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Antimony in the Soil-Plant System in an Sb Mining/Smelting Area of Southwest China

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The distribution, bioavailability, and accumulation of antimony (Sb) at the interface of rhizospheric soils and indigenous plants from a large Sb mining/smelting area in Southwest China were explored. Results showed that the local soil was severely polluted by Sb, and the aluminum magnesium silicate minerals and the carbonate fraction may mainly contribute to bound Sb. The sequential extraction results of soil samples revealed that the portion of bioavailable Sb was low, but the bioavailable Sb concentration was up to 67.2 mg/kg, due to high total Sb concentrations in the soil. The Sb content in local plants showed a wide range, from 21 to 21148 mg/kg. The species of *Chenopodium album* Linn., *Sedum emarginatum* Migo, and *Sedum lineare* Thunb showed high accumulation of Sb at levels of above 1000 mg/kg. The Sb contents in the tissues for most plants decreased with the order of root > leaf > stem. The bioaccumulation coefficients and/or the biological transfer factors for most plants were less than 1. All of the studied plant species were not identified as Sb-hyperaccumulators, but the species of *Chenopodium emarginatum* Migo, and Sedum lineare Thunb could be applied as alternative plants for phytoremediating Sb-polluted soils.

Keywords: antimony, soil, plant, phytoremediation, mine area

Introduction

Antimony (Sb), a non-essential and toxic heavy metal that is detrimental to plants, is classified as one of the 13 priority pollutant metals (Keith and Telliard 1979). Although widely distributed in the natural environment, Sb content in soil is generally on the order of a few mg/kg. The average Sb concentration in soil is around 1 mg/kg globally (Filella, Belzile, and Chen 2002), 1.06 mg/kg in Chinese soil (0.38-2.98 mg/kg) (Qi and Cao 1991), and 0.3-8.4 mg/kg in Dutch soil (Crommentuijn et al. 2000). However, elevated Sb in soil is observed in many areas of the world. For instance, Sb content is 1489 mg/kg in soil close to an Sb smelter in England (Ainsworth, Cooke and Johnson 1990), 700 mg/kg in soil around five discarded As, Cu, Pb, Zn and Sb mining and smelting areas throughout Britain (Flynn et al. 2003), and 101-5045 mg/kg in soil in the Xikuangshan Sb mine area in South China (He 2007). This elevated Sb content in soil is mainly of anthropogenic (i.e., mining, processing, and smelting) origin, and may contribute to accumulation of Sb in plants of the contaminated sites. For instance, higher content of Sb (267-1136 mg/kg) is observed in certain plants from the polluted Sb-mining areas in Spain (Murciego *et al.* 2007), and 1105–1367 mg/kg in plants from a former Sb-mining area in Italy (Baroni *et al.* 2000). The Sb-accumulated plants may serve as bio-indicators and phytoremediation to soil polluted by Sb.

China possesses the major mineral resource and industrial production of Sb in the world (He et al. 2012). Due to intensive Sb mining and smelting processes, large quantities of Sb mine/smelting wastes composed of barren rocks, tailings, and slags have been disposed in the local environments, and may cause serious Sb contamination and potential health effects (Wu et al. 2011). The native wild plants widely growing in the mining/smelting sites may provide clues to bio-monitor the mobility, migration, and accumulation of Sb throughout the soil-plant system. However, very few studies have targeted Sb mobility in soil-wild plant systems in Sb mining/smelting sites. The Sb content in wild plants from an Sb mine area in South China is reported from 3.92 to 143.7 mg/kg (Qi et al. 2011). Comparably, our preliminary study in an Sb mining/smelting area in Southwest China has observed much higher Sb content in local wild plants, i.e., 1–3 orders of magnitude higher than the reported values from Qi et al. (2011), which may correspond to high Sb content in local soil of karst terrain (Ning 2009).

Therefore, it is appropriate to conduct a follow-up study to further understand the mobility, migration, and accumulation of Sb through the soil-plant system in an Sb mining/smelting area in Southwest China. This study aims to investigate Sb distribution and bioavailability in soil, and bioaccumulation in various wild plants dominating the local mine dumps. The

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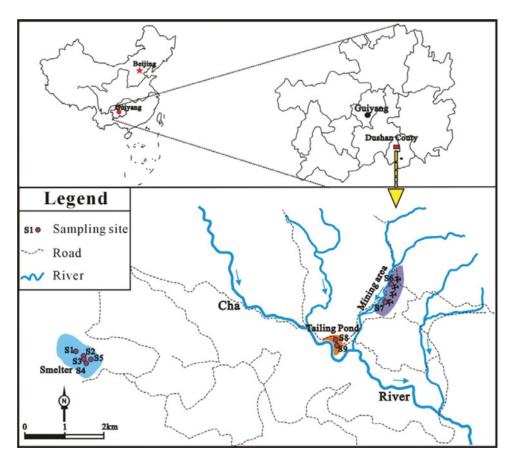


Fig. 1. Map showing the sampling sites.

findings would be significant for potential applications of autochthonous vegetation species for bio-monitoring or phytoremediating for Sb pollution.

Materials and Methods

Study Area

The study area of Banpo Sb Mine is located in Dushan County (107°30'–107°45'E, 25°40'–25°50'N) of south Guizhou Province, Southwest China. The Banpo Sb deposit is of clastic rock type, hosted by deep seated faults and fractures. The local strata are composed of arenites and quartz-zrenites, interbedded with sandy shale and dolomite, and intercalated limestone and silicarenite, gerruginous sandstone or oolitic hematite beds of the lower Devonian (Wu 1993). The main ore-bearing bed is a grey, thickly bedded, fine-grained quartzite of early Devonian age, unconformably overlying Silurian strata. The main wall rock alterations are silicification, calcilization, baritization, sericitization, arglillization, and carbonization. The main ore mineral is stibnite. The gangue minerals are mainly composed of pyrite, quartz, calcite, and dolomite.

The mine has been in operation for more than one century, and the current production is up to 3000 tons of refined Sb per year. Sb from the mine wastes presents a severe environmental problem. The sub-tropical continental monsoon climate is warm and humid with an annual precipitation of 1346 mm, with maximum precipitation occurring in July and August. The annual average temperature is $15 \,^{\circ}$ C.

Sample Collection and Treatment

A total of nine soil and 30 plant samples were collected at nine sites from the local mining, milling, and smelting areas (Fig. 1). At each site, the dominating wild plants and rhizospheric soil were sampled.

The soil samples were kept in polyethylene bags and airdried in the laboratory pending final processing. The soil was processed for geochemical analysis by disaggregation to pass through a 2-mm sieve. The sieved fractions were then ground in a Bico ceramic disc grinder followed by reduction to 200mesh ($<74 \mu m$) powder in a ceramic ball mill.

The collected fresh plant samples colonizing the waste rocks, tailings, slags, and polluted soil were partitioned into root and aboveground biomass on site. The aboveground biomasses were divided into two groups, one was preserved as a whole, and the other was further separated into leaf, stem, flower or fruit, if applicable. All of the plant materials were then cleaned using Milli-Q water (18.2 M Ω ·cm) to exclude any Sb contamination from dust or soil particles on the plants, and then air dried in labeled paper bags. All of the plant materials were crushed using a crushing machine (FZ102, TAISITE, China) into fragments capable of passing thorough a 60-mesh sieve for geochemical analysis. Species identification for plant samples was performed at Guizhou Normal University.

Soil and Plant Analyses

The soil pH was measured after suspending the soil in deionized water in a ratio of 1:2 (m/v) using a pH meter (AISI pHB9901, Taiwan, China). The cation exchange capacity (CEC) was computed after saturation of soil samples with 0.005 M EDTA, 1 M ammonium acetate mixture, and a standard titration solution of ammonia acid. Soil organic carbon (SOC) was determined by the Walkley Black method (Nelson and Sommers 1982). The mineral compositions of selected soil samples were determined by X-ray diffraction (XRD, D/Max-2200, Japan).

Approximately 50 mg of the sieved soil powder (< 74 μ m) was digested using a heated acid mixture (15 mL of 15 M HNO₃ and 5 mL of 10 M HF) to determine Sb. Additionally, 100 mg of the powdered plant samples were digested with a 10-mL mixture of strong acids (8 mL of 15 M HNO₃ and 2 mL of 10 M HF) for Sb determination. Milli-Q water (18.2 M Ω cm) was used for all experiments, and the reagents used were of super pure grades.

The content of Fe, Al, Mn, K, Mg, Ca, and Na in soil was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP6500, Thermo Scientific, Germany). The concentrations of Sb in soil and plants were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer, ELAN DRC-e, USA) (Qi, Hu, and Conrad 2000). The detection limit is calculated as the average of ten times the standard deviation of the ion counts obtained from the individual procedural reagent blanks (prepared in the same way as the sample decomposition), divided by the sensitivity of standard solution. The detection limit for Sb was 0.1 mg/kg, which is substantially lower than the Sb content in this study. The analytical precision, determined based on the standard quality control procedures using internationally certified reference materials (OU-6, AMH-1, and GBPG-1), internal standards (Rh at 500 μ g/L), and duplicates, was better than \pm 10%. The standard reference material GBW07405 (China National Research Center of CRM's soil) was used for analytical quality control. The average total Sb concentration of the GBW07405 was $37 \pm 6 \text{ mg/kg}$ (n = 6), which is comparable to the certified value of $35 \pm 7 \text{ mg/kg}$. The relative percentage differences of sample replicates for soil and plants were <10% (n = 3) and <6% (n = 3), respectively. The determined data for plants were reported as dry weight (DW).

Sequential Extraction Procedures

The full protocol for sequential extraction of Sb in three selected soil samples (S1, S6, and S8) was performed in accordance with the modified Tessier's procedure (Tessier, Campbell, and Bisson 1979), and consisted of the exchangeable fraction (1 mol/L MgCl₂, pH 7), carbonates fraction (1 mol/L, NaOAc/HAc, pH 5), Fe-Mn oxides fraction (0.4 mol/L, NH₂OH·HCl in 25% HAc), organic matter and/or sulfides fraction (0.02 mol/L, HNO₃ in 30% H₂O₂, pH 2, 3.2 mol/L NH₄OAc in 20% HNO₃), and residual fraction (15 mL of 15 M HNO₃ and 5 mL of 10 M HF). The exchangeable fraction provides information concerning the bioavailable Sb in the soil. The soil sample S8 was analyzed in triplicate in order to assess the uncertainty of the extraction procedure for Sb determination, and the coefficients of variation (CVs) were 4.0%, 2.8%, 3.2%, 6.4%, and 3.4% for all of the five sequential extraction fractions (steps 1 to 5), respectively. To evaluate the intensity of experimental contamination, blank experiments were performed under the same conditions, and the results suggested that no significant Sb contamination was introduced during the sequential extraction. The recovery of Sb was determined by comparing the amount of Sb extracted with the total amount indicated by its total digestion concentration: (sum/total) \times 100%. In this study, the recovery rate of Sb was found to be within the range of 88–105%.

Results and Discussion

Soil Characteristics and Trace Elements in Rhizospheric Soil

The results of the chemical analyses were listed in Table 1. All soil samples were neutral or near neutral, exhibiting pH from 6.3 to 7.4. Samples collected from sites S1, S2, S6, S8, and S9 had low content of SOC (0.35-0.93%); whereas, there was relatively higher SOC content (3.16-14.5%) at sites S3, S4, S5, and S7. The higher SOC content in the soil responded to dense vegetation coverage with higher biomasses and dense plant root systems. Soil samples yielded CEC values ranging from 0.22 to 2.31 cmol/kg (mean at 1.14 cmol/kg). The concentrations of Al, Fe, Mn, Mg, Ca, Na, and K were 18.2-74.3 g/kg, 6.43-98.7 g/kg, 28.8-4260 mg/kg, 2.35-36.1 g/kg, 8-77.4 g/kg, 1.11-23.0 g/kg, and 5.31–25.3 g/kg, respectively. The major element compositions in soil reflect the origin of parent rocks (Ning 2009). The XRD results for soil samples showed similar mineralogical compositions, composed of quartz, stibnite, montmoduonite, illtite, gaolinite, calcite, goethite, and some iron-bearing minerals.

The content of trace elements in soil was also listed in Table 1. The total Sb content in nine soil samples ranged from 267 to 5633 mg/kg, with an average of 1732 mg/kg. Especially, elevated Sb concentration in soil near calcinatory was as high as 5633 mg/kg, which is much higher than the maximum permissible pollutant concentration of Sb (36 mg/kg) in receiving soil (WHO 1996). Sb content has been observed to gradually decrease with soil depth at Sb mining/smelting sites (Ning 2009), which suggested atmospheric wet and/or dry depositions from the mining/smelting activities. In contrast, the concentrations of As, Co, Ba, Tl, and Pb were 0.6–54.7 mg/kg, 0.1–5.6 mg/kg, 272–966 mg/kg, 0.1–21.3 mg/kg and 3.9–28.1 mg/kg, respectively, and showed no significant pollution in local soils.

Geochemical Fractionation of Sb in Rhizospheric Soil

The results for geochemical partitioning of Sb based on Tessier's sequential extraction for three selected soil samples

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			CEC	SOC	Sb	As	C	Ba	F	Pb		Fe	Mn	Mg	Ca	Na	R
Site	Site Site description pH (cmol/kg)	Hd	(cmol/kg)	(%)	(%) (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(g/kg)	(g/kg)	(mg/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
S1	Smelting site	na	0.22	0.35	733	22.1	3	908	0.1	pu	18.2	16.4	232	3.02	11.2	2.67	6.72
S2	Smelting site	7.3	0.34	0.47	764	17.7	2.8	996	21.3	pu	16.5	7.55	155	5.25	18.2	2.52	6.39
S3	Smelting site	6.3	na	7.2	1657	0.6	3.3	351	0.4	7.9	57.4	98.7	465	4.22	65.3	13.3	5.31
$\mathbf{S4}$	Smelting site	7.1	2.31	3.2	5536	7.5	1.1	468	0.3	19.3	69.5	42	697	36.1	157	23	10.5
S5	Smelting site	6.6	na	14.5	3139	13.1	2.4	578	0.6	18	74.3	59.2	4260	12.5	77.4	5.49	5.31
S6	Waste rock pile	na	1.65	0.93	2666	54.7	5.6	893	0.5	pu	44.8	28.7	77.4	5.25	9.08	3.41	25.3
$\mathbf{S7}$	Waste rock pile	6.9	na	3.2	466	pu	0.8	291	0.2	9	18.2	15.1	232	2.41	9.36	1.11	6.56
$\mathbf{S8}$	Tailing pond	6.4	1.19	0.41	2705	20.7	4.2	554	3.53	28.1	33.2	11.8	28.8	5.42	26.2	4.93	10.9
S9	Tailing pond	7.4	na	0.5	267	nd	0.1	272	0	3.9	18.3	6.43	77.4	2.35	8	1.63	7.06
na: nc nd: nc	na: not analyzed nd: not detectable																

Table 1. Characteristics of rhizospheric soil and selected element contents in rhizospheric soil

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Table 2. Sb concentration in different fractions by sequential extraction (mg/kg)

					S 8	
Fraction	S 1	S 6	S 8(1)	S8(2)	S8(3)	$S8(mean \pm SD)$
T1	10.8	3.9	67.9	63.2	70.5	67.2 ± 3.7
T2	26.4	9.3	298	276	284	286 ± 11.1
T3	28.5	21.1	70.4	74.5	68.3	71.1 ± 3.2
T4	59	26.4	33.2	40.1	36.4	36.6 ± 3.5
T5	703.5	2470	2393	2170	2297	2287 ± 111.9
Sum	828	2530	2862	2623	2756	2747 ± 119.8
Recovery	88.5%	105.4%	94.5%	103.1%	98.1%	$98.5\% \pm 4.3\%$

T1: exchangeable fraction; T2: bound to carbonates fraction; T3: bound to poorly crystallized Fe-Mn oxides fraction; T4: bound to organic matter and/or sulfides fraction; T5: residual fraction.

(S1, S6, and S8) were listed in Table 2. Concentrations of Sb in various fractions in soil (S1 and S6) followed the order of residual fraction (85-97.6%, T5) > organic matter and sulfide fraction (1.04-7.13%, T4) > bound to Fe-Mn oxide fraction (0.83-3.44%, T3) > bound to carbonate fraction (0.37-3.19%, T2) > exchangeable fraction (0.15-1.3%) (Fig. 2). However, the soil at site S8 showed a different geochemical fraction pattern of residual fraction (83.2%) > bound to carbonate fraction (2.59%) > exchangeable fraction (2.45%) > organic matter and sulfide fraction (1.34%). This difference may result from some chemical reagents, such as lime and xanthate, applied during ore-processing, and elevated Sb content in the carbonate fraction in soil at site S8 impacted by ore-processing byproduct of tailings.

Overall, the majority of Sb (83.2–97.6%) was found to exit predominantly in the residual fraction in soil. The XRD results showed that the local soil (including samples taken from the tailing pond at S8 and S9) had very similar mineralog-

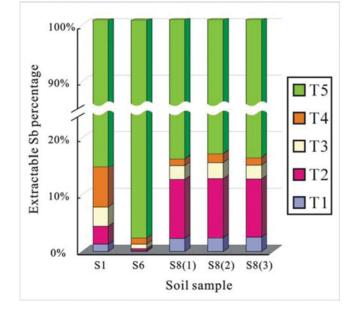


Fig. 2. The sequential extraction fractions of Sb in soil. T1: exchangeable fraction; T2: bound to carbonates fraction; T3: bound to poorly crystallized Fe-Mn oxides fraction; T4: bound to organic matter and/or sulfides fraction; T5: residual fraction.

ical compositions, mainly composed of quartz, stibnite and clay minerals, including montmorillonite, illite, kaolinite, calcite and goethite, and implied that Sb was mainly bound in the silicate minerals of soil. There was a significant positive correlation between total Sb and CEC (r = 0.961, p < 0.01) in the rhizospheric soil, but no similar correlation was found for Sb vs. SOM (Table 3). Generally, CEC is controlled by soil organic matter and clay minerals. Thus, it is deduced that the clay minerals would be an important factor that manages Sb in local soils. Furthermore, clay minerals were composed

Table 3. Pearson correlation coefficients among metals, pH, CEC, and SOC in soil

	pН	CEC	SOC	Sb	As	Со	Ва	Tl	Pb	Al	Fe	Mn	Mg	Ca	Na	K
pН	1															
CEC	2 - 0.18	1														
SOC	-0.511	0.825	1													
Sb	-0.252	0.961**	0.305	1												
As	0.27	0.047	-0.424	-0.116	1											
Со	-0.706	-0.115	-0.086	0.156	0.779*	1										
Ba	0.187 -	-0.724	-0.265	-0.012	0.664	0.634	1									
T1	0.399 -	-0.508	-0.254	-0.233	-0.038	0.115	0.523	1								
Pb	-0.437 -	-1.000^{**}	0.04	0.706	0.942	0.651	0.911*	0.8	1							
Al	-0.51	0.980**	0.736*	0.824*	* -0.311	0.137 -	-0.173	-0.356	0.411	1						
Fe	-0.667	0.869	0.707^{*}	0.352	-0.503	0.158 -	-0.28	-0.321	-0.078	0.759*	1					
Mn	-0.299	0.546	0.918**	0.34	-0.261	-0.091 -	-0.056	-0.161	0.213	0.655	0.426	1				
Mg	0.118	0.767	0.208	0.883*	* -0.329	-0.243 -	-0.104	-0.124	0.417	0.665	0.226	0.259	1			
Ca	-0.153	0.735	0.451	0.852*	* -0.588	-0.231 -	-0.252	-0.192	0.375	0.815**	0.536	0.396	0.931**	1		
Na	-0.19	0.781	0.228	0.794*	-0.548	-0.12 -	-0.258	-0.212	0.285	0.717*	0.571	0.093	0.859**	0.936**	1	
Κ	0.032	0.524	-0.337	0.322	0.882**	* 0.636	0.381	-0.153	0.683	0.109	-0.15	-0.275	0.057	-0.132	-0.022	21

**Correlation (two-tailed) is significant at p < 0.01 level

*Correlation (two-tailed) is significant at p < 0.05 level

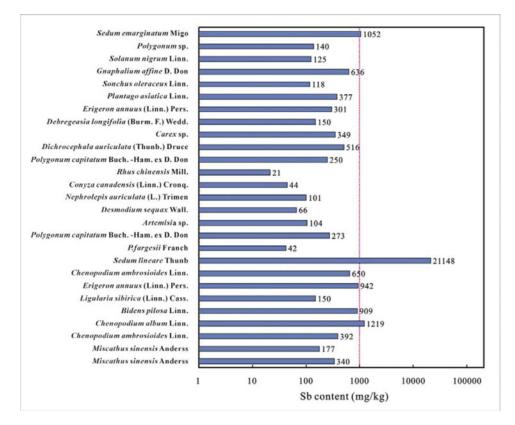


Fig. 3. Total Sb concentrations in plants.

of aluminium magnesium silicate minerals, and interestingly, a significantly positive correlation between Sb and Al (r = 0.824, p < 0.01), and Mg (r = 0.883, p < 0.01) was observed in local soil (Table 3).

Although previous studies have indicated that Fe oxides (Tighe, Lockwood, and Wilson 2005; Muller *et al.* 2007) and organic matter (Tighe *et al.* 2005; Van Vleek, Amarasiriwardena, and Xing 2011) could play important roles in bounding Sb in soil, the effect of Fe oxide and organic matter on bounding Sb was quite limited in this study, in which lower Sb concentrations ranged from 21.1–71.0 mg/kg and 26.4–36.6 mg/kg, respectively. A significant correlation was also observed between total Sb and Ca (r = 0.882, p < 0.01) in local soils (Table 3), which may suggest that carbonate is an important carrier to bind Sb in local soil.

The Sb concentrations in the exchangeable fraction varied from 3.9 to 67.2 mg/kg, which indicated high amounts of bioavailable Sb in rhizospheric soil. Generally, the total Sb contents in plant do not significantly correlate with those in soils, but they may positively correlate with the exchangeable Sb contents in soils, because plants tend to easily uptake the soluble or exchangeable Sb from soils (Baroni *et al.* 2000). He *et al.* (2007) also reports that Sb in the leaves of radish is positively correlated with Sb in soil. Although the portion of bioavailable Sb was only 0.15-2.45% of the total Sb in rhizospheric soil, the elevated Sb concentrations in the contaminated soil still resulted in elevated bioavailable Sb that may imply for high potential of uptake and accumulation by plants.

Bioaccumulation of Sb in Wild Plants

The Sb concentrations from a total of 30 wild plants in 27 species colonizing the waste rocks, tailings, waste residues, and polluted soils in the mining/smelting sites were presented in Fig. 3. Large variations of Sb contents in local wild plants were observed, ranging from 21 mg/kg in Rhus Chinensis Mill. to 21148 mg/kg in Sedum lineare Thunb. High Sb concentrations were also observed in species of Sedum emarginatum Migo (1052 mg/kg) and *Chenopodium album* Linn. (1219 mg/kg). These elevated Sb levels in the local plants suggested that plants growing on intensively contaminated soils with Sb tended to accumulate high amounts of Sb. The Sb contents in the local wild plants were remarkably higher than those (5.97–98.23 mg/kg) reported from other Sb mine areas in China (Qi et al. 2011), which may suggest a phytoavailability difference for Sb by plants, and/or the contents of coexisting ions, such as phosphorus and calcium, in soil (Biver, Krachler, and Shotyk 2011; Feng et al. 2013).

Antimony is non-essential to plant, and generally present in small amounts in plant. The background Sb content in terrestrial vascular plants generally ranges from 0.2 to 50 μ g/kg (Murciego *et al.* 2007). However, the Sb contents in the local wild plants were three orders of magnitude higher than the background values. Eikamann and Kloke (1993) report that 5 mg/kg Sb is a tolerable concentration in plants; whereas, the concentration of 150 mg/kg in mature leaves has been considered phytotoxic (Kabata-Pendias and Pendias 1984). However, no phytotoxic phenomenon exited in the investigated plants, even when Sb was up to 21,148 mg/kg in *Sedum lineare* Thunb

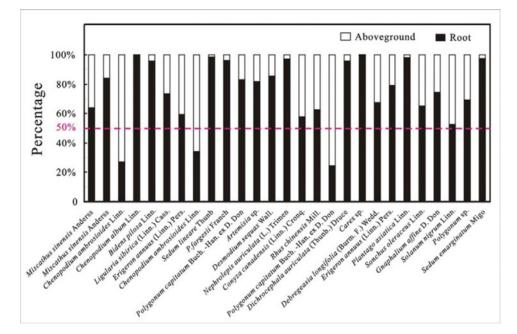


Fig. 4. Mass percentage cumulus histogram of Sb in aboveground part and root of plant.

in the study area. This implied that certain plants may have high phyto-tolerance to elevated Sb from contaminated soils.

The bioaccumulation of Sb in different parts of individual plant also varied widely. The Sb contents in roots were commonly higher than those in aboveground tissues, except for *Chenopodium ambrosicides* Linn. and *Polygonum capitatum* Buch. -Han. ex D. Don (Fig. 4). For most local plants, the Sb concentrations in plant tissues of aboveground parts showed the order of leaf > stem, which suggested that Sb tends to be transferred to upward tissues in aboveground parts of these plants, and stems may act as a transfer channel for Sb. Reproductive organs, such as flowers or fruits, may accumulate Sb to some extent, up to tens of mg/kg.

The species of *Sedum lineare* Thunb was found to strongly accumulate Sb in roots, with extremely elevated Sb of up to 23522 mg/kg. The Sb contents in roots of another four species, *Bidens pilosa* Linn., *Erigeron annuus* (Linn.) Pers., *Sedum emarginatum* Migo, and *Chenopodium album* Linn. were also observed to contain high levels of Sb at 909 mg/kg, 942 mg/kg, 1052 mg/kg, and 1219 mg/kg, respectively.

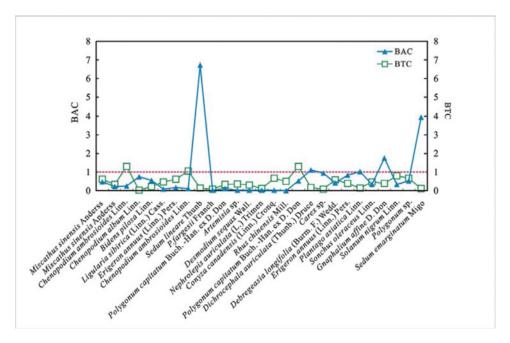


Fig. 5. Biological accumulation coefficient (BAC) and biological transfer coefficient (BTC) of different plants.

In aboveground tissues of the abovementioned plants, only *Sedum lineare* Thunb was observed to uptake high Sb at 3092 mg/kg.

The biological accumulation coefficient (BAC: total Sb concentration in plants to Sb in *rhizospheric* soil) was utilized to estimate the accumulation extent of Sb in different species of plants (Fig. 5). Most BACs of all of the plants were below 1, except for Sedum emarginatum Migo, Plantago asiatica Linn., Sedum lineare Thunb, Gnaphalium affine D. Don, and Dichrocephala auriculata (Thunb.) Druce, which had BACs at 3.9, 1.0, 6.7, 1.7, and 1.1, respectively. To estimate Sb transfer in plant tissues, the biological transfer coefficient (BTC: Sb concentration in aboveground tissues to Sb in underground tissues) was also calculated (Fig. 5). Almost all of the BTCs of the investigated plants were below 1; only the BTCs of *Chenopodium* ambrosioides Linn. (at sites S3 and S4) and Polygonum capitatum Buch. -Han. Ex D. Don were relatively higher, up to 1.3 (site S3), 1.1 (site S4), and 1.3, respectively. According to the definition of hyperaccumulator (Kramer 2010), concentrations of heavy metals must be higher than a designated value, and both BAC and BTC were higher than 1. Since the geochemical activity of Sb is similar to As, Murciego et al. (2007) recommend 1000 mg/kg as the threshold level of Sb for Sb-hyperaccumulator. To date, only a few plants, such as Achillea ageratum, Plantago lancelolata, Silene vugaris (Baroni et al. 2000), Dittrichiaviscose (Murciego et al. 2007), and Pteris cretica L. (Feng et al. 2011) have been identified to be potential Sb-hyperaccumulators. In this study, although some plants were found to strongly accumulate Sb, BACs and/or BTCs were lower than 1. Therefore, none of the investigated plants in this study were recognized as Sb hyperaccumulators. However, most wild plants had strong tolerance to high levels of Sb, especially Chenopodium album Linn., Sedum emarginatum Migo and Sedum lineare Thunb, which could be applied as alternative plants for phytoremediating Sb-polluted soil, and even be applied in industrial phytomining.

Conclusions

This study revealed the capacity of Sb transfer at the rhizospheric soil-plant system at Sb mining/smelting sites. In the rhizospheric soil, the majority of Sb was observed in the residual fraction bound to the silicate minerals, and the carbonate fraction may also contribute to bound Sb. Although there was a relatively low portion of bioavailable Sb, the bioavailable Sb content may reach up to 67.2 mg/kg due to high total Sb content in rhizospheric soil. For most indigenous plants, the distribution pattern of Sb concentration in plant tissues followed a descending order of root > leaf > stem. None of the investigated plants species in this study were recognized as Sb-hyperaccumulators, but certain plants had high phytotolerance to elevated Sb and can also highly accumulate Sb, up to thousands of mg/kg, such as *Chenopodium album* Linn., Sedum emarginatum Migo, and Sedum lineare Thunb. Thus, these specific plants could be applied as alternative plants for phytoremediating Sb-polluted soil, and even be applied in industrial phytomining.

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