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Arsenic, antimony and bismuth in human hair from potentially exposed individuals in the vicinity of antimony mines in Southwest China

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ABSTRACT

To study the effect of the environmental pollution in exposed population, human hair samples of residents were collected from two typical antimony mines (Xikuangshan antimony mine and Qinglong antimony mine, Southwest China) and one non-mining city (Guiyang, Southwest China), and the concentrations of arsenic, antimony and bismuth in these samples were analyzed by hydride generation-atomic fluorescence spectrometry. Arsenic concentrations for Xikuangshan, Qinglong, and Guiyang ranged 0.236–48.4 (mean 4.21), 0.130–16.1 (mean 2.96), and 0.104–0.796 (mean 0.280) $\mu\text{g/g}$, respectively. Antimony concentrations for Xikuangshan, Qinglong, and Guiyang ranged 0.250–82.4 (mean 15.9), 0.060–45.9 (mean 5.15), and 0.065–2.87 (mean 0.532) $\mu\text{g/g}$, respectively. Bismuth contents were found to be greater than the limit of detection ($\text{LOD} > 0.016 \mu\text{g/g}$) in all the human hair samples collected from residents from Qinglong antimony mine, 95.5% samples from Xikuangshan mine and only 22.7% samples from Guiyang. There were no significant differences in both arsenic and antimony concentrations between hair samples from male and female individuals in the same area ($P > 0.05$). Arsenic and bismuth were mainly present in samples from children (5–9 years) and adults aged 41–51 years. Relatively high antimony contents ($\geq 3 \mu\text{g/g}$) were detected mainly in samples from children and adults aged ≥ 41 years. Significant correlation was found between the concentrations of arsenic and antimony in the human hair samples ($r = 0.523$, $P < 0.05$). The results indicate that arsenic and antimony in antimony mining area may significantly affect human health.

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1. Introduction

Arsenic is a toxic and carcinogenic element that is widespread in the environment [1]. Arsenic pollution has been reported worldwide, and some areas in South-East Asia and South America are particularly polluted [2–4]. In contrast to arsenic, there is limited understanding of the behavior, ecotoxicology, and the extent of environmental dispersion of antimony [5,6]. Antimony is emitted into the environment through human activities such as waste incineration, mining, smelting, and the combustion of fossil fuels. Increasing use of antimony and its compounds has resulted in elevated antimony mining and smelting activities [7]. From 8000 years ago to present (i.e. 1989) the concentration of antimony in the environment increased by 50% [8–11]. Antimony has been classed as a priority pollutant by the

United States Environmental Protection Agency (US EPA) and the German Research Council [12].

In China, arsenic, antimony and bismuth pollution is a serious issue due to the presence of many large antimony mines. The Xikuangshan antimony mine is situated in Hunan Province, Southwest China, and is the largest antimony mine in the world [13]. It has annual average production capacities of 55,000, 40,000, and 40,000 metric tons of antimony ore, antimony products, and zinc ingots, respectively [13]. Antimony pollution from this mine is causing environmental problems in China [14]. The surface water around Xikuangshan antimony mine is heavily polluted by antimony, with concentrations significantly exceeding the limit for drinking water in China [15]. Another large and important antimony mine is located in Qinglong County, Guizhou Province, Southwest China [16]. It has 199,600 metric tons of antimony reserves [17]. Antimony pollution in Qinglong due to the antimony mine is also severe [17]. However, although many investigators have highlighted the importance of the environmental chemistry of arsenic, antimony and bismuth [7,9,18–23], little information is available on how antimony contamination affects exposed populations.

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The levels of arsenic, antimony and bismuth could be determined in human hair samples and used to determine the consequences of exposure to these compounds. Human hair samples can be collected easily and non-invasively, and they are convenient for storage. Furthermore, the concentrations of trace elements in the hair of an individual are possibly related to those of the elements in the human body [24]. Consequently, human hair has been used as an important biological material by the US Environmental Protection Agency (EPA), the World Health Organization (WHO) and the International Atomic Energy Agency (IAEA) for worldwide environmental monitoring [4,17].

The main objective of the present study is to estimate arsenic, antimony, and bismuth concentrations in hair samples from exposed populations in the vicinity of antimony mining areas in Southwest China. The information provided by this analysis will extend the information on the impact that environmental exposure to these heavy metals has on human health.

2. Experimental

2.1. Sampling sites

Human hair samples were collected from residents around the Xikuangshan antimony mine, Qinglong antimony mine, and Guiyang (Fig. 1). Residents from Guiyang were selected as a control group, because Guiyang was not influenced by any mining activities.

2.2. Chemicals and reagents

All of the chemicals and reagents used in this study were analytical grade or higher. All solutions were prepared with Milli-Q purified water (18.2 M Ω cm). Glassware was cleaned by soaking for a day in 20% (v/v) HNO₃ solution, and rinsing with deionized water prior to use. Arsenic, antimony and bismuth stock solutions of 100 mg/L were obtained from the Standard Reference Center of China, and were stored in polyethylene bottles in the refrigerator at 4 °C. Working standard solutions of arsenic, antimony and bismuth were prepared by appropriate dilution from their 100 mg/L stock solutions. These were prepared daily to prevent any possible species conversion. KBH₄ solution (2%, m/v) was prepared daily by dissolving KBH₄ powder in NaOH solution (0.5%, m/v). Diluted HCl solution (5%, v/v) was prepared from the concentrated acid.

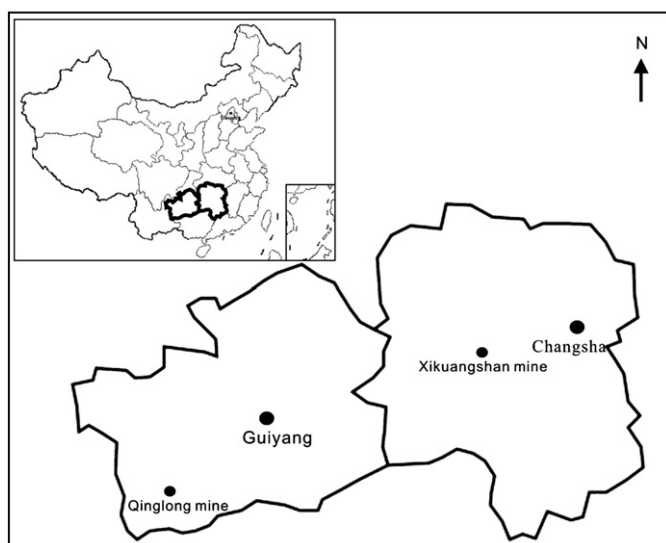


Fig. 1. Locations of the sampling sites in China. Antimony mines are located at Xikuangshan and Qinglong. Guiyang was selected as a control location due to the lack of antimony mining in this area.

2.3. Sampling and sample preparation

Hair samples were collected at barbershops located around the Xikuangshan ($n=67$) and Qinglong ($n=62$) antimony mines. Samples were only collected from long-term residents who had not colored or treated their hair. Control samples were collected from the residents of Guiyang ($n=22$). Samples were taken of hairs approximately 2–3 cm long that were cut from the nape of the neck near to the scalp with stainless steel scissors. All samples were kept in individual sealable polyethylene bags at room temperature. To remove surface contamination, the samples were soaked for >0.5 h in diluted HCl (5%, v/v), and then rinsed 10 times with tap water and three times with deionized water. Subsequently, all samples were dried in an oven at 60 °C for approximately 6 h. The dried hair was cut into small pieces (<1 mm) with stainless steel scissors, and stored in sealable bags at room temperature until analysis [25].

An aliquot (500 mg) of hair sample was transferred into a 50 mL flask for digestion. The digestion procedure was carried out by soaking with 10 mL of concentrated HNO₃ and 1 mL of concentrated HClO₄ for 12 h. The flasks were heated at 110 °C on an electric hot plate for approximately 3 h. Then the temperature was elevated to 160 °C. When the volumes of the sample solutions in the flasks were <0.5 mL, the solutions were immediately transferred to sample bottles and made up to 20 mL with 5% (v/v) HNO₃. Human hair certified reference material (GBW07601) from the National Research Center for Standard Materials (Beijing, China) and a reagent blank were digested following the same procedures for QC/QA purposes [25].

Following the digestion procedure, the bismuth concentration was detected directly by hydride generation-atomic fluorescence spectrometry (HG-AFS). For antimony and arsenic, an aliquot (1 mL) of the digestion solution was transferred to a sample bottle, and 0.5 mL of HCl, 1 mL of thiourea (20%, m/v), and 1 mL of 20% (m/v) ascorbic acid were added. Each sample was made up to 10 mL with purified water and left for 0.5 h before antimony and arsenic detection using HG-AFS. Some samples required further dilution. The reagent blank sample was made up using HCl (5%, v/v), thiourea (2%, m/v), and ascorbic acid. The reductant used for arsenic, antimony and bismuth was KBH₄ (2%, m/v) stabilized in NaOH solution (0.5%, m/v).

2.4. Apparatus

For signal detection purposes, a HG-AFS (AFS810, Beijing Jitian Co., China) equipped with arsenic, antimony and bismuth boosted-discharge hollow cathode lamp was used. The instrument was set to shield argon flow rate at 1000 mL/min, and the carrier gas (argon) flow rate was 400 mL/min. The lamp current for EDL was 60 mA. The analysis time and delay time were 10 s and 1 s, respectively.

3. Results and discussion

3.1. Calibration graph

Calibration graphs were set up in the range of 0–20 μ g/L for arsenic and 0–30 μ g/L for antimony in 5% (v/v) HCl, respectively. Optimal concentrated thiourea and ascorbic acid solutions were prepared. The linear equations were $Y = 19.92X - 9.1651$ ($R^2 = 0.9995$) for arsenic, $Y = 6.0399X - 14.6779$ ($R^2 = 0.9992$) for antimony, and $Y = 0.0104X - 2.0649$ ($R^2 = 0.9995$) for bismuth. At a signal-to-noise ration of three, the limit of the detection (LOD) was determined to be 0.36, 0.006, and 0.004 μ g/L for arsenic, antimony, and bismuth, respectively.

3.2. Accuracy and precision

Human hair certified reference material (GBW07601, National Research Center for Standard Materials, China) was used to check the accuracy of the chemical analyses (Table 1).

Table 1

Mean and standard deviation (SD) of arsenic, antimony, and bismuth concentrations in the standard reference sample.

Element	Concentrations ($\mu\text{g/g}$, dry wt.)			
	Certified values		Found values	
	Mean	S.D.	Mean	S.D.
Arsenic	0.28	0.05	0.28	0.06
Antimony	0.095	0.016	0.12	0.04
Bismuth	0.34	0.02	0.31	0.02

3.3. Distribution of arsenic in human hair

3.3.1. Frequency distribution of arsenic in human hair

The arsenic concentrations were quite variable between human hair samples from residents in the antimony mining areas and those from the control group in Guiyang (Fig. 2). The concentrations of arsenic in human hair samples from Xikuangshan, Qinglong, and Guiyang were 0.236–48.4, 0.130–16.1, and 0.104–0.796 $\mu\text{g/g}$, respectively. Lower arsenic concentrations were detected in human hair samples from the residents around Qinglong mine than those from Xikuangshan mine. However, residents from both mining areas had significantly higher hair arsenic concentrations than those from Guiyang ($P < 0.05$).

The mean arsenic concentration reported in hair samples from children living in Pian de' Gangani (Montalto di Castro, Latium, Italy) was 0.159 $\mu\text{g/g}$ and the median was 0.152 $\mu\text{g/g}$ [26]. Man et al. reported an arsenic concentration of $0.17 \pm 0.14 \mu\text{g/g}$ in hair samples from children aged 6–15 years [17]. The arsenic concentration in hair from blackfoot disease patients ($0.56 \pm 0.41 \mu\text{g/g}$) in Taiwan, China was significantly higher ($P < 0.001$) than that in hair from healthy people ($0.56 \pm 0.41 \mu\text{g/g}$) [27]. The arsenic content in human hair samples from individuals in arsenic-affected areas of West Bengal, India ranged 0.17–14.39 $\mu\text{g/g}$, with a mean of 3.43 $\mu\text{g/g}$ and median of 2.29 $\mu\text{g/g}$ [4]. The mean hair arsenic concentration for a patient group drinking contaminated water in Bangladesh was 14.1 $\mu\text{g/g}$, while in a group drinking uncontaminated water it was below 3.0 $\mu\text{g/g}$ [28]. Hair samples from patients in the Tumotezuqi area with minor and serious endemic arsenic poisoning contained 0.534 ± 0.106 and $1.87 \pm 1.48 \mu\text{g/g}$ of arsenic, respectively [29]. In comparison, hair samples from healthy male adults living in Beijing contained $0.087 \pm 0.057 \mu\text{g/g}$ of arsenic [29]. In a further Chinese study, hair arsenic contents ranged 0.004–9.999 $\mu\text{g/g}$ and the mean was $0.927 \pm 1.213 \mu\text{g/g}$ [30].

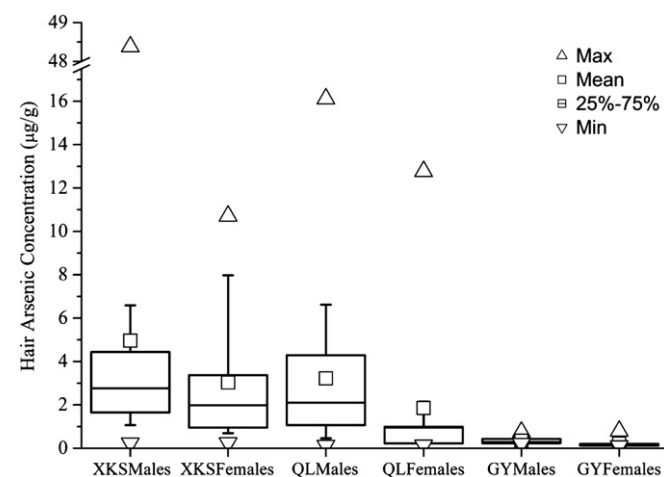


Fig. 2. Arsenic concentrations in human hair samples obtained in Xikuangshan (XKS), Qinglong (QL) and Guiyang (GY). The square represents the mean value, the box indicates the range 25–75% of the distribution, and the triangles represent the minimum and maximum values.

Some authors have claimed that arsenic levels in human hair from healthy individuals should be $< 1 \mu\text{g/g}$ [31]. However, others have suggested that the background concentration for human hair arsenic is $< 3 \mu\text{g/g}$ [28,32]. The levels of arsenic in human hair are perhaps variable because individuals live in areas with different background arsenic concentrations. In the present study, the average concentration of arsenic in human hair sampled from residents around Xikuangshan mine was $> 3.0 \mu\text{g/g}$ at 4.21 $\mu\text{g/g}$, which was lower than that in severely polluted Bangladesh while higher than those in other countries and areas. This suggests that antimony mining in this area presents a threat to public health.

Among the 129 hair samples obtained in this study from individuals living close to antimony mines, 48 (37.2%) were found to be suffering from various degrees of chronic arsenic poisoning ($> 3 \mu\text{g/g}$). Twenty-eight (41.8%) of the 67 residents from Xikuangshan and 20 (32.0%) of the 62 residents from Qinglong had high hair arsenic concentrations. For the individuals from Xikuangshan mine, 18 (26.9%) had hair arsenic concentrations of 3–6 $\mu\text{g/g}$, 6 (9.0%) had hair arsenic concentrations of 6–9 $\mu\text{g/g}$, 2 (3.0%) had hair arsenic concentrations of 9–12 $\mu\text{g/g}$, and 2 (3.0%) had hair arsenic concentrations of $\geq 15 \mu\text{g/g}$. For the residents around Qinglong mine, the numbers of individuals at each level were: 11 (17.7%) at 3–6 $\mu\text{g/g}$, 5 (8.1%) at 6–9 $\mu\text{g/g}$, 1 (1.6%) at 9–12 $\mu\text{g/g}$, 1 (1.6%) at 12–15 $\mu\text{g/g}$, and 2 (3.2%) at $\geq 15 \mu\text{g/g}$. The independent-samples *t*-test showed no significant differences for arsenic concentration between hair samples from males and females from the same area ($P > 0.05$).

3.3.2. Changes in human hair arsenic concentration according to age

Human hair arsenic concentrations in children are typically higher than in other age groups [33]. This phenomenon was observed in the present study (Table 2). Eighty percent of the children (5–9 years) and 69.6% of the adults aged 41–51 years had high hair arsenic concentrations ($\geq 3 \mu\text{g/g}$). This indicates that arsenic affected these ages' groups more than other age groups. This may be caused by different rates of arsenic metabolism resulting in differing accumulation of arsenic [34,35]. Arsenic accumulation in the human body is related to the strength of the metabolism [36]. Younger adults accumulate less arsenic than other age groups due to their robust metabolism. Children and the elderly have relatively weak metabolisms, and they may accumulate more arsenic than other age groups when exposed to the same levels.

3.4. Antimony concentrations in human hair

3.4.1. Frequency distribution of antimony in human hair

The concentrations of antimony in human hair samples from Xikuangshan, Qinglong, and Guiyang were 0.250–82.4 (mean 15.9, median 9.22), 0.060–45.9 (mean 5.15, median 3.48), and 0.065–2.87 (mean 0.532, median 0.240) $\mu\text{g/g}$, respectively. The mean antimony values in human hair samples from residents around the Xikuangshan antimony mine were significantly higher than those of residents from both Qinglong and Guiyang ($P < 0.05$) (Fig. 3).

A study of industrial occupational exposure found mean antimony values of 0.05, 0.57 and 0.36 $\mu\text{g/g}$ in hair from locomotive shed workers, industrial welders, and students and office workers,

Table 2

Frequency distribution of high hair arsenic concentrations in different age groups.

Age class for arsenic, years (<i>n</i>)	Frequency <i>n</i> (%)	
Children	5–9 (10)	8 (80.0)
Adolescent	10–18 (23)	3 (13.0)
Adult	19–29 (41)	8 (19.5)
	30–40 (46)	11 (23.9)
	41–51 (23)	16 (69.6)
	≥ 52 (8)	2 (25.0)
Total		48 (31.8)

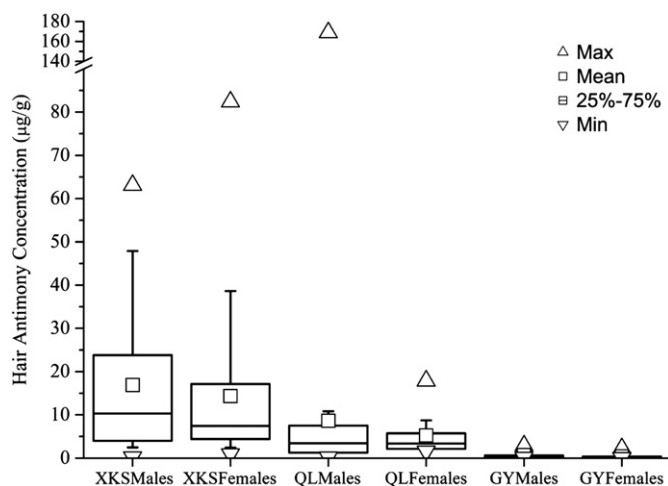


Fig. 3. Antimony concentrations in human hair samples obtained in Xikuangshan (XKS), Qinglong (QL), Guiyang (GY). The square represents the mean value, the box indicates the range 25–75% of the distribution, and the triangles represent the minimum and maximum values.

respectively [26]. Batzevich et al. studied hair samples from 17 ethnic and territorial groups in an unpolluted area of the former USSR, and found antimony concentrations in the 17 ethnic hair samples ranged 0.05–0.58 µg/g [37]. The concentration of antimony in the hair of healthy individuals from Taiwan, China was 0.078 ± 0.059 µg/g [27]. In our study, the average concentration of antimony in human hair sampled from residents around Xikuangshan and Qinglong mines were much higher than those in other countries and areas.

There is limited information as to what level of antimony in hair can be used to estimate whether individuals are suffering from chronic antimony poisoning. Some studies have found that hair arsenic levels are <3 µg/g [28,32]. Therefore, we use 3 µg/g as the normal hair antimony level. In this study, all the human hair samples from the residents of Guiyang contained <2.87 µg/g antimony. Among the 129 samples from residents around the antimony mines, 90 (69.8%) contained >3 µg/g antimony. In the samples from Xikuangshan, 38 (56.7%) contained 3–23 µg/g antimony, 9 (13.4%) contained 23–43 µg/g antimony, 5 (7.5%) contained 43–63 µg/g antimony, and 2 (3.0%) contained ≥ 63 µg/g antimony. Among the samples from Qinglong, 35 (56.4%) contained 3–23 µg/g antimony, and only 1 (1.6%) contained ≥ 23 µg/g antimony. The independent-samples *t*-test showed there was no significant difference for antimony concentration between hair samples from males and females in the same area ($P > 0.05$).

3.4.2. Changes in human hair antimony concentration according to age

High antimony concentrations (≥ 3 µg/g) were found in 80.0% of children (5–9 years) and 69.6% of adults aged 41–51 years (Table 3). More children (5–9 years) and adults aged 41–51 years were affected by antimony than individuals in other age groups.

Table 3
Frequency distribution of high hair antimony concentrations in different age groups.

Age class for antimony, years (n)	Frequency n (%)
Children 5–9 (10)	9 (90.0)
Adolescent 10–18 (23)	13 (56.5)
Adult 18–29 (41)	19 (46.3)
30–40 (46)	25 (54.3)
41–51 (23)	18 (78.3)
≥ 52 (8)	6 (75.0)
Total	90 (59.6)

3.5. Bismuth concentrations in human hair

3.5.1. Frequency distribution of bismuth in human hair

Among the 22 hair samples from residents of Guiyang, only 5 (22.7%) had bismuth concentrations higher than the minimum detection limit. In contrast, all of the hair samples from residents around Qinglong antimony mine and 95.5% of the hair samples from residents around Xikuangshan mine had bismuth concentrations higher than the minimum detection limit.

Jorgensen et al. reported that bismuth concentrations ranged <0.03 to <0.1 µg/g in mammalian tissues [38]. Park et al. found a mean bismuth level of 0.04 µg/g in hair samples from 655 children (3–6 years old) from metropolitan and small cities in Korea [39]. In our study, all of the 22 hair samples from Guiyang contained <0.1 µg/g bismuth. In the two mining areas, 37 (28.7%) of the 129 hair samples contained >0.1 µg/g bismuth. Among the 67 human hair samples from Xikuangshan, 8 (11.9%) contained 0.1–0.3 µg/g bismuth, 1 (1.5%) contained 0.3–0.5 µg/g bismuth, and 1 (1.5%) contained 0.7–0.9 µg/g bismuth. For the hair samples from Qinglong, 10 (16.1%) contained 0.1–0.3 µg/g bismuth, 5 (8.1%) contained 0.3–0.5 µg/g bismuth, 4 (6.5%) contained 0.5–0.7 µg/g bismuth, 2 (3.2%) contained 0.7–0.9 µg/g bismuth, 2 (3.2%) contained 0.9–1.1 µg/g bismuth, and 1 (1.6%) contained ≥ 1.1 µg/g bismuth.

No significant differences were found with the independent-samples *t*-test ($P > 0.05$) for bismuth concentration between hair samples from males and females in the same area.

3.5.2. Changes in human hair bismuth concentration according to age

High bismuth concentrations (≥ 0.1 µg/g) were observed in 90.0% of the children (5–9 years), 78.3% of adults aged 41–51 years, and 75.0% of adults aged ≥ 52 years (Table 4). More children (5–9 years) and adults aged ≥ 41 years were affected by bismuth exposure than individuals in other age groups.

3.6. Correlation between arsenic and antimony in human hair

A significant correlation was observed between arsenic and antimony concentrations in the human hair samples ($r = 0.523$, $P < 0.01$).

3.7. Arsenic and antimony in water and soil around the antimony mine area

The concentrations of arsenic and antimony were determined in water and soil from Xikuangshan antimony mine (Table 5). Arsenic and antimony concentrations in the water polluted directly by the antimony mine drainage were 21.0 and 9750 µg/L, respectively [40]. In the Xikuangshan mining area, the ratio of dissolved arsenic to total arsenic is 57.3%, and that for antimony is 85.2% [15]. Eikmann et al. reported that the maximum antimony content that could be tolerated in environmental samples was 5 µg/g [42], while Crommentuijn et al. reported a maximum permissible antimony concentration in standard soil of 3.50 µg/g [43]. Arsenic and antimony concentrations of 35.1 and 172 µg/g, respectively, in soil samples surrounding Xikuangshan mining area [41]. These results indicate that water and soil in the vicinity of antimony mining and smelting area contain elevated levels

Table 4
Frequency distribution of high hair bismuth concentrations in different age groups.

Age class for bismuth, years (n)	Frequency n (%)
Children 5–9 (10)	6 (60.0)
Adolescent 10–18 (23)	5 (21.7)
Adult 18–29 (41)	8 (19.5)
30–40 (46)	11 (23.9)
41–51 (23)	7 (30.4)
≥ 52 (8)	–
Total	37 (24.5)

Table 5

Arsenic and antimony concentrations ($\mu\text{g/g}$) in water and soil samples obtained around Xikuangshan antimony mine.

Element	Water [40]	Soil [41]	Human hair
Arsenic	21.0	35.1	4.21
Antimony	9750	172	17.6

of arsenic and antimony. They may be a health hazard for the residents in the surrounding area.

4. Conclusions

High levels of arsenic, antimony and bismuth were detected in human hair samples from residents in the vicinity of both Xikuangshan and Qinglong antimony mines. In comparison, lower levels of arsenic, antimony and bismuth were detected in human hair samples from residents of Guiyang, which was not affected by antimony mining activity. These results show that arsenic, antimony and bismuth concentrations in hair of residents living close to antimony mines are significantly higher than in those living in non-mining areas ($P < 0.05$).

There were no significant differences for both arsenic and antimony concentrations between hair samples from males and females from the same area ($P > 0.05$). Significant positive correlation was found between arsenic and antimony concentrations in the hair samples ($r = 0.523$, $P < 0.05$). Compared with other groups, arsenic, antimony and bismuth affected children (< 10 years) and older adults aged 41–51 years more than other age groups.

These results indicate that arsenic and antimony in antimony mining areas may largely impact human health when compared to non-mining areas. Further research is required to identify how arsenic, antimony and bismuth pass from food sources to the human body.

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