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Bioaccumulation of antimony, arsenic, and mercury in the vicinities of a large antimony mine, China

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ABSTRACT

To study the characteristics of antimony (Sb) bioaccumulation under high Sb background values, aquatic, amphibious and terrestrial biological samples were collected in the vicinity of the Xikuangshan (XKS) Sb mine area in China. Hydride generation-atomic fluorescence (HG-AFS) analysis showed that Sb concentrations in terrestrial invertebrates (average 30,400 μg kg^{-1} dry wt.) were higher than those in aquatic (average 5200 μg kg^{-1} dry wt.) and amphibian (average 2300 μg kg^{-1} dry wt.) biological samples. Within 1 km distance of the XKS Sb mine area, grasshoppers (*Acrida chinensis*) and earthworms (*Pheretima aspergillum*) had the highest Sb amounts of 17,300 ± 3200 and 43,600 ± 47,700 μg kg^{-1} dry wt., respectively. No Sb biomagnifications were observed. The bioavailability of Sb was found to be lower than those of As and Hg. A preliminary conclusion is that antagonistic effects exist between Sb and Hg accumulation in biological samples from aquatic environments. Our study is the first to report such antagonistic effects between Sb and Hg. If this deduction proves to be correct, it should be taken into consideration in assessing human health risks, especially when Sb and Hg concentrations in the aquatic environments are high.

1. Introduction

Antimony, which is a toxic element [1], and suspected to be carcinogenic[2,3], has been listed as a priority pollutant in both the United States and the European Union [4,5]. Because its abundance in the Earth's crust is generally low, the environmental behavior of Sb has received less attention than other toxic metals such as As, Hg, Pb and Cd. As an excellent flame retardant, pigment, and alloy-hardening material, Sb has been widely used in the manufacturing and chemical industries. In particular, the use of Sb in brake pads, and ongoing large-scale Sb mining/smelting activities, have contributed greatly to the increasing concentrations of Sb in the environment. Although the concentration ratio of Sb to As in the Earth's crust is 1/10, this ratio has been reversed in some contaminated environment [6–8]. Monitoring of Sb concentrations in Tokyo, Japan has shown that the level of Sb in atmospheric particles is at least 2 times those of As [9]. Environmental concerns with regard to Sb have therefore increased recently.

The bioaccumulation behavior of an element can reflect its bioavailability to organisms. Thus, an understanding of the bioaccumulation behavior of a toxic element can provide many clues as to how to protect a variety of biological species in the ecological food chain, and how to evaluate the human health risks of a toxic element. However, little experimental evidence regarding the bioaccumulation behavior of Sb has been available until now because concerns about Sb have only begun to increase in the past decade. It is generally believed that the bioaccumulation behavior of Sb may be similar to that of As. Thus the behavior of Sb is usually predicted from the observed behavior of As [10]. However, the validity of this analogy has not yet been demonstrated and it has some limitations existed. For instance, dimethylarsinic acid is very soluble in water, but dialkylstibinic acid is polymeric with poor water solubility [11]. Data on the bioaccumulation behavior of Sb have shown that in areas where Sb smelting operations are ongoing, Sb concentrations in plant leaves are usually higher than those in roots because of the impact of atmospheric pollution [8,12]. In contrast, no significant difference in Sb concentrations between plant leaves and roots was observed in abandoned Sb mine areas [13]. The results of some studies conducted in Sb mine areas are given in Table 1. The bioconcentration factors (BCFs: element concentrations in organism/element concentrations in the exposure source) of Sb were generally less than 1 [7,12,14,15]. No obvious biomagnification effects of Sb in the food chain were observed [7,15]. However, high Sb concentrations were found in the upper trophic levels of the aquatic food chain [7]. The bioavailability of Sb is generally lower than that of As [7,16]. Nevertheless, high Sb bioaccumulation can be observed in plants

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Table 1
Antimony concentrations and bio-concentration factors (BCFs) in biological samples from some Sb mine areas as reported in previous studies.

Organism	Area	Site description	n[a]	Organ	Concentration (mg kg^{-1}, dw)	BCFs			Reference
						Description	Mean ± S.D.	Range	
Radish	Hunan, China	Sb mine area, arable land	>6	Root	5.54 (3.02–10.5)	Organ/soil	0.45 ± 0.32	0.033–0.83	[8]
			>6	Leaf	54.1 (1.48–121)	Organ/soil	2.97 ± 2.99	0.281–8.71	
Wilding	Tuscany, Italy	Abandoned Sb mine area, old field, mine dumps and tailing ponds	>45	Root	236 (1.68–1150)	Organ/soil	9.55 ± 9.98	0.25–34.8	[13]
			>45	Leaf	275 (6.09–1367)	Organ/soil	7.4 ± 7.0	1.06–33.2	
Vegetable, grain, herbage	Bergland, Germany	Historical Sb/As/Hg mine area, garden and agricultural land	134	Leaf and shoot	0.31 (<0.02–2.2)	Organ/soil	0.006 ± 0.003	0.0005–0.01	[14]
Grass	North-east England	Sb mine area, grassland	24	leaf(100 M)	142 (48–336)	Organ/soil	0.34 ± 0.133	0.16–0.55	[12]
			24	leaf(250 M)	17.3 (8–30)	Organ/soil	0.07 ± 0.025	0.05–0.12	
			6	leaf(450 M)	17.3 (10–22)	Organ/soil	0.09 ± 0.02	0.06–0.12	
Vole (100 M)	North-east England	Sb mine area, grassland	21	Liver, lung, kidney	0.26 (0.18–0.31)	Organ/grass leaf	0.003 ± 0.0006	0.002–0.003	[15]
Rabbit (250 M)			5	Liver, lung, kidney, femur	0.36 (0.15–0.68)	Organ/grass leaf	0.015 ± 0.008	0.006–0.03	
Insectivore (450 M)			6	Liver, lung, kidney	0.31 (0.11–0.49)	Organ/insect	0.028 ± 0.014	0.01–0.05	
Aquatic rooted plant	NSW, Australia	Sb/Au/W mine area, stream	35	Root	342 (18–954)	Organ/sediment	0.93 ± 1.16	0.04–8.68	[7]
			35	Leaf	58 (1.1–212)	Organ/sediment	0.11 ± 0.11	0.002–0.31	
Carnivore			12	Total tissue	149 (0.3–302)	Organ/omnivore	0.66 ± 0.55	0.001–1.34	
Omnivore			9	Total tissue	225 (174–277)	Organ/detritivore	1.43 ± 0.33	1.1–1.75	
Detritivore			2	Total tissue	158 (0.3–316)	Organ/herbivore	1.1 ± 1.1	0.002–2.2	
Herbivore			2	Total tissue	143 (94–193)	Organ/autotroph	0.93 ± 0.32	0.61–1.25	
Macroalgae			5	Total tissue	96 ± 13	Organ/water[b]	0.25		

[a] n refers to the number of samples (same in the following Tables).
[b] Water concentrations in μg L^{-1}.

exposed to high concentrations of Sb [13]. This suggests that the bioaccumulation characteristics of Sb may differ significantly in different environmental contexts. Furthermore, little is known about the bioaccumulation behavior of Sb in different biological species. More information and related data are needed to clarify the characteristics and mechanisms of Sb accumulation in biological species.

Previous studies of Sb were carried out mainly in the context of low concentrations of Sb [10]. However, with increasing concentrations of Sb in the environment, humans and other organisms are being increasingly exposed to Sb. Research on Sb bioaccumulations in the context of higher concentrations can better reflect its behavior in the real environment. In addition, Sb bioaccumulation behavior can be highlighted and clarified under high levels of Sb. This study was therefore conducted on the bioaccumulation behavior of Sb in a large Sb mining/smelting area in Hunan, China, which had been seriously polluted by Sb. The literature showed that tailings, soil, crops [8,17], mine drainage materials [18] and the hair of residents [19] in the area contain high levels of Sb. The studies of Sb bioaccumulation in this area, and its effects, have focused mainly on crops [8,17], wild plants (Deng et al., unpublished data), and fish tissues [20]. These studies indicated that the phytoavailable fraction of Sb in soil is relatively lower; And Sb accumulations in radish leaves were mainly from atmospheric deposition [8,17]. Fish organs exhibited elevated Sb concentrations, and the extent of the accumulation varied with habitat [20]. However, no systematic research was conducted on the bioaccumulation behavior of Sb other than for plants and fishes. Because this area has been severely polluted by Sb, studies in this area of the migration and cycle of Sb in the food web, and their biological effects, are a matter of urgency. These studies provide preliminary data on the bioavailability of Sb, which can form the basis of further assessment of the risk to humans. In this study, Sb, As, and Hg accumulations were compared in aquatic, amphibious, and terrestrial species. Arsenic and Hg were integral to this study because the geochemical behavior and co-occurrence of As are similar to those of Sb. Moreover, elevated As and Hg concentrations have been determined in this Sb mining/smelting area [8,18,19].

2. Materials and methods

2.1. Study area

The Xikuangshan (XKS) Sb mine in Lenshuijiang, Hunan Province in central China is one of the largest Sb mine in the world. The XKS Sb mine covers a total area of 70 km^2, and has undulating topographic features with altitudes in the range 198–1072 m, mainly 200 to 400 m. The climate in this area is characterized by a typical subtropical continental monsoon with an average temperature and annual rainfall of 16.7 °C and 1354 mm, respectively. Antimony exploitation began in 1897 and the mining operations have continued until today. These long-term and large-scale Sb mining/smelting activities have resulted in Sb pollution of the local environment [8,17,18].

2.2. Sample collection and preparation

Between December 2007 and July 2008, water, soil, fish, algae, frog, snail, grasshopper, crab and earthworm samples were collected from the study area (for details, see Table 2 and Fig. 1). Water and soil samples were collected from each site at which fish and earthworms, respectively, were collected. None of the water sampling sites was polluted directly by Sb mine drainage. Organism and soil samples were stored in sealed-polyethylene bags and surface water samples were stored in acid-cleaned plastic bottles. All the samples were immediately stored in ice-packed coolers and then transported to the laboratory where they were stored at −20 °C for biological samples and 2 °C for water samples.

Frozen biological samples were thawed and rinsed individually with deionized water to remove possible impurities. Then organism organs including gill, liver, kidney, muscle, swim bladder and skin were taken out. Complete organs of smaller biological samples were obtained after removal of the viscera. All biological samples were freeze dried for 48 h, and then ground to a powder and stored at −5 °C until analysis. Soil samples were air-dried at the room temperature and ground to 100 mesh.

Table 2
Description of samples and sampling sites.

Site	Site name	Distance (km)[a]	Site description	Sample type (n)
A	Nankuang	1	Pond	Water (3), fish (4)
B	Shuichang	1	River	Water (12), algae (12), crab (9), frog (2)
C	Shuichang	1	Reservoir, grassland	Water (6), fish (19), river snail (3), grasshopper (4)
D	Yangjia	1.5	Pond	Water (6), fish (14)
E	Yangjia	3	Abandon field	Frog (1)
F	Shengli	3	Reservoir	Water (6), fish (15)
G	Shengli	3	Paddy field	Water (3), fish (2), frog (2)
H	Fuyuan	4	Reservoir	Water (6), fish (8)
I	Minzhu	5	Reservoir	Water (6), fish (8)
J	Tongxing	8	Pond	Water (3), fish (3)
1–7		1–7	Abandon or arable land	Earthworm (>100), soil (14)

[a] Distance refers to how far away the sampling site is from the Sb smelting site (the same in the following Tables).

2.3. Analytical methods

All chemical reagents used were purchased from Sinopharm Chemical Reagent Co., Shanghai, China, except KBH_4 (Sigma Chemical Co., St. Louis, MO., USA) and KI (Tianjin Fuchen Chemicals Reagents Co., Tianjin, China). The pH, electrical conductance (EC), and dissolved oxygen (DO) of the water samples were measured in the field. The dissolved organic carbon (DOC) of the water samples was measured using a High TOC II analyzer (Elementar, Germany). Total Sb, As, and Hg concentrations were analyzed on a hydride generation-atomic fluorescence spectrometer system (HG-AFS). Approximately 0.1 g of each biological sample were digested with 3 mL of high purity HNO_3 (65% v/v) in acid-cleaned digestion vessels and approximately 0.5 g of each soil sample were digested with 10 ml of aqua regia (3:1, HCl:HNO_3). These samples were digested by heating (<140 °C) in acid-cleaned digestion vessels. Antimony, As, and Hg in all the digested solutions were determined using an AFS-810 spectrometer (Beijing Jitian, China) (for detail, see reference [20]). The operating conditions of the AFS instrument were optimized, all calibration curves showed good linearity (r>0.999). Total and dissolved Sb, As, and Hg in the water samples were measured using the same method as that used for the digested solutions.

2.4. Quality control

Quality control consisted of method blanks, blank spikes, matrix spikes, blind duplicates and certified materials (CRMs). The CRMs were DOLT-3 (dogfish liver) from National Research Council, Canada, GBW08573 (yellow-fin tuna), GBW07603 (bush leaves) and GBW07406 (soil) from the National Research Centre for Certified Reference Materials, China. Recoveries (measured value/certified value × 100%) for Sb, As, and Hg in the CRMs were within the range of 85–107%, 92–112% and 89–117%, respectively. The relative standard deviations (RSD) of duplicated samples were less than 9%.

2.5. Statistical analyses

The statistical package SPSS for Windows 11.5 (SPSS Inc., Chicago, IL, USA) was used for data analysis. Correlation coefficients were studied by Pearson correlation analysis. Independent-samples t tests were performed to test the significance of different environmental compartments. Statistical tests were considered statistically significant if p<0.05.

3. Results and discussion

3.1. Aquatic organism

At distance of within 1 km the Sb mine area, the Sb concentrations of terrestrial organisms (grasshoppers and earthworms) were significantly higher than those of aquatic and amphibious organisms; fish and frogs had the lowest Sb concentrations (Fig. 2). Although fish, green algae, and river snails are all aquatic species, Sb accumulation levels were lower in fish than in green algae and river snails (Table 3). Antimony concentrations in fish muscles in this study (82.8 ± 20.1 (3.34–387) μg kg^{-1} dry wt.) were slightly higher than those in an abandoned Sb mine area in Corsica, France (75 ± 65 (23–179) μg kg^{-1} dry wt.) [21]. This report did not list the Sb concentration in water so differences in BCFs cannot be compared. Serious Sb pollution of water has been demonstrated in our study area [20]. Significant positive correlations (r = 0.14, p<0.05, n = 197) were found between Sb concentrations in fish tissues and those in the corresponding water samples. This may indicate that water was one of the principal Sb sources for fish. BCFs (fish/water) of Sb (2.34 ± 1.45 (0.11–6.99)) were significantly lower than those for As (48.3 ± 14.7 (1.84–193)) and Hg (127 ± 136 (1.04–727)) (Fig. 3a). This indicates that for fish, the availability of Sb in water was less than the availabilities of As and Hg. Although green algae are one of the main sources of food for crucian and wild carp in this area, Sb concentrations in both of species were only 1% of those in green algae. This suggests that there was no Sb biomagnification in fish/algae.

Antimony accumulations in green algae (Table 3) were significantly higher than the general level (100–200 μg kg^{-1} dry wt.) in unpolluted freshwater and marine algae [22–24]. This can be attributed to the high concentrations of Sb in water at the sampling sites (156 ± 3.92 (150–163) μg L^{-1}), which were significantly higher than the general Sb concentrations in oceans (0.2 μg L^{-1}) and in unpolluted freshwater systems (from a few ng L^{-1} to a few μg L^{-1}). In contrast, Sb levels in green algae in this study were lower than those in an Sb/Au/W mine area in Australia (96,000 ± 13,000 μg kg^{-1} dry wt.). This can be ascribed to a stream at the Australian site which had been polluted directly by the Sb/Au/W mine drainage, and had Sb concentrations up to 381 ± 23 μg L^{-1} [7]. Significant positive correlations between Sb concentrations in algae and those in river water have been found [25]. In our study, the BCFs (algae/water) of Sb (78.1 ± 28.6 (32.5–129)) were lower than those at the Australia site (251 ± 34.1) [7]. The BCFs of Sb were significantly lower than those of As (1366 ± 387 (900–2343)) and Hg (495 ± 284 (141–1118)) (Fig. 3b). Similarly, the Sb BCFs (algae/water) were about one order of magnitude lower than those of As in coastal areas of Mexico [24]. Telford et al. also found that BCFs (algae/water) of Sb (251) were significantly lower than those of As (1217) in a stream at the Australian site [7]. These results demonstrated that the bioavailability of Sb in algae or water is relatively low compared with that of As.

River snails, as expected, had higher concentrations of Sb (3542 ± 448 μg kg^{-1}) than fish (Table 3), probably because they inhabited the bottom layer of the sampling reservoir. Antimony concentrations in sediment are generally higher than those in water [26]. Antimony accumulations in channeled whelks (*Busycon canaliculatum*), on average 10 μg kg^{-1} dry wt., monitored in ocean dump sites in New York, USA [27], were significantly lower than the levels found in river snails in this study. This can be attributed to serious Sb pollution of water in the XKS Sb mine area. In this study, As concentrations in river snails were within the range of those occurring naturally in snails (800–2800 μg kg^{-1} dry wt.) [28]. In contrast, in our results, accumulations of As were lower than those in river snails in a seriously As-polluted areas, Kanker, India (11,000 μg kg^{-1} dry wt.) [29], where the As content of the surface water (74.4 μg L^{-1}) was higher than in our results (11.3 ± 0.5 μg L^{-1}). In our study, the BCFs (river snail/water) of As (117) were also slightly lower than those in the report on the India site(156) [29]. However, the As BCFs (river snail/water) of As in our study are high comparison with those reported in other studies. Irwin et al. [30] reported that the BCFs of snails (*Huernia campanulata*) exposed to As(III) (at 1000 μg L^{-1}) and As(V) (at 100 μg L^{-1}) were 83 and 99, respectively. Exposure of the snail (*Stagnicola emarginata*) to high concentrations of As(III) and As(V) resulted in BCFs ranging from 16 to 17. Our results coincide with this report as relatively low As

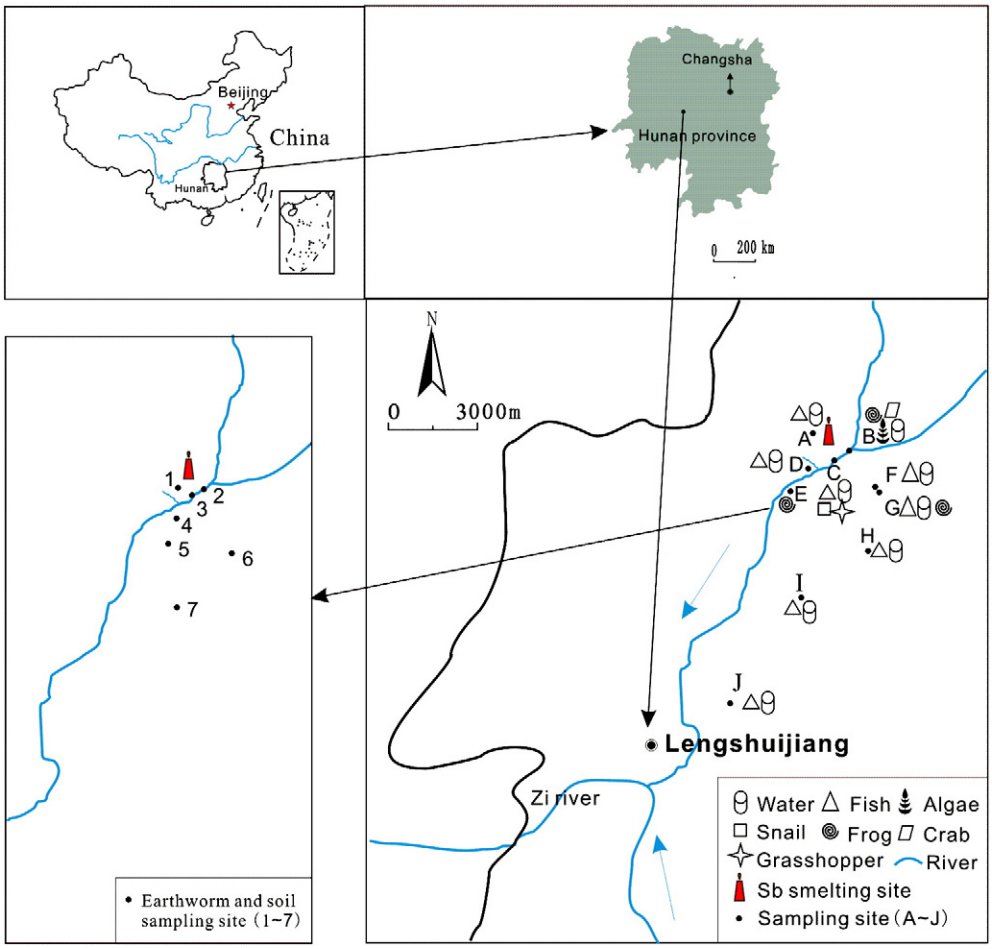

Fig. 1. Map and description of the study area.

concentrations in water were found at the XKS sampling sites. In our study, Hg concentrations in river snails (8.85 μg kg^{-1} wet wt.) were lower than those in apple snails (*Pomacea paludosa*) in water management areas in southern Florida, USA (63 μg kg^{-1} wet wt.) [31]. This can be contributed to the threefold increase in Hg pollution in sediment in southern Florida in the past few decades. In our study, the Sb BCFs (river snail/water) (34.4) were significantly lower than those for As (117), whereas they were unexpectedly higher than those of Hg (29.1). We ascribe the higher values for Sb to characteristics particular to river snails, because the Sb BCFs (fish/water and algae/water) of Sb were generally lower than those of Hg, as discussed above.

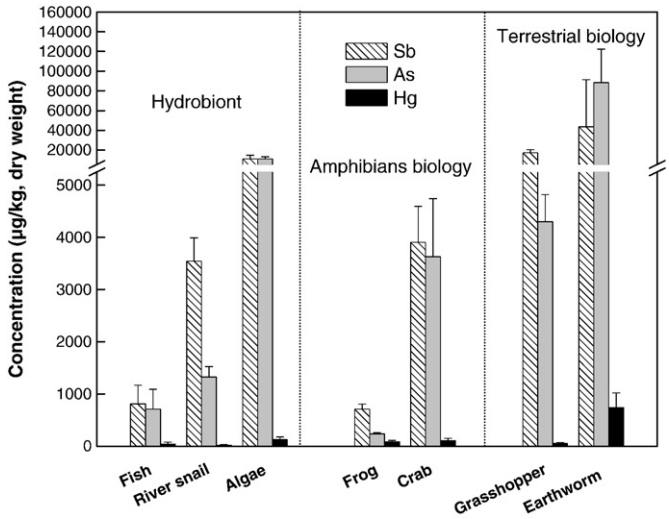

Fig. 2. Antimony, As, and Hg accumulations in biological species within 1 km from the Sb smelting site.

3.2. Amphibian organism

At distances within 1 km from the Sb smelting site, crabs had higher Sb concentrations than frogs (Table 3). This was probably due to the fact that crabs, like river snails, have benthic river habitats and are exposed to high concentrations of Sb in sediments. In fact, higher accumulations of other metals (Cr, Pb, Fe and Zn) have been found in crabs than in shrimp [32]. Although Sb concentrations in the water decreased with increasing distance from the Sb smelting site, the corresponding Sb accumulations in frogs did not show the same trend (Table 4). This result can be attributed to the differences in individual frogs. The weight (after removing the viscera) of younger frogs from site B (2.4 g and 3.2 g) were lower than those from site E (5.6 g and 12.3 g) and G (76.9 g). Thus younger frogs in site B probably had shorter exposure time to, and lower accumulations of, Sb. Elevated concentration of As in one frog (*Rana* sp.) have been reported in the Danube River in Paks, Hungary (2500 μg kg^{-1} dry wt.) [33], which were significantly higher than our results (Table 4). However, As concentrations in water reported in this study (1.1 ± 0.2 μg L^{-1}) were lower compared with those at our sampling sites (4.75 ± 4.02 (0.56–10.7) μg L^{-1}). This unexpected result may be attributed to various characteristics of individual frogs, as discussed above, such as the species, age, and As exposure time. Insects, small arthropods, or worms are the usual food sources of frogs. Grasshopper samples,

Table 3
Antimony, As, and Hg concentrations in biological species within 1 km distance from the Sb smelting site (μg kg^{-1} dry wt.).

Organism		Site	*n*	Sb		As		Hg	
Common name	Latin name			Mean	Range	Mean	Range	Mean	Range
Fish	Crucian *(Carassius auratus)*, Wild carp *(Hemiculter leucisculus)*	A,C	23	809 ± 360	195–1064	710 ± 383	281–1326	44.8 ± 34.2	0.05–95.3
Algae	*Hydrodictyon spp*	B	12	11,100 ± 3600	5700–17,600	11,000 ± 2100	7600–16,000	126 ± 53	43.6–268
Frog	*Rana chensinensis*	B	2	709 ± 95.2	614–804	240 ± 19.3	220–259	85.3 ± 7.21	78.1–92.5
River snail	*Cipangopaludina cathayensis*	C	3	3500 ± 448	3100–4100	1300 ± 201	1200–1600	22.1 ± 10.9	13.8–37.5
Crab	*Portunus pelagicus*	B	9	3900 ± 692	2700–5000	3600 ± 1100	1300–4600	107 ± 43.7	65.7–196
Grasshopper	*Acrida chinensis*	C	4	17,300 ± 3200	13,100–20,900	4300 ± 523	3600–4800	50 ± 19.5	35–77.5
Earthworm	*Pheretima aspergillum*	1,2,3	>50	51,100 ± 52,900	4700–127,800	82,800 ± 37,100	38,800–134,900	806 ± 288	377–1144

included in our study, are small arthropods. Antimony concentrations in grasshoppers were 24 times higher than those in frogs at the same sampling site (Table 3). Based on the assumption that each frog consumed mainly grasshoppers, no obvious biological amplification effect of Sb was found in frogs. This may also be one of the reasons for the unobvious trend for Sb accumulations in frogs with variations in Sb pollution at the sampling sites.

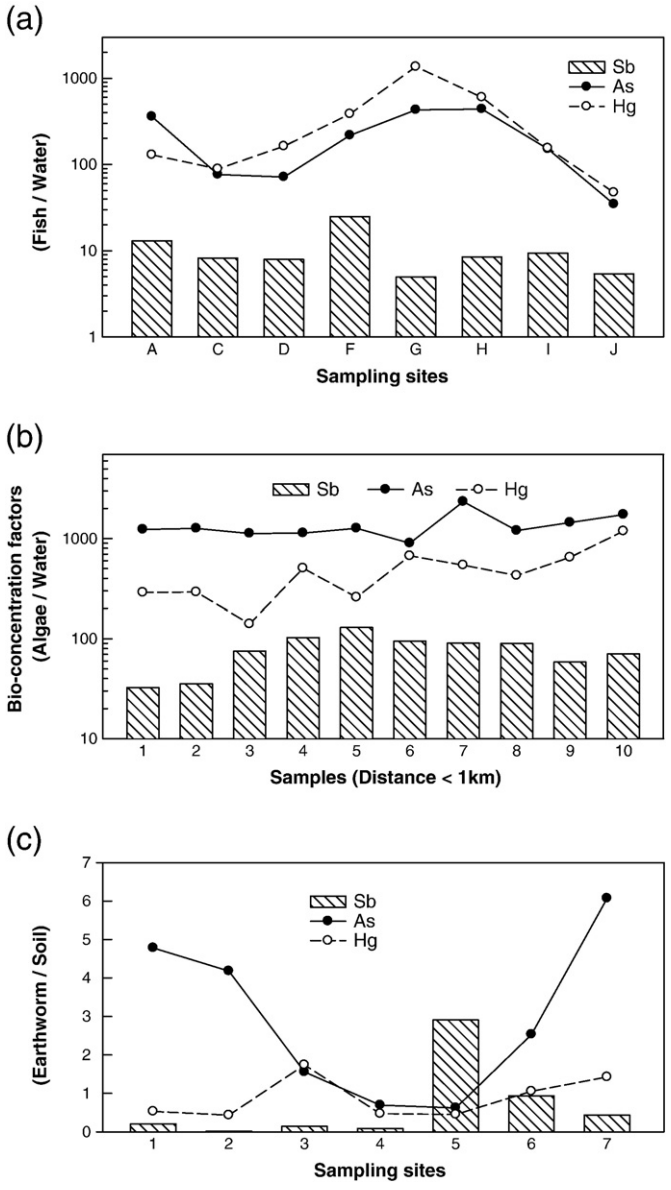

Fig. 3. BCFs of Sb, As, and Hg in different species.

Crabs exhibited elevated Sb accumulations (3901 ± 692 μg kg^{-1} dry wt.) (Table 3). In comparison, previous studies showed lower Sb concentrations (67.7 ± 46.6 (13–129) μg kg^{-1} dry wt.) in rock crabs in ocean dump sites in New York, USA [27]. Although the extent of Sb pollution at the American sampling sites is unknown, the Sb pollution was probably weaker than that in the XKS Sb smelting area. Arsenic and Hg concentrations in red king crabs (*Paralithodes camtschaticus*) in an offshore placer gold mining area in Alaska, USA were 16,090 ± 10,078 μg kg^{-1} and 58 ± 22 μg kg^{-1} dry wt., respectively; no significant differences in As and Hg concentrations were found between mining areas and non-mining areas [34]. In this study, the As levels in crabs were high but the Hg levels were low in comparison with data from the XKS mine area (Table 3), which may be ascribed to different extents of As and Hg pollution, although no data on the levels of As and Hg levels in the water are available in the literature. The Hg concentrations of Chinese mitten crabs in San Francisco Bay, CA, USA [35] were, as expected, higher (202 ± 236 μg kg^{-1} dry wt.) than those in the XKS mine area because the sampling area in the study was contaminated by Hg. The Sb BCFs (crab/algae) (0.35 ± 0.06) were similar to the As BCFs (0.35 ± 0.06), but lower than the Hg BCFs (0.85 ± 0.35). Crabs are omnivorous biological species and usually feed on algae and organic debris. Green algae and crabs were sampled at the same site in this study. Based on the assumption that green algae were the main food source of the crabs, no biological amplification effect of Sb was evident.

3.3. Terrestrial organism

Grasshoppers and earthworms are invertebrates, which have higher Sb accumulations than the other biological samples in this study (Fig. 2). Ainsworth et al., [15] reported that terrestrial invertebrates have high accumulations of Sb. The Sb concentrations were 1–2 orders of magnitude higher than those in other terrestrial animals such as rabbits and voles. In comparison with the levels of Sb (61,381 (2400–398,000) μg kg^{-1} dry wt.) found within 0.45 km of the Sb mine area in other Sb mine areas [15], Sb accumulations in grasshopper samples from the XKS mine area were lower but within the range of reported concentrations. Arsenic and Hg concentrations in grasshoppers within 1 km distance from the XKS mine area (Table 3) were higher than those in a polluted agricultural area in Arizona, USA (As: 823 (650–1400) μg kg^{-1} dry wt.; Hg: not detected–30 μg kg^{-1} dry wt.) [36]. In contrast, the concentrations of Hg we had obtained were significantly lower than those (200–600 μg kg^{-1} dry wt.) in grasshoppers in the Peloponnesus region of Greece [37]. This may be attributed to the relatively low Hg pollutions in the XKS mine area [20]. Grasshoppers generally constitute significantly large amounts of the arthropod biomass of grasslands [38], and they are also a common herbivorous invertebrates at our sampling site. In addition, they prey upon other insectivorous vertebrates and birds. Thus, the grasshoppers, which contained high levels of Sb and As in the XKS Sb mine area, could play a significant role in accumulating and further transferring Sb and As to higher trophic levels. In fact, previous

Table 4
Antimony, As, and Hg concentrations in frogs from different sites (μg kg^{-1} dry wt.).

Site	n	Sb		As		Hg	
		Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
B	2	709 ± 95.2	614–804	240 ± 19.3	220–259	85.3 ± 7.21	78.1–92.5
E	1	872		261		75.4	
G	2	1100 ± 35.5	1085–1156	492 ± 26.5	466–518	139 ± 21.4	119–161

studies have suggested that grasshoppers can be regarded as the bioindicators of heavy metal pollution [37].

The mean levels of Sb, As, and Hg accumulations in earthworms were 12,700 ± 22,200 μg kg^{-1}, 21,800 ± 14,900 μg kg^{-1} and 207 ± 157 μg kg^{-1} dry wt., respectively. In comparison, Gál et al. reported lower concentrations of Sb (27,000 μg kg^{-1} dry wt.) in earthworms in an abandoned Sb mine area in Glendinning, Scotland [39]. In contrast, As concentrations in their study were significantly higher (960,000 μg kg^{-1} dry wt.). The BCFs (earthworm/soil) of both Sb and As in their study were below 1, which is consistent with our results. Ainsworth et al. [15] showed that earthworms had high accumulations of Sb, correlated to the extent of Sb pollution in the soil. And they ascribed the high Sb accumulations to the significant contribution to the total body burden made by soil in the gut. Our study indicated that Sb and As concentrations (63,000 μg kg^{-1} and 55,100 μg kg^{-1} dry wt., respectively) in earthworm gut were significantly higher than the corresponding concentrations (47,900 and 35,200 μg kg^{-1} dry wt.) in the soil habitat. In contrast, Hg concentrations in the gut (599 μg kg^{-1} dry wt.) were slightly lower than those in the inhabit soil (671 μg kg^{-1} dry wt.). Our study showed that the Sb BCFs (earthworm except the gut/soil) (0.19) were significantly lower than those for As (0.83) and Hg (0.25) (Fig. 3c). The Sb BCFs were also lower than those in other Sb mine areas (0.89) [15], suggesting that the Sb bioavailability in soil may differ in different area. It should be noted that no significant positive correlation was found between Sb concentrations in earthworms and those in the corresponding soils ($r = 0.12$, $p > 0.05$). For instance, lower concentrations of Sb (20,700 μg kg^{-1} dry wt.) were found at sampling site 5, but the earthworm from that site exhibited relatively high Sb accumulations (55,800 μg kg^{-1} dry wt.) (Table 5). Previous studies indicated that more mobilized metals gradually migrated from the surface to the deeper layers of mine tailings after the tailings had been abandoned [40]. Sampling site 5 in our study included a larger number of Sb mine tailings which had been abandoned for years, so there was probably high mobility of Sb in its median layer, which was the layer inhabited by earthworms. This indicated that Sb accumulation in earthworms did not merely depend on the total concentrations of Sb in the soil, but depend mainly on the amount of bioavailable Sb.

3.3. Relationship between Sb and As accumulation in organism

Antimony contaminations have most frequently been reported on and around mining and smelting sites often co-occurring with As [41,42]. In our study, significant positive correlations were found between Sb and As in environmental compartments (soil and water) and those in organisms (Fig. 4). Clear linear relationships were shown between Sb and As in water, aquatic organisms and amphibian organisms. In contrast, relatively weaker linear correlations were found in soil and terrestrial organism. These results suggested that Sb and As in aquatic environments exhibited closed relationship.

Although the bioaccumulation behavior of Sb generally believed to be similar to that of As [10], our results suggested that lower BCFs, compared with As, were found in water and fish, in water and algae, and in soil and earthworm (Fig. 3). In fact, relatively low bioavailability of Sb has been reported in soils and plants [8,14], in grass and small mammals [15], in sediments and aquatic plants [7], and in soils and human [16].

Using the observed behavior of As to predicted the behavior of Sb has not yet been demonstrated and it has some limitations. For instance, dimethylarsinic acid is very soluble in water, but dialkylstibinic acid is polymeric with poor water solubility [11]. Wilson et al. reviewed some work on Sb contaminated soils and concluded that although the metalloids behave similarly at times, this cannot always be assumed in all environments [42].

3.4. Relationship between Sb and Hg accumulation in organism

The XKS Sb mine area was seriously polluted by Sb and slightly polluted by Hg [8,18]. This study showed that the antagonistic effects between Sb and Hg probably existed during their accumulation in organisms. This was in accord with the following pieces of evidence: (1) Fish gills exhibited the highest Sb accumulations in fish (gills/other organs = 1.56), but showed the lowest Hg concentrations (gills/other organs = 0.084) (Fig. 5). (2) Antimony concentrations in crab shells were significantly higher than those in other organs (shells/other organs = 1.67); however, the converse is seen for Hg levels (crab shells/other organs = 0.43) (Table 6); (3) Significant negative correlations were found between Sb concentrations in water and Hg concentrations in fish (Table 7).

Mercury concentrations in water did not correlate with Sb concentrations in fish (Table 7), probably because the relatively low levels of Hg in the water had less effect on the Sb accumulations in fish. However, the high concentrations of Sb in water can significantly inhibit the accumulation of Hg in fish.

Antagonistic effects between Hg and Se with regard to their toxic effects on organisms have been found. The mechanism is attributed mainly to the high affinity between Se and Me–Hg, which reduces the toxic effects of mercury on organisms. This affinity is a million times higher than that between S and Hg. [43–45].

Table 5
Antimony, As, and Hg concentrations in earthworms (*Pheretima aspergillum*) in different sites (μg kg^{-1} dry wt.).

Site	Site descriptions	Distance	Sb		As		Hg	
			Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
1	Abandoned field near Sb smelting site	0.5	125,300 ± 2100	125,300–127,800	80,100 ± 1700	78,000–82,200	1100 ± 116	899–1100
2	Abandoned field near river	0.8	22,300 ± 1800	21,100–24,800	129,500 ± 4400	124,200–134,900	952 ± 24.8	922–982
3	Grass land near pond	1	5800 ± 866	4700–6800	38,800 ± 43.5	38,800–38,900	404 ± 38.2	377–458
4	Arable land	2	5500 ± 546	5000–6500	27,900 ± 2700	24,200–32,000	369 ± 52	300–444
5	Wastes of Sb mine	3	55,700 ± 5400	49,100–62,300	38,400 ± 4400	33,000–43,800	528 ± 97.8	459–667
6	Abandoned field near pond	4	2700 ± 237	2400–2900	21,100 ± 2100	19,700–24,000	234 ± 26.9	196–253
7	Abandoned field near pond	6	25,200 ± 1700	23,100–27,300	90,400 ± 5000	84,300–96,400	580 ± 14.4	562–598

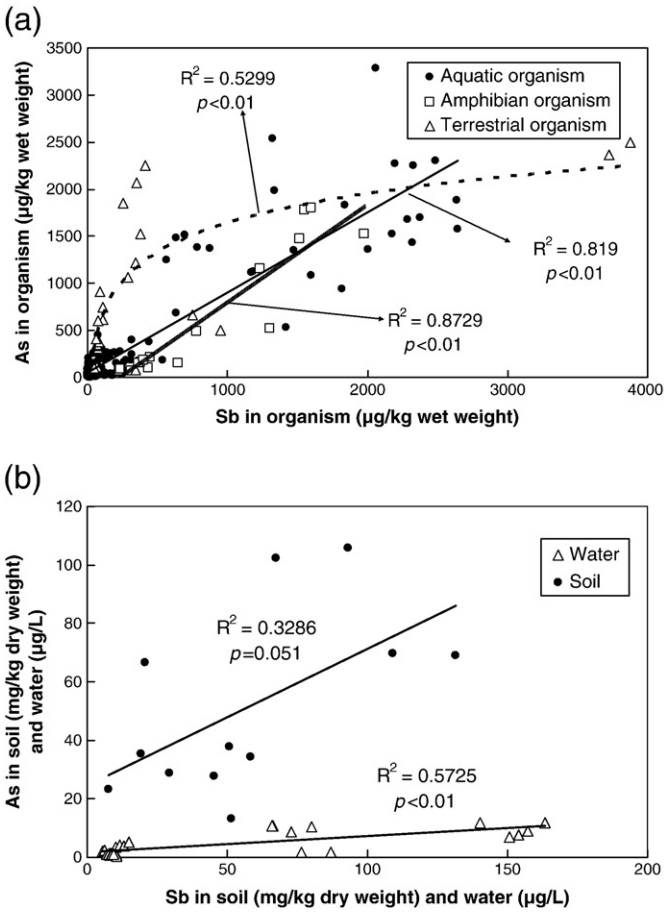

Fig. 4. (a) Relationship between Sb and As in organisms (concentrations in terrestrial organism expressed in μg kg^{-1} divided by 20). (b) Relationship between Sb and As in water and soils.

To our knowledge, no report has previously been published on antagonistic effects between Sb and Hg accumulations in organisms. Our study is the first to show the probable existence of such antagonistic effects between Sb and Hg. Bakir et al. [46] have found strong competitions among Sb, Zn, Ni and Al in adsorption on seaweeds; the presence of Sb(III) in multi-component metal solutions suppressed the removal of Ni(II), Zn(II), and Al(III) by seaweeds, reducing removal from 90, 90 and 74% to 28%, 17% and 24%, respectively. Therefore, in our study, strong adsorption competitions

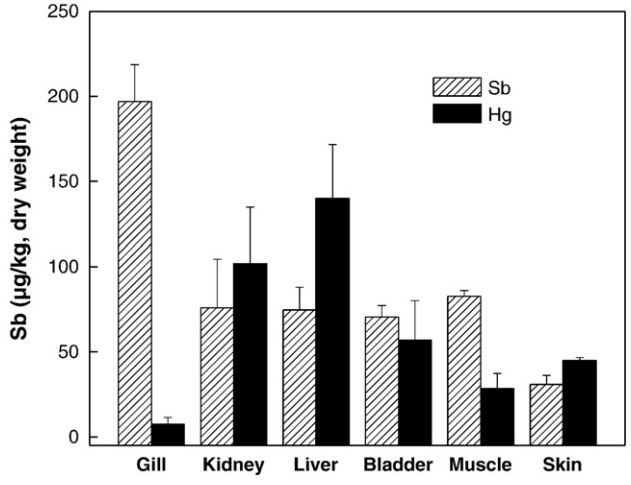

Fig. 5. Antimony and Hg accumulations in fish organs.

Table 6
Element distribution in the different organs of crabs (μg kg^{-1} dry wt.) (mean ± SD).

	Sb	As	Hg
Shell	6300 ± 260	2500 ± 345	89.6 ± 17.2
Other organs	3800 ± 88.7	2400 ± 58.5	211 ± 21.8

Table 7
Correlation coefficients of element concentrations between water and fish.

	Sb (W)	As (W)	Hg (W)	Sb (F)	As (F)	Hg (F)
Sb(W)	1					
As(W)	0.71**	1				
Hg(W)	0.03	0.18	1			
Sb(F)	0.14*	0.18**	−0.03	1		
As(F)	0.15*	−0.05	−0.29**	0.36**	1	
Hg(F)	−0.15*	0.25**	0.49**	0.07	−0.12	1

W: water. F: fish. Fish organ: $n = 197$. Water: $n = 45$.
* Significant correlation was observed at $p < 0.05$.
** Significant correlation was observed at $p < 0.01$.

probably also exists between Sb and Hg during their accumulations in organisms. In particular, for organs, with a high affinity to Sb, such as fish gills and crab shells, the antagonistic effects were outstanding, leading to low accumulations of Hg in these organs.

The antagonistic effect between Sb and Hg is only a preliminary conclusion, suggesting that further evidence and argumentation are required. Such antagonistic effects either were or were not prevalent, and a more specific study of the extent of these antagonistic effects is needed.

4. Conclusions

Antimony concentrations in biological species in the XKS Sb mine area were usually higher than those at other Sb mine and in unpolluted areas, whereas As and Hg levels in biological samples were close to those in other less-contaminated areas. Antimony concentrations in terrestrial invertebrates were higher than those in aquatic and amphibious species. No obvious Sb biomagnifications were observed. The bioavailability of Sb was found to be low comparison with As and Hg. Antagonistic effects probably exist between Sb and Hg accumulations in organisms in aquatic environments, and our study is the first to report these effects. If this conclusion is valid, this should be taken into consideration in assessing human health risks, especially when concentrations of Sb and Hg in aquatic environment are high.

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