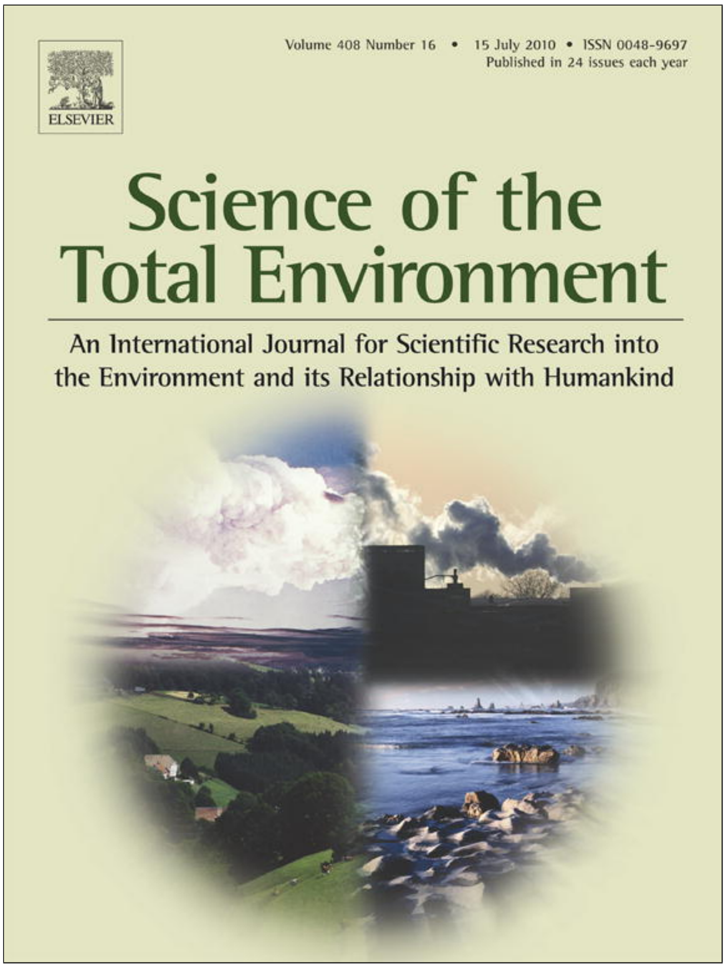

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Antimony, arsenic and mercury in the aquatic environment and fish in a large antimony mining area in Hunan, China

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ABSTRACT

Antimony (Sb) has received increasing attention recently due to its toxicity and potential human carcinogenicity. In the present work, drinking water, fish and algae samples were collected from the Xikuangshan (XKS) Sb mine area in Hunan, China. Results show that serious Sb and moderate arsenic (As) contamination is present in the aquatic environment. The average Sb concentrations in water and fish were $53.6 \pm 46.7\ \mu g\ L^{-1}$ and $218 \pm 113\ \mu g\ kg^{-1}$ dry weight, respectively. The Sb concentration in drinking water exceeded both Chinese and WHO drinking water guidelines by 13 and 3 times, respectively. Antimony and As concentrations in water varied with seasons. Fish gills exhibited the highest Sb concentrations but the extent of accumulation varied with habitat. Antimony enrichment in fish was significantly lower than that of As and Hg.

1. Introduction

As a toxic trace element and a suspected human carcinogen (Gebel, 1997), antimony (Sb) has been listed as a priority pollutant of interest in both the USA (USEPA, 1979) and EU (Council of the European Communities, 1976). Similar to As, Sb is a chalcophilic group V metalloid, and is assumed to have a comparable geochemical behavior and toxicity (Gebel, 1997; Wilson et al., 2004; Tighe et al., 2005). The principal global sources of anthropogenic Sb pollution are mining and smelting (Adriano, 1986; Li and Thornton, 1993). Antimony concentrations in Sb mine drainage can reach $6064–7502\ \mu g\ L^{-1}$ (Zhu et al., 2009). In contrast, in non-polluted water Sb concentrations are usually less than $1.0\ \mu g\ L^{-1}$ (Filella et al., 2002a). Like lead and mercury, antimony contamination is also a global environmental issue. Antimony enrichment and accumulation have been reported in peat bogs in Europe and in polar ice in the Canadian arctic during the past few decades (Shotyk et al., 1996; Krachler et al., 2005). Antimony has been reported as the most enriched trace element in some city aerosols (Shotyk et al., 2005). However, little attention has been paid to the environmental chemistry of Sb in comparison to metals and metalloids such as As, Pb and Hg (Shotyk et al., 2005), primarily because the Sb content of most environmental matrices is usually low (Bencze, 1994). Recently, environmental concerns regarding Sb has increased as a result of elevated concentrations around smelters, chemical plants, mining and mineralized areas, and the increased availability of Sb rich consumer products (i.e., use in fire retardants and brake pads) (Filella et al., 2002a).

Antimony is generally not readily mobilized in the environment despite high Sb soil concentrations at smelter sites (Flynn et al., 2003; Wilson et al., 2004). The “phytoavailable Sb” in contaminated soil was found to be only 0.06–0.59% of the total Sb content in German Sb/As/Hg mine area (Hammel et al., 2000) and 1.62–8.26% in Chinese Sb mine area (He, 2007). Relatively low Sb bioavailability has also been reported in soils, plants, invertebrates and small mammals around a smelter in England Sb mine area (Ainsworth et al., 1990a,b). Bioconcentration factors (BCFs, a ratio of element concentrations in organism to that in the exposure source) just ranged from 0.003 to 0.34 in these areas. Nevertheless, elevated Sb and As concentrations have been measured in the upper trophic level macroinvertebrates of an aquatic ecosystem contaminated by mining activity (Telford et al., 2009). Especially highly soluble Sb and methylantimony has been found in natural waters (Andreae et al., 1981). Although the distribution and chemical form of Sb in the terrestrial and aquatic environment probably has a strong influence on its uptake, the bioavailability and accumulation of Sb in aquatic environments

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remain unclear, and further investigation is required to fully understand the behavior of Sb in aquatic ecosystems.

China is one of the largest Sb producers in the world. The average production of Sb in these two years of 1999 and 2006 accounted for 85.5% of the global production (Carlin, 2000, 2006). The largest Sb mine in China is Xikuangshan (XKS) Sb mine, located in Lengshuijiang, Hunan province in central China. The XKS Sb mine is located on a large Sb deposit and is nicknamed the "World's Antimony Capital". Antimony was first mined at the site in 1897 and mining operations continue today. The climate in this area represents a typical subtropical continental monsoon with an average annual rainfall of 1354 mm. Significant seasonal differences in rainfall exist with highest rainfall in summer (approx 550–600 mm from May to July).

A number of previous studies have been undertaken in the area. These showed that mine tailings (He, 2007), mine drainage (Zhu et al., 2009), soils (He, 2007), crops (He and Yang, 1999; He et al., 2002) and hair of local residents (Liu et al., 2009) contain elevated Sb, As and Hg concentrations (Table 1). These studies focused mainly on Sb effects on crops, Sb accumulations and mobility in mine tailings, mine drainage and soils. However, to date, Sb in drinking water and its biogeochemical behavior in the aquatic environment of the mine area have not been investigated. The objectives of the present study were to investigate contamination and bioaccumulation of Sb, As and Hg in water and fish in the area of the XKS Sb mine.

2. Materials and methods

2.1. Sampling procedure

Between December 2007 and July 2008, 73 fish, 51 water and 12 algae samples were collected from the study area. The sampling sites included a river (Shuichang River), 3 ponds (Nankuang, Yangjia and Tongxing), and 4 reservoirs (Shuichang, Shengli, Fuyuan and Minzhu) (Table 2 and Fig. 1). These water sampling sites were not directly polluted by Sb mine drainage. Antimony smelting operations and subsequent atmospheric transportation of Sb may have contributed to pollution of these sites. All reservoirs are used as drinking water supplies. Water samples were divided at each site. One part was acidified to 1% v/v with ultrapure HCl in order to determine dissolved (filtered with 0.45-μm filtration membranes in the field) and total metal (unfiltered) concentrations; The other part was not acidified in order to measure dissolved organic carbon (DOC). Fish and algae samples were stored in sealed-polyethylene bags and water samples were stored in acid-cleaned plastic bottles. All samples were immediately placed in ice-packed coolers and transported to the laboratory where they were stored at −20 °C for fish and algae, and 2 °C for water.

Table 1

Mean Sb, As and Hg concentrations in environmental compartments in XKS Sb mine area reported by the previous literature (mg kg^{-1}).

	N	Sb	As	Hg	Reference
XKS area					
Mine tailing	–	1291	332	4.59	He (2007)
Seepage water[a]	–	(8.4–11.3)	(0.04–1.20)	–	He (2007)
Mine drainage	18	10.1 ± 7.39	0.127 ± 0.3	0.003 ± 0.003	Zhu et al. (2009)
Soil	–	(100.6–5045)	35.1	14.9	He (2007)
Radish root	36	5.6	(0.17–85.1)	(0.06–0.4)	He (2007)
Radish leaf	36	54	(0.98–34.5)	(0.19–2.52)	He (2007)
Residents' hair	67	15.9	4.21	1.79	Liu et al. (2009)
Control area					
Typical fresh water worldwide	–	<1 (μg L^{-1})	–	–	Filella et al. (2002b)
Typical Chinese soils	–	(0.8–3)	–	–	Qi and Cao (1991)
Plant in Sb/As/Hg mine area, Germany	134	0.31	–	–	Hammel et al. (2000)
Typical urban residents' hair	22	0.53	0.28	0.34	Liu et al. (2009)

N, number of analyzed samples.

ND, not determined.

[a] From the Sb smelter furnace clinker.

Frozen fish and algae samples were thawed and rinsed individually with deionized water to remove possible metal contaminants. The fish organs including gill, liver, kidney, muscle, swim bladder and skin were then extracted. Subsequently, gill and skin were washed successively with Milli-Q water to remove adsorptive impurities. All samples were freeze-dried for 48 h, and then ground into powders and stored at −5 °C until analysis.

2.2. Analytical methods

All chemical reagents used were purchased from Sinopharm Chemical Reagent Shanghai Co., China, except KBH_4 (Sigma Chemical Co., St. Louis, MO, USA) and KI (Tianjin Fuchen Chemicals Reagents Co., China). pH, electrical conductance (EC), and dissolved oxygen (DO) of water samples were measured in the field. Dissolved organic carbon (DOC) of the water samples was measured using a High TOC analyzer (Elementar, Germany). Total and dissolved Sb, As and Hg concentrations were determined using a hydride generation-atomic fluorescence spectrometer (HG-AFS). Approximately 0.1 g of fish and algae were oxidized with 3 mL of high purity HNO_3 (65% v/v) in acid-cleaned digestion vessels, the mixture allowed to digest overnight at room temperature (or for 2–3 h at 60 °C). The vessels were then heated slowly to 125 °C for 1 h and heated continuously to keep slightly boiling (<140 °C). When the solution decreased to approximately 1 mL, 1 mL H_2O_2 (30%, v/v) was added and samples were heated for an hour. Once cooled the solutions were carefully transferred and made up to the 25 mL volume with Milli-Q water. One hour later an aliquot of 5 mL was transferred into sample bottles, to which 1 mL of ultrapure HCl (30%, v/v) and 1 mL of preliminary reductant (10% (m/v) analytical grade KI + 2% (m/v) analytical grade ascorbic acid) was added. The samples were made up to 10 mL volume with Milli-Q water and left for 30 min until they were analyzed using the AFS-810 (Beijing jitian, China). The operating conditions of AFS instrument were optimized and all calibration curves demonstrated good linearity ($r > 0.999$). Total and dissolved Sb, As and Hg in the water were measured using the same method as that used for the digested solution.

2.3. Quality control

Quality control consisted of method blanks, blank spikes, matrix spikes, blind duplicates and certified materials (CRMs). The CRMs include DOLT-3 (Dogfish liver) (from National Research Council, Canada), GBW08573 (Yellow-fin tuna) and GBW07603 (Bush leaves) (both from National Research Centre for Certified Reference Materials, China). All samples with outlier were analyzed again, by repeating the digestion and measurement procedure. The recoveries (Measured value/Certified value × 100%) for Sb, As and Hg in CRMs were in the range of 85–107%, 92–112% and 89–117%, respectively. The relative standard deviation (RSD) of duplicated samples was less than 9%.

2.4. Statistical analyses

The statistical package SPSS for windows 11.5 (SPSS Inc., Chicago, Illinois, USA) was used for data analyses. Correlation coefficients were studied using Pearson correlation analysis. Independent-sample *t*

Table 2
Samples and sampling site description.

Site	Site name	Sampling date	Distance (km)[a]	Site descriptions	Water samples	Fish samples	Fish species
A	Nankuang	Jul. 2008	1	Pond	3	4	Crucian (*Carassius auratus*)
B	Shuichang	Dec. 2007, Jul. 2008	1	River	12	–	–
C	Shuichang	Dec. 2007, Jul. 2008	1	Reservoir	6	19	Crucian, wild carp (*Hemiculter leucisculus*)
D	Yangjia	Dec. 2007, Jul. 2008	1.5	Pond	6	14	Crucian, grass carp (*Ctenopharyngodon idellus*)
E	Shengli	Dec. 2007, Jul. 2008	3	Reservoir	6	15	Grass carp, Crucian, herring (*Mylopharyngodon Peters*)
F	Shengli	Jul. 2008	3	Paddy field	3	2	Grass carp
G	Fuyuan	Jul. 2008	4	Reservoir	6	8	Grass carp, Crucian, carp (*Cyprinus carpio*)
H	Minzhu	Dec. 2007, Jul. 2008	5	Reservoir	6	8	Grass carp, Crucian, bighead crap (*Aristichthys mobilis*)
I	Tongxing	Jul. 2008	8	Pond	3	3	Grass carp

[a] Distance was the sampling site away from the Sb smelting site (same in the following tables).

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. Sb, As and Hg in the water

The average concentrations of Sb, As and Hg in water were $53.6 \pm 46.7\ \mu g\ L^{-1}$, $4.75 \pm 4.02\ \mu g\ L^{-1}$ and $0.69 \pm 0.75\ \mu g\ L^{-1}$, respectively (Table 3). The percentage of dissolved Sb relative to total Sb in the water was larger than that of As and Hg (85.2%, 57.3% and 48.4%, for Sb, As and Hg, respectively). Antimony concentrations in water were significantly higher than those in some Sb and metal mine areas worldwide (Table 4). In contrast, Sb concentrations were within the range of values reported by other authors in mine contaminated waters (Telford et al., 2009), and were lower than those polluted directly by the Sb mine drainage (Zhu et al., 2009). However, As concentrations were lower than those generally reported in other contaminated areas (Frisbie et al., 2002; Culioli et al., 2009; Kazi et al., 2009; Telford et al., 2009). Mercury

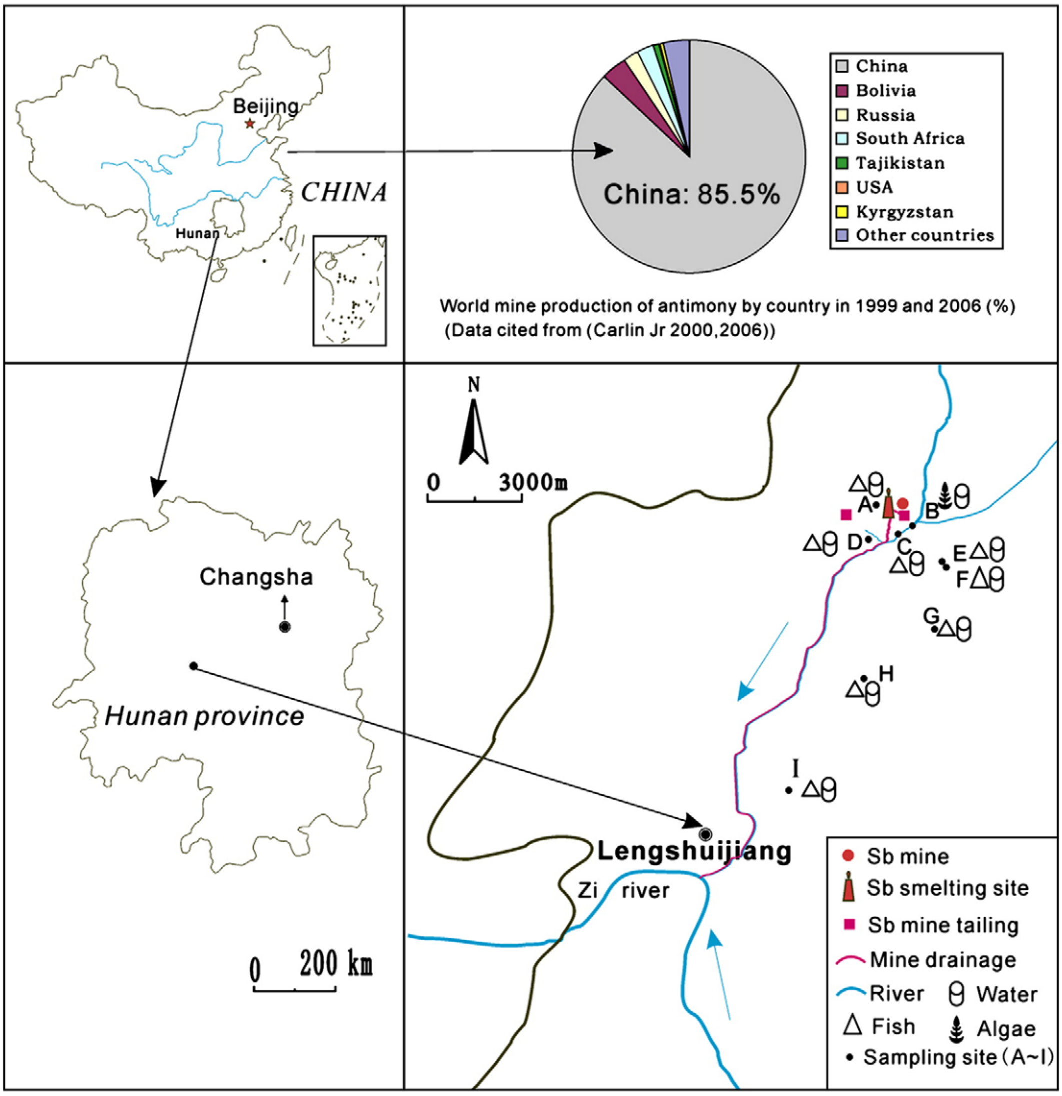

Fig. 1. Map of the study area and description.

Table 3
Total Sb, As and Hg levels in water in XKS Sb smelting area (μg L^{-1}).

Site	Site descriptions	Distance (km)	Sb	As	Hg	Sb/As
			Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean
A	Pond	1	81.8 ± 7.3	1.68 ± 0.08	0.05 ± 0.02	48.7
B	River	1	156 ± 4	8.91 ± 1.62	0.2 ± 0.1	17.5
C	Reservoir	1	103 ± 37	11.3 ± 0.5	0.76 ± 0.68	9.12
D	Pond	1.5	43.7 ± 32.7	6.6 ± 3	0.99 ± 0.75	6.62
E	Reservoir	3	6.67 ± 0.74	1.65 ± 0.55	0.76 ± 0.67	4.04
F	Paddy fied	3	8.7 ± 1.2	0.69 ± 0.05	0.05 ± 0.03	12.6
G	Reservoir	4	10.4 ± 0.1	0.56 ± 0.06	0.09 ± 0.01	18.6
H	Reservoir	5	8.66 ± 0.46	1.16 ± 0.08	0.68 ± 0.59	7.47
I	Pond	8	13.2 ± 1.7	4.41 ± 0.82	1.91 ± 0.35	2.99

concentrations in the water were slightly higher than those in some urban areas (Moore and Sutherland, 1980; Fang et al., 2004), but were significantly lower than those in Hg smelting (Li et al., 2008) and industrially polluted areas (Ferreira et al., 1979). In fact, He (2007) reported an elevated mean concentration of Hg of 14.9 (9.67–21.3) mg kg^{-1} in soils, compared with a baseline value in this area of 0.06 to 0.08 mg kg^{-1} (Wen and Chi, 2007). This suggests that, in addition to Sb, As and Hg contamination was also observed in the vicinity of the XKS Sb mine.

Concentrations of Sb, As and Hg in water have been compared with drinking water guidelines (Table 5) because the river (site B) and reservoirs are used as water supplies for local residents. The average Sb concentration exceeds the Chinese and WHO guidelines by 13 and 3 times, respectively. In contrast, As and Hg concentrations were near and below the WHO guidelines respectively.

Using elemental ratios to distinguish metals' source origin is a simple and theoretically possible approach and has been applied in other studies in Pb/Zn smelting impacted areas (Eckel et al., 2002; Bi et al., 2006). Antimony and As are generally spatially correlated in the environment (Byrd, 1990). The different behavior of Sb and As during the Sb smelting process (e.g. boiling points of Sb and As are 1587 and 603 °C respectively) will result in different Sb/As ratios in different environmental compartments. According to the literature related to the study site (Table 3), the data for mine drainage shows that Sb/As ratios were extremely high with an average of 79.5 (Zhu et al., 2009); Sb/As ratios in seepage water from the smelter furnace clinker (mean: 15.3) were also relatively higher in comparison to that of mine tailings (mean: 3.89) and soils (mean: 2.87) (He, 2007). Data suggest that the Sb smelting activities lead to the high Sb/As ratios in the polluted water. We postulate that most As (b.p. 603 °C) evaporated during the high temperature Sb (b.p. 1587 °C) smelting process due to its lower boiling point resulting in little retention in mine drainage. The Sb/As ratio in the pond (site A) located closest to the Sb smelting site is extremely high (mean: 48.9). The Sb/As ratios in the river (site B) in the vicinity of the Sb smelting site were also relatively high (mean: 18.2). This river (site B), despite no direct mine drainage input, had probably been polluted indirectly by the mine discharge. In fact, it is likely that Sb may gradually leach out from the abandoned mine tailings up stream of the river.

Trends in Sb, As and Hg concentrations in water with distances from the XKS Sb smelting site are shown in Fig. 2. Antimony and As concentrations near the Sb mine area (distance ≤ 1.5 km) were significantly higher than those reported at the other sites, indicating that Sb and As concentrations were highly affected by Sb smelting activities. However, a similar trend was not observed for Hg. In fact, the lowest Hg concentrations (mean: 0.049 μg L^{-1}) were found in the pond water (site A) affected to a great extent by Sb smelting operations. This mainly attributed to that Hg concentrations in water were less affected by the Sb smelting. Moreover, most Hg may also be evaporated and little retained in the mine drainage due to its low boiling point (357 °C). In fact, Sb mine tailing (He, 2007) and mine drainage (Zhu et al., 2009) were characterized by relatively lower Hg concentrations in this area compared to the soils. In general, Hg pollution appeared to have been derived mainly from metal smelting flue gas dusts, which subsided rapidly and resulted in significant decrease of Hg concentrations in soils with increasing distance from the metal mined areas (Sterckeman et al., 2002; Li et al., 2008).

Variations of Sb and As concentrations in the water with different seasons were also observed (Fig. 3). Water samples collected in the reservoir (site C) and pond (site D) closest to the smelter (distance < 1 km)

Table 4
Comparison of Sb, As and Hg concentrations in water and fish muscle.

Area	Water or fish	Sb[a]	As[a]	Hg[a]	Area description	Reference
China	River	152 (135–163)	8.7 (7.1–12)	0.22 (0.08–0.4)	Sb mine	This study
	Reservoir	36 (7.3–140)	3.6 (0.56–10)	0.89 (0.09–1.4)		
	Pond	48 (13–87)	4.1 (1.5–10)	0.96 (0.05–1.9)		
	Fish	25 (1.8–144)	49 (9–152)	35 (2.7–243)		
China[b]	River (mine drainage input)	7049 (6064–7502)	5.3 (5.5–7.3)	1.4 (0–5.9)	Sb mine	Zhu et al. (2009)
Australia	Stream (mine drainage input)	381 ± 23	46 ± 2	–	Sb–As mine	Telford et al. (2009)
New Zealand	River	25 (14–30)	8 (5.5–8.6)	–	Abandoned Sb smelting	Wilson et al. (2004)
Turkey[c]	River	0.02–0.1	–	–	Sb mine	Duran et al. (2007)
USA	River	0.17–8.3	0.11–1.6	–	Ag/Pb/Zn smelting	Mok and Wai (1990)
China	River	–	8.4 (0.06–21)	–	As smelting	Tao et al. (2007)
Pakistan	Lake	–	97 (35–158)	–	Village	Kazi et al. (2009)
Bangladesh	Tubewell water	0.0015–1.8	0.7–640	–	Countrywide	Frisbie et al. (2002)
China	Lake	–	–	0.16 (0.12–0.2)	Urban	Fang et al. (2004)
China	Stream water	–	–	0.94 (0.09–2.3)	Hg smelting	Li et al. (2008)
Canada	Lake	–	–	<0.2	Industrially polluted	Moore and Sutherland (1980)
	Fish	–	–	1220–3680		
France	River	–	1498 (18–2330)	–	Abandoned As smelting	Culioli et al. (2009)
	Fish	–	220–630	–		
Brazil	River	–	–	1.9 (0.01–10)	Industrially polluted	Ferreira et al. (1979)
	Fish	–	–	50		
Thailand	Pond	–	770 (550–990)	–	Abandoned tin mining	Jankong et al. (2007)
	Fish	–	3530 (2620–4440)	–		
France	Fish	80 (23–180)	980 (620–1370)	–	Abandoned As smelting	Foata et al. (2009)
Mediterranean	Fish	–	11,910 (2380–52,420)	–	Marine environment	Storelli and Marcotrigiano (2004)
Spain	Fish	–	100 (8–993)	–	Agricultural pollution	Bordajandi et al. (2003)
Argentina	Fish	–	–	189	Hg cell factory	Arribere et al. (2003)

[a] Water and fish muscle expressed in μg L^{-1} and μg kg^{-1} wet weight, respectively.

[b] The river is polluted directly by the Sb mining and smelting drainage from the same area as this study.

[c] Dissolved Sb.

Table 5
Risk-based drinking water guideline and element concentrations in the drinking water in the mine area (μg L^{-1}).

Element	Risk-based drinking water guideline			Concentrations in drinking water	
	WHO[a]	China[b]	USEPA[c]	Distance < 1 km	Distance > 1 km
Sb	20	5	6	127 (103–152)	10 (8.1–12)
As	10	10	10	9.4 (8.6–11)	1.1 (0.51–1.7)
Hg	6	1	2[d]	0.51 (0.22–0.79)	0.53 (0.09–0.79)

[a] WHO (2004).
[b] China drinking water standard (GB5749-2006) (2007).
[c] USEPA (2006).
[d] Inorganic Hg.

in July 2008 exhibited significantly higher Sb and As concentrations than those in December 2007. This can be attributed to fluctuations in precipitation between the different seasons. Summer, in this study area, has the highest rainfall approximately 42–44% of the annual amount. July is the peak of the rainy season and December is dry season. In July, more Sb and As from atmospheric emission precipitation due to the Sb smelting activities were accumulated in the reservoir and pond. In contrast, less variations in Sb and As concentrations were observed at the other reservoirs (sites E and H) (distance > 3 km). This suggests mine drainage and smelter wastes, rather than deposition of smelter dust, greatly impacted pollutant concentrations at these sites closest to the smelter. River water (site B) showed limited variations of Sb and As concentration partly due to its constant mixing and flow effects. Moreover, sediment entrainment and mixing were not important due to low sediment loads. This river is generally shallow (< 1 m) and mainly paved with small stones at the bottom.

No significant increase in Hg concentration in the water from reservoir (C) and pond (D) was detected during the rainy season. Instead, a slight decrease was observed due to the diluting process during the rainy season. This again suggests that Hg concentrations in the water were less affected by the Sb smelting. This study cannot exclude the possibility that Hg was derived from another source. In fact, the highest Hg concentrations in water were found in the pond (site I) which was probably greatly affected by other anthropogenic sources, being in close proximity to Lengshuijiang city.

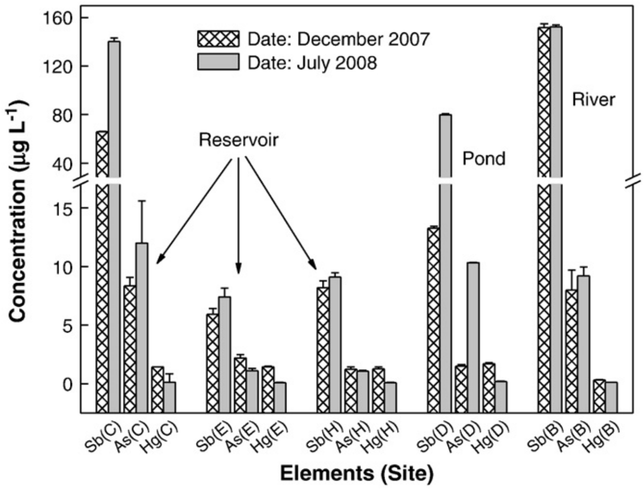

Fig. 3. Variations of total Sb, As and Hg concentrations in water in different seasons.

3.2. Sb, As and Hg in fish

The weighted average concentrations of Sb, As and Hg in fish were 218 ± 113, 266 ± 109 and 65.3 ± 34.7 μg kg^{-1} dry weight, respectively. As shown in Fig. 2, Sb concentrations were approximately one order of magnitude higher than As and Hg concentrations in all water samples. However, some fish samples had higher As and Hg concentrations, especially at downstream locations. The $BCFs_{(fish/water)}$ of Sb (mean: 10.8) have been significantly lower than As (mean: 193) and Hg (mean: 206). Relatively low bioavailability of Sb has been reported in soils and plants (Hammel et al., 2000; He, 2007), in grass and small mammals (Ainsworth et al., 1990b), in soils and human (Gebel et al., 1998), and in sediments and aquatic plants (Telford et al., 2009). Our observations also suggest lower bioavailability of Sb in water and fish.

Positive correlation was found between Sb and Hg concentrations in fish and those in the water ($r = 0.14$ and 0.49, $P < 0.05$ and 0.01, $n = 197$ and 181, respectively); Negative correlation was observed between As concentrations in fish and the water ($r = -0.05$, $P > 0.05$, $n = 190$). This possibly indicates that water was a principal source for Hg accumulation in fish. The correlations between fish and water for

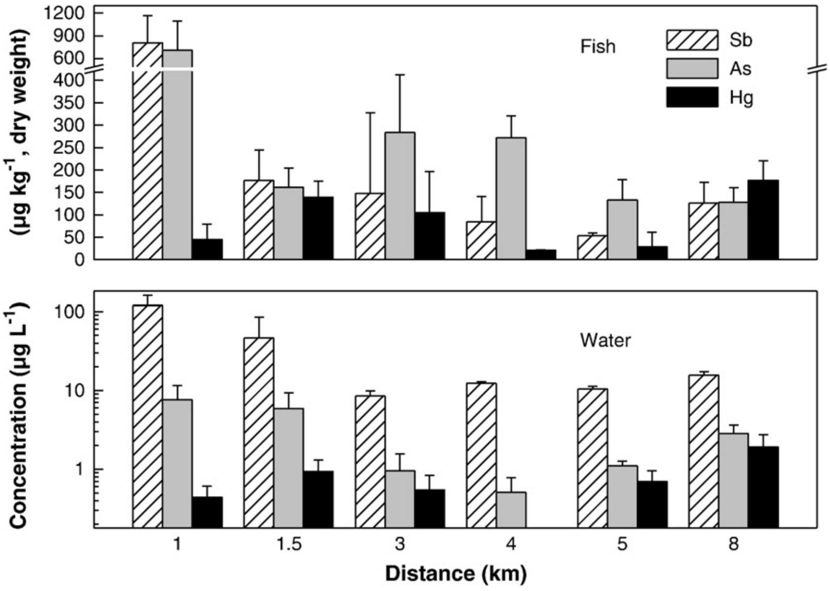

Fig. 2. Concentrations of total Sb, As and Hg in water and fish. The calculation of Sb, As and Hg concentrations in the fish was based on both weight and concentration of the organs: $\bar{x} = (x_1f_1 + x_2f_2 + \ldots\ldots + x_nf_n)/(f_1 + f_2 + \ldots\ldots f_n) = \sum xf/\sum f$ (x is the mean concentrations of Sb, As and Hg in each organ, f is weight of each organ).

Sb and As concentrations are very weak, suggesting other source (e. g. ingestion) may play an important contribution to the accumulation of Sb and As in fish, including algae. Algae are one of the major foods for the sampled fish, and algae (*Hydrodictyon* spp) (all sampled from site B) exhibited high Sb and As concentrations. The average concentrations of Sb, As and Hg in algae were 11,100 ± 3600, 11,000 ± 2100 and 126 ± 53 μg kg^{-1} dry weight, respectively. This suggestion is also supported by a previous study in Hungary where no clear relationship for As was observed between water and fish. Arsenic uptake was dominated by carp and catfish diet (Soeroes et al., 2005).

The Sb concentrations in algae were higher than the general concentrations 0.1–0.2 mg kg^{-1} dry weight, reported previously in freshwater and marine algae (Sánchez-Rodríguez et al., 2001; Filella et al., 2007). The As concentrations in algae were similar to those reported in freshwater in Hungary (7.2 mg kg^{-1} dry weight) (Schaeffer et al., 2006) and in shallow coastal zone in Mexico (13.2 mg kg^{-1} dry weight) (Sánchez-Rodríguez et al., 2001). Both Sb and As concentrations in algae were lower than those reported in a stream polluted by Sb–As mine drainage in Australia (Telford et al., 2009). In contrast, the BCFs of Sb and As (0.07 and 1.23 respectively) for water-algae were comparable (0.25 and 1.22 respectively) (Telford et al., 2009).

3.3. Sb, As and Hg in fish organ

The uptake and distribution characteristics of Sb, As and Hg in fish organs are shown in Table 6 and Fig. 4. Significantly higher Sb concentrations and BCFs in gills than in other organs were observed. Nevertheless, gills exhibited relatively low Hg concentrations. High concentrations of Sb in fish gills may be associated with ionic exchanges, and fish gills can produce mucus which can serve as a binding site to capture other metals such as aluminum (Handy and Eddy, 1989; Wilson et al., 1994); Moreover, Sb concentrations in fish gills may be attributed to the excretory roles of gills (Oladimeji et al., 1984). To our knowledge, there is only one report (Foata et al., 2009) published about Sb concentrations in fish in an abandoned As smelting area. This report showed that kidney and gill have highest Sb concentrations (kidney (701) > gills (618) > other organs (75–258) μg kg^{-1} wet weight). In contrast, results in our study show Sb concentrations in fish gill were exclusively higher than in any other organs including kidney (Fig. 5). The different results are probably attributable in part to the different fish species. In our study, Sb concentrations in crucian (*Carassius auratus*) gills were much higher than those in grass carp (*Ctenopharyngodon idellus*) and significant differences were observed in the same sites (D, E, F, and G sites, respectively) ($P<0.05$) (Fig. 5). In general, crucian (an omnivorous fish) and grass carp (an herbivorous fish) mainly inhabit the bottom and surface layer of aquatic environments, respectively. Sb concentrations in sediments are generally 100 times higher than those in the overlying water (Filella et al., 2002a). Therefore, those bottom feeders had more access to Sb. Moreover, the carp (at sampling site F), an omnivorous fish generally residing at the bottom, also exhibited an elevated Sb concentration in gills than that in grass carp gills. This suggests that Sb concentration in fish gills was closely related to their habitats.

Table 6
Antimony, As and Hg concentrations in different fish organs (μg kg^{-1} dry weight).

Fish organ	Sb	As	Hg
	Mean[a]	Mean[a]	Mean[a]
Gill	197 ± 163	161 ± 152	7.35 ± 2.87
Kidney	75.9 ± 8.51	286 ± 64	102 ± 44
Liver	74.7 ± 17.2	251 ± 37	140 ± 47
Bladder	70.5 ± 18.8	151 ± 33	56.9 ± 32.5
Muscle	82.8 ± 20.1	164 ± 17	28.4 ± 22
Skin	31 ± 13	141 ± 36	44.8 ± 9.2

[a] If the data showed normal distribution, arithmetic mean was calculated. If the data showed logarithmic normal distribution, geometric mean was calculated. If the data showed skewed distribution, the median was calculated.

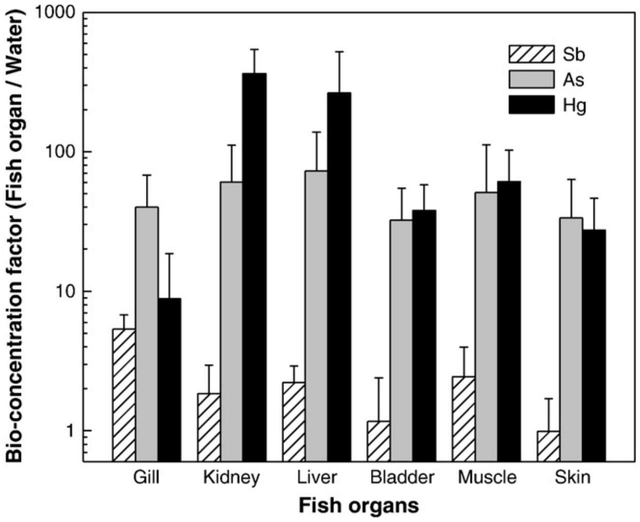

Fig. 4. Bio-concentration factors of Sb, As and Hg from water to fish organs.

The organs with the highest BCF$_{(\text{fish organ/water})}$ for As and Hg are liver and kidney, respectively (Fig. 4). Fish kidney and liver had similar BCFs for Sb, As and Hg, and high accumulation of As and Hg was more pronounced. High As and Hg concentrations in kidney and liver have been reported in control experiments (Pedlar and Klaverkamp, 2002) and other field experimental studies (Sindayigaya et al., 1994; Mason et al., 2000; Celechovska et al., 2005; Culioli et al., 2009). Many other studies (Karadede and Unlu, 2000; Alcorlo et al., 2006) have shown that muscle is not an active tissue for metal bioaccumulation. In fact, whether fish muscle will accumulate Sb, As and Hg is highly dependent on the environment's geochemical conditions and the fish species being considered. In addition to fish muscle, this study indicated that swim bladder and skin also exhibited relatively lower BCFs for Sb, As and Hg than other organs (Fig. 4). Fish skin exhibited the lowest Sb, As and Hg concentrations, except that the lowest Hg concentrations were observed in gills (Table 6). This indicates that swim bladder and skin were also not active tissue for the bioaccumulation of those elements.

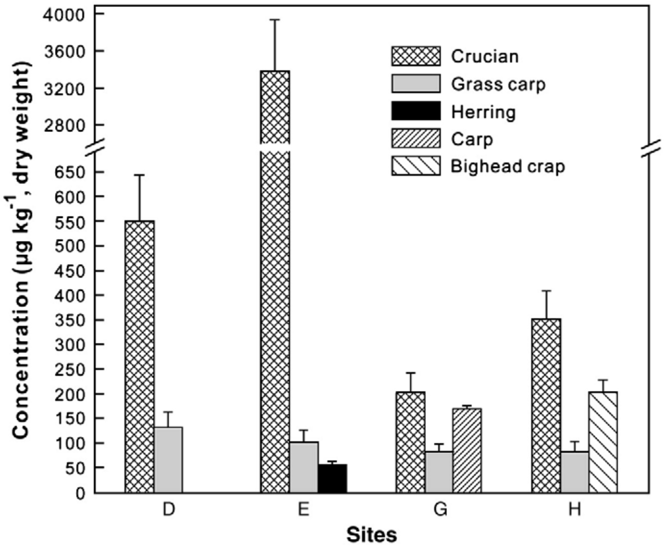

Fig. 5. Comparison of Sb concentrations (mean value) in fish gills at different sites.

Therefore, water was a principal source for Sb accumulations in fish. Moreover, Sb concentrations in liver ($r = 0.87$, $P < 0.01$, $n = 35$), kidney ($r = 0.91$, $P < 0.01$, $n = 31$) and gill ($r = 0.51$, $P < 0.05$, $n = 42$) were positively correlated with those in water. It can be considered that liver, kidney and gill were the principal fish organs in which Sb accumulated. However, no significant correlation for Sb was observed between muscle, skin, swim bladder and the water. This may be the reason for the worse correlations between Sb concentrations in whole fish and water. In spite of the fact that the kidney is generally recognized as an organ excreting some metabolic products/toxic material (Hedrick et al., 1993), our results demonstrate enhanced element concentrations in this critical organ. In comparison, As ($r = 0.28$, $P > 0.05$, $n = 42$) and Hg ($r = -0.11$, $P > 0.05$, $n = 42$) concentrations in fish gill do not exhibit significantly positive correlations with those in water. This again suggests that fish gill has unique Sb accumulation characteristics. Moreover, Sb and As concentrations in other fish organs (especially fish kidney) exhibit similar correlations with those in water. Only in fish muscle were Hg concentrations positively correlated with those in water ($r = 0.51$, $P < 0.01$, $n = 58$), in spite of fish muscle not being the most active tissue for Hg accumulation.

It should be noted that the elemental concentrations in fish organs not only reflect exposure to the elements, but the elemental excretion from the various organs by metabolic processes. In particular, fish kidney (Hedrick et al., 1993) and liver (Sorensen, 1991) were recognized as the excretory and detoxification organs respectively. Fish gill also has an excretory role (Oladimeji et al., 1984). Therefore the high elemental concentrations in organs also indicate their high metabolic activity to remove the toxic elements with the result that more contaminants are moved to these organs.

3.4. Factors affecting the elements BCFs$_{(fish/water)}$

The pH in all water samples averaged 7.1 (5.8–7.6) and showed significantly positive correlation with BCFs for Sb ($r = 0.19$, $P < 0.05$, $n = 197$). On the other hand, insignificant correlations were observed between pH and BCFs for As and Hg ($r = -0.08$ and 0.06, $P > 0.05$, $n = 190$ and 181, respectively). In terrestrial environments, a previous study reported that unlike the other trace elements such as Cd or Zn, the mobility of Sb decreases with decreasing pH in soils (Hammel et al., 2000). The literature (Filella et al., 2002b) has shown, under reducing conditions, the form of Sb present at low to intermediate pH values is Sb_2S_3(s); and where as at higher pH values, SbS_2^- species predominates. This can probably account for the dissimilar bioaccumulation of Sb in the aquatic environment.

The dissolved organic carbon (DOC) concentrations in water averaged 2.3 (0.9–9.9) mg L^{-1} and significant negative correlations between DOC concentrations and BCFs for Sb ($r = -0.16$, $P < 0.05$, $n = 197$), were higher than that for As and Hg ($r = 0.02$ and -0.08, $P > 0.05$, $n = 190$ and 181, respectively). Although some previous studies have shown that dissolved organic matter seems to play an insignificant role in fate of Sb in aquatic environment (Tanizaki et al., 1985; Tanizaki et al., 1992a,b), while two other studies reported that Sb was significantly associated with dissolved organic matter in polluted lakes (Deng et al., 2001) and coastal sea water (Gillain and Brihaye, 1985). Our results demonstrate that Sb in water is associated with the DOC fraction in the smelting water. In general, dominated Sb (V) form is anionic in natural waters, and predominant natural organic compounds are also negatively charged (Pilarski et al., 1995). A competition of absorption via fish gills probably exists between Sb (V) and DOC.

4. Conclusions

In addition to Sb, serious As contamination was observed in the XKS Sb mine area. More than 20% of sampling sites had elevated Sb and As concentrations in drinking water. Sb and As concentrations in water varied with seasons. Fish gills exhibited the highest Sb concentrations, which varied according to fish habitats. This study demonstrated that fish gills and liver were the principal bio accumulating routes for fish. Significantly lower bioavailability was observed for Sb compared with As and Hg in aquatic environments.

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