Environmental geochemical and spatial/temporal behavior of total and speciation of antimony in typical contaminated aquatic environment from Xikuangshan, China

Wenjing Guo [a,b], Zhiyou Fu [b,*], Hao Wang [a,b], Fanhao Song [b], Fengchang Wu [b], John P. Giesy [b,c]

[a] College of Water Sciences, Beijing Normal University, Beijing 100875, China
[b] State Key Laboratory of Environment Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[c] Department of Biomedical and Veterinary Biosciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

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ABSTRACT

Since environmental geochemical behavior of antimony (Sb), especially Sb speciation in aquatic system were largely unknown, studies were conducted in various waters and sediments from the world's largest antimony mine area at Xikuangshan (XKS). Based on samples collection, total and speciation of Sb and several aquatic environmental parameters were determined in waters from river, well, reservoir, wastewater and sediments. Sb(V) was found as the predominant speciation in the waters and sediments. The environmental geochemical behavior of Sb speciations were mainly controlled by the process of oxidation and adsorption/combination with environmental matrix, mainly as Fe/Al (hydr)oxide, and oxidation may has higher priority than adsorption in the aquatic system. Spatial distribution of decreased Sb concentrations in some surface waters resulted from the dilution effect of river/reservoir/tributary water and adsorption of environmental matrix. The declined temporal distributions of Sb in waters compared with previous studies were attributed to several restoration measures and less mining/smelting activities in XKS. Results suggested that tailings heaps in mining region should arouse much attention for its potential release of Sb.

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1. Introduction

Antimony (Sb) is a nonessential metalloid of increasing environmental concern, due to its increasing concentrations in the environment that resulted from rapid growth in use of Sb in batteries, flame retardants, paints, semiconductors and alloys [1–10]. For instance, Sb has been enriched to a greater extent than lead (Pb) in atmospheric particles in several cities [11], and in recent decades has been found accumulated in peat bogs in Europe and the Canadian Arctic [12,13]. Suspected carcinogenicity of Sb to humans has been reported [8,14]. Inhalation of Sb can damage respiratory systems, liver and skin [15,16]. Thus, Sb and its compounds have been listed as priority pollutants interest by the European Union (EU) and Environmental Protection Agency of the United States (USEPA), respectively [17,18]. Although concern about Sb has increased continuously over the last few decades, basic knowledge of environmental geochemical behavior of Sb in natural aquatic system was not adequate compared with other group V elements, such as arsenic (As) [19,20]. Especially, the distribution of Sb in sediment was largely unknown.

Various speciation of Sb(-III, 0, III, V) occur in environmental compartments, with common inorganic speciations being Sb(III) and Sb(V). These two common speciations of Sb exhibit remarkable differences in their environmental behaviors and toxic potencies. Over wide ranges of pH from 2 to 11, predominant speciations of Sb(III) and Sb(V) in aquatic environments are $Sb(OH)_3$ and $Sb(OH)_6^-$, respectively. Sb(III) can be strongly adsorbed on Fe/Mn (oxyhydr)oxide as inner-sphere complexes, and can be oxidized to Sb(V) rapidly at smaller concentrations, thus exhibiting high instability in environmental matrices [21–26]. Toxic potency of Sb(III) is 10-fold greater than that of Sb(V) [5]. Hence, speciation of inorganic Sb is a crucial issue determining geochemical behavior of Sb.

China, the largest producer of Sb worldwide, produced approximately 80% of global annual production in the last decade [19,27]. The XKS Sb mine in Hunan Province is one of the world's major producers of Sb. It is renowned as the "World's Antimony Capital". During the past approximately 100 years, mining and smelting activities in this region have resulted in contamination of water, soil and sediment by Sb and other metals [27]. Major sources of Sb included emission, seepage and runoff from mine wastewater and untreated mine tailings. Concentrations of Sb in waters of reservoirs, ponds and rivers in XKS were nearly two orders of magnitude greater than those in unpolluted waters of other regions [28–30]. Elevated contents of total Sb, much higher than that in

uncontaminated sediments, were found in the aquatic waters of XKS [4, 31]. In recent years, severe contamination around XKS has made this area the typical region of research on Sb [19,28,32–39]. Although large-scale and long-term mining/smelting activities in the area have occurred over the last 100 years, temporal and spatial distribution of Sb, especially speciation of Sb in aquatic environments in this area were still sparse. In addition, study on spatial/temporal distribution of Sb is necessary to understand environmental behavior of Sb and establish its global biogeochemical cycle [7].

Hence, the main objectives of the present study conducted in XKS were to investigate: (1) the temporal/spatial distribution of total and speciations of Sb in various waters of XKS, and (2) the influence factors of environmental behavior of Sb in natural waters and sediments.

2. Materials and methods

2.1. Site description

The XKS, which covers a total area of 70 km^2, is located between 27.7°N and 111.4°E near Lengshuijiang city, Hunan Province. The climate of this area is subtropical continental monsoon with an annual, mean temperature of 16.7 °C and annual rainfall of 1354 mm. The NE-trending Lianxi River flows through mining area, and Zijiang River, the second largest river of Hunan province, runs along the side of the mining area. Besides Sb, rich deposits of mercury (Hg), gold (Au), zinc (Zn), arsenic (As) and coal are contained in the XKS mineralization zone. Further details of sample locations are given elsewhere [29,35].

2.2. Samples collection

All 11 water samples (S1–S11) and 6 sediment samples (a–f) were collected in July 2016 and 2017 from the vicinity of the XKS smelter which covered the most area of South Mine, the upstream and downstream of Lianxi River (Fig. 1, Table 1). Water samples were collected from the reservoir, rivers and wells by use of acid-washed polyethylene

Table 1
Descriptions of sampling sites in the XKS area.

Station	Type	Station character
S1	River water	Contaminated by waste water
S2	River water	Located in downstream of S3, contaminated by waste water
S3	River water	Tributary located between S2 and S4, not contaminated by waste water
S4	River water	Located in upstream of S2, contaminated by waste water
S5	River water	Not contaminated by waste water directly
S6	River water	Located in upstream of S5, contaminated by waste water
S7	Reservoir water	Located in dam, near tailings heaps, not contaminated by waste water directly, drinking water
S8	River water	Located in upstream of dam, not contaminated by waste water directly, drinking water
S9	Tailing water	Outfall of waste water and waste residue
S10	Well water	Vicinity of tailing dam
S11	River water	Main river across the downtown, not contaminated by XKS waste water
a	Sediment of Lianxi river	Upstream of S4, about 0.5 km from S4
b	Sediment of Lianxi river	Upstream of S4, about 1.5 km from S4
c	Sediment of Lianxi river	Upstream of S4, about 2.2 km from S4
d	Sediment of Lianxi river	Downstream of S6, about 2.0 km from S6
e	Sediment of Lianxi river	Upstream of S6, about 0.4 km from S6
f	Sediment of tailing	Located in tailing dam

bottles. Electrical conductivity (EC), pH, dissolved oxygen (DO) were measured immediately in the field. Samples of water from each location were divided into two parts. Main anions, cations and total organic carbon (TOC) were measured in first sample. Samples were acidified to 1% (v/v) for quantification of metals. EDTA was added to another sample to
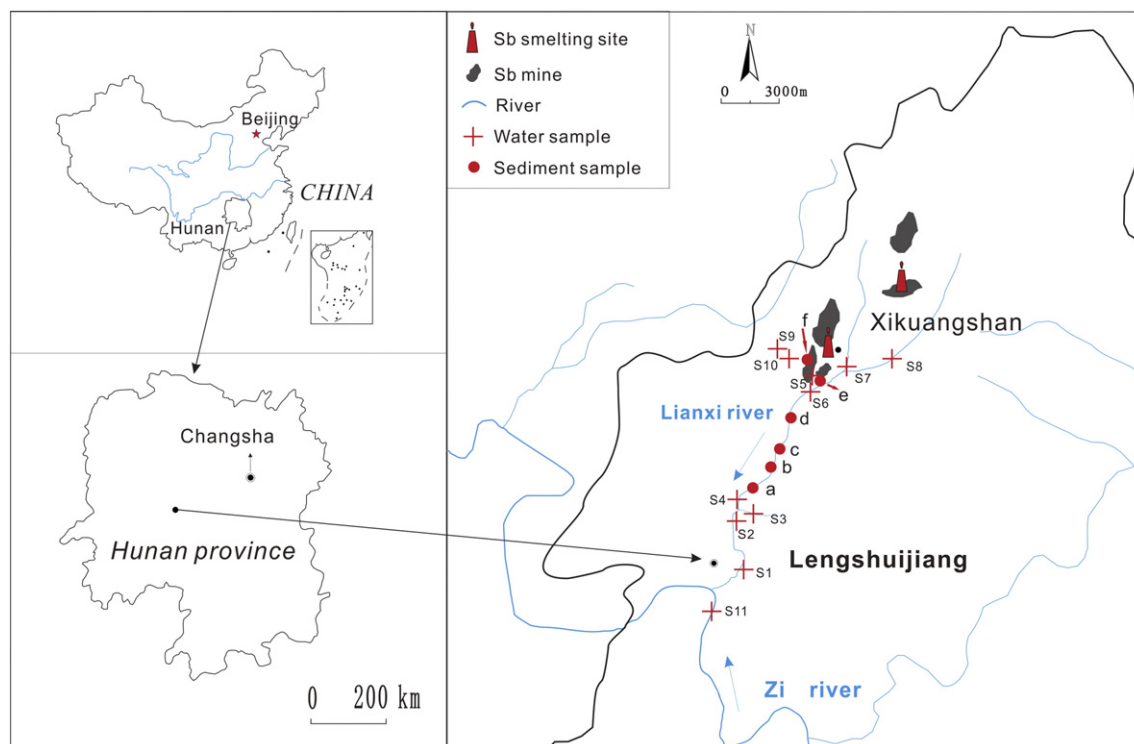

Fig. 1. Sampling locations in the XKS mine area.

prevent and decrease the oxidation of Sb(III) to Sb(V) in sampling [40]. Samples of water were kept at 4 °C in the dark until analysis and transported to the laboratory as soon as possible [41].

Sediment samples in Lianxi River were collected and sealed in pre-cleaned zip lock bags. Also, the sediment samples were delivered to the laboratory in the dark as soon as possible until analysis. These sediment samples were centrifuged, cool-dried, crushed, and passed through a 0.15 mm sieve for determination of total and speciations of Sb and other metals.

All chemicals and reagents used in this study were of analytical-reagent grade or greater purity and de-ionized water was obtained from a Milli-Q system. Vessels used were soaked in dilute nitric acid and washed using de-ionized water at least three times.

2.3. Analytical methods

2.3.1. Determination of several aquatic parameters

The pH of samples was measured by use of a pH meter (FE20K, Mettler Toledo, Switzerland). DO and EC were determined by quick detector (HORIBA D-54) prior to delivery to laboratory. Concentrations of NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ were measured by ion chromatograph (ICS-3000, Dionex) after samples were filtered through 0.45 μm nylon membrane filters (Whatman, UK). Concentrations of TOC were determined by total organic carbon analyzer (TOC-V CPH, SHIMADZU). Concentrations of Al, Cd, Cr, Fe, Al and Se in the acidified sample aliquots were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 5300 DV). Microwave digestion were applied to pretreat the sediment samples [42], ICP-OES was used to measure the concentrations of metals like Fe, Al, Mn, Zn and Se.

2.3.2. Determination of total Sb

Total concentrations of Sb in samples were measured by use of hydride generation-atomic fluorescence spectrometry (HG-AFS, Millennium Excalibur System, Kent, United Kingdom). A 0.5 mL volume of reducing agent, which consisted of 50% (m/v) KI and 10% (m/v) ascorbic acid (both purchased from Sinopharm Chemical Reagent Co., Ltd) and 15 mL hydrochloric acid (12 mol/L, Beijing Chemical Works) were added to 5 mL of filtered water. The carrier solution of HCl (1.8 mol/L) and $NaBH_4$ solution (0.8%) for HG-AFS was prepared with ultrapure hydrochloric acid and dissolving powdered $NaBH_4$ in 0.4% NaOH solution respectively (both purchased from Tianjin Fuchen Chemical Reagents Factory). Hydride generation was performed with a Millennium P.S. Analytical-10.055. Standard solutions with concentrations from 0 to 20 μg/L were prepared by diluting standard stock solutions (stored at 4 °C), which were obtained by dissolving appropriate amounts of antimony potassium tartrate ($K(SbO)C_4H_4O_6$) (Sinopharm Chemical Reagent Co., Ltd). Total concentrations of As in samples were measured using the same method as that used for Sb.

2.3.3. Determination of Sb speciation

High Performance Liquid Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry (HPLC-HG-AFS) was used to determine soluble speciation of Sb in the samples, all instruments were same as the determination of total Sb except HPLC was from Agilent (1200 Series preparative pump, USA). An anion exchange column (PRP-X100, 4.1 × 250 mm, 10 μm; Hamilton) was used to separate Sb(V) and Sb(III). Conditions for the HPLC-HG-AFS were as follows: ammonium tartrate solution (pH value was adjusted to 5, purchased from Sinopharm Chemical Reagent Co. Ltd) was used as mobile phase with a flow rate of 1.0 mL/min. The HCl carrier solution and $NaBH_4$ solution were prepared in the same method as for determination of total Sb. Sample injection volume was 200 μL and speciation of Sb were determined by PSA-10.055. Seven mixed standard solutions of 0 to 100 μg/L were obtained by mixing stock solutions, which were prepared by diluting stock solutions of hexahydroxy-antimoniate ($KSb(OH)_6$) (Sigma-Aldrich) and antimony potassium tartrate ($K(SbO)C_4H_4O_6$). Operating

conditions of the AFS instrument were optimized and calibration curves of Sb(V) and Sb(III) exhibited good linearity. Samples of water were injected into the AFS system after they were filtered through a 0.45 μm nylon membrane filters (Whatman, UK).

The concentrations of Sb speciations in sediments were conducted by using HPLC-HG-AFS consisting of UV irradiation. Citric acid was used to extract the Sb speciations in the sediments. The speciations of Sb were verified by retention times consistent with those of Sb speciations standard solutions. The details of method are available in previous report [43].

2.4. Quality control

Quality control included method blanks, blank spikes, matrix spikes and blind duplicates. CRM (certified reference standard) of stream sediments (Chinese National Standard, GSD-12) were used in the determination of total Sb. Due to the lack of CRM of Sb speciations, same stream sediments (GSD-12) spiked with standard solution of Sb(V)/Sb(III) was applied in this study. The recoveries of total Sb, Sb speciations and other metals in waters were 97–104%, and recoveries of Sb speciations in sediments were 63–79%. Standard solutions of total Sb and Sb speciations were prepared daily and calibrated with standard curves, in which coefficients of determination (r) were greater than 0.999. Limits of detection (LOD) of total Sb, Sb(V) and Sb(III) were 0.72, 0.015 and 0.55 μg/L, respectively. Relative standard deviations (RSDs) of duplicated samples in waters and sediments were <6%.

2.5. Statistical analyses

The ANOVA analysis was used to test the difference of Sb concentrations by using the statistical package SPSS 19.0 (SPSS Inc., Chicago, Illinois, USA), and $p < 0.05$ was considered statistically significant. Correlation coefficients were performed by using Pearson correlation analysis.

3. Results and discussion

3.1. Total Sb levels and other contaminants in waters and sediments

Total concentrations of Sb in water samples from XKS ranged from 16 to 38, 288 μg/L (Fig. 2, Table 2). Mean and ranges of Sb concentrations in various samples of water in decreasing order were: mine wastewater (S9) (38, 288 μg/L) > river water contaminated by mine wastewater (S1, S2, S4 and S6) (1373 (942–2137) μg/L) > reservoir water for drinking and its upstream of river (S7 and S8) (379 (344–415 μg/L) μg/L) > river water that was uncontaminated directly by mine waste water
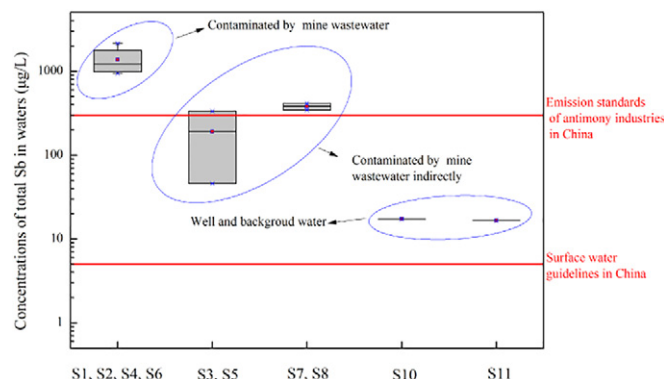

Fig. 2. Comparison of risk-based Chinese national water guideline and Sb concentrations in the water samples from the XKS area. S1, S2, S4 and S6 represent river that was contaminated by mine waste water; S3 and S5 represent river waters not directly affected by mine waste water; S7 and S8 represent reservoir water for drinking and its upstream of river; S10 represents well water for drinking; S11 represents Zijiang river water.

Table 2
Concentrations of Sb and other metals in the waters of XKS area (μg/L).

Sample	Sb	As	Cd	Cr	Zn	Fe	Al	Se
S1	942 ± 3[a]	23 ± 2	1.2	1.2	8.5	<LOD	<LOD	27[a]
S2	1014 ± 4[a]	20 ± 2	2	2.1	20	<LOD	<LOD	35[a]
S3	46 ± 5[a]	<LOD	0.40	5.7	4.3	<LOD	<LOD	11[a]
S4	1397 ± 29[a]	15 ± 1	2.5	3.6	19	<LOD	<LOD	26[a]
S5	335 ± 14[a]	<LOD	<LOD	4.4	8.5	<LOD	<LOD	9.5
S6	2137 ± 35[a]	502 ± 24[a]	8.5[a]	4.1	18.9	<LOD	3.49	49[a]
S7	344 ± 13[a]	83 ± 7[a]	1.4	3.8	6.9	<LOD	0.97	17[a]
S8	415 ± 15[a]	99 ± 10[a]	1.9	4.4	7.9	<LOD	<LOD	18[a]
S9	38,288 ± 363[a]	43 ± 5	0.60	1.9	12	302.1[a]	<LOD	45[a]
S10	17 ± 1[a]	<LOD	2.7	5.6	261	157.9	6679.7	1.3
S11	16 ± 2[a]	<LOD	0.71	6.5	5.4	<LOD	<LOD	5.3
Surface water guidelines in China	5.0	50	5.0	50	1000	300	Not mentioned	10

<LOD represented less than limit of detection.

[a] Concentration of metal was greater than the limit of surface water guidelines in China (Class III).

(S3 and S5) (191 (46–335) μg/L) > well water used for drinking (S10) (17 μg/L) > Zijiang river water (S11) (16 μg/L) (Fig. 2). These concentrations partly exceeded the maximum permissible concentration standard for emissions of Sb by industries in China (300 μg/L, GB 30770-2014) and all exceeded the surface water guidelines in China (5 μg/L, GB 3838-2002).

The greatest concentration of Sb was found in water of the tailing dam (S9, 38, 288 μg/L), which contained Sb mine wastewater and residues. Such seriously contaminated water was stored behind the tailings dam and was properly regulated, so limited ecological risk would be expected for the surrounding environment. Concentrations of Sb in river waters contaminated by mine wastewater (S1, S2, S4 and S6) were approximately 10-fold greater than those in river waters not contaminated directly by wastewater (S3 and S5). In comparison, concentrations of Sb in river waters contaminated by mine wastewater in XKS were greater than that in stream waters affected by mine wastewater (mean 381 ± 23 μg Sb/L) in water near the Hillgrove antimony–gold mine in NSW, Australia [44]. Concentrations of Sb in well water (S10) (17 μg/L), reservoir water (S7) (344 μg/L) and its upstream (S8) (415 μg/L), which used as local drinking water source, exceeded the drinking water guideline of Sb in China (5 μg/L, GB 5749–2006). Thus, that water was unsuitable for use as drinking water by local residents if not treated to less contents of Sb to safer concentrations. The high Sb concentrations in S7 and S8, uncontaminated directly by Sb mine waste water, may result from the influence of percolating water from tailings heaps near the reservoir.

Concentrations of As in natural waters except for S9 (tailing wastewater) and S10 (well water) which had a mean of 123 with a range of <LOD to 502 μg/L, were significantly greater than concentrations reported previously in this region with a range of 0.56 to 11 μg/L [19] and 1.1 to 7.3 μg/L [30]. The mean concentration of Zn was 34 with a range of 4.3 to 261 μg/L. The mean concentration of Se was 22 with a range of 1.3 to 49 μg/L, which not only exceeded the limit of surface water guidelines in China (10 μg/L), but also exhibited more serious pollution by Se than

that reported in 2006 (0.015–34 μg/L) [30]. Severe contaminations of Cd and Cr were not observed in the study area. Concentrations of Na$^+$ had a mean of 16.6 with a range of 1.6 to 74 mg/L (Table 3). The mean concentration of SO$_4^{2-}$ was 141.3 with a range of <LOD to 275.6 mg/L.

The concentration of Zn exhibited significantly positive correlation with total concentrations of Sb in waters ($r = 0.86$, $p<0.01$) (see Fig. S1). In fact, rich deposits of Zn and Sb are contained in XKS area, and a Zn smelting factory, which was affiliated with Hsikwang Shan Twinkling Star Co., Ltd, is located in the upper stream of Lianxi River and produced Zn products. Concentrations of Se were positively correlated with total concentrations of Sb in waters ($r = 0.94$, $p<0.01$) (see Fig. S1). This significant correlation, which was consistent with another study conducted in this area [30], can be attributed to the fact that both metals are strong chalcophile, and associated with sulfur that often occur together in deposits thus released by mining and smelting [45]. The high concentration levels of Na$^+$ and the positive correlation between concentrations of total Sb and Na$^+$ (Fig. S2) were caused by the Butyl Xanthate (C$_4$H$_9$OCSSNa) that was applied during mining and flotation. Elevated contents of SO$_4^{2-}$ were observed in this study and the survey of Nov. 2006 [30], which can be explained as the oxidation process of stibnite (Sb$_2$S$_3$, primary ore mineral of Sb mine [35]).

TOC was reported by several literatures that has complex relationship with Sb in aquatic environment [46,47]. In this study, TOC exhibited insignificant correlation with total Sb in waters ($r = -0.26$, $p > 0.05$, see Fig. S3, tailings wastewater of S9 and well water of S10 were eliminated). In addition, the previous report also showed that organic matter fraction of Sb constitute only a small proportion of total Sb in Lianxi river [31], so organic matter may serve a non-significant role in the environmental geochemical behavior of Sb in the aquatic system. The pH value of greater than 4 except well water were detected in study area (Table 3), which was different from the results of the acid mine drainage from the XKS mine area in the previous study [30]. The neutral pHs were resulted from the reaction of CaCO$_3$/MgCO$_3$ and H$^+$ and may facilitate the oxidation process of Sb(III) to Sb(V) [29].

Table 3
Several aquatic parameters in water samples from XKS.

Sample	EC (ms/m)	TOC (mg/L)	pH	DO (mg/L)	K$^+$ (mg/L)	Mg^{2+} (mg/L)	Na$^+$ (mg/L)	Ca^{2+} (mg/L)	NO$_3^-$ (mg/L)	SO$_4^{2-}$ (mg/L)
S1	61	1.8	7.5	5.6	2.3	14	11	96	7.8	174.2
S2	63	1.7	7.3	5.3	2.3	13	16	106	6.9	261.8
S3	41	2.0	7.4	5.5	0.99	4.8	1.6	64	3.2	51.4
S4	67	2.3	7.1	5.7	2.4	13	17	113	5.0	197.3
S5	61	1.2	7.5	6.4	2.1	15	7.6	100	5.8	275.6
S6	65	1.8	7.8	5.3	2.5	10	21	109	5.7	232.3
S7	38	2.7	7.8	4.9	1.1	5.4	6.6	69	3.5	81.7
S8	39	2.3	7.8	4.9	1.1	5.6	7.4	68	3.3	85.7
S9	196	2.2	7.1	3.2	10	31	74	321	<LOD	<LOD
S10	52	1.4	3.7	5.4	5.9	9.3	18	46	56.5	183.7
S11	16	2.8	7.4	5.2	1.7	2.3	2.1	26	2.4	10.5

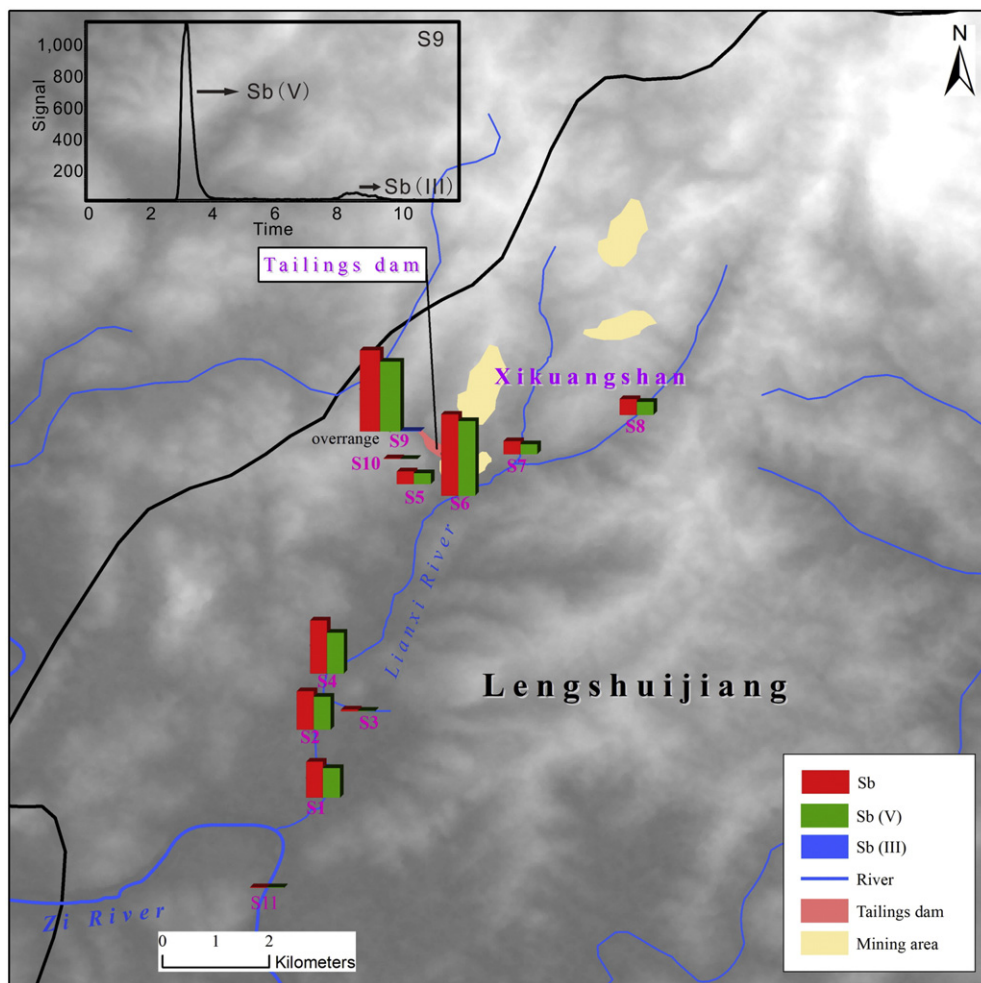<LOD represented less than limit of detection.

Fig. 3. Spatial distribution of Sb speciations in XKS waters. The concentration of S9 was not displayed in proportion since its content was several orders of magnitude greater than other sample sites. White and grey color represented high and low altitude area in the map. The liquid chromatogram image of dilution solution of water from S9 also demonstrated in this figure.

Abundant Fe and Al were detected in the sediments of Lianxi river, which have the elevated concentrations of 2.2×10^{-5}–5.5×10^{-5} and 9.4×10^{-4}–6.3×10^{-5} mg/kg. Similar with waters of this area, elevated levels of Zn and As were also found in the sediments of XKS.

3.2. Sb speciations in waters and sediments

Sb(V) was the predominant speciation in XKS water samples (Fig. 3), and almost no Sb(III) in the natural water were observed. This result

was supported by other previous reports in XKS [27,29,31], suggesting the high stability of Sb(V) in aquatic environments. The predominant Sb(V) in the surface waters may be attributed by the following mechanism: the Xikuangshan stibnite ores contained amounts of stibnite(Sb_2S_3) and pyrite (FeS_2) [35,48]. The former could generate abundant Sb^{3+} in the process of flotation (Reaction 1, Fig. 4). The latter could transform to ferric sulfate in the flotation process of stibnite, this acidic waste water could be neutralized by $CaCO_3$(calcite)/$MgCO_3$ and generated ferrihydrite [29,49]. The processes were showed as: FeS_2
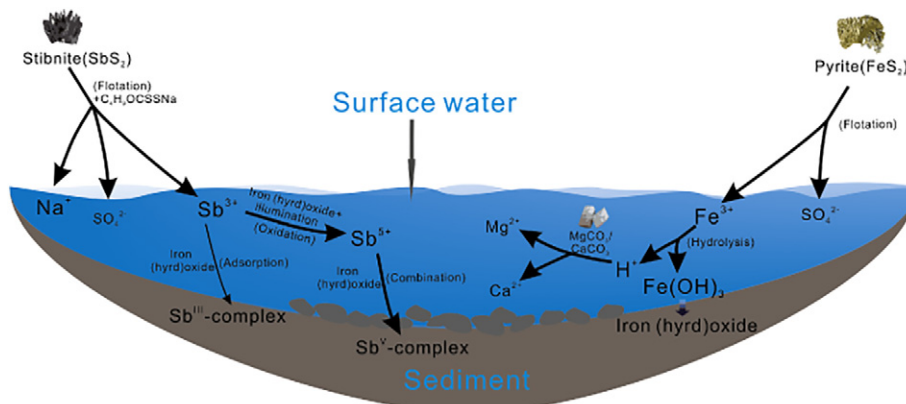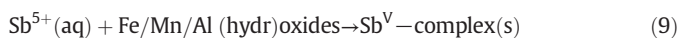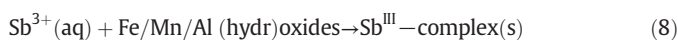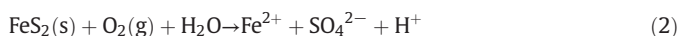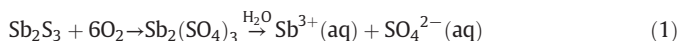

Fig. 4. The environmental geochemical cycle of Sb in the surface waters and sediments from XKS.

→ ferric sulfate → ferrihydrite (Reactions 2–6, Fig. 4). Sb(III) can be easily oxidized to Sb(V) with O_2 and catalyzed by particulate iron/manganese (hydro)oxides in the surface water [50]. Humic acid in natural waters and sediments also could catalyze the oxidation of Sb(III) to Sb(V) [51,52]. Several recent studies have revealed that photooxidation of Sb(III) occur rapidly in the presence of different Fe(III) species and organic Fe(III) complexes [53,54] (Reaction 7, Fig. 4). In addition, it was found that Sb(III) show higher affinity with iron (hydr)oxide than Sb(V) and adsorbed by iron (hydr)oxide as inner-sphere complex [21, 55,56] (Reactions 8 and 9, Fig. 4).

Sb(III) was only found in wastewater from the inlet pipe of tailings dam at S9 with concentration of 327 μg/L, suggesting that high concentration of Sb(III) had not sufficient time to be oxidized to Sb(V). Furthermore, wastewater of S9 containing the lowest concentration of dissolved oxygen (DO) (3.2 mg/L) seemed has limited contribution to the oxidation of Sb(III) (Table 3). It should be noticed that concentrations of soluble inorganic Sb speciations in filtered water samples accounted for only a portion of the total Sb averaged 72% (42–92%), suggesting that a considerable part of unidentified speciation of Sb, most probable is, particulate Sb existed in these waters from XKS. In fact, the previous study also reported that particulate Sb accounted for approximately 15% of total Sb [28].

The greatest concentration of Sb(V) and Sb(III) of 156.3 and 11.1 mg/kg extracted by citric acid were observed in the sediment of tailing dam. The concentrations of Sb(V) ranged from 34.3 to 96.1 mg/kg and Sb(III) has a range of <LOD to 7.4 mg/kg in the sediments of Lianxi river (Table 4). Elevated concentrations of Sb(V) and Fe/Al in sediments were in according with the report of Wang et al., which revealed that most of Sb combined with Fe/Al in the sediments [31]. Although Sb(III) showed higher affinity with iron (hydr)oxide than Sb(V) [57], relatively low concentrations of Sb(III) were observed in the sediments, this may indicate that oxidation of Sb(III) to Sb(V) has higher priority than adsorption in the surface water. Actually, there was a report revealed that ferrihydrite surface was a catalyst for the oxidation of Sb(III) in the process of adsorption [21]. It should be noticed that Sb(III) in the sediments were detected in the sediments while no Sb(III) were observed in waters, suggesting that Sb combined with matrix (i.e. iron/aluminum hydroxide) may be prevented for further transformation (Fig. 4). The relative reactions were shown as follows:

$$Sb_2S_3 + 6O_2 \rightarrow Sb_2(SO_4)_3 \xrightarrow{H_2O} Sb^{3+}(aq) + SO_4^{2-}(aq) \quad (1)$$

$$FeS_2(s) + O_2(g) + H_2O \rightarrow Fe^{2+} + SO_4^{2-} + H^+ \quad (2)$$

$$Fe^{2+}(aq) + O_2 + H^+ \rightarrow Fe^{3+} + H_2O \quad (3)$$

$$Fe^{3+}(aq) + H_2O \rightarrow Fe(OH)_3(s) + H^+ \quad (4)$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + CO_2(g) \quad (5)$$

$$MgCO_3 + H^+ \rightarrow Mg^{2+} + CO_2(g) \quad (6)$$

$$Sb^{3+}(aq) + O_2 \xrightarrow{catalyst} Sb^{5+}(aq) \quad (7)$$

$$Sb^{3+}(aq) + Fe/Mn/Al\ (hydr)oxides \rightarrow Sb^{III}-complex(s) \quad (8)$$

$$Sb^{5+}(aq) + Fe/Mn/Al\ (hydr)oxides \rightarrow Sb^{V}-complex(s) \quad (9)$$

3.3. Spatial distribution of Sb in waters

In the waters of Lianxi River (Fig. 5a), concentrations of Sb decreased sharply (approximately 50%) over approximately 6 km downstream from the XKS. Similar decreases in concentrations of Sb were also found in other reports of Liu et al. and Wang et al. [29,31]. Due to a large number of input of wastewater from XKS, almost no plants were found in main stream of Lianxi River [58]. Therefore, dilution effect of river water and adsorption/precipitation of matrix in river (i.e. Fe/Al hydr(oxide)) may be the main causes of decreased trend of Sb in river.

In tributary river not directly contaminated by mining wastewater (Fig. 5b), concentrations of Sb at S5 (about 1.5 km from mining site) was nearly 7-fold greater than that at S3 (about 5 km from mining site), indicating the decreased pollution of Sb from the Sb smelting site. The adsorption of Fe/Al (hydr)oxide in the sediment could serve as one of the significant roles in the decreased trend of Sb concentration in river. It has been widely reported that both Sb(V) and Sb(III) could combine with $Fe(OH)_3/Al(OH)_3(s)$ in the environmental compartments [21,25,57]. Moreover, in the main stream of Lianxi River feed by the tributary river (46 μg Sb/L with only about 50% river runoff compared with main stream), total concentrations of Sb decreased sharply from 1397 μg/L to 1014 μg/L (Fig. 5c). The results suggested the dilution effect by less contaminated tributary water have considerable contribution to the decreased trend of Sb concentration in main stream.

Concentrations of Sb in water at S8 (about 1 km upstream from reservoir S7) were greater than that at S7 (reservoir water, Fig. 5d), which were consistent with results of a previous study [28], suggesting that potential adsorption and precipitation of Sb occurred in the reservoir.

3.4. Temporal distribution of Sb in waters

Several previous studies, conducted by Wang et al., Liu et al. and Zhu et al. respectively in the XKS, were selected to compare the temporal distribution of Sb contamination of waters with the function of time (Fig. 6, Table 5). Concentration data only detected in the same region as this study were compared.

Overall, concentrations of Sb in river waters exhibited decreased trend with the function of time. Concentrations of Sb in river waters (S1, S2, S4 and S6) contaminated by mine wastewater had a mean of 1373 with a range of 942 to 2137 μg/L, which was slightly less than concentrations observed in Dec. 2008, when the mean was 1545 and a range of 1154 to 2099 μg/L. The Sb contamination in this study was much less than the concentrations in Jul. 2007 with the mean was 2803 and a range of 2500 to 3210 μg/L [29] and Nov. 2006 with the mean was 6745 and a range of 5928 to 7558 μg/L [30] (Fig. 6a).

Several factors such as seasonal variation and sampling period could influence the distribution of Sb. In the XKS area, previous study has revealed that Sb concentrations of rainy season were nearly same as

Table 4
Description and concentration of metals in sediments of XKS.

| Samples	pH	Sb(V) (mg/kg)	Sb(III) (mg/kg)	Zn (mg/kg)	Se (mg/kg)	As (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Mn (mg/kg)
a	7.8	55.4 ± 2.3	2.6 ± 0.6	1389.9 ± 190.4	<LOD	3295.9 ± 175.4	45,847.8 ± 1429.5	42,347.9 ± 2040.7	541.0 ± 85.8
b	7.9	34.3 ± 2.1	<LOD	124.2 ± 27.4	<LOD	542.8 ± 20.2	21,547.5 ± 2194.5	9434.1 ± 304.7	17.9 ± 1.9
c	7.5	78.6 ± 3.9	3.0 ± 0.8	2975.0 ± 135.6	<LOD	3033.8 ± 203.4	55,136.1 ± 523.5	43,373.4 ± 710	477.9 ± 127.9
d	7.4	96.1 ± 3.5	7.4 ± 2.3	2075.1 ± 126.0	<LOD	4534.9 ± 1108.9	33,663.8 ± 1121.1	62,824.8 ± 2053.3	715.5 ± 29.7
e	7.4	61.8 ± 4.2	0.7 ± 0.2	705.6 ± 60.7	<LOD	3034.7 ± 611.7	44,594.5 ± 1596.9	61,802.8 ± 2151.2	835.7 ± 27.8
f	7.3	156.3 ± 7.1	11.1 ± 0.3	40.9 ± 1.7	<LOD	434.9 ± 63.8	1118.3 ± 192.3	3021.6 ± 229.5	11.6 ± 1.3

<LOD represented less than limit of detection.
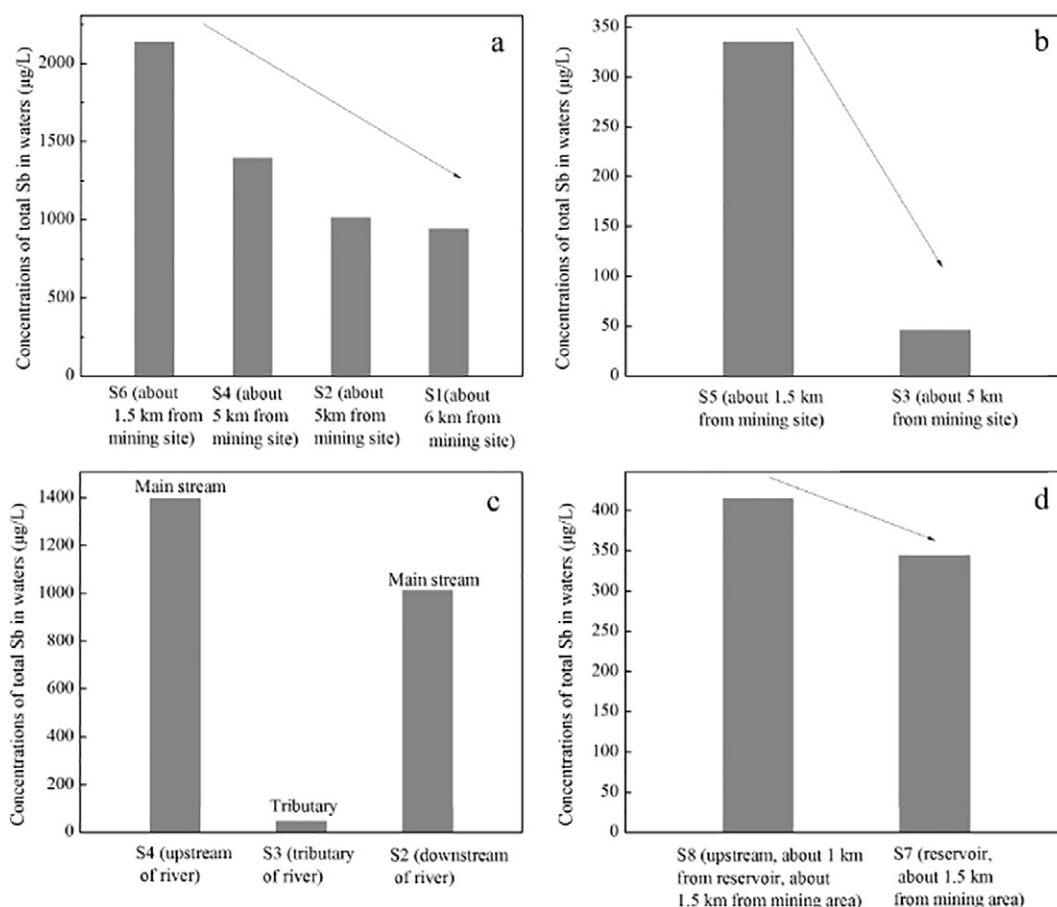
Fig. 5. a) Distribution of concentrations of Sb in main stream directly contaminated with Sb mine wastewater; b) tributary river not directly contaminated by Sb mine wastewater; c) upstream and downstream of contaminated river and uncontaminated tributary; d) reservoir used for drinking and its upstream of river.

that of dry season in river waters [28]. Hence seasonal factors on the variation of Sb concentration in rivers may be ignored. This decreased trend was mainly attributed to the following two aspects: 1) Large scale and long term mining/smelting activities have led to the serious

contamination of metals including Sb, therefore local government has attach much importance to environment protection to reduce release of contaminants to surrounding area. Several measures to restore the environment were witnessed in the past 7 years, like contaminated
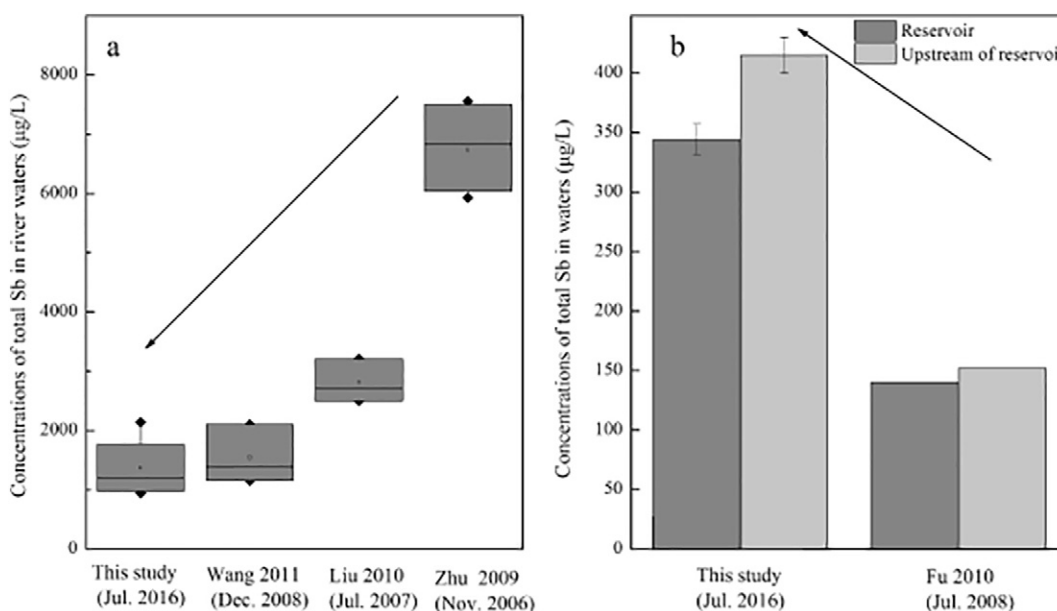

Fig. 6. a) Concentrations of Sb in river waters directly contaminated by mine wastewater in the XKS area; b) concentrations of Sb in the reservoir (S7) and its upstream location (S8) that were not directly contaminated by mine wastewater in the XKS area.

Table 5

Concentrations of total Sb and Sb speciations in waters of XKS conducted by previous reports.

	Sampling period	Number of water samples	Contaminant	Reference
1	Nov. 2006	15	Total Sb (4581–29,423 µg/L)	Zhu 2009 [29,30]
2	Jul. 2007	18	Total Sb (330–11,400 µg/L); Sb(V) (330–11,400 µg/L); Sb(III) (<LOD–trace level)	Liu 2010 [28,29]
3	Dec. 2007 and Jul. 2008	51	Total Sb (135–163 µg/L)	Fu 2010 [27,28]
4	Dec. 2008	6	Total Sb (224–2099 µg/L)	Wang 2011 [30,31]

<LOD represented less than limit of detection.

soil was fixed by plants and mineral deposits with low storage were shut down [59]. 2) With the continual mining activity in the Sb ore zone, XKS mineral deposits have consumed their limited stocks gradually. Statistical data from the statistics bureau of Lengshuijiang demonstrated that the Sb products from the XKS area have being suffered from decreased tendency in recent years (see Fig. S4), indicating the less mining/smelting activities in the contaminated area. Same declined trend also demonstrated in the China inventory of Sb emissions by Tian et al. [60], suggesting that Sb emissions declined gradually since 2005.

In comparison, concentrations of Sb in the reservoir (S7) and its upstream (S8) with a mean of 380 and range of 344 to 415 µg/L were greater than concentrations observed at the same sites in the same period of 2008 (130 µg/L) [28] (Fig. 6b). This inverse trend in reservoir may be attributed to indirect contamination with slow and continuous releases of Sb from tailings heaps near the reservoir. In particular, mobility of Sb has been demonstrated less than some other metals like As [19,61]. Thus, Sb can accumulate in the reservoir with time [31].

4. Conclusions

In the present study, elevated concentrations of Sb and other co-occurred contaminants were observed in waters and sediments from XKS. Sb(V) dominated the Sb speciations in various waters and sediments. The environmental geochemical behaviors of Sb in this typical aquatic system were mainly influenced by the processes of oxidation and adsorption/combination. Oxidation from Sb(III) to Sb(V) was suggested having priority than other process in the surface waters. The oxidation/combination of matrix and dilution effect of tributary played significant roles in the spatial distribution of Sb in natural water. The temporal decreased contamination level of Sb in Lianxi River was attributed to several restoration measures implemented by local government and less mining/smelting activities in the contaminated region of XKS. Our results suggested that tailings heaps in mining region should arouse much attention for its potential release of Sb.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2017.10.010.

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Supporting Information

Environmental geochemical and spatial/temporal behavior of total and speciation of antimony in typical contaminated aquatic environment from Xikuangshan, China

WenjingGuo[a, b], Zhiyou Fu [b*], Hao Wang [a, b], Fanhao Song [b], Fengchang Wu [b], John P. Giesy [b c]

[a] *College of Water Sciences, Beijing Normal University, Beijing 100875, China*

[b] *State Key Laboratory of Environment Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China*

[c] *Department of Biomedical and Veterinary Biosciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada*

* Corresponding author: Zhiyou Fu, zhiyoufu@126.com. +86-10-84915312
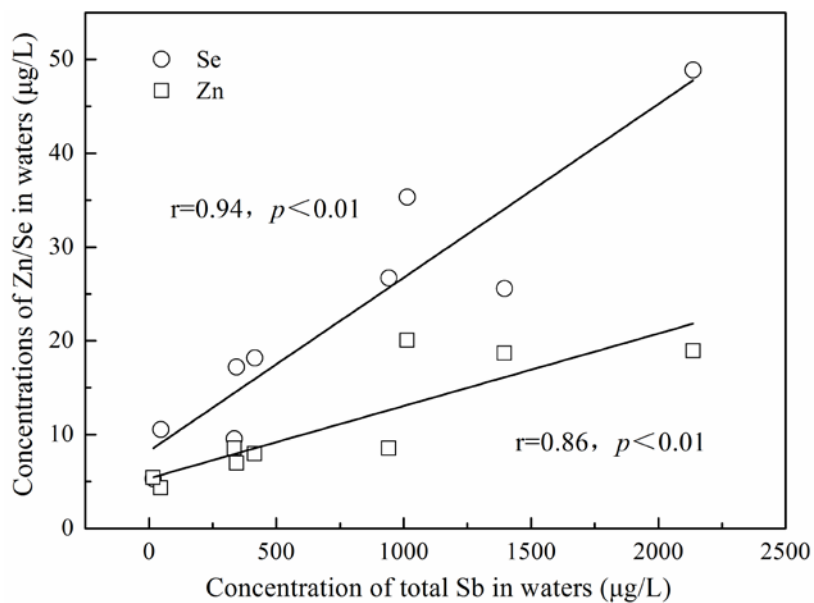
Fig. S1 Correlations between concentrations of Zn/Se and Sb in the XKS area (excluding tailings wastewater of S9 and well water of S10).
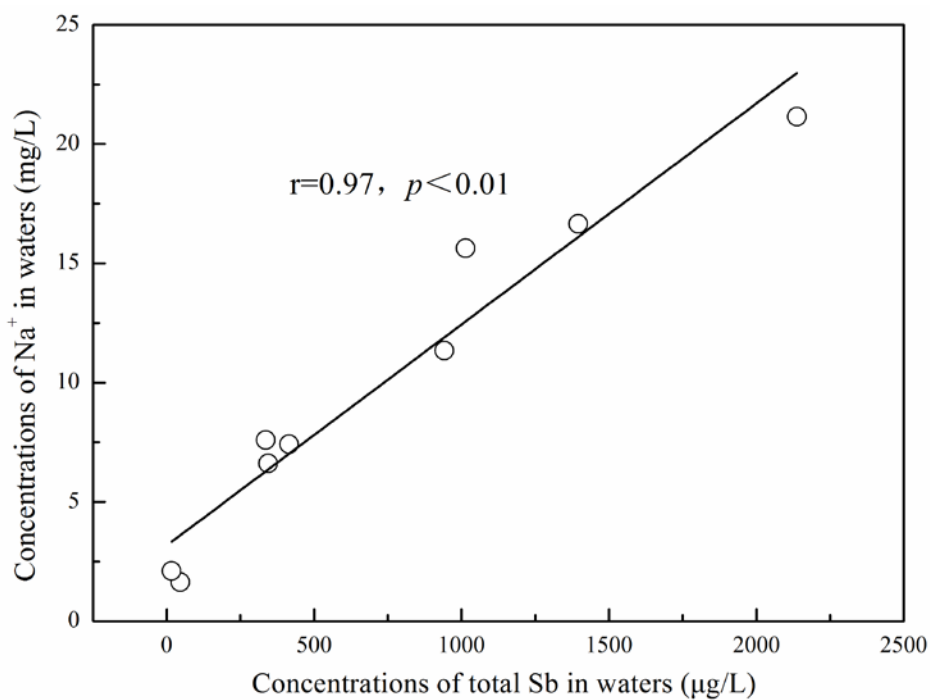

Fig. S2 Correlation between concentrations of total Sb and Na$^+$ (excluding tailing wastewater of S9 and well water of S10).
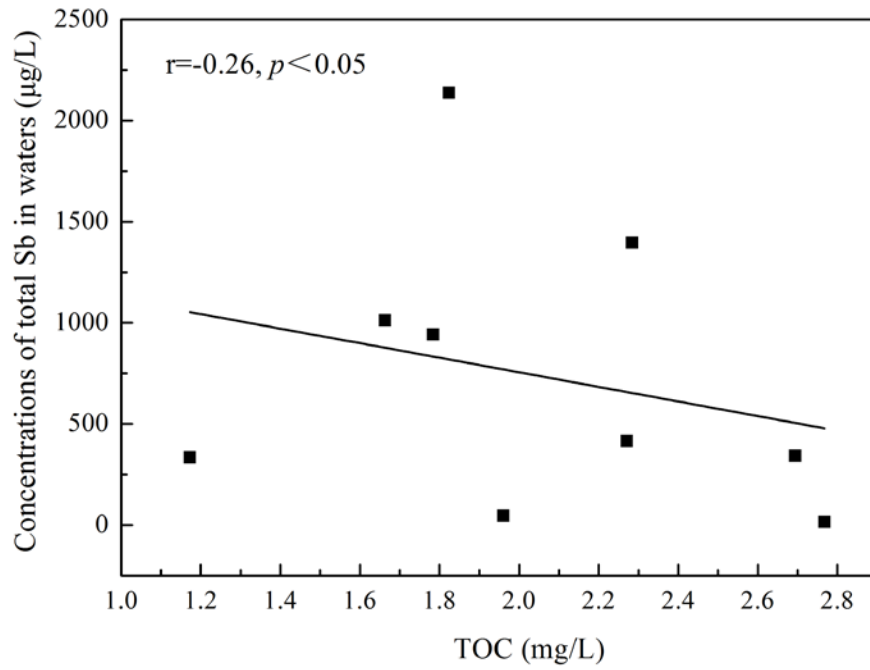
Fig. S3 Correlation between concentrations of total Sb and TOC (excluding tailing wastewater of S9 and well water of S10).
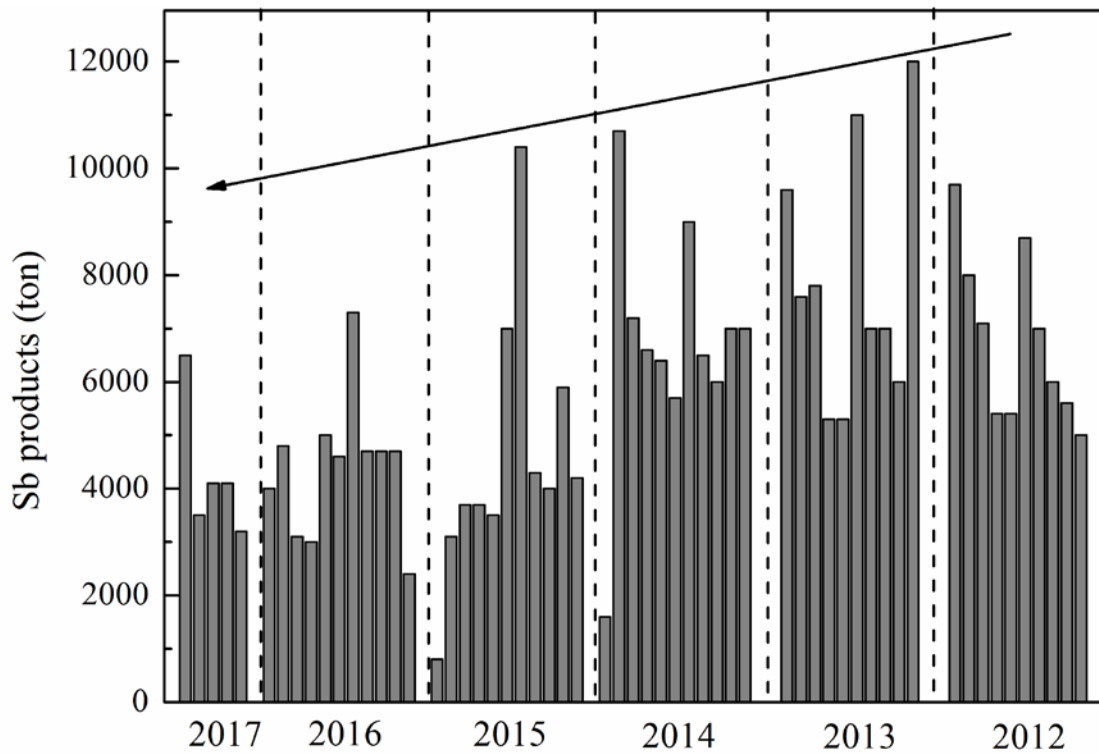

Fig. S4 The monthly Sb products from Feb. 2012 to Jun. 2017 of XKS mining area. The statistical data were obtained from the statistics bureau of Lengshuijiang [1], some of that data were not collected.

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[1] Statistics   bureau   of   Lengshuijiang,   Gate-way   website   of   Lengshuijiang city.http://www.lsj.gov.cn (accessed August 5, 2017).