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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 ± 46.7 μg L^{-1} and 218 ± 113 μg 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 μg L^{-1} (Zhu et al., 2009). In contrast, in non-polluted water Sb concentrations are usually less than 1.0 μg 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*