*Environ. Chem.* **2020**, *17*, 314–322 https://doi.org/10.1071/EN20003

**Research Paper** 

# Accumulation and transport of antimony and arsenic in terrestrial and aquatic plants in an antimony ore concentration area (south-west China)

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**Environmental context.** Phytoremediation requires an understanding of bioconcentration and translocation processes that determine behaviour and fate of potentially toxic elements. We studied the distribution of antimony and arsenic in terrestrial and aquatic soil-plant systems in an antimony ore zone. We found that the common climbing plant Kudzu (*Pueraria lobata*) is suitable for phyto-stabilisation of antimony-bearing tailings, while tiger grass (*Thysanolaena maxima*) was able to extract antimony and arsenic from contaminated soils.

**Abstract.** Antimony (Sb) pollution is a major environmental issue in China. Many historical abandoned tailings have released high concentrations of Sb and its associated element arsenic (As) to surrounding environments. This has prompted the need to understand accumulation and translocation processes that determine the behaviour and fate of Sb and As in contaminated soil–plant systems and to identify suitable plant species for phytoremediation. Here we investigate distribution of Sb and As in terrestrial and aquatic dominant plant species and associated soils, all of which are naturally found in an Sb ore concentration area in south-west China. Total Sb and As concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). The percentage of soluble Sb and As in the total concentrations were determined; the results showed that the basic soil environment facilitates the release of Sb and As from contaminated soils, and that Sb has higher mobility than As. Bioconcentration factor (BCF) and translocation factor (TF) were used for evaluating the ability of plants to accumulate and transport Sb and As, respectively. The results indicated that all selected plant species have the potential to tolerate high concentrations of Sb and As. Consequently, this study suggested that *Pueraria lobata* (PL) can be used as the preferred species for phytostabilisation of abandoned Sb-bearing tailings, given that PL has well-developed roots and lush leaf tissues and the ability to translocate Sb from roots to aboveground parts. *Thysanolaena maxima* (TM) is suitable for phyto-extraction of Sb and As in contaminated soils.

Additional keywords: abandoned tailings, antimony pollution, phytoremediation.

Received 9 January 2020, accepted 3 February 2020, published online 20 March 2020

# Introduction

Antimony (Sb) is widely used in textiles, papermaking, plastics, electronic products, and automobile brake pads, among other products, because of its flame-retardant properties. Antimony is also a toxic element, and the amount of Sb in the environment is strictly limited because of its toxicity, underscoring a global dilemma as to how antimony should be managed (Herath et al. 2017). China leads the world in terms of Sb reserves and production (USGS 2018), and Sb pollution has become one of the major environmental issues in China (He et al. 2012).

Antimony and arsenic (As) are in the same group of elements in the periodic table, and both share similar chemical properties (Filella et al. 2002; Wilson et al. 2010). Owing to this geochemical similarity, Sb often coexists with As in the natural environment (Arai 2010). Mining activities are one of the most important anthropogenic sources of Sb and As in the environment (Herath et al. 2017). Historical mine wastes and tailings produced by Sb mining have led to high concentrations of Sb and As in Sb mining areas and surrounding environments (Macgregor et al. 2015; Fu et al. 2016; Zhou et al. 2017; Li et al. 2018; Sun et al. 2019) due to diffusion and migration of Sb and As. This affects ecosystems around mining areas (Telford et al. 2009; Wei et al. 2015; Dovick et al. 2016) and promotes Sb and As exposure to humans and animals (Ungureanu et al. 2015; Wu et al. 2011; Fu et al. 2011; Liu et al. 2011).

Antimony, like As, is not an essential element for plant growth. Instead, both are considered to be elements of plant toxicity (Feng et al. 2013). In general, in terrestrial plants, the



Fig. 1. Location of the investigated mining areas and sampling sites.

background value of Sb ranges from 0.2 to 50  $\mu$ g kg<sup>-1</sup> (Baroni et al. 2000), and the background value of As ranges from 0.009 to  $1.5 \text{ mg kg}^{-1}$  (Baroni et al. 2004). Much higher levels of Sb and As are found in plants growing in mining areas. Early studies showed that when the Sb content in the extractable part of the soil was as high as 793 mg kg<sup>-1</sup>, plants exhibited high enrichment of Sb, with the highest levels reaching 1367 mg kg<sup>-</sup> (Baroni et al. 2000). Some plants and microalgae with high Sb enrichment were also found in later studies, with reported Sb levels reaching 1136 mg  $kg^{-1}$  (Murciego et al. 2007) and 1423 mg kg<sup>-1</sup> (Borovička et al. 2006). Antimony can also significantly accumulate in the roots of paddy rice (Ding et al. 2015; Zhang et al. 2017). However, some studies have shown that plants grown in soils contaminated with high Sb contained lower levels of Sb (Nakamaru et al. 2006; He et al. 2019). The uptake mechanisms and transport pathways of Sb are different in each plant and are poorly understood (Pierart et al. 2015).

Compared with Sb, much more is known regarding the behaviour, ecotoxicology, and distribution of As in soil-plant systems (Tschan et al. 2009; Fayiga and Saha 2016; Han et al. 2017; Suriyagoda et al. 2018). In light of the similar chemical properties of Sb and As and the elevated content of both elements in mine areas, this study examines the joint accumulation and transport of Sb with As. Drawing on measurements from one of the most important Sb ore concentration zones in China, the aims of this work are to: (1) investigate the distribution of Sb and As in the dominant plant parts and their corresponding contaminated soils; (2) reveal the transport and accumulation characteristics of Sb and As from contaminated soils to plants; and (3) study the bioconcentration factor (BCF) and translocation factor (TF) of these plant species. Our results have significant implications for exploring the feasibility of phytoremediation using suitable hyperaccumulator plants in Sb mining areas.

# Experimental

# Study area

The study area is the Guibei-Qiannan Sb ore concentration area, which is located at the junction of the northern Guangxi Zhuang Autonomous Region and southern Guizhou in south-west China (Fig. 1). The structure of this Sb ore concentration area is dominated by faults, and the location of Sb deposits is controlled by these structures. The Sb is highly enriched in the stratum and has a good geochemical background of Sb mineralisation (Wang et al. 2013). The area with the highest ore concentrations is mainly composed of a single stibnite deposit in Dushan county and a Sb deposit produced by the Dachang tin multi-metalliferous mine in Nandan county. This area has been mined for decades. Although most of the mines have been closed and abandoned, the wastes from early mining activities have caused serious Sb and As pollution in the surrounding environments (Li et al. 2018, 2019; Sun et al. 2016).

## Sampling and analysis

According to the distribution of dominant plant species in the two mining areas, five terrestrial and two aquatic plant species were taken from eight sites in the study area. The terrestrial plants are: *Pteris vittata L.* (PV), *Saccharum arundinaceum* (SA), *Miscanthus floridulus* (MF), *Thysanolaena maxima* (TM), and *Pueraria lobata* (PL). The aquatic plants are *Equisetum ramosissimum* (ER) and *Microstegium vimineum* (MV). PV, commonly known as the Chinese brake, is a fern species. ER, known as branched horsetail, is an evergreen horsetail species. PL is a perennial liane, MV is an annual herb, and the other three plant species are perennial herbs. Three to five plants per species were collected from each site, and their roots, stems, and leaves were separated for analysis. In total, 89 samples of terrestrial

Site	п	рН	Total Sb $(mg kg^{-1})$	Soluble Sb $(mg kg^{-1})$	Total As $(mg kg^{-1})$	Soluble As $(mg kg^{-1})$
1 <sup>A</sup>	3	$7.5\pm0.2$	$3196 \pm 1562$	$14.9 \pm 11.2$	$265.9\pm40.9$	$0.2 \pm 0.12$
2 <sup>A</sup>	3	$6.2\pm0.6$	$556.8\pm265.4$	$0.37\pm0.01$	$19013\pm3539$	$0.78\pm0.29$
3 <sup>A</sup>	2	$4.1 \pm 1.9$	$1774 \pm 1880$	$0.26\pm0.31$	$14971 \pm 4612$	$0.43\pm0.01$
$4^{A}$	1	7.5	19.85	0.06	150.8	0.04
5 <sup>A</sup>	3	$8.3 \pm 0.1$	$615.2 \pm 847.4$	$4.7\pm5.7$	$309.3\pm200.5$	$1.4 \pm 1.1$
6 <sup>B</sup>	2	$7.1 \pm 0.1$	$2183 \pm 1731$	$5.9 \pm 5.2$	$7606\pm797.8$	$0.64\pm0.18$
$7^{\mathrm{B}}$	2	$7.1 \pm 0.2$	$1379.6 \pm 519.6$	$1.6\pm0.27$	$9952 \pm 381.6$	$1.1\pm0.17$
$8^{\mathrm{B}}$	3	$4.1\pm0.6$	$2494\pm988.4$	$0.26\pm0.17$	$16790\pm7853$	$0.99 \pm 0.65$

 Table 1. The pH and Sb and As concentrations in soils collected from eight sampling sites

 n, number of samples; entries are shown as mean  $\pm$  standard deviation (s.d.)

<sup>A</sup>Terrestrial soils.

<sup>B</sup>Aquatic soils.

plants and 18 samples of aquatic plants were collected. Meanwhile, a total of 12 soil samples from abandoned mine tailing dumps and 7 soil samples from around the roots of riparian plants were collected.

#### Sample preparation

The roots, stems, and leaves of the studied plants were thoroughly washed with tap water and rinsed more than three times with deionised water. After the sample was dried at 60 °C, the roots, stems, and leaves were pulverised and ground with an electric mill (IKA A11 Basic, Germany) and stored in precleaned sealable bags (Telford et al. 2009). Soil samples were collected by using a stainless-steel trowel and sealed in polythene bags. Each sample was dried in an oven at 60 °C and then milled so that it passed through a 150- $\mu$ m sieve (Guo et al. 2018).

## Sample digestion

The milled samples (plant: 0.05 g; soil: 0.01 g) were digested in a mixture of HNO<sub>3</sub>: HF (2:1, v/v) in a polytetrafluoroethylene (PTFE) crucible and heated at 170 °C (internal pressure:  $\sim$ 7.9 bar) for 9 h (plant samples) or 12 h (soil samples). The digested solution was heated to dryness. Finally, the digested residue was dissolved in 1 mL of HNO<sub>3</sub> and diluted to 100 mL with deionised water (Milli-Q, 18.2 MW cm).

## Sample analysis

The digested solution was analysed for Sb and As by inductively coupled plasma mass spectrometry (ICP-MS, NexION 300X, PE). A 10-g dry soil sample was stirred with 25 mL deionised water and analysed for pH (Tan et al. 2018; He 2007). A 2-g dry soil sample was shaken with 20 mL deionised water for 2.5 h, centrifuged at room temperature at 10956 g (relative centrifugal force) for 10 min, filtered through 0.22- $\mu$ m membrane filter paper, and analysed for soluble Sb and As (Ettler et al. 2007).

#### Bioconcentration factor

The BCF was calculated by the ratio of concentration ( $mg kg^{-1}$ ) of metalloid in plant parts to that in soil:

$$BCF = C_{plant}/C_{soil}$$

## Translocation factor

The TF was calculated by the ratio of the content  $(mg kg^{-1})$  of metalloid in aboveground parts of the plant to that in the roots:

$$TF = C_{aboveground parts}/C_{root}$$

Generally, BCF reflects the accumulation capacity of plants to metalloids in the soils, whereas TF indicates the translocation ability of plants to metalloids from the roots to the aboveground parts (Baroni et al. 2004; Wang et al. 2019).

## Reagents and quality control

All acids and reagents used were analytical grade. Sub-boiling distilled (DST-1000, Savillex, USA) nitric acid and hydro-fluoric acid were used for sample digestions. Multi-element standard solutions (AccuTrace ICP-MS Calibration Standard, 10  $\mu$ g mL<sup>-1</sup> each element) for ICP-MS analysis were purchased from AccuStandard Incorporation, New Haven, USA. Rigorous quality control procedures included analysis of reagent blanks, water blanks, replicate samples, and certified national reference material of plant (GBW-07604), soil (GBW-07404), and sediment (GBW-07305). The precision of determination of elements was better than 5 %.

## **Results and discussion**

## Sb and As concentrations in contaminated soils

All the dominant plants were taken from abandoned mine tailing dumps, and the contaminated soils associated with the rhizosphere environment of those plants were essentially composed of mine tailings. The pH values and concentrations of Sb and As of both terrestrial and aquatic soils from the eight sites are displayed in Table 1. The pH of soils on sites 3 and 8 were (4.1  $\pm$  1.9) and (4.1  $\pm$  0.6) respectively, revealing an acidic soil environment; the pH of site 2 was ( $6.2 \pm 0.6$ ), being a mildly acidic environment. However, other sites showed a neutral-to-basic pH (7.1  $\pm$  0.1 to 8.3  $\pm$  0.1), which are similar to the pH of the background river waters in the associated study areas (Li et al. 2018, 2019). In fact, the acidic pH arises due to oxidation of metal sulfide minerals, including Sb-bearing and As-bearing minerals such as stibnite, arsenopyrite, orpiment, and realgar in the mine tailings, leading to the formation of acidic solutions while releasing a large amount of Sb and As into the solution (Wilson et al. 2010). Furthermore, the acid is easily neutralised by the abundant carbonate present in the surrounding environment, resulting in elevated Sb and As concentrations detected in a neutral environment (Paikaray 2015; Ashley et al. 2003). As can be seen from Table 1, soil environments of terrestrial and aquatic plants at all sampling sites except site 4 contained high levels of total Sb and As concentrations, regardless of the pH of the soils. The mine tailing dump where site 4 is located is the oldest of all the



**Fig. 2.** Relationship between pH values and soluble Sb (a) and As (b) percentages in the terrestrial and aquatic soils.

tailing dumps, and it has been seriously weathered, and the mine tailings have been substantially eroded.

Soil pH is the most important factor affecting the mobility of metalloids in soils (McBride et al. 1997; de Matos et al. 2001). Fig. 2 shows the relationship between the pH value of contaminated soil and the percentage of soluble Sb and As to the total concentrations. Obviously, the percentage of soluble Sb and As content gradually increases with the variation of pH from acidic to basic, indicating that the weak alkaline environment is more conducive to the release of Sb and As from contaminated soils. This is related to the fact that Sb and As are metalloids that commonly have oxidic, hydroxidic, and oxyanionic forms in their natural state. Both Sb and As often occur in hydrothermal sulfide deposits, their common minerals including Sb sulfides and As sulfides (Wilson et al. 2010). When  $Sb^{III}$  and  $As^{III}$ sulfide minerals dissolve in water, then the 'hydroxides' Sb(OH)<sub>3</sub> and As(OH)<sub>3</sub> are formed respectively. They do not occur as discrete Sb<sup>3+</sup> and As<sup>3+</sup> ions in solutions but as H<sub>3</sub>SbO<sub>3</sub> and H<sub>3</sub>AsO<sub>3</sub>. Both H<sub>3</sub>SbO<sub>3</sub> and H<sub>3</sub>AsO<sub>3</sub> can dissociate in alkaline solutions to form the charged anions (H<sub>2</sub>SbO<sub>3</sub><sup>-</sup> and H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> respectively), which are very soluble in water (Biver and Shotyk 2012; Brown 2011). The results of an experimental study on the leaching of Sb from Sb-bearing ores also indicated that alkaline conditions (pH 9-10) are more conducive to the release of Sb from the ores than acidic (pH < 4) or neutral conditions (Hu et al. 2016).



Fig. 3. Soluble percentage of Sb and As to the total concentrations in the terrestrial and aquatic soils.

The soluble Sb and As in the soils can easily migrate and diffuse and are also easily absorbed by the plant roots and transported to the aboveground parts of the plants (Baroni et al. 2000; Murciego et al. 2007). The results of total and soluble Sb and As are presented in Table 1. The contents of soluble Sb and As were indeed relatively high in the weakly alkaline soil environments. Furthermore, to compare the mobility of Sb and As in contaminated soil samples more directly, the percentage of soluble Sb and As is plotted relative to the total concentrations (Fig. 3). The results showed that although the average value of As in the soil environment of the terrestrial and aquatic plants was much higher than that of Sb, the percentage of soluble As was lower than that of Sb, which indicates that the mobility of Sb in soils of the study area is greater than that of As. The same phenomenon has been reported elsewhere (Gál et al. 2006; Casiot et al. 2007; Hiller et al. 2012; Li et al. 2019).

## Sb and As concentrations in plants

To investigate whether dominant plants growing in the mine tailing dumps were resistant to high concentrations of Sb and As, we analysed the concentrations of Sb and As in the roots, stems, and leaves of those plant species collected from each sampling site (Table 2). Most of these plants naturally grew in high Sb-contaminated and As-contaminated environments (Table 1) and were mainly annual or perennial plants with large biomass. Differences in plant species and metal supply levels can affect the distribution of metalloids in different tissues of plants (Midhat et al. 2019) and can also cause differences in the concentration of metalloids absorbed by the same plant, resulting in a variable concentration range of Sb and As in the roots, stems, and leaves of the same plant form.

In the terrestrial plants, PV and MF contained high levels of Sb in roots, stems, and leaves, ranging respectively  $(1.2-140.1, 1.0-29.7, 6.0-73.4) \text{ mg kg}^{-1}$  for PV and (0.49-546.7, 0.19-3.1, 1.6-129.9) mg kg<sup>-1</sup> for MF. For the absorption of As, PV showed the highest contents of As, and the range of As concentrations in roots, stems, and leaves were (207.8-1877.2, 54.9-1228.7, 69.6-1535.1) mg kg<sup>-1</sup> respectively. In the aquatic plants, ER, as a leafless evergreen horsetail, contained the highest levels of Sb and As. Total concentrations of Sb and As in the roots and stems of ER ranged respectively (141.3-2183.4, 10.0-44.0) mg kg<sup>-1</sup> for Sb and (168.1-1353.3, 30.8-316.6) mg kg<sup>-1</sup> for As. The specific average values of Sb and As absorbed by different plants are shown in Table 2. Regarding the

 Table 2.
 Sb and As concentrations in the roots, stems, and leaves of dominant plant species collected from eight sampling sites (data in mg kg<sup>-1</sup> DW)

 Entries are shown as mean ± s.d.; DW, dry weight; PV, Pteris Vittata L.; SA, Saccharum arundinaceum; MF, Miscanth floridulus; TM, Thysanolaena maxima; PL, Pueraria lobata; ER, Equisetum ramosissimum; MV, Microstegium vimineum

Plant species		Sb concentration			As concentration	n
	Root	Stem	Leaves	Root	Stem	Leaves
PV <sup>A</sup>	$50.4 \pm 10.7$	$8.3 \pm 2.1$	$33.6 \pm 6.3$	$872.6 \pm 146.1$	$330.9\pm77.4$	$624.9 \pm 118.1$
SA <sup>A</sup>	$20.2\pm7.2$	$3.0\pm0.95$	$13.7 \pm 4.1$	$72.4\pm36.6$	$15.1 \pm 5.3$	$24.9\pm7.5$
MF <sup>A</sup>	$34.4\pm30.2$	$1.1 \pm 0.18$	$29.1 \pm 8.2$	$16.9 \pm 5.1$	$3.4\pm0.70$	$58.0\pm25.2$
TM <sup>A</sup>	$11.7 \pm 2.6$	$1.5\pm0.59$	$25.9\pm7.7$	$69.2 \pm 24.3$	$8.4 \pm 3.7$	$37.3 \pm 13.1$
PL <sup>A</sup>	$4.7 \pm 2.4$	$2.4\pm0.81$	$6.3 \pm 0.79$	$3.1 \pm 0.44$	$3.9 \pm 2.2$	$6.1 \pm 1.8$
ER <sup>B</sup>	$595 \pm 333.6$	$21.7 \pm 5.1$	_	$609 \pm 194.2$	$130.8\pm40.9$	_
$MV^B$	$24.9\pm9.3$	$2.7\pm1.6$	$10.5\pm2.8$	$120.5\pm57.8$	$14.6\pm7.9$	$18.9\pm4.3$

<sup>A</sup>Terrestrial plants.

<sup>B</sup>Aquatic plants.

high Sb and As concentrations in these plants, we can think of these plants (PV, MF, and ER) as hyper-tolerant species to accumulate Sb and As. In addition, although the other four plant species did not show strong ability to accumulate Sb and As, they also had a certain tolerance to high concentrations of Sb and As. To some extent, they can reduce the leaching and diffusion of Sb and As in the soil polluted by high Sb and As.

To further analyse the distribution characteristics of Sb and As in different plant tissues, we used BCF to evaluate the ability of plant parts to uptake Sb and As from soils. Fig. 4 shows the BCFs of plant roots, stems, and leaves for accumulating Sb and As from contaminated soils. For the terrestrial plants, the BCF of Sb is similar in leaves and roots in MF, SA, and PV, but in PL and TM there is more in the leaves than the roots (Fig. 4a). The BCF of As in these terrestrial plants differed from that of Sb. Arsenic is significantly accumulated by PV; the BCF of As in the roots and leaves of PV is greater than 1 (Fig. 4b, Table 2). The BCF of As in the tissues of plants in SA is almost similar, whereas the order of that in MF, TM, and PL is leaves > roots > stems (Fig. 4b). For the aquatic plants, the concentrations of Sb and As in ER were significantly higher than that in MV (Table 2). In ER, the BCF of Sb and As is more in the roots than the stems; the order in MV is roots > leaves > stems (Fig. 4c). Comparing the distribution of Sb and As in plant tissues, we found that almost all plant stems have much lower ability to absorb Sb than As.

## Sb and As accumulation and translocation in plants

BCF reflects the accumulation capacity of plants to elements in the soils, whereas TF indicates the translocation ability of plants to elements from the roots to the aboveground parts (Baroni et al. 2004; Chandra and Kumar 2017; Wang et al. 2019). By calculating the BCF and TF values of a plant species, the accumulative efficiency of the contaminating element in the plant can be evaluated, and whether the plant is suitable for phytostabilisation or phyto-extraction for the contaminated soils can be determined (Ali et al. 2013). The greater the BCF and TF values, the greater the ability of the plant to accumulate and translocate the elements.

The BCF (all parts including roots, stems, and leaves) and TF of seven kinds of plant species to Sb and As are shown in Fig. 5. For Sb, all plants have BCF values less than 1; all terrestrial plants have TF values greater than 1 (Fig. 5a). For As, except for the BCF value of PV being greater than 1, the BCF of other plants is less than 1; the TF values of all terrestrial plants are also

greater than 1 (Fig. 5b). The BCF and TF values of Sb and As in aquatic plants collected in this study were less than 1 (Fig. 5a, b). These results suggest that all of the terrestrial plant species collected can effectively transport Sb and As from the roots to the aboveground parts, indicating that these plants have the potential to translocate Sb and As from their roots.

The concentrations of heavy metals in the aboveground parts of a plant is one of the important factors for evaluating whether the plant can be used to remove heavy metals from contaminated soil, which means that the higher the TF value, the more suitable for phytoremediation (Fischerová et al. 2006). All of the TF values of the terrestrial plants in this study exceeded 1, indicating that these plants can effectively translocate Sb and As to the aboveground parts. It seems that these terrestrial plants have bioconcentration ability to remove Sb and As from mine tailings. However, we need to identify whether the sources of Sb and As in the aboveground parts of the plant are consistent with its roots. Aboveground parts of plants, especially plant leaves, can accumulate trace elements from both root-mediated transportation and also atmospheric deposition (De Temmerman et al. 2015; Yalaltdinova et al. 2018). To test the source, we developed a linear correlation between element contents in the roots and aboveground parts for each plant (Table 3).

The best linear correlations for Sb were observed in TM (R = 0.6604) and PL (R = 0.8857) (Table 3), indicating that the source of Sb in the aboveground parts of TM and PL was consistent with their roots. Both TM and PL have high levels of TFs (3.96  $\pm$  1.06 and 2.99  $\pm$  1.13 respectively), indicating that TM and PL have a greater ability to translocate Sb from the roots to the aboveground parts than other plants. In addition, PL is a perennial vine with very developed roots and lush leaf tissues, which can increase the slope stability of the tailing dump to some extent. Therefore, we suggest that PL may be suitable for phytostabilisation in Sb mine tailings. For other plant species in the study area, although they have weak ability to transfer Sb to the aboveground parts, their roots are still enriched with elevated concentrations of Sb, indicating that the roots of these plants can act as a barrier to prevent Sb translocating to the aboveground parts.

The best linear correlations for As were found in PV (R = 0.8396), TM (R = 0.8194), and MV (R = 0.9777) (Table 3), suggesting that the As in the aboveground tissues of these three kinds of plants mainly comes from their roots. However, the BCF and TF values of As in MV were less than 1, indicating that MV does not have bioaccumulation efficiency



Fig. 4. Comparison of Sb and As BCFs in the terrestrial (a, b) and aquatic (c) plant tissues.

for As. Thus, it can be concluded that PV and TM in the study area have strong ability to translocate As from the roots to the aboveground parts, indicating that these plants could be suitable for phytoremediation of As-contaminated soil. Like for Sb, other plant species also have a barrier function in the roots to prevent the translocation of As to the aboveground parts.

For a plant to be considered a hyperaccumulator, both the BCF and TF values must be greater than 1, and also the

concentration in the aboveground parts should be greater than 1 % (Baker and Brooks 1989; Wang et al. 2019). In this study, only the accumulation of As in PV was consistent with this hyperaccumulator definition (Fig. 5b), which showed that PV is indeed a very effective As hyperaccumulator plant (Ma et al. 2001). PV not only has a strong ability to accumulate As, but it also effectively transports As from the roots to the aboveground parts (Mathews et al. 2011; Müller et al. 2013), suggesting that



Fig. 5. BCF (all parts including roots, stems, and leaves) and TF of the plants to Sb (a) and As (b).

 Table 3. Linear correlation between total concentrations in the epigeal parts and in the roots of the plant samples

 R, linear correlation index

R	Terrestrial plants					Aquatic plants	
	Pteris vittata L. (PV)	Saccharum arundinaceum (SA)	Miscanthus floridulus (MF)	Thysanolaena maxima (TM)	Pueraria lobata (PL)	Equisetum ramosissimum (ER)	Microstegium vimineum (MV)
Sb	0.3883	0.2600	0.2520	0.6604	0.8857	0.4192	0.2766
As	0.8396	0.6351	0.4020	0.8194	0.4728	0.1414	0.9777

PV is the potential species for phytoremediation in Ascontaminated soils.

## Conclusions

Production, reservation, and consumption of Sb in China rank the first in the world; thus, Sb pollution in China is a critical issue currently. Historical mine tailings derived from Sb mining activities is the most important source of Sb and its associated element As pollution. Phytoremediation is a feasible method to treat mine tailings and contaminated soils, but it requires an understanding of the transport and bioaccumulation processes that determine the behaviour and fate of Sb and As in the soil– plant system. In this study, five kinds of terrestrial and two kinds of aquatic dominant plant species, and their corresponding soils, were collected from an Sb ore concentration area in south-west China. The growing environment of all plants was subject to acute Sb and As pollution and contained very high concentrations of Sb and As. The extraction of water-soluble Sb and As was studied in the corresponding soil of all plants; the results showed that mobility of Sb was greater than that of As. At the same time, solubility of Sb and As increased with the pH of soil, which varied from neutral to alkaline. The bioconcentration of Sb and As in all the terrestrial plants mainly occurred in the roots and leaves, whereas that of Sb and As in the aquatic plants mainly accumulated in the roots. *Pteris vittata L.* (PV) is a

well-deserved As hyperaccumulator and is the only plant species studied for which both the BCF and TF exceeded 1. This study did not identify a Sb hyperaccumulator but found that Pueraria lobata (PL) had a high TF level with a well-developed root system and lush leaf tissues, indicating that PL could be used as the preferred species for phytostabilisation of abandoned tailings in the Sb mining areas. PL could translocate Sb to the aboveground parts from the roots; its developed root system can increase the stability of the abandoned tailings, and its dense leaves can also beautify the mine environment. In addition, Thysanolaena maxima (TM) also has the ability to translocate Sb and As from the roots to the aboveground parts and is therefore suitable for phyto-extraction for Sb- and Ascontaminated soils. Other dominant plant species had weak ability to translocate Sb and As but can naturally grow and survive in high Sb and As environments. This indicates that these native and dominant plant species have a strong tolerance to Sb and As and can be used as suitable plant species in the high Sb and As environments of the mining areas.

## **Conflicts of interest**

The authors declare no conflicts of interest.

#### Acknowledgements

The authors would like to acknowledge comments from the editors and the reviewers. In particular, the authors would like to thank Dr Montserrat Filella for her constructive comments and suggestions on their manuscript. The authors also sincerely appreciate Professor Gordon Grant, a Research Hydrologist in the USDA Forest Service and a Courtesy Professor in Oregon State University, for his instructive suggestions on the writing of this paper. This work was funded by the National Natural Science Foundation of China (No. U1612442), the Project of Science and Technology Department of Guizhou Province (ZHICHENG[2019]2838; RENCAI[2016]5664), the Opening Fund of the State Key Laboratory of Environmental Geochemistry (SKLEG2019712), and the National Key Research and Development Project (2018YFC1801705).

#### References

- Ali H, Khan E, Sajad MA (2013). Phytoremediation of heavy metalsconcepts and applications. *Chemosphere* **91**, 869–881. doi:10.1016/ J.CHEMOSPHERE.2013.01.075
- Arai Y (2010). Arsenic and antimony. In 'Trace elements in soils'. (Ed. PS Hooda) pp. 384–400. (Wiley-Blackwell: London)
- Ashley P, Craw D, Graham B, Chappell DA (2003). Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. *Journal of Geochemical Exploration* 77, 1–14. doi:10.1016/S0375-6742(02)00251-0
- Baker AJM, Brooks RR (1989). Terrestrial higher plants which hyperaccumulate metallic elements. A review of their distribution, ecology and phytochemistry. *Biorecovery* 1, 81–126.
- Baroni F, Boscagli A, Protano G (2000). Antimony accumulation in Achillea ageratum, Plantago lanceolata and Silene vulgaris growing in an old Sbmining area. Environmental Pollution 109, 347–352. doi:10.1016/ S0269-7491(99)00240-7
- Baroni F, Boscagli A, Di Lella LA (2004). Arsenic in soil and vegetation of contaminated areas in southern Tuscany (Italy). *Journal of Geochemical Exploration* 81, 1–14. doi:10.1016/S0375-6742(03)00208-5
- Biver M, Shotyk W (2012). Stibnite (Sb<sub>2</sub>S<sub>3</sub>) oxidative dissolution kinetics from pH 1 to 11. *Geochimica et Cosmochimica Acta* **79**, 127–139. doi:10.1016/J.GCA.2011.11.033
- Borovička J, Řanda Z, Jelínek E (2006). Antimony content in macrofungi from clan and polluted areas. *Chemosphere* 64, 1837–1844. doi:10.1016/ J.CHEMOSPHERE.2006.01.060
- Brown K (2011). Antimony and arsenic sulfide scaling in geothermal binary plants. 'Proceedings International Workshop on Mineral Scaling 2011', Manila, Philippines, 25–27 May 2011, pp. 103–106.

- Casiot C, Ujevic M, Munoz M, Seidel JL, Elbaz-Poulichet F (2007). Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). *Applied Geochemistry* 22, 788–798. doi:10.1016/J.APGEOCHEM.2006.11.007
- Chandra R, Kumar V (2017). Phytoextraction of heavy metals by potential native plants and their microscopic observation of root growing on stabilised distillery sludge as a prospective tool for in situ phytoremediation of industrial waste. *Environmental Science and Pollution Research International* 24, 2605–2619. doi:10.1007/S11356-016-8022-1
- de Matos AT, Fontes MPF, da Costa LM, Martinez MA (2001). Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. *Environmental Pollution* 111, 429–435. doi:10. 1016/S0269-7491(00)00088-9
- De Temmerman L, Waegeneers N, Ruttens A, Vandermeiren K (2015). Accumulation of atmospheric deposition of As, Cd and Pb by bush bean plants. *Environmental Pollution* 199, 83–88. doi:10.1016/J.ENVPOL. 2015.01.014
- Ding YZ, Wang RG, Guo JK, Wu FC, Xu YM, Feng RW (2015). The effect of selenium on the subcellular distribution of antimony to regulate the toxicity of antimony in paddy rice. *Environmental Science and Pollution Research International* 22, 5111–5123. doi:10.1007/S11356-014-3865-9
- Dovick MA, Kulp TR, Arkle RS, Pilliod DS (2016). Bioaccumulation trends of arsenic and antimony in a freshwater ecosystem affected by mine drainage. *Environmental Chemistry* 13, 149–159. doi:10.1071/EN15046
- Ettler V, Mihaljevic M, Šebek O, Nechutný Z (2007). Antimony availability in highly polluted soils and sediments – a comparison of single extractions. *Chemosphere* 68, 455–463. doi:10.1016/J.CHEMOSPHERE. 2006.12.085
- Fayiga AO, Saha UK (2016). Arsenic hyperaccumulating fern: implications for remediation of arsenic contaminated soils. *Geoderma* 284, 132–143. doi:10.1016/J.GEODERMA.2016.09.003
- Feng R, Wei C, Tu S, Ding Y, Wang R, Guo J (2013). The uptake and detoxification of antimony by plants: a review. *Environmental and Experimental Botany* 96, 28–34. doi:10.1016/J.ENVEXPBOT.2013. 08.006
- Filella M, Belzile N, Chen YW (2002). Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth-Science Reviews* 57, 125–176. doi:10.1016/S0012-8252(01)00070-8
- Fischerová Z, Tlustoš P, Száková J, Šichorováa K (2006). A comparison of phytoremediation capability of selected plant species for given trace elements. *Environmental Pollution* 144, 93–100. doi:10.1016/ J.ENVPOL.2006.01.005
- Fu ZY, Wu FC, Mo CL, Liu B, Zhang Y (2011). Bioaccumulation of antimony, arsenic, and mercury in the vicinities of a large antimony mine, China. *Microchemical Journal* 97, 12–19. doi:10.1016/ J.MICROC.2010.06.004
- Fu ZY, Wu FC, Mo CL, Deng QJ, Meng W, Giesy JP (2016). Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China. *The Science of the Total Environment* 539, 97–104. doi:10.1016/J.SCITOTENV.2015.08.146
- Gál J, Hursthouse AS, Cuthbert SJ (2006). Chemical availability of arsenic and antimony in industrial soils. *Environmental Chemistry Letters* 3, 149–153. doi:10.1007/S10311-005-0022-1
- Guo WJ, Fu ZY, Wang H, Song FH, Wu FC, Giesy JP (2018). Environmental geochemical and spatial/temporal behavior of total and speciation of antimony in typical contaminated aquatic environment from Xikuangshan, China. *Microchemical Journal* **137**, 181–189. doi:10.1016/ J.MICROC.2017.10.010
- Han Y, Liu X, Rathinasabapathi B, Li H, Ma LQ (2017). Mechanisms of efficient As solubilization in soils and As accumulation by Ashyperaccumulator *Pteris vittata*. *Environmental Pollution* 227, 569– 577. doi:10.1016/J.ENVPOL.2017.05.001
- He MC (2007). Distribution and phytoavailability of antimony at an antimony mining and smelting area, Hunan, China. *Environmental Geochemistry and Health* **29**, 209–219. doi:10.1007/S10653-006-9066-9
- He MC, Wang XQ, Wu FC, Fu ZY (2012). Antimony pollution in China. *The Science of the Total Environment* 421–422, 41–50. doi:10.1016/ J.SCITOTENV.2011.06.009

- He MC, Wang N, Long X, Zhang C, Ma C, Zhong Q, Wang A, Wang Y, Pervaiz A, Shan J (2019). Antimony speciation in the environment: recent advances in understanding the biogeochemical processes and ecological effects. *Journal of Environmental Sciences* **75**, 14–39. doi:10. 1016/J.JES.2018.05.023
- Herath I, Vithanage M, Bundschuh J (2017). Antimony as a global dilemma: geochemistry, mobility, fate and transport. *Environmental Pollution* 223, 545–559. doi:10.1016/J.ENVPOL.2017.01.057
- Hiller E, Lalinská B, Chovan M, Jurkovič L, Klimko T, Jankulár M, Hovorič R, Šottník P, Fl'aková R, Ženišová Z, Ondrejková I (2012). Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. *Applied Geochemistry* 27, 598–614. doi:10.1016/J.APGEO CHEM.2011.12.005
- Hu XY, Guo XJ, He MC, Li SS (2016). pH-dependent release characteristics of antimony and arsenic from typical antimony-bearing ores. *Journal of Environmental Sciences* 44, 171–179. doi:10.1016/J.JES.2016.01.003
- Li L, Liu H, Li HX (2018). Distribution and migration of antimony and other trace elements in a Karstic river system, Southwest China. *Environmental Science and Pollution Research International* 25, 28061–28074. doi:10.1007/S11356-018-2837-X
- Li L, Tu H, Zhang S, Wu L, Wu M, Tang Y, Wu P (2019). Geochemical behaviors of antimony in mining-affected water environment (Southwest China). *Environmental Geochemistry and Health* **41**, 2397–2411. doi:10.1007/S10653-019-00285-8
- Liu B, Wu F, Li X, Fu Z, Liao H (2011). Arsenic, antimony and bismuth in human hair from potentially exposed individuals in the vicinity of antimony mines in Southwest China. *Microchemical Journal* 97, 20–24. doi:10.1016/J.MICROC.2010.07.008
- Ma LQ, Komart KM, Tu C, Zhang W, Cai Y, Kennelly ED (2001). A fern that hyperaccumulates arsenic. *Nature* 409, 579. doi:10.1038/35054664
- Macgregor K, MacKinnon G, Farmer J, Graham M (2015). Mobility of antimony, arsenic and lead at a former antimony mine, Glendinning, Scotland. *The Science of the Total Environment* **529**, 213–222. doi:10. 1016/J.SCITOTENV.2015.04.039
- Mathews S, Rathinasabapathi B, Ma LQ (2011). Uptake and translocation of arsenite by *Pteris vittata* L.: effects of glycerol, antimonite and silver. *Environmental Pollution* **159**, 3490–3495. doi:10.1016/J.ENVPOL. 2011.08.027
- McBride M, Sauve S, Hendershot W (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science* **48**, 337–346. doi:10.1111/J.1365-2389.1997.TB00554.X
- Midhat L, Ouazzani N, Hejjaj A, Ouhammou A, Mandi L (2019). Accumulation of heavy metals in metallophytes from three mining sites (Southern Centre Morocco) and evaluation of their phytoremediation potential. *Ecotoxicology and Environmental Safety* **169**, 150–160. doi:10.1016/J.ECOENV.2018.11.009
- Müller K, Daus B, Mattusch J, Vetterlein D, Merbach I, Wennrich R (2013). Impact of arsenic on uptake and bio-accumulation of antimony by arsenic hyperaccumulator *Pteris vittata*. *Environmental Pollution* **174**, 128–133. doi:10.1016/J.ENVPOL.2012.10.024
- Murciego AM, Sanchez AG, Gonzalez MAR (2007). Antimony distribution and mobility in topsoils and plants (*Cytisus striatus, Cistus ladanifer* and *Dittrichia viscosa*) from polluted Sb-mining areas in Extremadura (Spain). *Environmental Pollution* 145, 15–21. doi:10.1016/ J.ENVPOL.2006.04.004
- Nakamaru Y, Tagami K, Uchida S (2006). Antimony mobility in Japanese agricultural soils and the factors affecting antimony sorption behavior. *Environmental Pollution* 141, 321–326. doi:10.1016/J.ENVPOL.2005. 08.040
- Paikaray S (2015). Arsenic geochemistry of acid mine drainage. *Mine Water* and the Environment 34, 181–196. doi:10.1007/S10230-014-0286-4
- Pierart A, Shahid M, Séjalon-Delmas N, Dumat C (2015). Antimony bioavailability: knowledge and research perspectives for sustainable agricultures. *Journal of Hazardous Materials* 289, 219–234. doi:10. 1016/J.JHAZMAT.2015.02.011
- Sun WM, Xiao EZ, Dong YR, Tang S, Krumins V, Ning ZP, Sun M, Zhao YL, Wu SL, Xiao TF (2016). Profiling microbial community in a

watershed heavily contaminated by an active antimony (Sb) mine in Southwest China. *The Science of the Total Environment* **550**, 297–308. doi:10.1016/J.SCITOTENV.2016.01.090

- Sun W, Sun X, Li B, Häggblom MM, Li F (2019). Bacterial response to antimony and arsenic contamination in rice paddies during different flooding conditions. *The Science of the Total Environment* 675, 273– 285. doi:10.1016/J.SCITOTENV.2019.04.146
- Suriyagoda LDB, Dittert K, Lambers H (2018). Mechanism of arsenic uptake, translocation and plant resistance to accumulate arsenic in rice grains. *Agriculture, Ecosystems & Environment* 253, 23–37. doi:10. 1016/J.AGEE.2017.10.017
- Tan D, Long J, Li B, Ding D, Du H, Lei M (2018). Fraction and mobility of antimony and arsenic in three polluted soils: a comparison of single extraction and sequential extraction. *Chemosphere* 213, 533–540. doi:10.1016/J.CHEMOSPHERE.2018.09.089
- Telford K, Maher W, Krikowa F, Foster S, Ellwood MJ, Ashley PM, Lockwood PV, Wilson SC (2009). Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia. *Environmental Chemistry* 6, 133–143. doi:10.1071/EN08097
- Tschan M, Robinson B, Schulin R (2009). Antimony in the soil–plant system – a review. *Environmental Chemistry* 6, 106–115. doi:10.1071/ EN08111
- Ungureanu G, Santos S, Boaventura R, Botelho C (2015). Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption. *Journal of Environmental Management* 151, 326–342. doi:10.1016/J.JENVMAN.2014.12.051
- USGS (2018). Antimony: statistics and information. Available at https:// minerals.usgs.gov/minerals/pubs/commodity/antimony/mcs-2018-antim. pdf [verified 30 June 2019].
- Wang YL, Chen YC, Wang DH, Xu J, Chen ZH, Liang T (2013). The principal antimony concentration areas in China and their resource potentials. *Geology in China* 5, 1366–1378. [in Chinese].
- Wang Z, Liu X, Qin H (2019). Bioconcentration and translocation of heavy metals in the soil-plants system in Machangqing copper mine, Yunnan Province, China. *Journal of Geochemical Exploration* 200, 159–166. doi:10.1016/J.GEXPLO.2019.02.005
- Wei C, Ge Z, Chu W, Feng R (2015). Speciation of antimony and arsenic in the soils and plants in an old antimony mine. *Environmental and Experimental Botany* **109**, 31–39. doi:10.1016/J.ENVEXPBOT.2014. 08.002
- Wilson SC, Lockwood PV, Ashley PM, Tighe M (2010). The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review. *Environmental Pollution* **158**, 1169–1181. doi:10.1016/J.ENVPOL.2009.10.045
- Wu FC, Fu ZY, Liu B, Mo CL, Liao H (2011). Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area. *The Science of the Total Environment* 409, 3344–3351. doi:10.1016/J.SCITOTENV.2011.05.033
- Xiao EZ, Krumins V, Tang S, Xiao TF, Ning ZP, Lan XL, Sun WM (2016). Correlating microbial community profiles with geochemical conditions in a watershed heavily contaminated by an antimony tailing pond. *Environmental Pollution* **215**, 141–153. doi:10.1016/J.ENVPOL.2016. 04.087
- Yalaltdinova A, Kim J, Baranovskaya N, Rikhvanov L (2018). *Populus nigra L*. as a bioindicator of atmospheric trace element pollution and potential toxic impacts on human and ecosystem. *Ecological Indicators* **95**, 974–983. doi:10.1016/J.ECOLIND.2017.06.021
- Zhang L, Yang Q, Wang S, Li W, Jiang S, Liu Y (2017). Influence of silicon treatment on antimony uptake and translocation in rice genotypes with different radial oxygen loss. *Ecotoxicology and Environmental Safety* 144, 572–577. doi:10.1016/J.ECOENV.2017.06.076
- Zhou J, Nyirenda MT, Xie L, Li Y, Liu H (2017). Mine waste acidic potential and distribution of antimony and arsenic in waters of the Xikuangshan mine, China. *Applied Geochemistry* 77, 52–61. doi:10.1016/J.APGEO CHEM.2016.04.010

Handling Editor: Montserrat Filella