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

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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 pollutants 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-(oxy)hydr(o)oxides (Johnson et al., 2005; Mitsuobu 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...
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; Murciego 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 MΩcm). Total Sb in soils or plants (Sbₜ𝑜𝑡) 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-oxide 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 <0.2%, except 57 (48%), 58 (50%) and 510 (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, Membrane), conserving 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 MΩcm) 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 (Sbₜₒ𝑡) conserved in 3% HCl; (ii) sample for Sb(III) analysis conserved in

### 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.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Soil texture</th>
<th>UTM coordinates</th>
<th>Site description</th>
<th>TOC (%)</th>
<th>pH¹</th>
<th>Sbₜₒ𝑡 (mg kg⁻¹)</th>
</tr>
</thead>
</table>
| S1        | Clay loam    | 27°45'00.97"N; 111°29'21.90"E | Waste rock/tailings, (industrial area) | 3.5      | 6.08 | 1062  
| S2        | Sand         | 27°45'00.67"N; 111°29'12.20"E | Waste rock (industrial area) | 2.7      | 6.94 | 1179  
| S3        | Sand         | 27°45'37.48"N; 111°29'08.66"E | Waste rock (industrial area) | 0.6      | 6.28 | 11230  
| S4        | Loam         | 27°45'31.31"N; 111°29'12.21"E | Waste rock/tailings (industrial/residential) | 7.2      | 6.96 | 7487   
| S5        | Clay loam    | 27°45'32.06"N; 111°29'11.33"E | Waste rock/tailings (industrial/residential) | 6.3      | 7.05 | 9433   
| S6        | Clay loam    | 27°45'03.33"N; 111°28'46.60"E | Waste rock/tailings (industrial/residential) | 7.9      | 7.39 | 1938   
| S7        | Sand         | 27°45'01.52"N; 111°28'27.97"E | Close to tailing dam (industrial/residential) | 1.8      | 7.26 | 1960   
| S8        | Sand         | 27°44'58.72"N; 111°28'28.02"E | Close to tailing dam (industrial/residential) | 0.9      | 7.46 | 1575   
| S9        | Loam         | 27°45'01.30"N; 111°28'28.67"E | Vegetable field close to tailing dam (residential area) | 11.6     | 6.02 | 1837   
| S10       | Loam         | 27°43'08.60"N; 111°27'08.68"E | Former paddy field, downstream mining area (residential area) | 5.7      | 5.81 | 527    
| NCS DC 73324 | Reference soil material | -    | -  | - | - | 54.6   |

¹ Measured in water extracts (liquid solid ratio 10:1, 24 h shaking).
² Dry weight.
³ One replicate.

### Table 2

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

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extractant</th>
<th>Extraction conditions</th>
<th>SSR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 mol l⁻¹ (NH₄)₂SO₄</td>
<td>4 h shaking, 25 °C</td>
<td>1:25</td>
</tr>
<tr>
<td>2</td>
<td>0.05 mol l⁻¹ (NH₄)H₂PO₄</td>
<td>16 h shaking, 25 °C</td>
<td>1:25</td>
</tr>
<tr>
<td>3b</td>
<td>0.2 mol l⁻¹ NH₄-oxalate buffer and 0.1 mol l⁻¹ ascorbic acid; pH 3.25</td>
<td>30 min in a water basin at 96 ± 3 °C in the light</td>
<td>1:25</td>
</tr>
<tr>
<td>4</td>
<td>Concentrated HNO₃, HCl and HF in a ratio 6:3:1 Microwave digestion, 190 °C, 15 min</td>
<td>Residue</td>
<td></td>
</tr>
</tbody>
</table>

* 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 carbonate (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 aerobic 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 (Mira 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(V) in water 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 Sb(IV) by mixing with NaBH4 (0.095 M, dissolved in 0.05M NaOH, flow rate 2.5 ml min⁻¹). Sb(II) was determined in 0.5 M disodium hydrogen carbonate. Sb(V) 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 (Andrae et al., 1981). Sb(V) was calculated from the difference of Sb(III) and Sb(III) concentrations. Concentrations of Na, K, Mg, Ca and Fe in solution were determined by ICP-OES. Concentrations of Sb(III) 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 (Liqiu TOC1 Elementar). 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 SkCl₃, Sb₂S₅, Sb₂O₃ and Sb₂O₅ were recorded in transmission mode with a Lytle detector, and the reference compound Ca(SbOH)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 spectra were 0.5 and 0.25 eV for pre-edge and XANES regions, respectively. The soil samples and references were ground and mounted (undusted) 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 (Tawatt et al., 2009). Spectra from the reference compounds Sb₂O₅, Sb₂O₃, Sb₂O₄ and Sb₂O₅, as well as for the LCF analysis of Sb(V) using the reference compounds of the Sb XANES spectra were performed 100 eV over the adsorption edge. The goodness of the fits are expressed as a statistical measure of the accuracy of the fit (Eq. 1)

\[ K = \frac{\sum (data - fit)^2}{\sum (data)^2} \]  

Reference compounds were provided from Aldrich (Sb₂O₅, Sb₂O₃, SbCl₃) and Sinopharm Chemical Reagent (Sb₂O₃, Ca(SbOH)₂) was synthesized in the laboratory by precipitation of a solution containing Ca-acetate and K₂Sb(OH)₄. The precipitate was washed thoroughly with de-ionized water before drying. All chemicals, except the synthesized Ca(SbOH)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)₄)₂. The databases thermo.com.v8.r6.dat and thermo.com.mining.dat provided with the software, were used for the calculations. Solubility data for Ca(Sb(OH)₄)₂ (Ksp = 10⁻¹².5) 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 Mintab15 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) (Filolla 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>
<thead>
<tr>
<th>Sb(III) (mg kg⁻¹)</th>
<th>Sb(V) (mg kg⁻¹)</th>
<th>Total water extractable Sb (mg kg⁻¹)</th>
<th>Water extractable Sb of total Sb in soil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>S1</td>
<td>&lt;</td>
<td>33.0</td>
<td>0.5</td>
</tr>
<tr>
<td>S2</td>
<td>0.012</td>
<td>0.002</td>
<td>435.3</td>
</tr>
<tr>
<td>S3</td>
<td>4.152</td>
<td>0.320</td>
<td>246.5</td>
</tr>
<tr>
<td>S4</td>
<td>&lt;</td>
<td>44.5</td>
<td>0.9</td>
</tr>
<tr>
<td>S5</td>
<td>0.092</td>
<td>0.003</td>
<td>748</td>
</tr>
<tr>
<td>S6</td>
<td>&lt;</td>
<td>43.3</td>
<td>0.5</td>
</tr>
<tr>
<td>S7</td>
<td>0.006</td>
<td>0.002</td>
<td>199</td>
</tr>
<tr>
<td>S8</td>
<td>0.017</td>
<td>0.003</td>
<td>125.8</td>
</tr>
<tr>
<td>S9</td>
<td>&lt;</td>
<td>12.5</td>
<td>0.8</td>
</tr>
<tr>
<td>S10</td>
<td>&lt;</td>
<td>6.29</td>
<td>0.04</td>
</tr>
</tbody>
</table>

< Below limit of detection (LOD) for Sb(III) — 0.0007 mg kg⁻¹.
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 (S4) eV, respectively. This lies between the peak maximum of the reference materials Ca [Sb(OH)6]2 (30 520.9 eV) and Sb2O3 (30 501.1 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(II) 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 (Fililella et al., 2009c). No reference material of possible Sb mixed-oxidation state minerals as stibonitite (Sb3O7(OH)2) and lewisite (Na2Sb3O7(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 fraction in the soil, which represents the non-specifically bound 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 increase 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
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 (0.04–28.3 mg kg$^{-1}$, 0.04–0.56% 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 (39–769 µg Sb (mg Fe)$^{-1}$), and much higher than expected for adsorption alone. Sorption studies of Sb(OH)$_6^{3-}$ 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 µg 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$_2$O$_3$ 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 (1–129 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$_2$S$_3$, 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 soil 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$_2$S$_3$ mine-impacted soils in Japan (Mitsunobu et al., 2006).

![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).](image1)

![Fig. 2. Sequential extraction of Sb in Xikuangshan soil samples. For sample codes reference is made to Table 1.](image2)
Oxidized to Sb(OH)$_6^-$

SO$_4^{2-}$

The oxidation of Sb$_2$S$_3$ is an acidifying process (Eq. (2)), with the acid being neutralized by CaCO$_3$ dissolution (Eq. (3)). Antimony is precipitated as Ca[Sb(OH)$_6$]$_2$, which may control concentrations of Sb in soils. The Sb solubility is governed by several phases in soil water (Johnson et al., 2005). Compared to other Sb(V)-oxides like Mg(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ (brandholzite), Ni(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ (botitnoite), NaSb(OH)$_6$ (mopungite) (Filella et al., 2009c) and K$_2$Sb(OH)$_6$, Ca[Ca(OH)$_6$]$_2$ has the lower solubility. Pb$_2$Sb$_2$O$_7$ (bindheimite) has the lowest 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 Ca[Ca(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 Ca[Ca(OH)$_6$]$_2$, whereas S10 (paddy soil) is undersaturated (Fig. 4). Thus, it is likely that Ca[Ca(OH)$_6$]$_2$ precipitation occurs in the Xikuangshan soil system. Other possible Sb mineral phases in soil include Sb$_2$O$_3$ (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 stibonite (Sb$^{11+}$Sb$^{5+}$O$_6$OH) and lewisite (Ca$_2$Na$_2$Sb$^{11+}$Sb$^{5+}$O$_6$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 Ca[Ca(OH)$_6$]$_2$, while Sb(III) is present in minor proportion in the soils, possibly occurring as Sb$_2$S$_3$, the ore material in the Xikuangshan mining area.

### 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$_2$S$_3$) to Sb and SO$_4^{2-}$ and a simultaneous dissolution of CaCO$_3$. Dissolution and oxidation of Sb$_2$S$_3$ is an acidifying process (Eq. (2)), with the acid being neutralized by CaCO$_3$ dissolution (Eq. (3)).

\[
\text{Sb}_2\text{S}_3 + 7\text{O}_2 + 10\text{H}_2\text{O} = 3\text{SO}_4^{2-} + 2\text{Sb(OH)}_6^- + 8\text{H}^+ \tag{2}
\]

\[
\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \tag{3}
\]

The solutions are not saturated with respect to gypsum (CaSO$_4\cdot$2H$_2$O), which commonly is found as secondary mineral in Sb mining areas (Filella et al., 2009a). Thus dissolution followed by equilibrium with gypsum is not suggested. In soils with high contamination levels of Sb(V) and elevated concentrations of Ca, precipitation of Ca[Sb(OH)$_6$]$_2$ may control concentrations of Sb in soil water (Johnson et al., 2005). Compared to other Sb(V)-oxides like Mg(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ (brandholzite), Ni(H$_2$O)$_6$[Sb(OH)$_6$]$_2$ (botitnoite), NaSb(OH)$_6$ (mopungite) (Filella et al., 2009c) and K$_2$Sb(OH)$_6$, Ca[Ca(OH)$_6$]$_2$ has the lower solubility. Pb$_2$Sb$_2$O$_7$ (bindheimite) has the lowest 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 Ca[Ca(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 Ca[Ca(OH)$_6$]$_2$, whereas S10 (paddy soil) is undersaturated (Fig. 4). Thus, it is likely that Ca[Ca(OH)$_6$]$_2$ precipitation occurs in the Xikuangshan soil system. Other possible Sb mineral phases in soil include Sb$_2$O$_3$ (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 stibonite (Sb$^{11+}$Sb$^{5+}$O$_6$OH) and lewisite (Ca$_2$Na$_2$Sb$^{11+}$Sb$^{5+}$O$_6$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 Ca[Ca(OH)$_6$]$_2$, while Sb(III) is present in minor proportion in the soils, possibly occurring as Sb$_2$S$_3$, 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 considerably higher compared to previously

<table>
<thead>
<tr>
<th>Soil sample ID</th>
<th>Plant sample</th>
<th>Sb(II) mg kg$^{-1}$</th>
<th>Sb(V) mg kg$^{-1}$</th>
<th>Sb(III) mg kg$^{-1}$</th>
<th>Citric acid extracted Sb mg kg$^{-1}$</th>
<th>Total Sb (digested) mg kg$^{-1}$</th>
<th>Sb(V) mg kg$^{-1}$</th>
<th>Citric acid extractable Sb mg kg$^{-1}$</th>
<th>Bioaccumulation factor (BAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Phytolacca acinosa Roxb</td>
<td>4.2</td>
<td>0.2</td>
<td>50.8</td>
<td>1.9</td>
<td>55.0</td>
<td>1.8</td>
<td>190</td>
<td>0.18</td>
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<tr>
<td>S2</td>
<td>Boehmeria nivea</td>
<td>27.0</td>
<td>0.8</td>
<td>506.7</td>
<td>45.1</td>
<td>524.7</td>
<td>29.5</td>
<td>4029</td>
<td>13.0</td>
</tr>
<tr>
<td>S3</td>
<td>Miscanthus floridulus</td>
<td>37.3</td>
<td>1.7</td>
<td>97.3</td>
<td>3.3</td>
<td>134.6</td>
<td>4.8</td>
<td>683</td>
<td>19.7</td>
</tr>
<tr>
<td>S4</td>
<td>Eremochloa ophiroides (Munro) Hack.</td>
<td>1.1</td>
<td>0.1</td>
<td>20.1</td>
<td>0.4</td>
<td>21.2</td>
<td>0.5</td>
<td>128</td>
<td>64</td>
</tr>
<tr>
<td>S5</td>
<td>Lactuca tatarica (L.) C.A.Mey</td>
<td>16.7</td>
<td>1.4</td>
<td>188.4</td>
<td>6.8</td>
<td>205.1</td>
<td>8.1</td>
<td>357</td>
<td>142</td>
</tr>
<tr>
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<td>Leersia hexandra Swartz</td>
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<td>0.2</td>
<td>73.3</td>
<td>2.4</td>
<td>88.3</td>
<td>2.6</td>
<td>292</td>
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<tr>
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<td>Hygropyza aristata (Retz.) Nees</td>
<td>3.6</td>
<td>0.2</td>
<td>55.2</td>
<td>2.3</td>
<td>58.9</td>
<td>2.5</td>
<td>109</td>
<td>22</td>
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<tr>
<td>S8</td>
<td>Phytolacca acinosa Roxb</td>
<td>0.95</td>
<td>0.01</td>
<td>14.8</td>
<td>0.8</td>
<td>15.5</td>
<td>1.3</td>
<td>314</td>
<td>49</td>
</tr>
<tr>
<td>S9</td>
<td>Comynya canadensis (L.) Cronq.</td>
<td>0.05</td>
<td>0.03</td>
<td>2.50</td>
<td>0.03</td>
<td>2.55</td>
<td>0.05</td>
<td>461</td>
<td>87</td>
</tr>
<tr>
<td>S10</td>
<td>Comynya canadensis (L.) Cronq.</td>
<td>0.05</td>
<td>0.03</td>
<td>2.50</td>
<td>0.03</td>
<td>2.55</td>
<td>0.05</td>
<td>461</td>
<td>87</td>
</tr>
</tbody>
</table>

**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 %.

**Fig. 3**: Percentage of Sb(III) and Sb(V) in plant extracts from citric acid extraction. Concentrations are shown in Table 6.
reported values from abandoned Sb mining areas (Tschan et al., 2009a), suggesting higher Sb bioavailability and bioaccumulation in the Xikuangshan active Sb mining area. Comynza 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 $6 \text{mg/kg}$ 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.
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References