V solution volume, mL
m soil weight taken in the sorption experiment, g.

3. Results and discussion

3.1. Antimony extraction and wheat germination

The previous survey showed that the sampling sites were affected by both agricultural and smelting activities. Antimony accumulation

was high in the surface soils and decreased with depth (Tserenpil and Liu, 2011). The SWEs of topsoils contained 518 μg·L^{-1} (site 1), 3077 μg·L^{-1} (site 2), 660 μg·L^{-1} (site 3) and 635 μg·L^{-1} (site 4) of Sb by soil/water = 1/10 extraction. The water extractable amounts were estimated to be 0.70–1.63% of total Sb. The amounts of water soluble Sb were comparable to the typical distribution of its mobile form in the soil environment (usually less than 2% of Sb total concentration, Wilson et al., 2010). The DOC content fluctuated between 26 and 150 mg·L^{-1}. The greatest concentration was measured at the formerly cultivated site (operated till 2004) and it was consistent with evidence of DOC accumulation as a result of land usage change or abandonment (Poulton et al., 2003).

Tschan et al. (2009) reported that a half maximum toxicity effective concentration (EC$_{50}$) of Sb to wheat was 630 mg·kg^{-1} (total Sb concentration in the soil). The Sb level at site 2 (see Table 1) is expected to be toxic to wheat development as it is around 5 times the EC$_{50}$ value. However, the EC$_{50}$ in the soil solution was not given by Tschan et al. (2009) and is not possible to predict the toxicity of SWEs. In our experiments, two types of winter wheat MaiFeng 1 and MaiFeng 2 germinated in media of SWEs and Sb water solutions containing 5 mg·L^{-1} Sb (V) or Sb (III). The germination rates for MaiFeng 1 and MaiFeng 2 were compared to the control trials in Table 2. Wheat germination rates were rapid and reached the maximum in all trials after 3 days. MaiFeng 1 was similarly influenced by SWEs and Sb spiked solutions and deionized water, and virtually all seeds germinated (Table 2). In the trials with MaiFeng 2 (wheat grains with the lower mass than Mai Feng 1), a slight decrease was observed in germination rates and the final germination percentage was 80–90% as compared to 100% in the control (Table 2). In an analogous study, Shtangeeva et al. (2011) found that Sb concentrations of 50–150 mg·L^{-1} delayed biomass growth as well as the distribution of essential elements; their results showed that concentrations of 100 and 150 mg·L^{-1} were more toxic than 50 mg·L^{-1}. In the present study, the concentration of 5 mg·L^{-1} Sb in the spiked solutions was comparable to the maximum Sb concentration (i.e., around 3 mg·L^{-1} for site 2) in the natural soil–water sample. Although, these concentrations were not as high as the severe toxic doses mentioned above, grains with the lighter weight were sensitive to the effects of Sb.

It was reported that during a short term treatment of 5 mg·L^{-1} of Sb (V) the growth of roots and sprouts in rice was insignificantly retarded, while Sb (III) slightly stimulated the growth (He and Yang,

Table 2
Wheat seed germination in the soil water extracts and Sb water solutions.

Solutions	Concentration of Sb in SWE[a], μg·L^{-1}	Total number of germinated seeds for MaiFeng 1				Total number of germinated seeds for MaiFeng 2			
		Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Site 1	518	19	19	20	20	16	16	16	16
Site 2	3077	19	19	19	19	16	17	17	17
Site 3	660	18	18	18	19	16	16	16	16
Site 4	635	18	20	20	20	16	17	18	18
Sb (III)	5000	15	17	18	19	16	17	18	18
Sb (V)	5000	15	18	18	19	15	17	17	17
Deionized water		18	19	19	19	18	19	20	20

[a] SWE—soil water extract.

1999). The SWE experiments did not produce fatal effect on the elongation of roots and sprouts for both types of wheat seeds. The lengths of roots were 20–27 mm and 30–35 mm for MaiFeng 1and MaiFeng 2, whereas sprout elongation reached 45–58 mm and 46–58 mm, respectively (Fig. 1). As indicated in the reference materials Sb (V) toxicity is 10 fold lower than its reduced form (Smichowski et al., 1998). In the current work, this tendency was revealed on the root and sprout growth at the Sb amount of 5 mg·L^{-1}. In the spiked trials with Sb (V), bimodal effect was revealed that showed longer roots but shorter sprouts for MaiFeng 1 and MaiFeng 2 compared to the controls. Rather significant delay on the growth was observed in the Sb (III) treatments, which showed retarded growth both on roots and sprouts these were even shorter than observed during the Sb (V) treatments. For seeds treated by SWEs, the roots and sprouts were always longer than the control (Fig. 1A and B).

This study showed low toxicity of Sb amount in the SWEs for wheat seed growth. Antimony can be transported from roots to the aerial parts of wheat, and that accumulation increases with time as reported by Shtangeeva et al. (2011). Therefore, wheat may be a potential extractor as it showed the ability to grow at the polluted site and importantly produces large amounts of biomass in the wheat kernels.

3.2. Antimony adsorption onto soil

The K_d value of Sb (III) ranged between 10 and 56 mL·g^{-1} over pH values of 3–7. The sorption isotherm at Sb concentration of $0.14 \cdot 10^{-4}$ mol·L^{-1}, as shown in Fig. 2A, revealed that the sorption maximum was at pH 3 and continuously decreased up to pH 7. The K_d value of the studied soil was the same order of magnitude as the mean K_d value of Sb for 110 Japanese agricultural soil specimens where it was determined to be 62 mL·g^{-1} (Nakamaru et al., 2006).

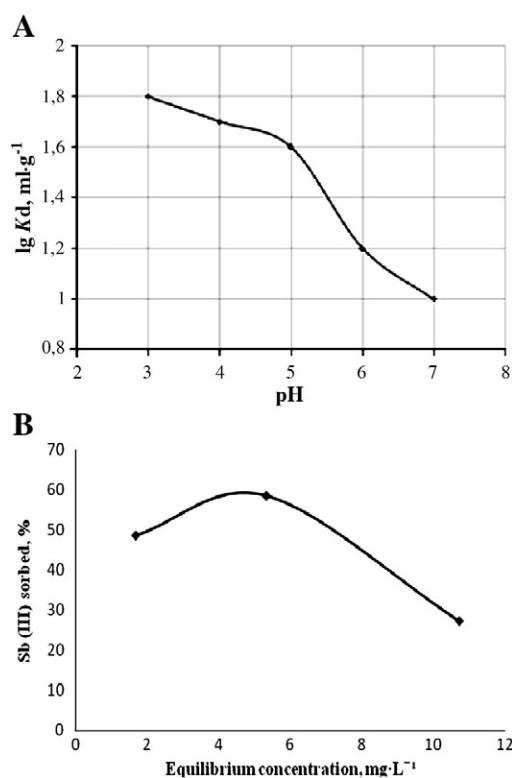**Fig. 2.** (A) Sb adsorption on the soil (site 1) as a function of pH of soil water system, $C_{Sb} = 0.14 \cdot 10^{-4}$ mol·L^{-1}; (B) proportion of sorbed Sb at equilibrium concentrations of 1.66, 5.32 and 10.73 mg·L^{-1}, pH 6.42.

Nakamaru et al. (2006) also reported that Sb distribution coefficient was negatively correlated with the system pH for two distinct soil groups (totally 86 soils), i.e. the same as the results of our present study. The topsoils from the smelting site possess medium to strong acidic characteristics (4.2–5.5) which could retard Sb mobility in the surface layer. Therefore, soil pH alteration from acidic to neutral leads to greater Sb concentration in soil solution, and this will produce a more toxic effect and negatively affect plant growth. In the wheat grain germination experiment (Section 3.1), Sb concentration of the spiked solution was prepared to be higher (1.7 times) than the maximum concentration in the soil solution in case of increased Sb availability.

Although smelter release is in the form of antimonite its major proportion easily oxidizes to antimonate under most environmental pH–Eh ranges of soil. Therefore, a comparison with Sb (V) sorption was undertaken here. The negative correlation between K_d and soil pH was also observed on Sb (V) sorption at various pH values, different amounts of organic matter and Fe (Martinez-Llado et al., 2011; Tighe et al., 2005). In that sense, the general pattern of the Sb sorption isotherm should not be strongly affected by the oxidation state change [if Sb (III) oxidizes to Sb (V)]. In calcareous soils, sorption was slow and K_d was estimated to be low as 0.45–1.55 mL·g^{-1} (Martinez-Llado et al., 2011). Two organic rich soils with high amorphous Fe content, in contrast, showed larger bonding affinity and fluctuated between 85 and 1230 mL·g^{-1} (Tighe et al., 2005). This variability was clearly related to the soil compositions e.g., organic and amorphous Fe phases.

In Fig. 2A, K_d increased by a factor of 1.2–2.2 per unit decrease of pH (significant increase between pH 6 and pH 5) and it was hard to predict which species existed over certain pH ranges since Sb is easily hydrolyzed in aqueous solutions, except in highly acidic mediums. Low pH enhances anion adsorption with an increasing variable positive charge in the soil. Thus, Sb sorption could be dominated by anion sorption.

The batch adsorption experiment was, moreover, conducted with different amounts of Sb (III). The Sb (III) equilibrium concentrations were 1.66, 5.32 and 10.73 mg·L^{-1} (pH was the same at 6.42 in all the trials) and sorption levels were 454.9, 3116.4 and 5224.6 mg·kg^{-1} soil in each individual trial, respectively. The proportion of adsorbed Sb increased from 48.7 to 58.6% with increasing Sb concentration from 1.66 to 5.32 mg·L^{-1}. However, at the highest concentration it decreased up to 27.4% (Fig. 2B). The similar decrease on Sb (V) sorption (at pH of around 6.5) appeared as the concentration increased (Tighe et al., 2005).

4. Conclusions

The water extracts of topsoils from the polluted site due to the smelting operations, contained 518–3077 μg·kg^{-1} soluble Sb which was 0.7–1.63% of the soil Sb total concentration. The soil from the abandoned polluted site contained higher DOC, indicating its restoration. In studying the Sb toxicity, both the water extracted Sb level and Sb spiked solutions (i.e., 5 mg·L^{-1}) had no fatal effect on wheat grain germination. However, there was an insignificant decrease (by 10–20% compared to the control) of the germination rate of MaiFeng 2 (grains with the smaller mass), suggesting that Sb toxicity may be related to grain size. Moreover, both species of Sb (at the level of 5 mg·L^{-1}) produced minor effect on the sprout elongation of wheat seeds and Sb (III) tended to have more negative effect than its oxidized form.

The adsorption behavior of Sb (III) in the smelter site soil showed a negative relation with pH of the soil water system, and suggested that maintaining soil pH at neutral would moderately increase Sb mobility. As bioavailability and mobility of metal are related, the higher concentration of mobile Sb in the soil column could increase the potential of plant uptake.

Acknowledgments

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