

## Distribution and phytoavailability of antimony at an antimony mining and smelting area, Hunan, China

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Received: 19 January 2006 / Accepted: 30 October 2006 / Published online: 10 March 2007  
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**Abstract** An investigation of the distribution, fractionation and phytoavailability of antimony (Sb) and other heavy metals in soil sampled at various locations in the vicinity of a Sb mine revealed elevated levels of Sb, most certainly due to the mining activities. The concentration of Sb in the soil samples was 100.6–5045 mg kg<sup>-1</sup>; in comparison, the maximum permissible concentration for Sb in soil in The Netherlands is 3.5 mg kg<sup>-1</sup>, and the maximum permissible concentration of pollutant Sb in receiving soils recommended by the World Health Organization is 36 mg kg<sup>-1</sup>. The soil sampled near the Sb mine areas had also contained high concentrations of As and Hg. Root and leaf samples from plants growing in the Sb mine area contained high concentrations of Sb, with the concentration of Sb in the leaves of radish positively correlating with Sb concentrations in soil. The distribution of Sb in the soil showed the following order: strongly bound to the crystalline matrix > adsorbed on Fe/Mn hydrous oxides, complexed to organic/sulfides, bound to carbonates > weakly bound and soluble. Solvents showed varying levels of effectiveness in extracting Sb (based on concentration) from the soil, with

Sb<sub>NH<sub>4</sub>NO<sub>3</sub></sub> > Sb<sub>EDTA</sub> > Sb<sub>HAc</sub>, Sb<sub>H<sub>2</sub>O</sub> > Sb<sub>NH<sub>4</sub>OAc</sub>, in decreasing order. The concentration of easily phytoavailable Sb was high and varied from 2.5 to 13.2 mg kg<sup>-1</sup>, the percentage of moderately phytoavailable Sb ranged from 1.62 to 8.26%, and the not phytoavailable fraction represented 88.2–97.9% of total Sb in soils.

**Keywords** Antimony mine area · Antimony pollution · Phytoavailability · Soil · Speciation

### Introduction

Antimony (Sb) is a toxic element that is found throughout the environment. This trace element has an estimated average abundance of 0.2 mg kg<sup>-1</sup> in the earth's crust (Smith and Huyck 1999) and background concentrations in soils of <0.3–8.4 mg kg<sup>-1</sup> (Crommentujin et al. 2000). Antimony background concentrations in Chinese soils vary between 0.8 and 3.0 mg kg<sup>-1</sup> (Qi and Cao 1991), with surface soils tending to be enriched with Sb (Kabata-Pendias and Pendias 1985). Much concern has been expressed regarding increasing levels of Sb pollution into the environment, primarily due to anthropogenic activities and the extensive use of Sb compounds. The important anthropogenic sources of Sb in soils are emissions – from vehicles, smelters and the burning of municipal waste (Dietl 1997;

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Fowler and Goering 1991; Shotyk et al. 2005b). Agricultural soils may become polluted with Sb through wet and dry deposition, from mining, manufacturing and municipal discharges and through the addition of soil amendments such as chemical fertilizers, sewage sludge and fly-ash (Crecelius et al. 1974). Various studies have reported high concentrations of Sb in the soil, vegetation and herbivorous and insectivorous mammals at sites around an Sb smelter (Ainsworth et al. 1990a, b; De Gregori et al. 2003; Wilson et al. 2004).

Some Sb compounds are considered to be hazardous – or even carcinogenic – to human health (Fowler and Goering 1991; Gebel 1997). Although Sb is a non-essential element for plants, it can be readily taken up by the roots of plants from soils in a soil solution – i.e. when it is soluble – and as such has the potential to act as a significant plant contaminant in mining and industrial areas (Ainsworth et al. 1991). The toxicity of Sb to plants has been described as moderate, with phytotoxic levels of 5–10 mg kg<sup>-1</sup> in plant tissue being reported (Kabata-Pendias and Pendias 1985). Eikamann and Kloke (1993) reported that 5 mg Sb kg<sup>-1</sup> dry weight is a tolerable concentration, while Crommentuijn et al. (2000) suggested that 3.5 mg Sb kg<sup>-1</sup> was the maximum permissible concentration in their standard soil samples. Based on the Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture, the World Health Organization (WHO) suggests that the maximum permissible pollutant concentration for Sb in receiving soils is 36 mg kg<sup>-1</sup> (Chang et al. 2002). The toxicity and physiological behavior of Sb are expected to depend not only on its oxidation state (He and Yang 1999), but also on the presence of organic constituents bound to the metal (Iffland 1988).

In recent years Sb has attracted increasing attention from researchers, primarily due to its industrial applications, its toxicity to humans and the bioaccumulation of Sb in plants grown in areas of mining activities (Byrd 1990; De Gregori et al. 2004; Dietl 1997). Efforts have been directed towards methodology for its determination (Ji et al. 2003) and assessing its occurrence and geochemistry (Belzile et al. 2001; Filella et al.

2002a, b, 2003a, b; Shotyk et al. 2005a, b; Wagner et al. 2003). The identification of Sb speciation in fresh plant extracts (Dodd et al. 1996), the mobility (Ashley et al. 2003; Hammel et al. 2000) and speciation of Sb in soil and its availability to plants (Flynn et al. 2003; He and Wan 2004; Koch et al. 2000; Lintschinger et al. 1998; Picard and Bosco 2003), Sb(III) binding to humic substances (Buschmann and Sigg 2004) and the biomethylation of inorganic Sb compounds by an aerobic fungus (Jenkins et al. 1998) have been investigated. In May of 2005, the First International Workshop on Sb in the Environment was held in Germany (Shotyk et al. 2005a).

China is rich in Sb mineral resources. The Xikuangshan Sb mine, located near Lenshuijiang City, Hunan Province, China, is one of the largest Sb mines in the world, and has for a long time been designated rather descriptively the “World Antimony Capital”. It is believed that Sb pollution from this particular mine and from Sb mining activities in China in general is very severe, resulting in significant environmental problems in China (He et al. 1994; Yang 1992).

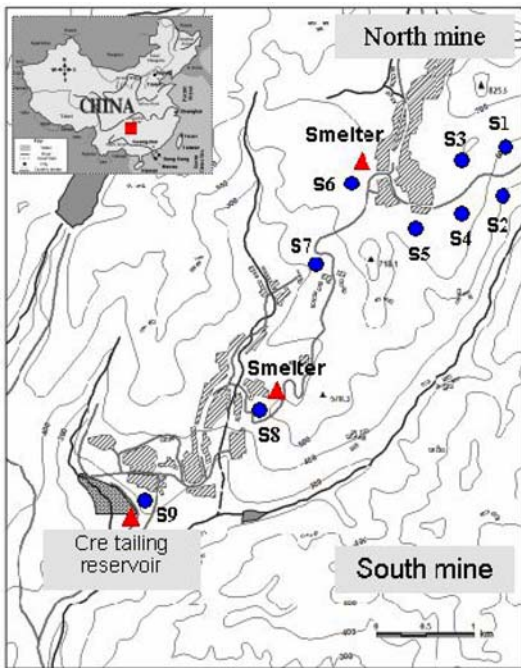
The main aims of this study were: (1) to investigate the distribution of Sb and accompanying elements near a Sb mine; (2) to analyze the fractionation of Sb in soils; (3) to assess the phytoavailability of Sb to plants.

## Material and methods

### Field sites and sample collection

The study area, Xikuangshan Sb mine and its surrounding area, is located between 27.7°N and 111.4°E near Lenshuijiang City, Hunan Province, in the southern part of China (Fig. 1). The Xikuangshan deposit covers an area of about 16 km<sup>2</sup> and follows the axis of a short anticline that strikes N30°E and plunges north and south. The deposit is located at the intersection between the NNE-trending Chengbu-Xinhua fault and the NW-trending Shuangfeng-Xikuangshan fault.

The Xikuangshan Sb deposit is hosted by dark-gray chert in the black shale series of the Upper Devonian Shetianqiao Formation. The deposit consists of the south mines and the north mines,



**Fig. 1** Research area and sampling scheme (located between 27.7°N and 111.4°E)

which are located on the east limb of the anticline. A 10-km-long lamprophyre dike is situated to the southeast. The mining area is composed of Devonian system that shows a rhythmic lithological combination of thick limestone, thin shale and/or sandstone (Shi et al. 1993).

Ore textures range from massive to disseminated, and from drusy to coarsely crystalline. Stibnite ( $Sb_2S_3$ ) is the only ore mineral. Trace amounts of pyrite, pyrrhotite and sphalerite occur in the ore along with the main primary gangue minerals, quartz and calcite, and secondary barite and fluorite. Ores can be divided into four types: quartz-stibnite, calcitestibnite, barite-quartz-stibnite and fluorite-quartz-stibnite. The first two types are economically the most important and occupy 90% of the total Sb reserves of the deposit. Stibnite occurs in the form of columnar and radiating aggregates distributed in a dark-gray chert (Fan et al. 2004). The ores are characterized by a very high content of Sb – 121,570-fold higher than the levels found in its continental crust (Taylor 1964; Taylor and McLennan 1985), 5930-fold higher than the levels

found in Devonian Ohio Shale (Kane et al. 1990) and 4863-fold higher than those found in average black shale (Yudovich and Ketris 1994).

The annual production capacity of the Xikuangshan Sb mine is 55,000 metric tons of ores, 40,000 metric tons of Sb products and 40,000 metric tons of zinc (Zn) ingots. The industrial applications of Sb are steadily increasing; in addition to the classical products of Sb ingots, Sb trioxide, Sb sulfide, etc., other products, such as sodium antimonate, dust-free antimony trioxide, antimony pentoxide, golden yellow antimony, antimony series flame-retardant master batch are also now being produced (<http://www.hksts.com/en/>).

The description of the sampling site is shown in Table 1. Site 1 (S-1) and Site 2 (S-2) were located at a 1-km distance from mine area; Site 3 (S-3), Site 4 (S-4) and Site 5 (S-5) were in the area of the North Sb mine; Site 6 (S-6) was near the alkali arsenic furnace residue, which contains high levels of sodium arsenate; Site 7 (S-7) was near smelting furnace residue containing sodium arsenate; Site 8 (S-8) was in the area of the South Sb mine and near the Sb smelter; Site 9 (S-9) was near the ore tailing reservoir that stores the tailing waste from the concentrating mill. Soil samples (0–20 cm from the surface) were collected with a stainless steel scoop and packed into aluminum boxes. Some radish plants growing in the soils were sampled (at least four individuals per sampling site). The radish plants are a popular vegetable (*Brassica campestris* L) in the research area; in the study period they were planted as normal in September and harvested in November (2000). Some ore-tailing particles of stibnite were collected from the Sb mine area. The perennial

**Table 1** Description of sampling site

Sample	Soil type	Site description
S-1	Paddy field	1 km away from mine area
S-2	Dry land	1 km away from mine area
S-3	Paddy field	In the antimony mine area
S-4	Dry land	In the antimony mine area
S-5	Dry land	In the antimony mine area
S-6	Dry land	Near alkali arsenic furnace residue
S-7	Dry land	Near smelting furnace residue
S-8	Dry land	Near antimony smelter
S-9	Dry land	Near ore tailing reservoir

prevailing wind direction is northeast, while in the summer the prevailing wind direction is south-east.

#### Sample preparation and analysis of soil properties

Soil samples were air-dried and sieved to pass a 2-mm mesh before analysis. Plant samples were thoroughly washed in tap water and then placed in an ultrasound bath to remove soil particles. This was followed by repeated rinses with acidified (HCl 3%) deionized water and a final rinse with double distilled water. Roots and leaves were separated, and dried at room temperature and then ground into fine powder.

Soil pH was determined in a 1:2.5 (w:v) soil:deionized water suspension that was stirred for 15 min. Carbonates, organic matter and cation exchange capacity (CEC) determinations were carried out following standard methods of Chinese Society of Soil Sciences (Chinese Society of Soil Sciences 2000). The range and mean values of the characteristics of topsoil samples are given in Table 2.

#### Analysis of Sb and other metals

Standards stock solutions of Sb(III) (1000 mg Sb l<sup>-1</sup>) were prepared by dissolving the appropriate amounts of potassium antimony tartrate and potassium pyroantimonate in water. Standard solutions of lower concentrations were prepared daily by making the appropriate dilution with water. All chemicals used for analysis were of analytical reagent or higher purity.

Total Sb concentrations in the soil samples, plants and soil extracts were obtained after digestion with HCl-HNO<sub>3</sub> (1:1, v/v); the Sb(V) in the sample digests and extracts was reduced to Sb(III) using KI (5%), and total Sb(III) determination was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (JY-Ultima, France). The measurements were calibrated using standards of similar chemical composition and corrected for blank values. The method was tested by the recovery of Sb. The detection limits of Sb were 0.63 ng ml<sup>-1</sup>, and the mean recovery rates were 94–108%. Standard

**Table 2** Properties of the studied soil sample

Sample	Soil texture	pH	Organic matter (%)	CEC <sup>a</sup> (cmol 100 g <sup>-1</sup> )
S-1	Clay loam	7.05	4.28	5.80
S-2	Loam soil	7.12	2.94	2.56
S-3	Clay loam	7.14	3.61	4.26
S-4	Clay loam	4.65	0.70	5.36
S-5	Loam soil	5.30	2.95	6.52
S-6	Clay loam	5.46	2.96	2.23
S-7	Loam soil	5.26	1.92	5.92
S-8	Clay loam	5.54	4.68	7.01
S-9	Loam soil	6.00	3.23	2.91

<sup>a</sup> CEC, Cation exchange capacity

reference plant (GBW07605), soil and water samples (manufactured by Chinese Academy of Environmental Science) were used to verify the quality of the analysis of the plants, soil samples and soil extracts.

#### Antimony fractionation in soils

The samples were extracted by a modified sequential extraction procedure for the fractionation of heavy metals (Tessier et al. 1979) after air-drying and passage through a 100-mesh nylon sieve. The method yields to six operationally-defined fractions: a water-soluble fraction (distilled water), a cation exchangeable fraction (1 mol l<sup>-1</sup> MgCl<sub>2</sub>, pH 7), a fraction bound to carbonates (1 mol l<sup>-1</sup>, NaOAc/HAc, pH 5), a fraction bound to poorly crystallized Fe-Mn oxides (0.4 mol l<sup>-1</sup>, NH<sub>2</sub>OH.HCl in 25% HAc), a fraction bound to organic matter and/or sulfides (0.02 mol l<sup>-1</sup>, HNO<sub>3</sub> in 30% H<sub>2</sub>O<sub>2</sub>, pH 2, 3.2 mol l<sup>-1</sup> NH<sub>4</sub>OAc in 20% HNO<sub>3</sub>) and a residual fraction (HNO<sub>3</sub>-HClO<sub>4</sub>-HF).

#### Assessment of the phytoavailability of Sb in soils

The availability of Sb in soils was evaluated by referring to related methods for the assessment of phytoavailability of heavy metals (Brun et al. 2000; DIN 19730 1997; Hammel et al. 2000). Four procedures commonly used to assess the availability of heavy metals in soil were used to extract the soil samples: leachability by water and determination of mobile trace elements in mineral soils

using an ammonium nitrate extraction [both recommended by the DIN (Deutsches Institut fuer Normung)]; from the plant available fraction, an EDTA extractant [recommended by the “Measurement and Testing Programme” of the European Community (formerly BCR)] and an  $\text{NH}_4\text{OAc}$  extractant (recommended by French standard NF X 31-108). The list below described the procedures in more detail.

1.  $\text{H}_2\text{O}$  extraction: 2 g of soil with 20 ml  $\text{H}_2\text{O}$  with gentle stirring for 2 h, followed by filtration;
2.  $\text{NH}_4\text{NO}_3$  extraction (DIN 19730 1997; Hammel et al. 2000): 20 g of soil with 50 ml 1 M  $\text{NH}_4\text{NO}_3$  for 2 h, followed by filtration;
3. EDTA extraction (French standard NF X 31-120; Afnor 1994): 7.5 g of soil was extracted with 50 ml of  $\text{Na}_2\text{-EDTA}$  0.01 M +  $\text{CH}_3\text{COONH}_4$  1 M for 2 h at  $20^\circ\text{C}$  with stirring, followed by filtration;
4.  $\text{NH}_4\text{OAc}$  extraction (French standard NF X 31-108; Afnor 1994): 10 g of soil was extracted with 200 ml of  $\text{CH}_3\text{COONH}_4$  1 M for 1 h at  $20^\circ\text{C}$  with stirring, followed by filtration.

## Results

### Pollution source analysis

The main sources of contamination at the studied locations are from ore tailing particles, smelter furnace clinkers, alkali arsenic smelting residues, wastewater and atmosphere deposition. Large amounts of ore tailing particles and ore-dressing residue are produced during the mineral separation and smelting processes. These ultimately contain high concentrations of Sb, As, and other heavy metals due to the weathering process. Table 3 shows the concentrations of metalloids and heavy metals in ore tailing particles. The concentrations of Sb and As in ore tailing particles were  $1291 \text{ mg kg}^{-1}$  and  $332.1 \text{ mg kg}^{-1}$ , respectively, and heavy metals such as Cr, Hg, Cu, Zn, Cd and Pb were also present. Only Hg is significantly anomalous (about  $100\times$  crystal abundance). The concentrations of Sb and As in the seepage water originating from leakage of the

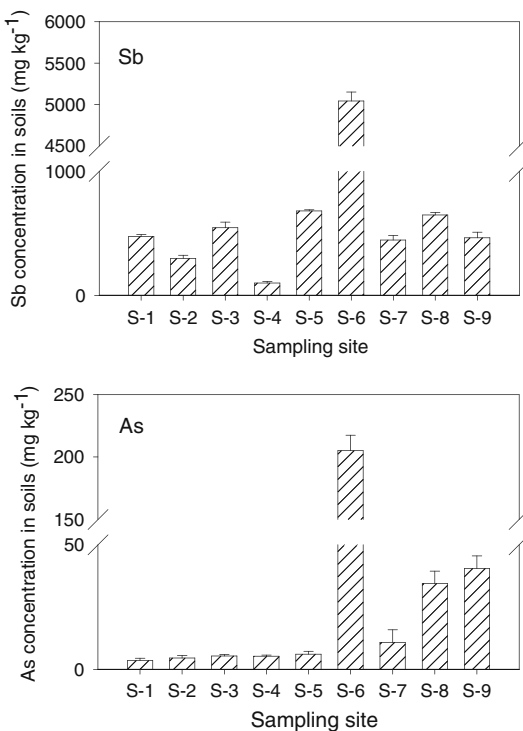
**Table 3** Distribution of Sb and other heavy metals in ore tailing particles ( $\text{mg kg}^{-1}$ )

Elements	Sb	As	Hg	Cr	Zn	Cd	Pb	Cu
Content	1291	332	4.59	46.4	12.4	0.3	16.2	9.1

smelter furnace clinker were very high and ranged between  $8.4$  and  $11.3 \text{ mg l}^{-1}$ , and between  $0.04$  and  $1.20 \text{ mg l}^{-1}$ , respectively. For the alkali arsenic smelting residues, the proportions of Sb and As varied between  $12.0$  and  $41.1\%$  and between  $1.7$  and  $15.0\%$ , respectively (Yang 1992).

### Distribution of Sb, As and other heavy metals in soils

The distribution of Sb and As in the soil samples taken nearby the Sb mine area is shown in Fig. 2. All samples contained notably higher concentrations than the background value of Sb in Chinese soils ( $0.8\text{--}3.0 \text{ mg kg}^{-1}$ ) (Qi and Cao 1991), with concentrations ranging between  $101$  and  $5045 \text{ mg kg}^{-1}$ . Soil samples from S-1 and S-2, which were located at a 1-km distance from the mine area, had a high Sb concentration relative to background levels in Chinese soils (Qi and Cao 1991) and typical world background soil values for Sb (Smith and Huyck 1999). The concentrations are also high compared with the maximum permissible concentration for Sb in soil in The Netherlands ( $3.5 \text{ mg kg}^{-1}$ ; Crommentuijn et al. 2000) and the maximum permissible pollutant concentrations ( $36 \text{ mg kg}^{-1}$ ) for Sb in receiving soils recommended by the World Health Organization (WHO) (Chang et al. 2002). These samples may have been contaminated by the dust from wet and dry deposition, mining activities and the nearby Sb smelter (Creelius et al. 1974). Sites S-3 and S-4 were located in the Sb mine area, and the corresponding soil samples contained  $652$  and  $101 \text{ mg Sb kg}^{-1}$ , respectively. Soil samples from S-6, which was located near the alkaline furnace clinker, contained high levels of Sb ( $5054 \text{ mg kg}^{-1}$ ), those from S-7, near the smelting furnace clinker, contained up to  $406 \text{ mg Sb kg}^{-1}$ , those from S-8, near the south smelter, contained up to  $852 \text{ mg Sb kg}^{-1}$ , and those from S-9, near the ore-tailing reservoir, contained  $513 \text{ mg Sb kg}^{-1}$ .



**Fig. 2** The distribution of Sb and As concentrations in soils. The data are the mean  $\pm$  standard errors ( $n=3$ )

When the levels of metals and metalloids found in the soil samples near the mine areas are compared to the maximum permissible and negligible concentrations in soil for metals and metalloids in the Netherlands [(in mg kg<sup>-1</sup>soil); As, 34; Hg, 2.2; Cr, 100; Cd, 1.6; Pb, 140; Zn, 160; Cu, 40] (Crommentuijn et al. 2000) and the maximum permissible pollutant concentrations recommended by WHO in receiving soils (in mg Sb kg<sup>-1</sup>soil) (As, 8; Hg, 7; Cd, 4; Pb, 84;) (Chang et al. 2002), the soils near the Sb mine areas can be assessed as containing elevated levels of As and Hg. The average As concentration was 35.1 mg As kg<sup>-1</sup> (range: 3.56–205 mg As kg<sup>-1</sup>), with the highest concentration at S-6, where it reached 205.1 mg As kg<sup>-1</sup> due to the pollution from the alkali arsenic furnace residue. The average concentration of Hg was 14.9 mg Hg kg<sup>-1</sup> (range: 9.67–21.3 mg Hg kg<sup>-1</sup>), while may be due to the influence of smelter emissions and atmosphere deposition. The levels of other heavy metals (Cr, Zn, Cd, Pb and Cu) were low, with average concentrations for Cr, Zn, Cd, Pb and Cu of 63.9 (range: 52.6–86.4), 174 (range: 30.3–946),

1.58 (range: 0.73–5.55), 61.7 (range: 15.1–150) and 47.2 (range: 19.4–66.4) mg kg<sup>-1</sup> soil, respectively.

#### Antimony, As and other heavy metals in plants

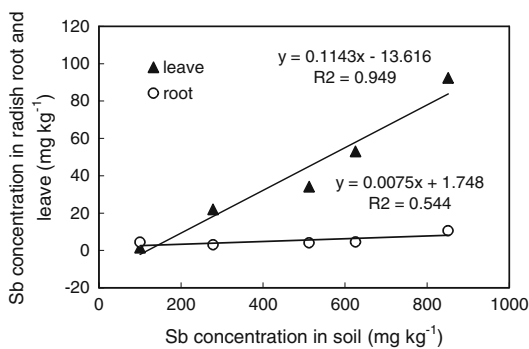
Table 4 shows concentrations of Sb and other heavy metals in the root and leaves of radish. Based on our analyses, these plant tissues contained high concentrations of Sb, with an average of 5.6 mg Sb kg<sup>-1</sup> (range: 3.0–10.5 mg Sb kg<sup>-1</sup>) in roots, and 54.0 mg Sb kg<sup>-1</sup> (range: 1.5–121.4 mg kg<sup>-1</sup>) in the leaves. Trace concentrations of As, Hg, Cr, Zn, Cd, Pb and Cu were also measured. The concentrations of As varied from 0.17 to 85.1 mg As kg<sup>-1</sup> in the radish roots, and from 0.98 to 34.47 mg kg<sup>-1</sup> in the radish leaves. The concentrations of Hg, Zn, Cd, and Pb in the radish roots were in the range of 0.06–0.40, 37.36–282.8, 0.09–1.32, 1.1–5.39 mg kg<sup>-1</sup>, respectively. The concentrations of Hg, Zn, Cd and Pb in the radish leaves were in the range of 0.19–2.52, 49.89–1563, 0.23–12.02, 1.57–50.19 mg kg<sup>-1</sup>, respectively. Although high levels of Sb were found in the radish leaves, no phytotoxicity was observed. There was a significant correlation between the Sb content of the radish leaves and total Sb concentration in the soil ( $r = 0.949$ ,  $P < 0.01$ ,  $n=5$ ) (Fig. 3), thereby demonstrating that Sb can be taken up from the soil into the roots and leaves. Previous studies suggested that Sb could be considered to be geochemically immobile (Ainsworth et al. 1990a,b, 1991); however, when present in soluble forms, it can be readily absorbed by plants. One radiological assessment of Sb distribution in plants showed a concentration of the element in roots, older leaves and the lower parts of the shoots (Coughtrey et al. 1983).

#### Antimony chemical forms and its phytoavailability

Using the method of sequential extraction (Tessier et al. 1979), we examined the distribution of Sb in soils (Table 5). The distribution of the different fractions/phases in order of decreasing abundance was: residual phase (Sb<sub>2</sub>S<sub>3</sub>) > Fe/Mn hydrous oxides, organic/sulphidic phase, carbonate

**Table 4** The distribution of Sb and other heavy metals in the roots and leaves of radish plants (mg kg<sup>-1</sup>)

Sample/site		Sb	As	Hg	Cr	Zn	Cd	Pb	Cu
S-2	Root	3.02	1.12	0.16	0.53	37.36	0.09	3.50	4.42
	Leaf	21.89	1.40	0.53	0.62	49.89	0.23	2.74	4.84
S-4	Root	4.40	1.70	0.40	1.12	71.88	0.41	3.71	4.48
	Leaf	1.48	0.98	0.19	0.67	53.52	0.56	1.57	1.33
S-5	Root	4.55	85.07	0.28	0.57	55.67	0.13	1.10	3.41
	Leaf	52.91	4.16	0.81	0.81	64.97	0.50	10.12	2.75
S-6	Root	6.82	0.28	0.12	0.72	72.09	0.26	4.97	3.14
	Leaf	121.40	34.47	2.52	0.42	194.8	1.30	9.99	3.80
S-8	Root	10.49	1.26	0.06	0.49	282.8	1.32	5.39	3.17
	Leaf	92.34	9.59	0.54	0.31	1563	12.02	50.19	14.55
S-9	Root	3.96	0.17	0.14	0.46	77.42	0.18	4.68	3.98
	Leaf	34.11	6.10	0.56	0.94	231.6	1.00	20.32	12.02



**Fig. 3** The relationship between Sb concentrations in the soil samples and the roots and leaves of radish

fraction > cation exchangeable, water-soluble fraction. Most of the Sb was found in the residual fraction, with values ranging from 88.2 to 97.9%.

The percentages of Fe/Mn hydrous oxides and organic/sulphidic phase were 0.52–3.9% and 0.91–4.59%, respectively. The carbonate fraction, cation exchangeable and water-soluble fraction constituted 0.19–2.76%, 0.43–2.11% and 0.09–2.50% of the Sb in the soil, respectively.

The sequential selective chemical extraction fractions of Sb in soils can be classified into three categories: easily phytoavailable (water soluble plus cation exchangeable fraction), moderately phytoavailable (carbonate fraction, Fe/Mn hydrous oxide fraction and sulphidic/organic bound metals) and not phytoavailable (residual fraction) (Table 6). There was a relatively high concentration of easily phytoavailable Sb in the soil samples (2.5–158.9 mg kg<sup>-1</sup>), the percentage of which varied from 0.47 to 3.54%. The percentage of

**Table 5** The sequential extraction fraction of Sb in soils

Speciation	Distribution of Sb in soils in mg Sb kg <sup>-1</sup> (%) <sup>a</sup>								
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Water soluble	3.29 (0.70)	2.25 (0.76)	2.95 (0.54)	0.65 (0.67)	1.10 (0.16)	112.3 (2.50)	0.62 (0.14)	8.51 (1.32)	0.42 (0.09)
Exchangeable	3.24 (0.68)	3.10 (1.05)	3.62 (0.66)	2.05 (2.11)	2.12 (0.31)	46.61 (1.04)	2.16 (0.49)	4.71 (0.73)	2.04 (0.43)
Carbonatic fraction	6.94 (1.47)	3.82 (1.29)	10.16 (1.85)	0.56 (0.58)	1.27 (0.19)	124.1 (2.76)	3.93 (0.89)	11.64 (1.80)	2.05 (0.43)
Fe/Mn oxides fraction	10.62 (2.24)	6.82 (2.30)	12.31 (2.24)	1.04 (1.07)	3.52 (0.52)	152.3 (3.39)	3.93 (0.90)	18.50 (2.86)	6.78 (1.44)
Sulphidic/organic	5.64 (1.19)	3.23 (1.09)	6.34 (1.16)	2.70 (2.78)	6.21 (0.91)	94.56 (2.11)	5.01 (1.14)	29.74 (4.59)	7.59 (1.61)
Residual fraction	443.6 (93.7)	277.1 (93.5)	513.3 (93.6)	90.7 (93.5)	667.2 (97.9)	3960 (88.2)	423.6 (96.4)	574.2 (88.7)	453.4 (96.0)
Total concentration	473.3 (100)	296.3 (100)	548.7 (100)	97.1 (100)	681.4 (100)	4489.9 (100)	439.2 (100)	647.3 (100)	472.3 (100)

<sup>a</sup> Percentage is given in parenthesis

moderately phytoavailable Sb ranged from 1.62 to 9.24%, and not phytoavailable fraction varied from 88.2 to 97.9%.

In the present study, the available Sb was also assessed using chemical extractants of H<sub>2</sub>O, HAc, EDTA, NH<sub>4</sub>OAc and NH<sub>4</sub>NO<sub>3</sub> (Table 7). The concentrations of Sb (Sb<sub>EDTA</sub>, Sb<sub>NH<sub>4</sub>OAc</sub>, Sb<sub>NH<sub>4</sub>NO<sub>3</sub></sub>, Sb<sub>H<sub>2</sub>O</sub> and Sb<sub>HAc</sub>) in soils extracted by the various solvents varied. The extractable Sb concentration for NH<sub>4</sub>NO<sub>3</sub> ranged between 0.20 and 95.9 mg kg<sup>-1</sup>. As a percentage of total Sb, the extractable fraction of Sb averaged 0.57% (range: 0.06–1.9%), which is consistent with the levels of 0.06–0.59% reported by Hammel et al. (2000). The percentages of extractable Sb for EDTA, HAc, H<sub>2</sub>O and NH<sub>4</sub>OAc were 0.50, 0.22, 0.19 and 0.09%, respectively.

## Discussion

Chemical extractions have been used in an attempt to evaluate the fraction of the solid phase, which is the potential source of metal available to biota (Qian et al. 1996). The relationship between the fractions (Sb<sub>EDTA</sub>, Sb<sub>NH<sub>4</sub>OAc</sub>, Sb<sub>NH<sub>4</sub>NO<sub>3</sub></sub>, Sb<sub>H<sub>2</sub>O</sub> and Sb<sub>HAc</sub>) in soils extractable by the various solvents and Sb content in soils (Sb<sub>Total</sub>), and the relationship between extractable fractions and soil characteristics (pH, CEC and organic matter content) were tested by the Pearson correlation coefficient. The correlations between extractable fractions by various solvents and Sb content in soils (Sb<sub>Total</sub>) were significant ( $r=0.667-0.778$ ,  $P<0.01$ ,  $n=9$ ).

In contrast to the high total levels, extractable levels of Sb were very low. The availability of Sb was low at different sites across a range of pH values (4.65–7.14), with no relationship between pH and extractable Sb levels, but there was a moderate correlation between extractable Sb for all solvents and soil organic matter content ( $r=0.500-0.611$ ,  $P<0.05$ ,  $n=9$ ). There was a good correlation between extractable Sb concentration for all solvents and Sb concentration in radish leaves ( $r=0.600-0.733$ ,  $P<0.05$ ,  $n=6$ ). The metal lability in contaminated soils and its availability to the plants is highly dependent on the metal speciation in soil and on the type of plant. The

**Table 6** The assessment for phytoavailability of Sb in soils

Bioavailable forms	Pytoavailability of Sb in soils in mg Sb kg <sup>-1</sup> (%) <sup>a</sup>								
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Easily bioavailable fraction	6.5 (1.38)	5.4 (1.81)	6.6 (1.20)	2.7 (2.78)	3.2 (0.47)	158.9 (3.54)	2.8 (0.63)	13.2 (2.05)	2.5 (0.52)
Moderately bioavailable fraction	23.2 (4.90)	13.9 (4.68)	28.8 (5.25)	4.3 (3.76)	11.0 (1.62)	371.0 (8.26)	12.9 (2.93)	59.9 (9.24)	16.4 (3.48)
Inert bioavailable fraction	443.6 (93.7)	277.1 (93.5)	513.3 (93.6)	90.7 (93.5)	667.2 (97.9)	3960.0 (88.2)	423.6 (96.4)	574.2 (88.7)	453.4 (96.0)

<sup>a</sup> Percentage is given in parenthesis



**Table 7** Extractable fractions of Sb in soils by various solvents

Sample/site	Sb <sub>Total</sub>	Sb <sub>EDTA</sub>		Sb <sub>NH<sub>4</sub>Oac</sub>		Sb <sub>NH<sub>4</sub>NO<sub>3</sub></sub>		Sb <sub>H<sub>2</sub>O</sub>		Sb <sub>HAc</sub>	
	(mg kg <sup>-1</sup> )	(mg kg <sup>-1</sup> )	(%) <sup>a</sup>	(mg kg <sup>-1</sup> )	(%)	(mg kg <sup>-1</sup> )	(%)	(mg kg <sup>-1</sup> )	(%)	(mg kg <sup>-1</sup> )	(%)
S-1	543.2	2.93	0.54	0.43	0.08	2.61	0.48	1.03	0.19	0.87	0.16
S-2	278.2	1.53	0.55	0.28	0.1	1.28	0.46	0.50	0.18	0.70	0.25
S-3	652.1	5.09	0.78	0.52	0.08	3.26	0.50	0.85	0.13	1.37	0.21
S-4	100.6	0.20	0.20	0.06	0.06	0.20	0.20	0.04	0.04	0.02	0.02
S-5	625.5	0.63	0.10	0.13	0.02	0.38	0.06	0.75	0.12	0.13	0.02
S-6	5045	60.5	1.20	13.6	0.27	95.9	1.90	28.3	0.56	41.4	0.82
S-7	405.8	0.57	0.14	0.12	0.03	0.49	0.12	0.57	0.14	0.20	0.05
S-8	851.5	6.30	0.74	1.11	0.13	10.98	1.29	2.72	0.32	3.66	0.43
S-9	512.8	1.49	0.29	0.10	0.02	0.67	0.13	0.31	0.06	0.26	0.05

<sup>a</sup> Percentage of total soil Sb

most labile forms (soluble, exchangeable, chelated) represent the immediate and potentially available fractions (Kabata-Pendias 1993; Maiz et al. 2000; Qian et al. 1996; Singh et al. 1998). Previous studies have shown that Sb tends to be present in soil as low-solubility sulphides (Hammel et al. 2000), bound to immobile Fe and Al oxides or associated with organic matter (Lintschinger et al. 1998; Tighe et al. 2005). Baroni et al. (2000) reported low levels of soluble Sb in soils from an old Sb mining area. Relatively insoluble or mobile fractions reflect a low bio-availability and uptake into biological systems, resulting in a low bioaccumulation in food chains (Ainsworth et al. 1990b; Flynn et al. 2003; Hammel et al. 2000). However, where Sb is present in more mobile forms in the soil, it can be accumulated by plants (Baroni et al. 2000; Hammel et al. 2000; He and Yang 1999). In the current study, there was a low concentration of extractable Sb and a low availability in the mine soils, but since Sb concentrations in the soil were extremely high (e.g. up to 0.5%), even low mobilities would still result in a significant uptake and accumulation by plants. The conclusion drawn by this author is, therefore, that both the apparent heavy Sb pollution in the mining soils and the accumulation of Sb in plants represent a potential ecological risk.

**Conclusion**

The results of the present study show that the soil samples near/adjacent to an Sb mine contain elevated Sb concentrations and are contaminated

with other potential toxicants, especially As and Hg. Radish plants collected in the area contained high concentrations of Sb; in particular, the leaves had a high Sb concentration that was positively correlated to soil Sb concentration. The sequential leaching procedure revealed that Sb was distributed in the soil samples in a series of residuals, followed by small fractions of Fe/Mn oxides, organic/sulphidic phase and carbonate phase. Easily phytoavailable Sb was present at a high concentration, reaching up to 2.5–13.2 mg kg<sup>-1</sup>, while the percentage of moderately phytoavailable Sb varied between 1.62 and 8.26% and the not phytoavailable fraction ranged between 88.2 and 97.9%. The extractable Sb concentrations varied, depending on the solvent. The percentage for the extractable fraction of Sb showed the following order: NH<sub>4</sub>NO<sub>3</sub> (0.57%) > EDTA (0.50%) > HAc (0.22%), H<sub>2</sub>O (0.19%) > NH<sub>4</sub>OAc (<0.09%). There was a moderate correlation between the extractable Sb concentration for various solvents and Sb concentration in the radish leaves ( $r=0.600-0.733$ ,  $P<0.05$ ,  $n=6$ ). There was also a moderate correlation between extractable Sb by various solvents and soil organic matter content ( $r=0.500-0.611$ ,  $P<0.05$ ,  $n=9$ ), but there was no relationship between pH and extractable Sb levels.

**Acknowledgments** The author is grateful to Dr. Dave Craw (University of Otago) and a second anonymous editor and to the reviewers for their constructive comments. The author was a visiting scholar (2005–2006) in the Department of Geography and Environmental Engineering, Johns Hopkins University and acknowledges Prof. William P. Ball, Johns Hopkins University, for his assistance during the visit and in writing the manuscript.

The project was supported by Natural Science Foundation of China (No. 29977002) and National Basic Research Program of China (No. 2004CB418502).

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