Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area

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ABSTRACT

Here, we present one of the first studies investigating the mobility, solubility and the speciation-dependent in-situ bioaccumulation of antimony (Sb) in an active Sb mining area (Xikuangshan, China). Total Sb concentrations in soils are high (527–11,798 mg kg⁻¹), and all soils, including those taken from a paddy field and a vegetable garden, show a high bioavailable Sb fraction (6.3–748 mg kg⁻¹), dominated by Sb(V). Elevated concentrations in native plant species (109–4029 mg kg⁻¹) underpin this. Both chemical equilibrium studies and XANES data suggest the presence of Ca[Sb(OH)₆]₂, controlling Sb solubility. A very close relationship was found between the citric acid extractable Sb in plants and water or sulfate extractable Sb in soil, indicating that citric acid extractable Sb content in plants may be a better predictor for bioavailable Sb in soil than total acid digestible Sb plant content.

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1. Introduction

The metalloid antimony (Sb) is an element of growing environmental concern. Its rapid growth in industrial use (e.g. flame retardants, alloys, pigments, semiconductors) is associated with an increased and often uncontrolled release of Sb compounds into the environment, e.g. mining and smelting activities, incineration of waste, combustion of fossil fuels, and spent ammunition (Filella et al., 2002a; Wilson et al., 2010). Worldwide, Sb is the ninth most mined metal and its compounds are listed as priority pollutant by the US Environment Protection Agency (USEPA, 1979). In soils Sb concentrations may be high, due to improperly disposed mine tailings and waste rocks (Filella et al., 2009a, 2009c; Wilson et al., 2010), often by far exceeding reported background values for soils (Filella et al., 2002a; Reimann et al., 2010). Despite high total concentrations, the mobility and bioavailability of Sb is generally low (Casado et al., 2007; Flynn et al., 2003). Earlier studies have, however, almost exclusively been carried out in abandoned mining areas rather than in active mines.

Antimony exists in a variety of oxidation states (–III, 0, III, V), with oxidation states III and V being most common inorganic

species in the natural environment with Sb(OH)₃ and Sb(OH)₆[–] being the dominant chemical species in wet environments. In general, inorganic Sb compounds were found to be more toxic than organic ones, with Sb(III) more toxic than Sb(V) species (Filella et al., 2002b). In soil solution Sb is mainly present as pentavalent oxyanion, Sb(OH)₆[–] (Filella et al., 2009c; Oorts et al., 2008). This is also the dominant form observed in contaminated soils near smelters and at shooting ranges (Johnson et al., 2005; Takaoka et al., 2005). Methylated Sb species may also play a role in soil depending on biological activity and the bioavailable inorganic Sb pool (Duester et al., 2005). Important natural sorbents of Sb in soil are Fe and Mn-(oxyhydr)oxides (Johnson et al., 2005; Mitsunobu et al., 2010; Wilson et al., 2010). Due to its neutral character over a wide pH range, Sb(III) is more strongly sorbed than the anionic Sb(V), making the latter more mobile in neutral and alkaline soils (Johnson et al., 2005). Thus, determination of the chemical speciation of Sb is crucial with regard to environmental fate and behavior. However, studies on the chemical speciation of Sb in soils and which parameters governing the Sb availability in soil are scarce. Here we address this knowledge gap by using different speciation studies including classical, functional and operational speciation (Bacon and Davidson, 2008; Ure, 1991). Classical speciation of Sb, referring to the specific chemical compounds or oxidation states, was studied in both soil water extracts and solid

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Table 1

Selected soil properties of the Xikuangshan site (soil on waste rock and tailings, garden and paddy soil). Standard deviation (SD) is based on triplicates.

Sample ID	Soil texture	UTM coordinates	Site description	TOC (%)	pH ^a	Sb _{tot} (mg kg ⁻¹) ^b	
						Mean	SD
S1	Clay loam	27°45'00.97"N; 111°29'21.90"E	Waste rock/tailings, (industrial area)	3.5	6.08	1062	101
S2	Sand	27°45'00.67"N; 111°29'12.20"E	Waste rock (industrial area)	2.7	6.94	11798	71
S3	Sand	27°45'37.48"N; 111°29'08.66"E	Waste rock (industrial area)	0.6	6.28	11230	715
S4	Loam	27°45'31.51"N; 111°29'12.21"E	Waste rock/tailings (industrial/residential)	7.2	6.96	7487	1966
S5	Clay loam	27°45'32.06"N; 111°29'11.33"E	Waste rock/tailings (industrial/residential)	6.3	7.05	9433	4324
S6	Clay loam	27°45'03.33"N; 111°28'46.60"E	Waste rock/tailings (industrial/residential)	7.9	7.39	1938	256
S7	Sand	27°45'01.52"N; 111°28'27.97"E	Close to tailing dam (industrial/residential)	1.8	7.26	1960	137
S8	Sand	27°44'58.72"N; 111°28'28.02"E	Close to tailing dam (industrial/residential)	0.9	7.46	1575	84
S9	Loam	27°45'01.30"N; 111°28'28.76"E	Vegetable field close to tailing dam (residential area)	11.6	6.02	1837	c
S10	Loam	27°43'08.60"N; 111°27'08.66"E	Former paddy field, downstream mining area (residential area)	5.7	5.81	527	100
NCS DC 73324				—	—	54.6	—
Reference soil material				—	—	60(±7)	—
Certified values, NCS DC 73324				—	—	60(±7)	—

^a Measured in water extracts (liquid solid ratio 10:1, 24 h shaking).^b Dry weight.^c One replicate.

soil samples using X-ray absorption near edge structure (XANES) analysis, whereas the functional speciation, e.g. bioavailability, and the operational speciation of Sb in soil were investigated by sequential chemical extractions of soil and by including the soil to plant transfer.

Antimony is not essential for plants but can be readily absorbed by plant roots when it occurs in soluble form (Baroni et al., 2000). Background Sb levels in terrestrial vascular plants range from 0.2 to 50 µg kg⁻¹ in plant tissue (Bowen, 1979). However in mining areas substantially higher Sb concentrations (up to 1600 mg kg⁻¹) have been found in vegetation (Ainsworth et al., 1990b; Baroni et al., 2000; Hammel et al., 2000; Murciago et al., 2007). Very little is known about the uptake mechanisms of Sb and which Sb species are taken up by terrestrial plants (Tschan et al., 2009b). Only few studies include chemical speciation analysis of Sb in plant extracts so far and hence the present study addresses this subject.

China is the largest Sb producer in the world with approximately 90% of the world production of 187,000 ton (U.S. Geological Survey, 2010). Based on the lack of information on Sb mobility, bioavailability and speciation in active Sb mining areas, we carried out a study in Xikuangshan, Hunan province (China), the largest active mining area in the world. The main objectives of this study were to investigate (i) the distribution and speciation of Sb in soil in an active mining area, where both waste rock, tailing-impacted sites, vegetable garden and paddy soils were considered, (ii) the solubility-governing phases of Sb in mining impacted soil and (iii) the speciation-dependent in-situ bioaccumulation of Sb in native plants from Sb impacted soils.

2. Materials and methods

2.1. Soil and plant sampling procedure

Soil and plant samples were collected in the Xikuangshan Sb mining area in June 2009. Stibnite (Sb₂S₃) is the dominant ore mineral. Sources of contamination in the study area are from mine tailings, waste rock, waste water and dust deposition after

atmospheric transport. A comprehensive description of the mineralogy of the mining area is given in He (2007) and Liu et al. (2010). The pH value of the soils was 5.8–7.5 (Table 1) due to naturally occurring calcareous minerals.

The plant samples consisted of dominant species of the vegetation community. The whole plant (1–3 individual plants of each species per location), was sampled, packed in PE bags, and stored cold before washing carefully with de-ionized water. Roots and shoots were separated and dried at 60 °C (48 h) and then ground to powder with liquid N₂. Soil samples (0.5–1.0 kg, one sub-sample) were collected from the exact same location as the plant samples (upper 10 cm), packed in separate plastic bags and stored cold (4 °C). The soil samples were air-dried at room temperature and sieved at 2 mm. Selected properties are given in Table 1.

2.2. Soil and plant extractions

Total acid digestion of soil and plant samples was carried out in a closed microwave digestion device (MarsXpress, CEM) using concentrated HNO₃ (65–68%), HCl (36–38%) and HF (>40%) (Supplier: Sinopharm Chemical Reagent, p.a.) in a ratio 6:3:1 with 0.2 g sample and 6 ml acid (190 °C, 15 min). After cooling to room temperature, the samples were filtered (quantitative filter paper, Hangzhou Paper Mill) and diluted to 50 ml with ultrapure water (>18 MΩ*cm). Total Sb in soils or plants (Sb_{tot}) refers to Sb digested by this method. Digestion of certified soil reference material (NCS DC 73324) was carried out for quality control (Table 1). Sequential chemical extraction of soil (Table 2) was carried out using a modified method developed for As based on extractants commonly used for the oxyanions selenium (Se) and phosphorous (P) (Wenzel et al., 2001). Earlier this procedure was used by Muller et al. (2007) for Sb and As and found to be suitable for evaluating the possible mobilization processes from samples contaminated by ore processing waste. The ammonium-oxalate buffer extraction in the original method to remove amorphous Fe, Al and Mn-oxides was excluded in the modified method because Sb also desorbs from crystalline Fe oxides in the presence of oxalate (Leuz, 2006). The sum of extracted Sb after full sequential extraction was checked against results from the single total digestion. The difference between the methods were <±20%, except S7 (48%), S8 (50%) and S10 (37%) based on average values. Soil (1 g, air dried) was placed in 50 ml tubes and 25 ml of extraction reagents (Beijing Chemical Works, p.a.) were added sequentially. After each extraction step the suspension was centrifuged (4000 rpm, 15 min). The solution was removed and filtered at 0.45 µm (Micro PES, Membrana), conserved in 3% HCl and stored in the fridge prior to analysis. For water extractions 1.6 g of soil sample (air dried) was weighed into a 50 ml tube and mixed with ultrapure water (>18 MΩ*cm) in a liquid solid (L/S) ratio 10:1 using a rotary shaker (24 h, 100 rpm, 25 °C). Next the samples were centrifuged (4000 rpm, 15 min) and filtered at 0.45 µm. The filtrate was split into three different fractions: (i) sample for total Sb (Sb_{tot}) conserved in 3% HCl; (ii) sample for Sb(III) analysis conserved in

Table 2

Modified sequential extraction procedure for soil samples (after Wenzel et al., 2001).

Fraction	Extractant	Extraction conditions	SSR ^a	
1	0.05 mol l ⁻¹ (NH ₄) ₂ SO ₄	4 h shaking, 25 °C	1:25	Non-specifically sorbed
2	0.05 mol l ⁻¹ (NH ₄)H ₂ PO ₄	16 h shaking, 25 °C	1:25	Specifically sorbed
3 ^b	0.2 mol l ⁻¹ NH ₄ -oxalate buffer and 0.1 mol l ⁻¹ ascorbic acid; pH 3.25	30 min in a water basin at 96 ± 3 °C in the light	1:25	Amorphous and crystalline Fe and Al oxides bound
4	Concentrated HNO ₃ , HCl and HF in a ratio 6:3:1	Microwave digestion, 190 °C, 15 min		Residue

^a SSR: soil to solution ratio.^b Wash step after fraction 3: NH₄-oxalate buffer (0.2 mol l⁻¹); pH 3.25; SSR 1:12.5; 10 min shaking in the dark.

0.5 M disodium hydrogen citrate (Sigma Aldrich, p.a.) to avoid oxidation to Sb(V); (iii) samples for other elements conserved in 3% HNO₃. All samples were stored at 4 °C prior to analysis. The risk of species shift (oxidation of Sb(III)) during air drying of the soil samples was considered to be low since the samples were obtained from the soil surface layer under oxic conditions. Changes in the Sb(III) concentrations during extraction and storage were negligible (<2.8%). For water extraction with 7 days equilibrium time, 1 g of soil sample (air dried) and 10 ml ultrapure water (>18 MΩ·cm) were shaken on a rotary shaker (100 rpm, 25 °C). After centrifugation (4000 rpm, 15 min) and filtration (0.45 μm) the filtrates were conserved as previously described and stored at 4 °C prior to analysis. Antimony minerals have shown slow dissolution kinetics (Leuz, 2006), and 7 days of shaking time were chosen to achieve equilibrium.

For speciation analysis of Sb(III) and Sb(V), plant samples were shaken (100 rpm, 25 °C) with 0.1 M citric acid (Sinopharm Chemical Reagent, p.a.) for 4 h and 1 h sonication at an L/S ratio of 10, as described in (Miravet et al., 2005). Extracts were centrifuged (4000 rpm, 15 min), filtered (<0.45 μm) and analyzed with HG-ICP-OES as previously described within 24 h. Total digestion of plant samples was carried out as described for soil samples. All extractions were carried out in triplicates unless stated otherwise.

2.3. Analytical methods

Concentrations of Sb(III) and Sb_{tot} in water extracts, extracts from the sequential extractions and the plant extracts were measured using hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES; Optima, 2000 DV, Perkin Elmer) using the method adapted from Perkin Elmer. Sb(III) was converted to SbH₃ by mixing with NaBH₄ (0.095 M, dissolved in 0.05M NaOH, flow rate 2.5 ml min⁻¹). Sb(III) was determined in 0.5 M disodium hydrogen citrate. Sb_{tot} was analyzed by reducing Sb(V) to Sb(III) with KI-ascorbic acid solution (5% KI, 5% ascorbic acid, 10% HCl) in 10% HCl prior to analysis (Andreae et al., 1981). Sb(V) was calculated from the difference of Sb_{tot} and Sb(III) concentrations. Concentrations of Na, K, Mg, Ca and Fe in solution were determined by ICP-OES. Concentrations of Sb_{tot} in soil were measured using inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies, 7500a). Total organic carbon (TOC) in soil was analyzed by an Organic Carbon Analyzer (USA Tekmar – Dohrmann Co). Concentrations of total inorganic carbon (TIC) in liquid samples were analyzed by carbon analyzer (Liqui TOCII Elemental). TIC results were used for calculating concentrations of HCO₃⁻, Sulfate (SO₄²⁻) and chloride (Cl⁻) were measured by Ion Chromatograph (USA Dionex). All analytical measurements were carried out with blanks and samples with known concentrations for quality control. Standards were matrix matched.

2.4. Calculation of BSAF and BAC

The biota to soil accumulation factor (BSAF) was calculated by the ratio of the total Sb content in plant shoot (mg kg⁻¹ dry weight (DW)) and total soil concentration (mg kg⁻¹ DW). Calculation of the bioaccumulation coefficient (BAC) was based on the ratio of the total content in plant shoot (mg kg⁻¹ DW) and water extractable soil Sb (mg kg⁻¹ DW).

2.5. X-ray absorption near edge structure (XANES) analysis

XANES provides a powerful method of characterizing the chemical speciation of an element associated with various minerals and phases in the solid phase, and is an especially valuable tool when the sample is sensitive to redox changes during sample preparation. Antimony K-edge XANES spectra were collected at the 14W1 beamline of the Shanghai Synchrotron Radiation Facility with a Si (311) double-crystal monochromator. The electron storage ring was operated with the energy of 3.5 GeV with a beam current of approximately 200 mA. Reference compounds of SbCl₃, Sb₂S₃, Sb₂O₃ and Sb₂O₅ were recorded in transmission mode with a Lytle detector, and the reference compound Ca[Sb(OH)₆]₂ and soil samples S3 and S4 were recorded in fluorescence mode. The photon energy was calibrated against the adsorption edge of Sb foil at an energy of 30 491 eV. Recorded steps were 0.5 and 0.25 eV for pre-edge and XANES regions, respectively. The soil samples and references were ground and mounted (undiluted) on plastic sample holders and sealed with Kapton tape for XANES analysis. All presented spectra were measured at ambient air conditions. Data analysis was performed using ATHENA software (Ravel, 2007). The position of the XANES peak was used to distinguish Sb(III) and Sb(V) (Mitsunobu et al., 2006; Scheinost et al., 2006; Takaoka et al., 2005). Linear combination fitting analysis (LCF) was used to fit a combination of model compounds to unknown spectra. This approach is commonly used to determine the relative proportions of model compounds present in heterogeneous samples (Fawcett et al., 2009). Spectra from the reference compounds Sb₂S₃, Sb₂O₃, Sb₂O₅ and Ca[Sb(OH)₆]₂ were used for the LCF analysis. LCF of the Sb XANES spectra was performed 100 eV over the adsorption edge. The goodness of the fits are expressed in the R-factor (R), which is a statistical measurement of the accuracy of the fit (Eq. 1)

$$R = \frac{\sum(\text{data} - \text{fit})^2}{\sum(\text{data})^2} \quad (1)$$

Reference compounds were provided from Aldrich (Sb₂S₃, Sb₂O₅, SbCl₃) and Sinopharm Chemical Reagent (Sb₂O₃). Ca[Sb(OH)₆]₂ was synthesized in the laboratory by precipitation of a solution containing Ca-acetate and KSb(OH)₆. The precipitate was washed thoroughly with de-ionized water before drying. All chemicals, except the synthesized Ca[Sb(OH)₆]₂, were of analytical grade.

2.6. Data processing

The computer program Geochemist Workbench Standard version 8.0 was used to determine the saturation indexes (SI) of various Sb phases based on data from water extracts from the 7-days equilibrium experiment and to establish a solubility diagram for Ca[Sb(OH)₆]₂. The databases *thermo.com.v8.r6.dat* and *thermo.com.minteq.dat* provided with the software, were used for the calculations. Solubility data for Ca[Sb(OH)₆]₂ ($K_{sp} = 10^{-12.55}$) from Johnson et al. (2005) was added to the database and used for the calculations. Values were corrected for ionic strength by using activity coefficients calculated by the “B-dot” equation which is an extended form of the Debye–Hückel equation (Bethke, 2008). Statistical data treatment was performed using the Minitab15 software.

3. Results

3.1. Total Sb concentrations in soil

The pH of the soil was between 5.81 and 7.46, and the TOC level varied between 0.6 and 11.6%. Total Sb concentrations in the Xikuangshan soil samples reached concentrations up to 11.8 g kg⁻¹ (Table 1). Even in paddy and garden soil, substantial concentrations were found varying from 527 (S10) to 1837 (S9) mg kg⁻¹. These values were in the upper range of those previously reported for primarily abandoned Sb mining areas (Wilson et al., 2010), and more than double the total Sb concentrations previously measured in soil samples from the same area (He, 2007; Wang et al., 2010). Our Sb_{tot} values were several orders of magnitude larger than background concentrations in unpolluted soils in Europe and North America (<10 mg kg⁻¹) (Filella et al., 2002a) and China (0.8–3.0 mg kg⁻¹) (He, 2007).

3.2. Water extraction of soil samples

Water-soluble Sb in all soil samples from the 24 h water extraction varied between 6.3 and 748 mg kg⁻¹ (0.6–10.2% of the total Sb content, Table 3), mainly occurring as Sb(V) (>98%). Results from the water extractions with 7 days equilibrium time showed higher Sb solubility, except for samples S5 and S10 (Table 4). High concentrations were also found for Ca (7.2–282 mg L⁻¹) and SO₄²⁻ (11.5–491 mg L⁻¹) while concentrations of Mg, K, Na and Cl were much lower. pH varied between 4.94 and 7.94. Cross-correlation of the measured data in Table 4, showed a good correlation between Sb and Ca (correlation coefficient = 0.81, $p < 0.05$), between Sb and

Table 3

Water extractable Sb(III), Sb(V) and total water extractable Sb in Xikuangshan soil samples (liquid solid ratio 10:1). Concentrations are given in mg kg⁻¹ dry weight. Dividing values by 10 gives concentrations in mg L⁻¹. Standard deviation (SD) is based on triplicates.

	Sb(III) (mg kg ⁻¹)		Sb(V) (mg kg ⁻¹)		Total water extractable Sb (mg kg ⁻¹)		Water extractable Sb of total Sb in soil (%)
	Mean	SD	Mean	SD	Mean	SD	
S1	<		33.0	0.5	33.0	0.5	3.1
S2	0.012	0.002	453.5	1.5	453.5	1.5	3.8
S3	4.152	0.320	246.5	5.2	250.7	5.1	2.2
S4	<		44.5	0.9	44.5	0.9	0.6
S5	0.092	0.003	748	18	748	18	7.9
S6	<		43.3	0.5	43.3	0.5	2.2
S7	0.006	0.002	199	5	199	5	10.2
S8	0.017	0.003	125.8	5.4	125.8	5.4	8.0
S9	<		32.3	0.8	32.3	0.8	1.8
S10	<		6.29	0.04	6.29	0.04	1.2

< Below limit of detection (LOD) for Sb(III) = 0.0007 mg kg⁻¹.

Table 4

Results from the 7 days water extractions (liquid solid ratio 10:1) of the Xikuangshan soils. Standard deviation (SD) is based on triplicates.

Sample	Sb mg L ⁻¹		Ca mg L ⁻¹		Mg mg L ⁻¹		K mg L ⁻¹		Na mg L ⁻¹		Cl ⁻ mg L ⁻¹		SO ₄ ²⁻ mg L ⁻¹		pH mmol L ⁻¹		HCO ₃ ⁻ mmol L ⁻¹	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
S1	5.34	0.22	78.7	3.2	17.4	0.9	3.53	0.64	0.49	0.18	12.0	2.2	142	5	6.64	0.01	0.34	0.02
S2	103	8	282	38	5.82	0.19	3.25	0.25	0.64	0.05	8.83	0.42	491	80	7.20	0.05	0.52	0.01
S3	44.0	4.9	17.6	2.5	2.67	0.22	0.85	0.01	0.79	0.25	9.50	0.87	41.4	0.6	4.94	0.06	0.06	0.00
S4	10.6	0.8	42.4	1.1	5.36	0.03	0.90	0.24	1.55	0.07	9.39	0.86	20.3	2.4	7.94	0.04	0.50	0.01
S5	17.1	1.1	126	5	27.8	0.9	3.03	0.17	9.86	0.28	10.5	0.8	154	9	7.21	0.02	1.24	0.03
S6	5.65	0.08	62.5	1.2	10.5	0.3	1.71	0.77	4.35	0.27	13.2	0.6	34.9	0.9	7.60	0.04	0.74	0.01
S7	36.1	0.7	126	15	1.16	0.01	1.25	0.19	0.30	0.02	9.06	—	228	36	7.52	0.03	0.27	0.01
S8	27.9	1.8	60.1	3.9	1.64	0.02	0.86	0.08	1.28	0.30	8.86	0.29	83.9	5.8	7.68	0.04	0.26	0.01
S9	4.33	0.07	7.19	0.16	0.99	0.01	4.06	0.33	0.49	0.02	9.02	—	15.43	—	5.63	0.09	0.09	0.00
S10	0.58	0.02	7.26	0.04	0.94	0.01	2.45	0.03	0.84	0.02	9.17	0.63	11.5	0.0	5.71	0.03	0.16	0.01

SO₄²⁻ (correlation coefficient = 0.88, $p < 0.05$), and between Ca and SO₄²⁻ (correlation coefficient = 0.98, $p < 0.05$), whereas low correlation was found between Sb and the other parameters.

3.3. XANES analysis

In Fig. 1 it is apparent that the adsorption edge shifts to higher energy at the higher oxidation state of Sb. The shape of the XANES spectra and the position of the peak maximum of the two soil samples are quite similar, with positions of the peak maximum at 30 502.5 eV (S3) and 30 501.9 eV (S4), respectively. This lies between the peak maximum of the reference materials Ca [Sb(OH)₆]₂ (30 502.9 eV) and Sb₂O₃ (30 500.1 eV), which indicates the presence of both valence states in the samples. However, it is not possible to distinguish between mixed-oxidation state minerals and single minerals containing Sb(III) or Sb(V) (Fawcett et al., 2009).

In the linear combination fitting analysis, the best fit scenario carried out on the normalized energy spectra for soil sample S3 is 90.1% Ca[Sb(OH)₆]₂ and 9.9% Sb₂S₃ (R-factor = 0.0003). For sample S4 this is 83.7% Ca[Sb(OH)₆]₂ and 16.3% Sb₂S₃ (R-Factor = 0.0012). Based on the key features in the XANES regions shown in Fig. 1 (marked with arrows), the presence of Sb₂O₃ could be excluded, and Sb₂O₅ does not occur naturally in the environment (Filella et al., 2009c). No reference material of possible Sb mixed-oxidation state minerals as stibiconite (Sb^{III} Sb^V₂O₆(OH)) and lewisite (Ca,Na,Sb^{III}, Sb^V₂O₆(OH)) were available. However, results from the water extractions showed almost exclusively Sb(V), making precipitation of Sb(III) and Sb(V) secondary minerals less likely.

3.4. Sequential chemical extraction of soil samples

Sequential extractions (Fig. 2) show that the SO₄²⁻ extractable Sb fraction in the soil, which represents the non-specifically bound

Table 5Sb (μg g⁻¹ soil) and Fe (mg g⁻¹ soil) concentrations and Sb to Fe ratio in oxalate-ascorbic acid extracts of Xikuangshan soil samples.

Sample	Sb μg g ⁻¹		Fe mg g ⁻¹		μg Sb (mg Fe) ⁻¹
	Mean	SD	Mean	SD	
S1	590	13	15.1	0.7	39.1
S2	5579	272	24.1	4.5	231.9
S3	4284	143	5.6	0.2	768.7
S4	1319	49	14.5	1.4	91.2
S5	4333	123	17.9	1.5	241.8
S6	1302	24	27.1	0.3	48.0
S7	1726	97	2.86	0.12	603.6
S8	930	95	2.10	0.13	442.5
S9	1364	31	6.7	0.5	203.2
S10	478	10	23.1	1.4	20.7

and easily leachable fraction in the soil (Wenzel et al., 2001; Muller et al., 2007), varied between 5 (S10) and 493 (S5) mg kg⁻¹. Compared to the total Sb concentration (sum of all fractions), the SO₄²⁻ extractable fractions were small (0.5–4.8%) and less (7–52%) than the concentrations measured in the water extracts (L/S ratio 10:1) of the same soil samples except S1 and S6. This may be due to shorter extraction time (4 h SO₄²⁻ extraction, compared with 24 h and 168 h for water extractions) and larger L/S ratio in the SO₄²⁻ extraction (25:1). In addition the decrease in pH associated with the addition of (NH₄)₂SO₄ may increase Sb sorption as suggested by Nakamaru and Sekine (2008), due to larger anion sorption capacity of the soil. Phosphate (PO₄³⁻) extractable Sb in the Xikuangshan soil samples varied between 6.7 mg kg⁻¹ (S9) and 864 mg kg⁻¹ (S2). These values were in the same range as the SO₄²⁻-extractable fraction.

Extraction with oxalate and ascorbic acid, which represents the fraction associated with amorphous and crystalline Fe, Al and Mn oxides, dissolved a relatively large fraction of total Sb (22–66%) (Table 5). Antimony concentration in the residue of the soil samples (acid digestion) varied between 24 and 77% of total Sb. This fraction is strongly bound to the soil matrix and is considered geochemically immobile.

3.5. Sb concentrations and speciation in plants

Total concentrations of Sb in the plants sampled in the Xikuangshan mining area were between 108 and 4029 mg kg⁻¹ (Table 6). The speciation analysis show that Sb(III) in plant extracts accounted for 1.8–28% of total Sb (Fig. 3). This was higher than the Sb(III) fraction in the water extracts of the soils. Highest Sb(III) concentration was found in *Miscanthus floridulus* (S3), where also Sb(III) was detected in elevated concentrations in the water extract of the corresponding soil sample.

4. Discussion

4.1. Distribution and mobility of Sb in soil

Total concentrations of Sb in the Xikuangshan soils were high and considerably higher than the Dutch Maximum Permissible Concentration (MPC) of 3.5 mg kg⁻¹ (factor 150 to 3370), and the Ecological Soil Screening Level (EcoSSL) for soil invertebrates of 78 mg kg⁻¹ (factor 7 to 150), identified by U.S. EPA. MPC represents the concentration of a contaminant in soil above which the risk of adverse effects is considered unacceptable (Crommentuijn et al., 2000), whereas EcoSSL are protective of ecological receptors that commonly come into contact with and/or consume biota that live in or on soil (USEPA, 2005). Leaching the soil with water or SO₄²⁻ solution showed high leachable amount of Sb, exceeding the

Fig. 1. Normalized Sb K-edge XANES spectra for reference materials and Xikuangshan soil samples (S3 and S4) and the linear combination fitting analysis (LCF) results (dot lines).

leaching limit for hazardous waste landfills according to the European landfill directive (5 mg kg^{-1} in 10:1 water to soil extracts). This was also true for paddy field soil and vegetable garden soil (S9 and S10). In the study of (He, 2007) for the same area, significantly lower concentrations in the water extracts were found ($0.04\text{--}28.3 \text{ mg kg}^{-1}$, $0.04\text{--}0.56\%$ of total Sb in the soil). This difference is probably due to lower soil to water ratios and shorter equilibration times (2 h), as adopted by He (2007). Earlier, Leuz and Johnson (2005) have shown slow dissolution kinetics of antimony minerals.

The sequential chemical extractions of the soil showed that Sb mainly was associated with the oxalate-ascorbic acid extractable fraction considered as strongly bound to oxides (Gleyzes et al., 2002). However the Sb concentrations related to the oxalate-ascorbic acid extractable Fe (Table 5) were high ($39\text{--}769 \text{ } \mu\text{g Sb (mg Fe)}^{-1}$), and much higher than expected for adsorption alone. Sorption studies of Sb(OH)_6^- on freshly precipitated and highly reactive ferrihydrite (Fe(OH)_3), which represents a good sorbent for Sb, have shown a Sb sorption capacity of $108 \text{ } \mu\text{g Sb (mg Fe)}^{-1}$ (Mitsunobu et al., 2010). Thus dissolution of Sb minerals by the oxalate – ascorbic acid solution is suspected. In studies conducted by Leuz (2006) it was shown that salts like Sb_2O_3 and KSb(OH)_6 were completely dissolved in oxalate –

ascorbic acid extractions. The dissolution of Sb minerals may explain the elevated oxalate – ascorbic acid extracted amount of Sb in some of the soil samples, thus indicating a higher mobile fraction of Sb in the soil than estimated based on the sequential extractions. This fact highlights the operational function of the sequential extraction.

Previous studies of soils from abandoned mining areas have shown low levels of soluble Sb in soil (Baroni et al., 2000; Casado et al., 2007; Flynn et al., 2003; Gal et al., 2007; Hammel et al., 2000), indicating that Sb is geochemically immobile (Ainsworth et al., 1990a, b; Diemar et al., 2009; Flynn et al., 2003). The present results show that the mobility of Sb may be substantial higher in active mining areas like Xikuangshan, indicating a high level of bioavailable Sb in soil. This is also supported by Ashley et al. (2003), who found considerable solubility of Sb (up to 37.3 mg L^{-1}) in equilibrium studies of stibnite from the Stoker deposit (Otago, Australia) with water (L/S ratio 1.5:1) and in stream sediments downstream the recently mined Hillgrove mine area, Australia (up to 6 mg L^{-1}). Moderate Sb mobility ($1\text{--}129 \text{ mg kg}^{-1}$) in water extracts of soil (L/S ratio 10:1, 24 h shaking) from an abandoned Sb mining area in Extremadura, Spain was also found by Murciego et al. (2007).

4.2. Speciation of Sb in soil

In the study area, Sb is mainly emitted as trivalent Sb in Sb_2S_3 , which is the main ore mineral. However, Sb occurred mainly as Sb(V) in the soil water extracts. This is in accordance with thermodynamic data for Sb and findings from the Ichinokawa Sb mine showing that Sb in soil and soil water was exclusively present in the pentavalent form over a wide redox range (360 to -140 mV) (Mitsunobu et al., 2006). The dominance of Sb(V) in the water extracts may be due to desorption of Sb(V) from soil surfaces and the preferential sorption of Sb(III) to soil particles, particularly Fe-oxides (Johnson et al., 2005; Wilson et al., 2010), or by rapid oxidation of Sb(III) by Fe-oxides as demonstrated by Belzile et al. (2001) and Leuz et al. (2006). Dominance of the pentavalent form of Sb in the Xikuangshan soil samples was also shown by the XANES analyses. A similar Sb(V) dominance was shown by XANES data reported for Sb_2S_3 mine-impacted soils in Japan (Mitsunobu

Fig. 2. Sequential extraction of Sb in Xikuangshan soil samples. For sample codes reference is made to Table 1.

Table 6
Content and speciation of Sb in terrestrial plants sampled at sites S1–S10. Extractable amounts in mg kg^{-1} DW. Relative amount of citric acid extractable Sb related to total Sb in %. Standard deviation (SD) is based on triplicates.

Soil sample ID	Plant sample	Sb(III) mg kg^{-1}	SD mg kg^{-1}	Sb(V) mg kg^{-1}	SD mg kg^{-1}	Citric acid extracted Sb mg kg^{-1}	SD mg kg^{-1}	Total Sb (acid digested) mg kg^{-1}	SD mg kg^{-1}	Citric acid extractable Sb of total %	Biota to soil accumulation factor (BSAF)	Bioaccumulation coeff. (BAC)
S1	<i>Phytolacca acinosa</i> Roxb	4.2	0.2	50.8	1.9	55.0	1.8	190	14	29.0	0.18	5.91
S2	<i>Boehmeria nivea</i> (L.) Gaudich.	27.0	0.8	506.7	45.1	524.7	29.5	4029	546	13.0	0.34	9.13
S3	<i>Miscanthus floridulus</i> (Labill.) Warb.	37.3	1.7	97.3	3.3	134.6	4.8	683	103	19.7	0.06	2.74
S4	<i>Eremochloa ophiuroides</i> (Munro) Hack.	1.1	0.1	20.1	0.4	21.2	0.5	128	64	16.5	0.02	2.90
S5	<i>Lactuca tatarica</i> (L.) C.A.Mey	16.7	1.4	188.4	6.8	205.1	8.1	357	142	57.5	0.04	0.48
S6	<i>Leersia hexandra</i> Swartz	15.0	0.2	73.3	2.4	88.3	2.6	292	33	30.3	0.15	6.88
S8	<i>Hygroryza aristata</i> (Retz.) Nees	3.6	0.2	55.2	2.3	58.9	2.5	109	22	54.2	0.07	0.87
S9	<i>Arachis hypogaea</i> L.	0.95	0.01	14.8	0.8	15.5	1.3	314	261	4.9	0.17	9.95
S10	<i>Comniza canadensis</i> (L.) Cronq.	0.05	0.03	2.50	0.03	2.55	0.05	461	87	0.6	0.87	75.08

et al., 2006). The Sb in soils from shooting ranges was found to be in the Sb(V) and Sb⁰ state (Scheinost et al., 2006). In addition, Fawcett et al. (2009) carried out XANES analysis on sediment samples from a mine-impacted pond and found both Sb(V) (70%) and Sb(III) (30%) in the sample.

4.3. Solubility-governing phases of Sb

Significant correlations between water extractable Sb, SO_4^{2-} and Ca indicate oxidation and dissolution of stibnite (Sb_2S_3) to Sb and SO_4^{2-} and a simultaneous dissolution of CaCO_3 . Dissolution and oxidation of Sb_2S_3 is an acidifying process (Eq. (2)), with the acid being neutralized by CaCO_3 dissolution (Eq. (3)). Antimony is oxidized to $\text{Sb}(\text{OH})_6^-$ which is the dominant Sb species found in the water extracts of the Xikuangshan soils.

The solutions are not saturated with respect to gypsum ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$), which commonly is found as secondary mineral in Sb mining areas (Filella et al., 2009a). Thus dissolution followed by equilibrium with gypsum is not suggested. In soils with high contamination levels of Sb(V) and elevated concentrations of Ca, precipitation of $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ may control concentrations of Sb in

soil water (Johnson et al., 2005). Compared to other Sb(V)-oxides like $\text{Mg}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$ (brandholzite), $\text{Ni}(\text{H}_2\text{O})_6[\text{Sb}(\text{OH})_6]_2$ (botinoite), $\text{NaSb}(\text{OH})_6$ (mopungite) (Filella et al., 2009c) and $\text{KSb}(\text{OH})_6$, $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ has the lower solubility. $\text{Pb}_2\text{Sb}_2\text{O}_7$ (bindheimite) has a lower solubility, but since concentrations of Pb and Ni (data not shown), Mg, K and Na (Table 4) are low compared to Ca in the water extracts of the Xikuangshan samples, they are not likely to control the Sb solubility. Based on the solubility product (K_{sp}) of $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ reported in Johnson et al. (2005) of $10^{-12.55}$, 9 of the 10 samples are oversaturated (samples S1–S8) or close to saturation (S9) with regard to $\text{Ca}[\text{Sb}(\text{OH})_6]_2$, whereas S10 (paddy soil) is undersaturated (Fig. 4). Thus, it is likely that $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ precipitation occurs in the Xikuangshan soil system. Other possible Sb mineral phases in soil include Sb_2O_3 (valentinite, senarmontite), which are both found to a great extent as secondary minerals in Sb mining areas (Filella et al., 2009b). However, the water extracts are not saturated with respect to these minerals. Mixed valency species as stibiconite ($\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}_2\text{O}_6(\text{OH})$) and lewisite ($\text{Ca}, \text{Na}, \text{Sb}^{\text{III}}, \text{Sb}^{\text{V}}_2\text{O}_6(\text{OH})$) may also occur as secondary minerals, but no thermodynamic data for these minerals have been found in literature.

Findings from the water extractions are supported by the XANES results, where Sb(V) is shown to predominate in the Xikuangshan soils most likely as $\text{Ca}[\text{Sb}(\text{OH})_6]_2$, while Sb(III) is present in minor proportion in the soils, possibly occurring as Sb_2S_3 , the ore material in the Xikuangshan mining area.

4.4. Uptake of Sb in plants

High Sb concentrations were found in plants from the Xikuangshan mining area. They were substantially higher than the concentrations reported by He (2007) in leaves of radish plants from the same area (range 1.5–121 mg kg^{-1}), and higher than values previously reported for abandoned mining areas (Baroni et al., 2000; Murciego et al., 2007). An exceptionally high value was found in *Boehmeria nivea* (L.) Gaudich (4029 mg kg^{-1}). This value is in the range of earlier reported EC_{50} values (maximum effective concentration) of Sb, indicating toxicity to terrestrial plants (Tschan et al., 2009a). No literature data on the Sb uptake in *B. nivea* was found, but this plant species is known to have a high tolerance with respect to As (Huang et al., 2008). The average biota to soil accumulation factor (BSAF) and the bioaccumulation coefficient (BAC) were 0.13 and 4.86, respectively (Table 6), which is considerable higher compared to previously

Fig. 3. Percentage of Sb(III) and Sb(V) in plant extracts from citric acid extraction. Concentrations are shown in Table 6.

Fig. 4. Stability diagram of $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ based on a K_{sp} of $10^{-12.55}$. Black dots show log activity of antimony and calcium in water extracts from the 7 days equilibrium experiment.

reported values from abandoned Sb mining areas (Tschan et al., 2009a), suggesting higher Sb bioavailability and bioaccumulation in the Xikuangshan active Sb mining area. *Comnyza canadensis* (S10) seems to have hyper accumulative properties with BSAF and BAC values of 0.87 and 75.1 respectively, and was not included in the average calculations. The World Health Organization (WHO) agreed on a Tolerable Daily Intake (TDI) of $6 \mu\text{g}/\text{kg}$ of body weight for Sb (WHO, 2003), which corresponds to a tolerable daily intake of 0.36 mg for a person with body weight of 60 kg. If the concentrations of Sb in plants from the Xikuangshan mining area are representative for the level in the edible plants in the area, the TDI most likely will be exceeded for humans living in the area consuming vegetables grown on site. In our study *Arachis*

hypogaea (peanut plant) is used as a food source, but only shoots and no fruits were analyzed.

Speciation analysis of the plant extracts showed that Sb(III) accounted for up to 30% of the total Sb concentration in plant shoots (Fig. 3). This is significant higher than the Sb(III) percentage in water extracts of the soil samples. Possible explanations for this may be that uptake of trivalent Sb species is facilitated by the plant, or that a reduction from pentavalent to trivalent Sb occurs after uptake. Muller et al. (2009) carried out a speciation analysis on aqueous extracts of Chinese brake fern *Pteris vittata* growing in Sb(V) spiked composites, and found beside Sb(V) considerable concentrations of Sb(III) and trimethylated antimony, TMSb(V). Sb extracted by citric acid accounts for 0.6–57.5% of total acid digested Sb in plants (Table 6). Except for the citric acid extractable Sb fraction in plant samples at S9 and S10, this fraction is in the same range (13.7–40.2%) as reported by Miravet et al. (2005). The high variation in the relative proportion of Sb extracted by citric acid is due to strong influence of the matrix composition.

4.5. Relationship between Sb concentrations in plants and Sb in soil

Based on numerous data from the literature, a close relationship between soluble Sb concentrations in soil and total Sb concentrations in plants has been shown by Tschan et al. (2009b). The corresponding results from the Xikuangshan samples (white dots in Fig. 5a and b) are in the same range (except S10). However, for our samples the best relationship was found between the citric acid extractable Sb in plants and the water as well as SO_4^{2-} -extractable Sb in soil (black triangles in Fig. 5a and b, respectively). These relationships are described well by a linear log–log regression model with $R^2 = 0.8$ (water extractable) and $R^2 = 0.9$ (SO_4^{2-} -extractable). The slope of the regression line is close to 1, over the full range of observations, extending over three orders of magnitude of Sb concentration. Citric acid is a mild extractant, and possible, this closer relationship is due to citric acid extractable Sb being less strongly bound in plants and thus better reflects Sb concentration in soil water. Digestion of the plant samples with strong acids also includes Sb which is more strongly bound and incorporated into the plant tissue accumulated over time. These results indicate that citric acid extractable Sb content in plants may be a better predictor for bioavailable Sb in soil than total acid digestible Sb plant content.

Fig. 5. Relationships between water extractable Sb (a) and $(\text{NH}_4)_2\text{SO}_4$ -extractable Sb (b) and Sb in plants (shoot) grown in these soils. Total acid extractable Sb ($\circ$) and citric acid extractable Sb ($\blacktriangle$) in plants are shown on the X abscissa. The points represent averages of replicate samples (the error bar of the citric acid extractable Sb is within the symbol). Regression was performed on the log-transformed data. The slope of the log–log regression line is not significantly different from 1. The dotted line represents a slope of one.

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References

- Ainsworth, N., Cooke, J.A., Johnson, M.S., 1990a. Distribution of antimony in contaminated grassland.2. Small mammals and invertebrates. *Environmental Pollution* 65, 79–87.
- Ainsworth, N., Cooke, J.A., Johnson, M.S., 1990b. Distribution of antimony in contaminated grassland.1. Vegetation and soils. *Environmental Pollution* 65, 65–77.
- Andreae, M.O., Asmode, J.F., Foster, P., Vantdack, L., 1981. Determination of Antimony(III), Antimony(V), and Metholantimony species in natrual-waters by atomic-absorption spectrometry with hydride generation. *Analytical Chemistry* 53, 1766–1771.
- Ashley, P.M., Craw, D., Graham, B.P., Chappell, D.A., 2003. Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. *Journal of Geochemical Exploration* 77, 1–14.
- Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? *Analyst* 133, 25–46.
- Baroni, F., Boscagli, A., Protano, G., Riccobono, F., 2000. Antimony accumulation in *Achillea ageratum*, *Plantago lanceolata* and *Silene vulgaris* growing in an old Sb-mining area. *Environmental Pollution* 109, 347–352.
- Belzile, N., Chen, Y.W., Wang, Z.J., 2001. Oxidation of antimony (III) by amorphous iron and manganese oxyhydroxides. *Chemical Geology* 174, 379–387.
- Bethke, C.M., 2008. *Geochemical and Biogeochemical Reaction Modeling*, second ed. Cambridge University Press, Cambridge.
- Bowen, H.J.M., 1979. *Environmental Chemistry of the Elements*. Academic Press, London.
- Casado, M., Anawar, H.M., Garcia-Sanchez, A., Santa-Regina, I., 2007. Antimony and arsenic uptake by plants in an abandoned mining area. *Communications in Soil Science and Plant Analysis* 38, 1255–1275.
- Crommentuijn, T., Sijm, D., de Bruijn, J., van den Hoop, M., van Leeuwen, K., van de Plassche, E., 2000. Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations. *Journal of Environmental Management* 60, 121–143.
- Diemar, G.A., Filella, M., Leverett, P., Williams, P.A., 2009. Dispersion of antimony from oxidizing ore deposits. *Pure and Applied Chemistry* 81, 1547–1553.
- Duester, L., Diaz-Bone, R.A., Koster, J., Hirner, A.V., 2005. Methylated arsenic, antimony and tin species in soils. *Journal of Environmental Monitoring* 7, 1186–1193.
- Fawcett, S.E., Gordon, R.A., Jamieson, H.E., 2009. Optimizing experimental design, overcoming challenges, and gaining valuable information from the Sb K-edge XANES region. *American Mineralogist* 94, 1377–1387.
- Filella, M., Belzile, N., Chen, Y.W., 2002a. Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth-Science Reviews* 57, 125–176.
- Filella, M., Belzile, N., Chen, Y.W., 2002b. Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. *Earth-Science Reviews* 59, 265–285.
- Filella, M., Chanudet, V., Philippo, S., Quentel, F., 2009a. Particle size and mineralogical composition of inorganic colloids in waters draining the adit of an abandoned mine, Goesdorf, Luxembourg. *Applied Geochemistry* 24, 52–61.
- Filella, M., Philippo, S., Belzile, N., Chen, Y.W., Quentel, F., 2009b. Natural attenuation processes applying to antimony: a study in the abandoned antimony mine in Goesdorf, Luxembourg. *Science of the Total Environment* 407, 6205–6216.
- Filella, M., Williams, P.A., Belzile, N., 2009c. Antimony in the environment: knowns and unknowns. *Environmental Chemistry* 6, 95–105.
- Flynn, H.C., Meharg, A.A., Bowyer, P.K., Paton, G.I., 2003. Antimony bioavailability in mine soils. *Environmental Pollution* 124, 93–100.
- Gal, J., Hursthouse, A., Cuthbert, S., 2007. Bioavailability of arsenic and antimony in soils from an abandoned mining area, Glendinning (SW Scotland). *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering* 42, 1263–1274.
- Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *TrAC-Trends in Analytical Chemistry* 21, 451–467.
- Hammel, W., Debus, R., Steubing, L., 2000. Mobility of antimony in soil and its availability to plants. *Chemosphere* 41, 1791–1798.
- He, M.C., 2007. Distribution and phytoavailability of antimony at an antimony mining and smelting area, Hunan, China. *Environmental Geochemistry and Health* 29, 209–219.
- Huang, Z.C., Chen, T.B., Lei, M., Liu, Y.R., Hu, T.D., 2008. Difference of toxicity and accumulation of methylated and inorganic arsenic in arsenic-hyperaccumulating and -hypertolerant plants. *Environmental Science & Technology* 42, 5106–5111.
- Johnson, C.A., Moench, H., Wersin, P., Kugler, P., Wenger, C., 2005. Solubility of antimony and other elements in samples taken from shooting ranges. *Journal of Environmental Quality* 34, 248–254.
- Leuz, A.K., 2006. Redox Reactions of Antimony in the Aquatic and Terrestrial Environment. Swiss Federal Institute of Technology Zurich, Zurich.
- Leuz, A.K., Johnson, C.A.R., 2005. Oxidation of Sb(III) to Sb(V) by O₂ and H₂O₂ in aqueous solutions. *Geochimica Et Cosmochimica Acta* 69, 1165–1172.
- Leuz, A.K., Monch, H., Johnson, C.A., 2006. Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization. *Environmental Science & Technology* 40, 7277–7282.
- Liu, F.Y., Le, X.C., McKnight-Whitford, A., Xia, Y.L., Wu, F.C., Elswick, E., Johnson, C.C., Zhu, C., 2010. Antimony speciation and contamination of waters in the Xikuangshan antimony mining and smelting area, China. *Environmental Geochemistry and Health* 32, 401–413.
- Miravet, R., Bonilla, E., Lopez-Sanchez, J.F., Rubio, R., 2005. Antimony speciation in terrestrial plants. Comparative studies on extraction methods. *Journal of Environmental Monitoring* 7, 1207–1213.
- Mitsunobu, S., Harada, T., Takahashi, Y., 2006. Comparison of antimony behavior with that of arsenic under various soil redox conditions. *Environmental Science & Technology* 40, 7270–7276.
- Mitsunobu, S., Takahashi, Y., Terada, Y., Sakata, M., 2010. Antimony(V) incorporation into synthetic ferrihydrite, goethite, and natural iron oxyhydroxides. *Environmental Science & Technology* 44, 3712–3718.
- Muller, K., Daus, B., Morgenstern, P., Wennrich, R., 2007. Mobilization of antimony and arsenic in soil and sediment samples - Evaluation of different leaching procedures. *Water Air and Soil Pollution* 183, 427–436.
- Muller, K., Daus, B., Mattusch, J., Stark, H.J., Wennrich, R., 2009. Simultaneous determination of inorganic and organic antimony species by using anion exchange phases for HPLC-ICP-MS and their application to plant extracts of *Pteris vittata*. *Talanta* 78, 820–826.
- Murcigo, A.M., Sanchez, A.G., Gonzalez, M.A.R., Gil, E.P., Gordillo, C.T., Fernandez, J.C., Triguero, T.B., 2007. Antimony distribution and mobility in topsoils and plants (*Cytisus striatus*, *Cistus ladanifer* and *Dittrichia viscosa*) from polluted Sb-mining areas in Extremadura (Spain). *Environmental Pollution* 145, 15–21.
- Nakamaru, Y.M., Sekine, K., 2008. Sorption behavior of selenium and antimony in soils as a function of phosphate ion concentration. *Soil Science and Plant Nutrition* 54, 332–341.
- Oorts, K., Smolders, E., Degryse, F., Buekers, J., Gasco, G., Cornelis, G., Mertens, J., 2008. Solubility and toxicity of antimony trioxide (Sb₂O₃) in soil. *Environmental Science & Technology* 42, 4378–4383.
- Ravel, B., 2007. *ATHENA User's Guide*.
- Reimann, C., Matschullat, J., Birke, M., Salminen, R., 2010. Antimony in the environment: lessons from geochemical mapping. *Applied Geochemistry* 25, 175–198.
- Scheinost, A.C., Rossberg, A., Vantelon, D., Xifra, I., Kretzschmar, R., Leuz, A.K., Funke, H., Johnson, C.A., 2006. Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. *Geochimica Et Cosmochimica Acta* 70, 3299–3312.
- Takaoka, M., Fukutani, S., Yamamoto, T., Horiuchi, M., Satta, N., Takeda, N., Oshita, K., Yoneda, M., Morisawa, S., Tanaka, T., 2005. Determination of chemical form of antimony in contaminated soil around a smelter using X-ray absorption fine structure. *Analytical Sciences* 21, 769–773.
- Tschan, M., Robinson, B.H., Nodari, M., Schulin, R., 2009a. Antimony uptake by different plant species from nutrient solution, agar and soil. *Environmental Chemistry* 6, 144–152.
- Tschan, M., Robinson, B.H., Schulin, R., 2009b. Antimony in the soil-plant system - a review. *Environmental Chemistry* 6, 106–115.
- Ure, A.M., 1991. Trace-Element speciation in soils, soil extracts and solutions. *Mikrochimica Acta* 2, 49–57.
- U.S. Geological Survey, 2010. *Mineral Commodity Summaries 2010*. U.S. Geological Survey, Washington.
- USEPA, 1979. *Water Related Fate of the 129 Priority Pollutants*. USEPA, Washington, DC, USA.
- USEPA, 2005. *Ecological soil screening levels for antimony*. Interim final OSWER Directive 9285.7–61, (2005), in: Response, OoSWaE. (Ed.), Washington, DC, USA.
- Wang, X.Q., He, M.C., Xie, J., Xi, J.H., Lu, X.F., 2010. Heavy metal pollution of the world largest antimony mine-affected agricultural soils in Hunan province (China). *Journal of Soils and Sediments* 10, 827–837.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* 436, 309–323.
- WHO, 2003. *Antimony in Drinking Water*. Background Document for Development of WHO Guidelines for Drinking Water Quality. World Health Organization.
- Wilson, S.C., Lockwood, P.V., Ashley, P.M., Tighe, M., 2010. The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. *Environmental Pollution* 158, 1169–1181.