

Distribution and health risk assessment to heavy metals near smelting and mining areas of Hezhang, China

Meryem Briki · Yi Zhu · Yang Gao ·
Mengmeng Shao · Huaijian Ding · Hongbing Ji

Received: 12 February 2017 / Accepted: 27 July 2017 / Published online: 19 August 2017
© Springer International Publishing AG 2017

Abstract Mining and smelting areas in Hezhang have generated a large amount of heavy metals into the environment. For that cause, an evaluative study on human exposure to heavy metals including Co, Ni, Cu, Zn, Cr, As, Cd, Pb, Sb, Bi, Be, and Hg in hair and urine was conducted for their concentrations and correlations. Daily exposure and non-carcinogenic and carcinogenic risk were estimated. Sixty-eight scalp hair and 66 urine samples were taken from participants of different ages (6–17, 18–40, 41–60, and ≥ 65 years) living in the vicinity of an agricultural soil near mine and smelting areas. The results compared to the earlier studies showed an elevated concentration of Pb, Be, Bi, Co, Cr, Ni, Sb, and Zn in hair and urine. These heavy metals were more elevated in mining than in smelting. Considering gender differences, females were likely to be more affected than male. By investigating age differences in this area, high heavy metal concentrations in male's hair and urine existed in age of 18–40 and ≥ 66 , respectively. However, females did not present homogeneous age distribution. Hair and urine showed a different distribution of heavy metals in different age and gender. In some cases, significant correlation was found between heavy

metals in hair and urine ($P > 0.05$ and $P > 0.01$) in mining area. The estimated average daily intake of heavy metals in vegetables showed a great contribution compared to the soil and water. Non-carcinogenic and carcinogenic risk values of total pathways in mining and smelting areas were higher than 1 and exceeded the acceptable levels. Thus, the obtained data might be useful for further studies. They can serve as a basis of comparison and assessing the effect of simultaneous exposure from heavy metals in mining and smelting areas, and potential health risks from exposure to heavy metals in vegetables need more consideration.

Keywords Heavy metals · Scalp hair · Urine · Age · Gender · ADD · Risk assessment

Introduction

Heavy metal pollution originating from industrial mining and smelting activities contaminates the environment and poses significant health concerns (Gray et al. 2002; Kuo et al. 2015; Li et al. 2008, b). Mining and smelting processes discharge large quantities of heavy metals into the environment. The metals accumulate in the soil, are transported into groundwater, enter the food chain, and can cause adverse health effects in humans (Li et al. 2014) and animals (Sonne et al. 2009). Therefore, exposure to heavy metals has attracted attention from the research community (Campbell et al. 2003; Feldmann et al. 1999; Li et al. 2009; Li 2013; Mortada et al. 2002; Massaquoi et al. 2015; Nam et al. 2003;

M. Briki · Y. Gao · H. Ding · H. Ji (✉)
School of Energy and Environmental Engineering, University of
Science and Technology Beijing, Xueyuan Road No. 30, Haidian
District, Beijing 100083, People's Republic of China
e-mail: ji.hongbing@hotmail.com

Y. Zhu · M. Shao
College of Food Science and Nutritional Engineering, China
Agricultural University, Beijing 100083, China

Umbangtalad et al. 2007; Vimercati et al. 2016; Wang et al. 2017; Zhang and Wong 2007). The toxicity of metals such as Pb, Cd, Be, As, Co, Cr, Ni, and Sb is dependent on their chemical forms (Baselt 2000; Cullen and Reimer 1989), and those elements can be harmful to human health (Bernard and Lauwerys 1984; Infante and Newman 2004; WHO 2010). Heavy metal poisoning leads to complications such as renal tubular damage, kidney and liver dysfunction, and brain and nervous system disorders. Common symptoms of acute Zn poisoning are stomach cramps, nausea, anemia, and damage to the pancreas (Bhattacharya et al. 2004). The toxicity of Hg varies significantly with the exposure route. Inhalation of high concentrations of Hg causes severe respiratory irritation, digestive disturbances, and marked kidney damage (Natural Healing Site 2010). From 2009 to 2013, over 5000 children in China were affected by Pb poisoning (Cao et al. 2015; Chuang et al. 2008; Ji et al. 2011). Nickel in drinking water can cause allergic reactions and eczema (Filon et al. 2009). Absorbed Bi is distributed throughout the soft tissues and bone, with the highest concentrations found in the kidney and liver (Fowler and Sexton 2007). In adults and newborns, the highest concentrations of Cu have been found in the liver and brain (Ellingsen et al. 2007). After metabolism, elements are generally eliminated within 3–4 days in the urine (Buchet et al. 1981; Li et al. 2009; WHO 1991). A variety of elements accumulates in the body and may be excreted through hair, nails, skin scaling, feces, and sweat (Mandal et al. 2004).

Scalp hair and urine are used to assess levels of heavy metal exposure in environmental risk assessments because hair is considered as a suitable indicator for estimating long-term metal exposure (Bencko 1995; Foo et al. 1993; Mortada et al. 2002; McDowell et al. 2004; Yasutake et al. 2004). We carried out a study on human exposure in Hezhang County, China. In this studied area, there is a considerable body of works such as Briki et al. (2015), Feng et al. (2004, 2006), and Ying and Qin (2001) who focused on the environmental pollution caused by heavy metals, but limited research focused on human exposure; human biomonitoring can reveal the absorbed dose into human body and give a measure of integrated exposure (Angerer et al. 2011; Zidek et al. 2016). According to Briki et al. (2015), the concentration of heavy metals in soil samples exceeded the standard limit of CNEMC (1990), so it is necessary to assess human health risks from exposure to soil heavy metals

and identify the main contamination sources in order to improve the environment of these areas and protect human health. The three main objectives of the present study were as follows: (1) to investigate the concentration of 12 and 11 heavy metals in human scalp hair and urine, respectively; (2) to evaluate age- and gender-related variations in levels of heavy metals; and (3) to estimate the average daily doses (ADD) and risk assessment using the results from our earlier study in this area (Briki et al. 2015) on heavy metals in vegetables (potato, garlic bolt, corn, and Chinese cabbage), along with metal levels in soil and water.

Materials and methods

Study area and participants

Hezhang County (104° 10' E to 105° 35' E, 26° 46' N to 27° 28' N) is famous for artisanal zinc smelting from the seventeenth century until 2004, when zinc smelting ceased. Large quantities of heavy metals were released into the environment and have spread (Bi et al. 2006a, b, 2007, 2009; Feng et al. 2004; Li et al. 2008, b). In our study, smelting areas were characterized by artisanal zinc smelting activities. And mining area was an active mine of Pb and Zn. We randomly chose people of different sex (male and female) and different ages (6–17, 18–40, 41–60, and ≥ 65 years) living in agricultural soil near mining and smelting areas. Study participants were general population lived in the selected study areas in Shangermachong (MM), Shehucun (ZB), and Haimeicun (LA). LA and ZB are considered smelting areas (SM) and MM represents a mining area; mean values from LA and ZB were compared with mean values from MM (Fig. 1). We divided the participants into four age groups based on the standard division of ages in China: 6–17, 18–40, 41–65, and above ≥ 66 . The distribution and descriptions of subjects in different sites in the sampled areas are presented in Table 1. The present study obtained ethic approval from the Committee of the Human Research Ethics, Agricultural University of China.

Sample collection

Urine and hair samples from participants were used to assess metal exposure. Participants had to be local residents and to have lived in their homes for at least

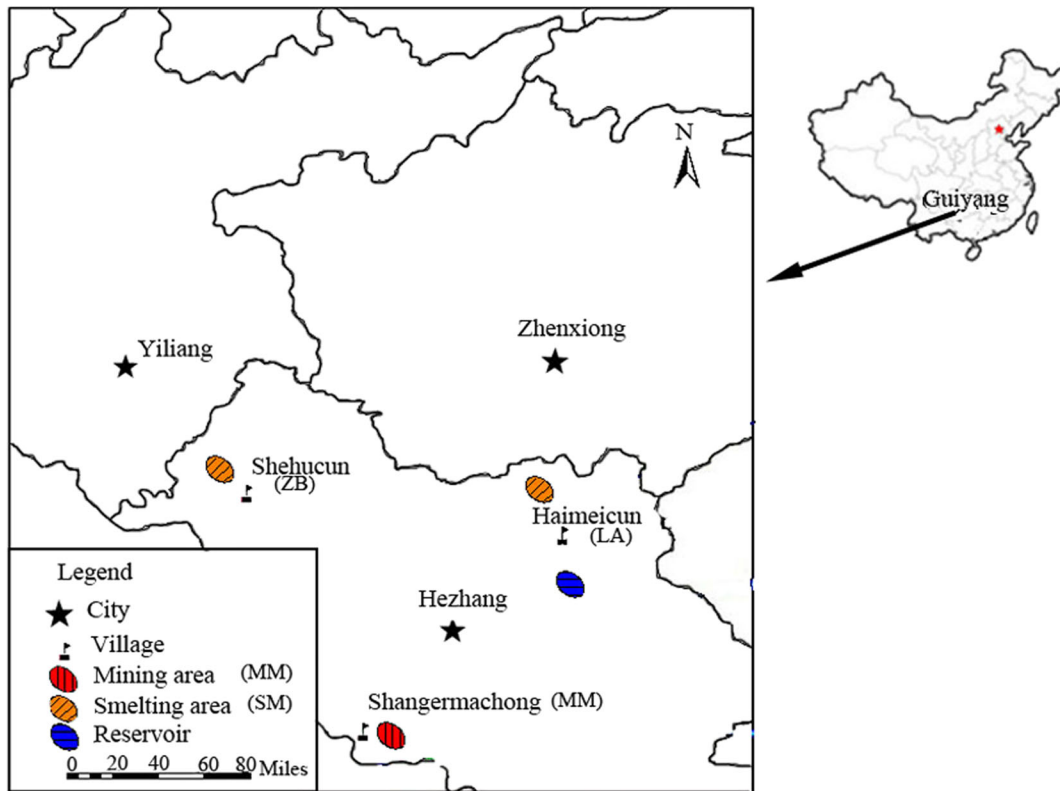


Fig. 1 Location of study areas in Hezhang County, China

3 months prior to the sampling time. Information such as age and gender was collected from all participants via a questionnaire.

Urine sample handling

The collected samples were stored in a cold pack immediately and refrigerated as soon as possible. Urine samples were stored at 4 °C without any additives according to the method of Feldmann et al. (1999).

Hair collection

The procedures for hair sampling were conducted according to Li et al. (2011). Hair samples were acquired using stainless steel scissors. All samples were stored individually in sealed plastic bags at room temperature.

Analytical method

To avoid surface contaminants, hair was cleaned using tap water and distilled water, then dried in an oven at

Table 1 Description of subjects in different sites in Hezhang County in mining and smelting areas

Sites	Occupation of subjects	Hair				Urine			
		Total population	Gender		Ages Ranges	Total population	Gender		Ages Ranges
			Male	Female			Male	Female	
ZB	Smelting areas	24	10	14	8–76	20	8	12	13–76
LA	Smelting areas	20	11	9	9–73	22	14	8	8–81
MM	Mining areas	24	7	17	6–77	24	7	17	6–68

The ages for hair and urine are divided to four groups, (6–17), (18–40), (41–65), and ≥ 66 for female and male

60 °C overnight. Stadlbauer et al. (2005) found that there was no significant difference between metal concentrations in the hair before and after washing. So the washing with water was to remove some external deposition like dust or organic matter which could skew the analysis.

The methods used to analyze heavy metals and determine the detection limit, quality control, precision, and sensitivity, along with validation of the procedure, were conducted as described by Stadlbauer et al. (2005). Urine analysis was performed in accordance with the method of Llerena et al. (2012). In brief, approximately 50 mg of hair was digested using microwave-assisted digestion with 2 mL HNO₃ and 1 mL H₂O₂. For urine, 0.8 mL HNO₃ and 0.4 mL H₂O₂ were added to 2 mL of urine and heated for 10 h at 90 °C. The samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS ELEMENT, Finnigan MAT). The accuracy and precision of the analysis were monitored by performing reagent blank analysis, analyzing 10% of samples in duplicate, and analyzing standard reference materials (Ji et al. 2004). Total Hg in urine was not measured because the sample quantity was insufficient. Total Hg (THg) concentrations in hair were determined using an RA-915+ mercury analyzer, equipped with a PYRO 915+ pyrolysis attachment and an automated Hg vapor detector (Ohio Lumex, Twinsburg, OH, USA), and analytical measurements were performed as described by Briki et al. (2015). Quality assurance and quality control measures included the analysis of duplicate samples, method blanks, and standard reference materials (GBW 07601 [GSH-1] for hair, from the Chinese Institute of Geophysical and Geochemical Exploration). The mean THg concentration found in GBW 07601 was $0.360 \pm 0.02 \text{ mg kg}^{-1}$ ($n = 11$), which is comparable to the certified concentration of $0.360 \pm 0.08 \text{ mg kg}^{-1}$. The relative difference between concentrations in the replicate samples was 6% for hair. All experiments were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (Guiyang, China).

Exposure pathway calculation method

Estimated values of human exposure to toxic metals in water, soil, and vegetables in Hezhang County were taken from Briki et al. (2015). According to the *Exposure Factors Handbook* (USEPA 2011), the ADD

values were calculated as milligrams per kilogram per day according to the following (Eq. 1):

$$\text{ADD} = (C \times \text{IR} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT}) \quad (1)$$

where C is the concentration (mg L^{-1} for water and mg g^{-1} for soil and plants), IR is the intake rate (L day^{-1} for water and g day^{-1} for soil and plants), EF is the exposure frequency (days year^{-1}), ED is the exposure duration (years), BW is the body weight (kg), and AT is the average time (days). The IR, ED, BW, and AT parameters were obtained from the literature (Li et al. 2015; Lim et al. 2008; Wongsasuluk et al. 2014; Wang et al. 2012). Table 2 displays the input parameters in ADD formulas.

Risk calculation

Non-carcinogenic risk

Non-carcinogenic (HQ) risk for a single substance is calculated by the following equation (Eq. 2)

$$\text{HQ} = \text{ADD} / \text{RfD} \quad (2)$$

where RfD is reference dose of metals ($\text{mg kg}^{-1} \text{ day}^{-1}$). If the HQ is ≤ 1 , it is at an acceptable level, while potential non-carcinogenic effects would happen in case of $\text{HQ} > 1$ and/or the risk of cancer exists (Cao et al. 2014; Gao et al. 2016). Hazard index (HI) for multiple substances and/or exposure pathways is calculated by the following equation (Eq. 3):

$$\text{HI} = \sum \text{HQ} \quad (3)$$

For the risk assessment of a mixture of chemicals, if $\text{HI} > 1$, it means that there is an unacceptable risk of non-carcinogenic effects on health, whereas $\text{HI} < 1$ means that there is an acceptable level of risk (Wongsasuluk et al. 2014).

Carcinogenic risk

For the carcinogenic risk (R), which can be associated with ingestion exposure, it is calculated using the following equation (Eq. 4):

$$R = \text{ADD} \times \text{SF} \quad (4)$$

where R is the excess probability of developing cancer over a lifetime as a result of exposure to a contaminant

Table 2 Input parameters to characterize the ADD value (exposure parameters)

Exposure parameters	Description	Unit	Value
C	Contamination concentration		
	Water	mg/l	
	Soil	mg/g	
IR	Plant	mg/g	
	Ingestion rate per unit time		
	Water	l/day	2 ^a
EF	Soil	mg/day	450 ^b
	Vegetables	g/day	303 ^a
	Exposure frequency	Days/year	365 ^{c,d}
ED	Exposure duration	Years	42 ^e
BW	Body weight	Kg	60 ^a
AT	Average time	Days	70 years ^{c,d}

^aLi et al. (2015)

^bLi et al. (2008, b)

^cWongsasuluk et al. (2014)

^dWang et al. (2012)

and SF is cancer slope factor ((mg kg⁻¹ day⁻¹)⁻¹). If *R* is in the range of 1 × 10⁻⁶ to 1 × 10⁻⁴, it indicates an acceptable level. While if it is ≤ 1 × 10⁻⁶, environmental and regulatory agencies consider the risk unacceptable (USEPA 1989). Slope Factor and RfD values employed in this study were obtained from the USEPA IRIS (Jiang et al. 2016; Wongsasuluk et al. 2014).

Statistical analysis

The concentrations of each heavy metal are presented as mean, SD, and medians. The correlation coefficients, *r*, between the contents of heavy metals in different biological samples were calculated by the Spearman’s method. To compare the difference between metal concentrations groups and identify significantly difference among heavy metals in studied areas, statistical analyses were conducted using one-way analysis of variance (ANOVA) and statistical significance set at *P* < 0.05. The statistical analysis was conducted using SPSS 19.

Results and discussion

Characterization of heavy metals in hair and urine

Concentrations of heavy metals in hair and urine of people living near smelting and mining areas are summarized in Table 3. Mean, SD, median, and percentile values are given to allow comparisons with other studies. The highest mean level of metal in hair and urine

was in the mining area, although Be and Cu levels were higher in the smelting areas. Conversely, most high urinary concentrations were found in the smelting areas, except for As, Cd, and Pb, which were higher in the mining area. Zn and Cr median values and Be and Bi means in hair and urine were higher in the smelting areas. The mean metal concentrations found in the hair samples from smelting areas (SM) decreased in the order Zn > Cu > Cr > Pb > Ni > Co > Cd > Be = Sb > Bi > As > Hg; Zn, Cu, Cr, Pb, Ni, and Co were also high in the soils from smelting areas (Briki et al. 2015). The mean metal concentrations found in the hair samples from mining area (MM) decreased in the order Zn > Cr > Pb > Ni > Cu > Cd > Co > As > Sb = Hg > Bi > Be. The mean metal concentration found in urine samples from smelting areas decreased in the order Zn > Cr > Ni > Cu > Pb > As > Co > Cd > Be > Sb > Bi. The mean metal concentrations found in the urine samples from mining area decreased in the order Zn > Cr > Ni > Cu > Pb > As > Cd > Co > Be > Bi > Sb. The concentration of some metals in hair and urine was in the range of published data from unexposed population (i.e., Goullé et al. 2005; Heitland and Koster 2004). Hair levels of Cu and Hg and urinary levels of As, Cd, Cu, Co, and Zn were similar to those found by Goullé et al. (2005) in a non-exposed population. The concentrations of Cd, Cu, and Cr in hair from smelting and mining areas and Pb in mining area were higher than Chinese resident normal hair content (Table 3).

The ANOVA of total means (Co, Ni, Cu, Zn, Cr, As, Cd, Pb, Sb, Bi, and Be) showed different levels of

significance among hair and urine metals in studied areas. The total mean values for heavy metals of hair in smelting and mining areas showed that differences in Cd and Co were significant, and the total mean values for urine in smelting and mining areas showed that Cd, Co, As, and Ni had significant effects $P < 0.05$. From smelting areas, the differences between group elements in hair and urine are higher than in hair and urine from mining area. The elements found to be significant are As, Be, Bi, Cd, Cu, Cr, Ni, Pb, and Zn in smelting areas and Be, Cd, Co, Cu, Cr, Ni, and Zn.

Urinary As concentrations in both the smelting ($0.40 \mu\text{g L}^{-1}$) and mining ($0.53 \mu\text{g L}^{-1}$) areas were not high compared with a control population ($8.6 \mu\text{g L}^{-1}$, Mandal et al. 2004). As levels in hair were $0.23 \mu\text{g g}^{-1}$ in the smelting areas and $0.40 \mu\text{g g}^{-1}$ in the mining area, compared with a lower $0.07 \mu\text{g g}^{-1}$ in a control population (Mandal et al. 2004). However, our values are lower than those found by Qin 2004.

In the mining and smelting areas, hair and urine concentrations of Be concentration were higher than those in an unexposed population of Goullé et al. 2005. Urinary Be was higher than the detection limits found by Jakubowski and Palczynski (2007) (0.03 and $0.06 \mu\text{g L}^{-1}$).

Bismuth levels in hair and urine in the mining area were higher than those found in an unexposed population (Goullé et al. 2005), while excreted urinary Bi levels were higher than hair levels in both the smelting and mining areas. This is in accordance with the findings of Fowler and Sexton (2007), who concluded that Bi is excreted mainly via urine. The retention time of Bi in the body is approximately 5 days, although it may persist for years in the kidneys of patients treated with Bi compounds (Fowler and Sexton 2007).

The mean concentration of Cd in urine samples from both areas ranged between 0.16 and $0.33 \mu\text{g L}^{-1}$, which are at below ($< 1.0 \mu\text{g L}^{-1}$ level) concentrations in human urine (Donati et al. 2008). However, Cd 5–95th range levels in hair were higher than 5–95th range levels in an unexposed population of Goullé et al. 2005. Cadmium mean values in the mining area ($0.84 \mu\text{g g}^{-1}$) were higher than those found previously in Hezhang (Ke et al. 1985, $0.15 \mu\text{g g}^{-1}$), Guizhou Province (Qin 2004, $0.45 \mu\text{g g}^{-1}$), and Bandarlampung City, Indonesia (Rivai 2001, $0.57 \mu\text{g g}^{-1}$). The major source of Cd exposure is food, especially vegetables and cereals (Molina-Villalba et al. 2014).

When comparing Co levels in urine and hair with values from an unexposed population of Goullé et al. 2005, Co levels in urine were lower; however, Co levels were high in the hair samples from the mining and smelting areas. Lison (2007) found that in occupational sites, workers were exposed to Co by inhalation of dusts.

Chromium hair values in the mining and smelting areas were very high compared with those in steel workers ($3.43 \pm 1.16 \mu\text{g g}^{-1}$, Afridi et al. 2006). Langard and Costa (2007) found that Cr was excreted through multiple pathways such as urine and feces.

The Cu levels in hair and urine were in range 5–95th of an unexposed population of Goullé et al. 2005. Ellingsen et al. (2007) found that Cu excretion occurred mainly through bile, and very little absorbed Cu was found in urine.

Qin (2004) reported that an average concentration of Hg from literature review in the hair of Chinese residents was approximately $1.36 \mu\text{g g}^{-1}$. In the present study, Hg contents in hair were 0.19 and $0.17 \mu\text{g g}^{-1}$ in the mining and smelting areas, respectively. In total, Hg concentrations found in the study area did not exceed the $1.0 \mu\text{g g}^{-1}$ limit recommended by the US Environmental Protection Agency (Hightower and Moore 2003, USEPA corresponding reference).

Nickel values in hair of residents from the mining area were higher than those in the smelting areas. Nickel values in urine of residents from the smelting areas were higher than those of the mining area. The 5–95th percentile range was higher than that measured in an unexposed population of Goullé et al. 2005 (Table 3).

Hair and urine Pb levels in all studied areas were higher than those found by Qin (2004) and Tang et al. (2009). They were also higher than those found in an unexposed population (Goullé et al. 2005). Hair Pb levels in the mining area were higher than those of steel and iron workers (Afridi et al. 2006; Gil et al. 2011). Cao et al. (2014) found that children living near a coking plant were exposed to high levels of Pb.

Antimony hair values in the mining area and urinary values in the smelting areas were higher than those reported in an unexposed population (Table 3). Absorbed Sb is generally excreted rapidly through the urine and feces. Some data indicate that low quantities of Sb may possess a long biological half-life, particularly in the lung. Antimony has also been found in the thyroid, adrenals, liver, and kidney (Tylanda and Fowler 2007).

Table 3 Total concentration of heavy metals in hair ($\mu\text{g g}^{-1}$) and urine ($\mu\text{g L}^{-1}$) of all participants, mean, SD, median, and range 5–95th percentile

Biological samples	Areas			Elements				
				As	Be	Bi	Cd	Co
Hair	Our study	Smelting areas (n = 44)	Mean \pm SD	0.23 \pm 0.24	0.05 \pm 0.05	0.03 \pm 0.05	0.33 \pm 0.26	0.35 \pm 0.32
			Median	0.17	0.03	0.03	0.25	0.14
			Range 5–95th	0.03–0.74	0.04–0.17	0.004–0.07	0.08–0.83	0.045–0.91
		Mining areas (n = 24)	Mean \pm SD	0.4 \pm 0.62	0.02 \pm 0.02	0.05 \pm 0.06	0.84 \pm 0.89	0.74 \pm 0.61
			Median	0.22	0.02	0.03	0.49	0.49
	Other works' results	- ^a - ^b	Mean	nd	nd	nd	0.15	nd
			Mean	1.03	nd	nd	0.45 ^f	nd
		- ^c - ^d	Range 5–95th	0.03–0.08	0.003–0.012	0.0004–0.14	0.004–0.17	0.004–0.14
			Mean	nd	nd	nd	0.25 \pm 0.14	nd
			Mean	nd	nd	nd	0.25 \pm 0.14	nd
Urine	Our study	Smelting areas (n = 42)	Mean \pm SD	0.4 \pm 0.18	0.1 \pm 0.09	0.07 \pm 0.06	0.16 \pm 0.09	0.34 \pm 0.23
			Median	0.41	0.07	0.06	0.14	0.29
			Range 5–95th	0.13–0.64	0.01–0.22	0.003–0.23	0.07–0.32	0.07–0.80
		Mining area (n = 24)	Mean \pm SD	0.53 \pm 0.32	0.07 \pm 0.05	0.06 \pm 0.06	0.33 \pm 0.43	0.22 \pm 0.08
			Median	0.52	0.06	0.05	0.21	0.22
	Other works' results	- ^a - ^c	Range 5–95th	0.18–1.18	0.02–0.15	0.004–0.16	0.07–0.58	0.11–0.37
			Mean	nd	nd	nd	3.5	nd
		- ^c	Range 5–95th	2.3–161	0.008–0.042	0.0005–0.009	0.06–0.79	0.16–1.14
			Mean	nd	nd	nd	0.6	nd
			Mean	nd	nd	nd	0.6	nd

Biological samples	Elements							
	Cr	Cu	Hg	Ni	Pb	Sb	Zn	
Hair	12.75 \pm 26.8	15.78 \pm 14.2	0.17 \pm 0.12	3.58 \pm 5.1	5.41 \pm 4.58	0.05 \pm 0.04	112 \pm 52.9	
	5.71	10.4	0.14	2.69	4.46	0.04	104	
	0.45–21.8	6.11–56.1	0.06–0.32	0.85–3.17	0.73–13.8	0.01–0.11	51.4–222	
	43.71 \pm 57.5	12.5 \pm 15	0.19 \pm 0.23	20.53 \pm 24.8	32.3 \pm 71.2	0.19 \pm 0.53	130.6 \pm 76.4	
	2.16	7.9	0.14	3.82	12.6	0.06	98.72	
	1.98–106.7	3.02–32.5	0.06–0.29	1.79–47.7	2.07–66.8	0.006–0.25	62.1–280	
	nd	nd	nd	nd	nd	nd	nd	
	nd	nd	1.56	nd	10.39	nd	nd	
	0.11–0.52	9.0–61.3	0.31–1.66	0.08–0.90	0.13–4.57	0.003–0.13	129–209	
	1.21 \pm 0.63	11.0 \pm 3.5	nd	nd	7.1 \pm 3.2	nd	130 \pm 30	
	Urine	26.5 \pm 16.6	4.29 \pm 3.6	nd	8.62 \pm 6.10	3.2 \pm 1.97	0.08	32.3
		29.1	4.08	nd	7.88	3.35	0.03	29.4
		0.79–51.4	1.04–7.99	nd	1.46–21.7	0.14–6.40	0.07–0.1	17.3–54.8
19.1 \pm 10.4		4.2 \pm 3.94	nd	4.61 \pm 1.71	3.26 \pm 1.64	0.02 \pm 0.01	32.9 \pm 20.6	
23.6		3.79	nd	4.23	3.72	0.01	26.6	
0.63–26.7		0.90–5.37	nd	1.84–8.02	0.56–5.12	0.004–0.04	12.8–68.4	
nd		nd	nd	nd	nd	nd	nd	
nd		4.3–12.1	-	0.59–4.06	0.01–2.14	0.02–0.08	44–499	
nd	nd	nd	5.3	0.01	0.3	259		

The bold entries of data represent higher value

nd no data

^aKe et al. (1985), Hezhang (control area)

^bQin (2004) (China and Guizhou province)

^cGoullé et al. (2005), unexposed population (France)

^dStandards from Chinese Trace Element Scientific Society from Wang et al. (2017)

^eTang et al. (2009) (control area)

^fGuizhou province

The Zn hair values in this study were higher than those in an unexposed population (Goullé et al. 2005). Mean concentrations of Zn in hair were 112 and 130 $\mu\text{g g}^{-1}$ in the smelting and mining areas, respectively. These values are lower than the 406.85 $\mu\text{g g}^{-1}$ reported by Rivai (2001). Urinary Zn levels were much lower than those of Tang et al. (2009) (Table 3). According to Sandstead and Au (2007), human Zn toxicity is relatively low, and Zn is environmentally ubiquitous and essential for life.

Overall, comparing this study results with those unexposed population described by Goullé et al. (2005), Ke et al. (1985), Qin (2004), and Tang et al. (2009), Be, Bi, Ni, Cr, and Pb were higher. The latter displayed the highest levels found in hair and urine. Co values were higher in hair in both the mining and smelting areas. Cd and Sb were much higher in hair samples from the mining area.

Age- and gender-related differences in heavy metal levels

Total distributions of heavy metals in female and male hair and urine in mining and smelting areas are drawn in Fig. 2. Male and female urinary and hair levels in both mining and smelting areas decreased in the same order: Zn > Cr > Ni > Cu > Pb > As. However, there are some differences for some metals, i.e., Cr, Ni, and Pb in female's hair from mining area were higher than other areas. Furthermore, Cr and Ni concentration in female's urine in smelting areas was higher than other areas.

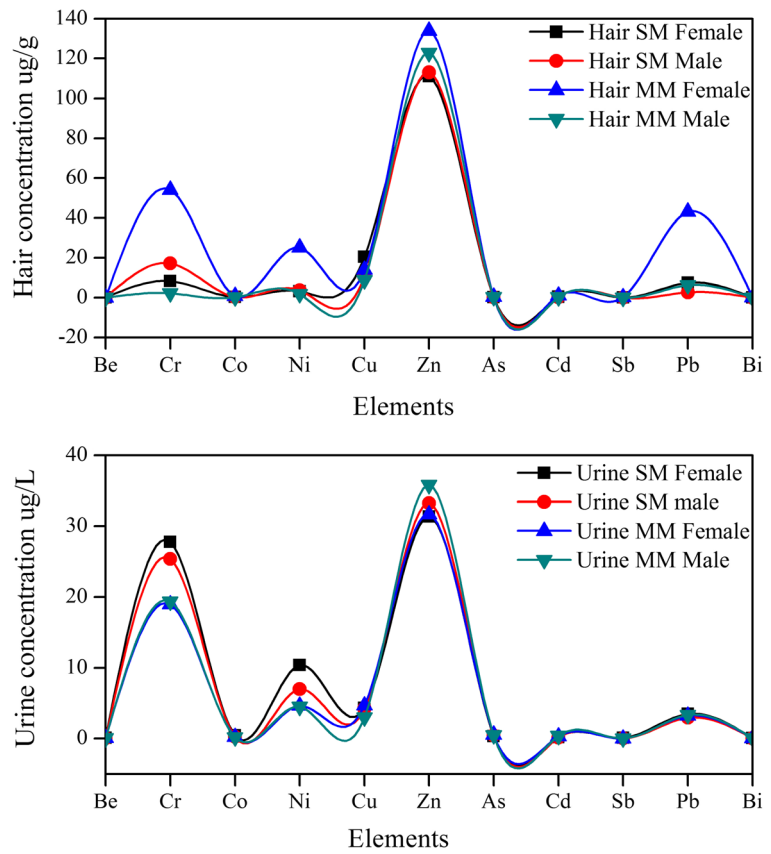
The analysis of variance showed different levels of significance among hair and urine metals of male and females in studied areas. Bi, Cd, Cu, and Pb are significant in female's and male's hair of smelting areas, and only Cd is significant in female's and male's hair of mining area. Cd and Co are significant different in female's and male's urine from smelting areas. Be and Pb in female's hair and Pb in male's hair from mining and smelting areas were significantly different. As, Cd, Co, Cr, and Ni in female's urine from mining and smelting areas were significant. And there are two cases where means are not significantly different: first is when comparing between urine of males in mining and smelting areas and the second is when comparing to urine of female and male of mining areas.

For a better description of distribution of heavy metal concentrations in urine and hair, participants are stratified by age and gender as presented in Fig. 3. Some

elements such as Zn, Pb, Ni, Cu, and Cr have high concentrations compared with the other elements (As, Be, Bi, Cd, Co, Hg, and Sb). Thus, for a better analysis, two histograms were drawn separately. The analysis by gender revealed that female participants had higher heavy metal concentrations in hair than male participants, especially in the age ranges of 18–40 and 41–65 years in both areas. Hair metal levels in males were higher among the participants aged 18–40 in both sampling areas. Urinary levels in males were higher among participants aged ≥ 66 years. Among females, urine and hair concentrations differed in the two sampling areas: High levels in hair were found in women aged 18–40 in the smelting areas and 41–65 in the mining area. High levels in urine were found in women aged 6–18 in the smelting areas and ≥ 66 years in the mining area.

Figure 3 shows that As, Be, Bi, Cd, Cu, Pb, Sb, and Zn levels were higher in female hair in the smelting areas, and Co, Cr, Hg, and Ni were higher in male hair. Li et al. (2009) and Shimomura et al. (1980) found lower levels of Hg in females. In our study, this was observed only in the smelting areas. High urinary levels of Bi, Co, Pb, and Sb were found in females in the smelting areas and As, Be, Cd, Cr, Cu, Ni, and Zn in males. Higher levels of heavy metals in female hair in the mining area were observed for As, Bi, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, and Zn and Be in males. Urinary levels of Be and Cu were high in females in the mining area, while As, Bi, Cd, Co, Cr, Ni, Pb, Sb, and Zn levels were high in men. Filon et al. (2009) found higher levels of Ni, Co, and Cr in females (0–15% higher than in males), while in smelting areas, male hair contained higher levels of these three metals. In both mining and smelting areas, female hair and urine samples contained higher mean concentrations of almost all tested metals; this finding was also observed by Moon et al. (1986). However, the urine of males aged ≥ 66 years in both the mining and smelting areas contained the highest values; this may be attributed to faster clearance and activities of daily living, particularly food choices. The elderly in China are known for consuming soup and other liquids. Li et al. (2009) and Feng et al. (2008) attributed high levels of metals in Chinese to a high daily consumption of rice, and elderly living in the south of China are also known for daily consuming of rice. Wu and Chen 2010 found that there are differences in As distribution for different ages, young and old people had high concentration; this could be related to the rate of

Fig. 2 Total heavy metal in female's and male's hair and urine in mining and smelting areas



metabolism. Khaliq et al. (2005) found that the levels of some metals such as Cu, Co, and Cr were accumulated in hair of the elderly donors; this may be related to different food habits of the different studied communities and to the geological and geographical differences in the different studied locations.

Arsenic, Bi, Cd, Cu, Pb, Sb, and Zn were higher in female's hair in both sampling areas. Molina-Villalba et al. (2014) found that girls aged 6–9 living near mining and industrial areas exhibited significantly higher heavy metal concentrations in hair than boys. When comparing our urine results of women (18–65 years) from smelting and mining areas with those of Callan et al. (2016), we found that some elements such as As, Cd, Cu, Co, and Zn were lower, some metals such as Sb and Be are moderate, and some metals such as Bi, Cr, Pb, and Ni were much higher. Higher heavy metal levels in female (18–65 years) hair may originate from external contamination, such as artificial hair treatments. According to Gil et al. (2011), hair grows approximately 10 mm/month and gives information on past and recent exposure.

When compared with other male group, Pb levels in the urine and hair of male children aged 6–17 years in the mining area was elevated. This finding is in accordance with numerous epidemiologic studies indicating that living near mining waste is major risk factor for Pb exposure (Dutkiewicz et al. 1993; Moreno et al. 2010). In this study, Pb levels in hair and urine did not increase with age, contrasting with the finding of Castaño et al. (2012). In this study, we found that lead in hair was related to the gender differences: females contain high levels comparing to males. A different finding was found by Strumylaite et al. (2004).

Cao et al. (2015) found that Pb was one of the most abundant elements in the blood of children living near a lead-acid battery plant. Lead largely persists in contaminated environments and is more dangerous for young and unborn children. It can affect normal growth, lead to learning disabilities, and damage the male reproductive system (Molina-Villalba et al. 2014; Natural Healing Site 2010).

Cd and Cr values did not increase with age, contrasting with the findings of Khlifi et al. (2014) and Langard

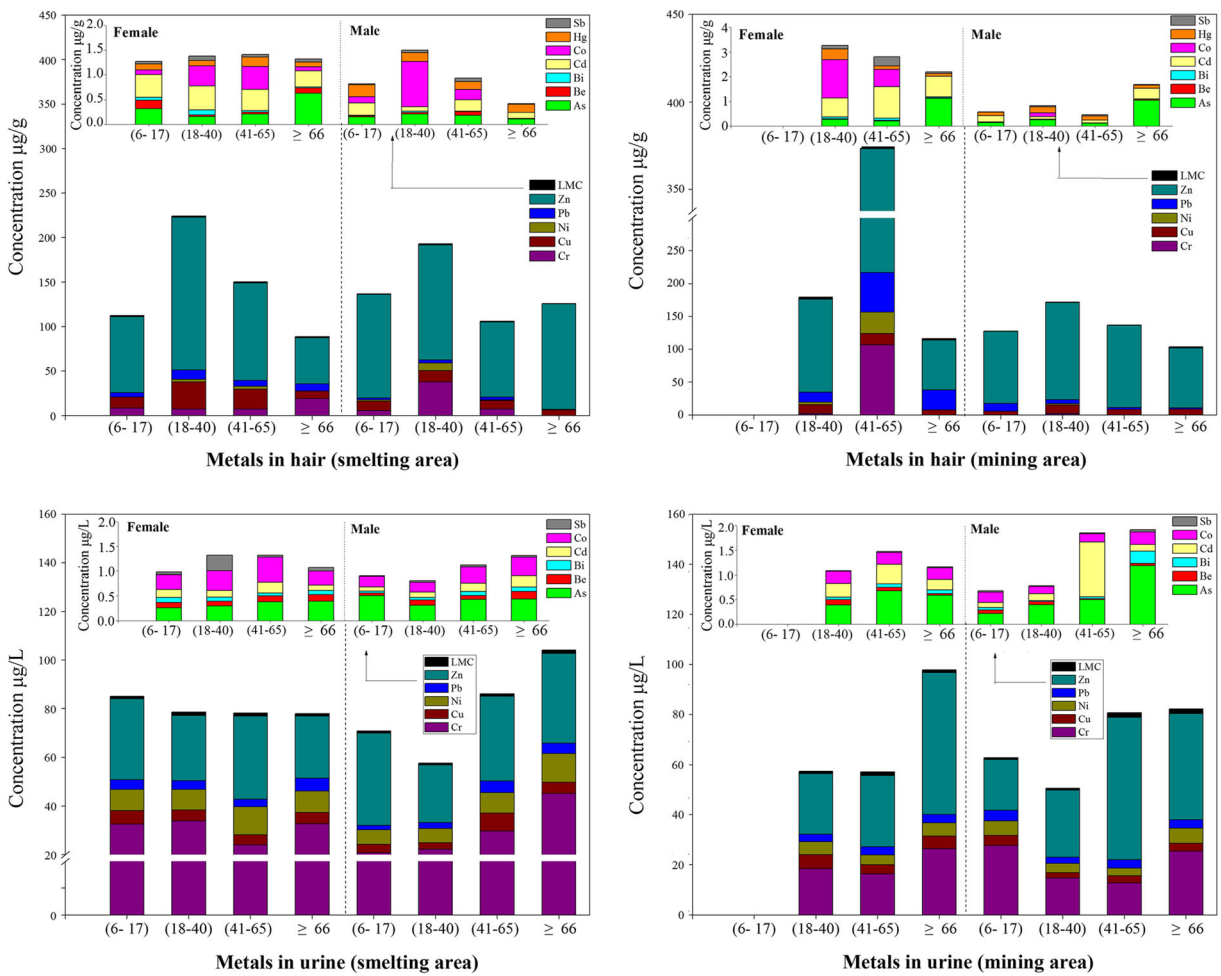


Fig. 3 Heavy metal concentrations in the urine and hair of participants stratified by age and gender. *LMC* low metal concentration

and Costa (2007). However, As in urinary samples from females in the smelting areas increases with age. According to Nam et al. (2003), accumulation of As in the body may be due to intake through various pathways, although the main routes are occupational exposure and diet (BerzasNevado et al. 2010). Furthermore, the growth rate of hair is affected by nutritional status and parallels the rate of heavy metal deposition (Rivai 2001). However, Halder et al. (2013) showed that As exposure could be related to the relationship between consumption of rice and tainted drinking water. Mercury levels in hair displayed no age- or gender-related differences. Li et al. (2009) found that Hg levels in hair varied significantly by gender but had no obvious correlation with age. In this study, metal levels were high in hair samples from females. This finding may be explained by longer residence periods,

compared with men, who may be more mobile and inclined to migrate in search of employment, and in 2002, Wu and Chen (2010) found that As concentration in female’s hair was higher than in male. The authors estimating that it could be due to professional disparities. Metal hair contents varied notably by hair color, hair care habits, gender, age, smoking status, and racial or ethnic factors (Barbosa et al. 2006; Esteban and Castaño 2009). The data from this study are in consistent with those reported earlier such as Kazi et al. (2009), Khalique et al. (2005), Vahter et al. (2007), Vimercati et al. (2016), and Wu and Chen (2010) who found that females contain higher level of heavy metal. Wu and Chen (2010) in 2002 found that As concentration in the hair of peasants was significantly higher than non-peasants, and other authors such as Khalique et al. (2005) explained the difference

Table 4 Spearman correlation coefficients for heavy metal concentrations in the two biological samples (urine and hair) in mining and smelting areas

Elements	(a) Mining area										(b) Smelting areas												
	Be U	Cr U	Co U	Ni U	Cu U	Zn U	As U	Cd U	Sb U	Pb U	Bi U	Be U	Cr U	Co U	Ni U	Cu U	Zn U	As U	Cd U	Sb U	Pb U	Bi U	
Be H																							
Cr H				0.975^b									0.397^a										
Co H		-.843^b		-.964^b			0.747^a																
Ni H																							
Cu H																							
Zn H																							
As H																							
Cd H																							
Sb H																							
Pb H																							
Bi H																							
Hg H																							

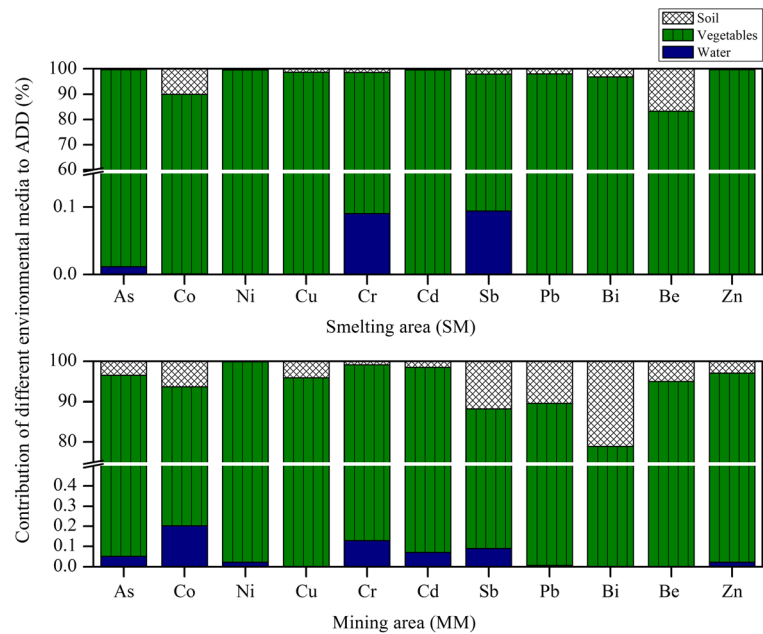
Blank cells indicate lack of statistically significant correlation. The bold entries of data represent higher value

U urine samples, H hair samples

^a Correlation is significant at the 0.05 level (two-tailed)

^b Correlation is significant at the 0.01 level (two-tailed)

Fig. 4 The contribution of soil, vegetables, and water to the average daily exposure dose



was in the basis of differentiation in metabolism and physiological function of the metals for male and female.

Overall, urinary metal concentrations were lower than metal concentrations found in hair in this study. Generally, urine provides an assessment of recent exposure. According to Gil et al. (2011), human hair has been shown to be a good vehicle of excretion from the human body, and multiple research groups found that heavy metal concentrations in hair were up to 10-fold higher than levels found in blood or urine (Bader et al. 1999; Kono et al. 1990). Factors such as gender and age are important in measuring exposure. We found differences among genders and age groups in our study; other factors, such as lifestyle habits of smoking and physical activity, should also be explored.

Heavy metal correlations in hair and urine

To identify a common source for the different metals in urine and hair found in this study, we performed a Spearman rank correlation analysis. Table 4 presents statistical correlation data for the analysis of heavy metal concentrations in the two biological samples (urine and hair) in the mining and smelting areas. The analysis showed that hair and urine heavy metal levels were highly correlated in mining area compared to those in smelting areas; however, it is clearly noted that in

mining areas the correlation is mostly negative. In the mining area, Ni U-Cr H and Cd U-Co H were highly positively correlated in urine and hair ($r = 0.975$ and $P < 0.01$ and $r = 0.747$ and $P < 0.05$). A highly negative correlation was found between Co H, Ni U, and Cr U in both hair and urine samples, and As U and Cd H were negatively ($r = -0.964$, $r = -0.843$, and $r = -0.574$, respectively; $P < 0.01$). The same results were found in Molina-Villalba et al. 2014 study that revealed a significant negative correlation between hair Cd and urine As. And a weak significant correlation exists between Bi H-As U and Cu U-Sb H ($r = -0.519$ and $r = -0.502$; $P < 0.05$) in mining area. The reason for this correlation is unclear. Zinc, Pb, and Be concentration in hair and urine did not show any significant correlations with other metals. An earlier study in Hezhang showed that As, Bi, Cd, Pb, Sb, and Zn in mining and smelting areas originated mainly from anthropogenic sources (Briki et al. 2015).

In Table 4, hair and urine samples from the smelting areas display only some elements such as Cr U and As H, Be U, and Hg H ($r = 0.436$ and $r = -0.495$; $P < 0.01$) and between Zn U and Sb H, As H-Ni U and Pb U, Cu U and Zn H, and Bi H-Sb U and Pb U ($P < 0.05$). Foo et al. (1993) found that there is a positive significant correlation between some metal concentrations in hair and their respective concentration in blood and urine. Co and Cd concentration in hair and urine did not show

Table 5 Total concentration of heavy metals in water ($\mu\text{g L}^{-1}$)

Elements	As	Be	Bi	Cd	Co	Cu	Cr	Ni	Pb	Sb	Zn
MM <i>n</i> = 2	Mean \pm SD 0.67 \pm 0.8	BL	BL	0.17 \pm 0.17	0.17 \pm 0.04	BL	3.97 \pm 1.85	2.57 \pm 0.95	2.4 \pm 1.67	0.57 \pm 0.73	16.4 \pm 8.7
SM <i>n</i> = 2	Mean \pm SD 0.14 \pm 0.12	0.01	BL	BL	0.06 \pm 0.04	BL	2.51 \pm 2.21	BL	BL	0.01 \pm 0.006	BL
Guideline value for drinking water quality ^a	10 $\mu\text{g L}^{-1}$	Rarely found in drinking water	-	3 $\mu\text{g L}^{-1}$	-	-	50 $\mu\text{g L}^{-1}$ but generally less than 2 μg	70 $\mu\text{g L}^{-1}$ but generally less than 0.02 mg L ⁻¹	10 $\mu\text{g L}^{-1}$	20 $\mu\text{g L}^{-1}$	-

BL below 0, - no guideline values

^aWHO (2011)

any significant correlation with other metals. Hair and urine samples contain different concentrations; the variation may be due to metabolic factors, as well as to the properties of individual metals. However, the associations between the correlation of the elements in hair and urine are hard to elucidate.

Heavy metal daily exposure levels

Risk assessment is the estimate of the nature and probability of adverse health effects in humans who may be exposed to pollutants. Human exposure to heavy metals is principally derived from food (Islam et al. 2014), drinking water, soil ingestion, inhalation rates, and pica (USEPA 1997). Figure 4 lists the contribution of each exposure route to estimated ADD values in this area. According to Cao et al. (2014), the daily intake of heavy metals is mainly derived from food such as vegetables and staple food. In our study, vegetables made an important contribution to the participants' total ADD for all heavy metals, accounting for > 70% in the mining area and 80% in the smelting areas. Vegetables provided 99.8% of the Ni values and 99% of the Cr values computed for the mining area. In the smelting areas, vegetables provided 99.7, 99.6, 99.6, and 99.6% of the ADD values for Zn, As, Ni, and Cd, respectively.

The most prevalent metals in the soil of the mining area were Bi, Sb, Pb, Co, and Be, accounting for 21, 11.7, 10.4, 6.3, and 5%, respectively. In the smelting areas, the same metals were most prevalent in a different order: Be (16.7%), Co (9.9%), Bi (3.2%), Sb (2.1%), and Pb (2%). These concentration levels were higher than background levels recorded in Guizhou (CNEMC 1990). Massadeh et al. (2010) found that smokers had higher Pb levels than non-smokers. Pb is known to exert toxic effects on the central and peripheral nervous systems, kidney, cardiovascular system, immune system, gastrointestinal tract, and male reproductive system. Furthermore, Pb can infiltrate the placenta and may affect the nervous system of the developing fetus (Skerfving and Bergdhal 2007). Drinking water did not represent any important contributions to the measured ADD. This is because drinking water samples contain low concentration of heavy metals as presented in Table 5. In Table 5, the monitored concentrations of heavy metals Co, Ni, Cu, Zn, Cr, As, Cd, Sb, Pb, Bi, and Be are found below the permissible levels of WHO (2011), indicating the water to be free from heavy metal pollution.

Table 6 Estimation of non-carcinogenic (hazard quotient, HQ) and carcinogenic health risks (cancer risk, *R*) from heavy metals in soil, vegetables, and water

	Smelting areas				Mining area			
	Soil ingestion	Vegetables	Drinking water	Total pathways	Soil ingestion	Vegetables	Drinking water	Total pathways
Hazard quotient								
As	2.92E-01	8.13E+01	9.36E-03	8.16E+01	3.05E+00	8.50E+01	4.48E-02	8.81E+01
Co	5.22E-01	4.75E+00	3.96E-03	5.28E+00	3.56E-01	5.29E+00	1.15E-02	5.66E+00
Ni	1.71E-02	4.25E+00		4.27E+00	1.53E-02	1.08E+01	2.57E-03	1.08E+01
Cu	1.25E-02	9.35E-01		9.47E-01	3.56E-02	8.41E-01		8.76E-01
Cr	2.63E-01	1.82E+01	1.67E-02	1.85E+01	1.72E-01	2.02E+01	2.65E-02	2.04E+01
Cd	4.10E-03	9.81E-01		9.85E-01	7.23E-02	4.80E+00	6.90E-03	4.88E+00
Sb	1.21E-02	5.74E-01	5.52E-04	5.87E-01	3.68E+00	2.76E+01	2.83E-02	3.14E+01
Pb	5.31E-02	2.64E+00		2.70E+00	1.96E+01	1.70E+02	1.37E-02	1.89E+02
Bi								
Be	8.35E-03	4.16E-02		5.00E-02	7.34E-03	1.40E-01		1.47E-01
Zn	2.78E-03	7.96E-01		7.99E-01	1.35E-01	4.48E+00	1.09E-03	4.61E+00
Total metals	1.19E+00	1.14E+02	3.06E-02	1.16E+02	2.71E+00	3.29E+02	1.35E-01	3.32E+02
Cancer risk								
As	1.31E-04	3.66E-02	4.21E-06	3.67E-02	1.37E-03	3.83E-02	2.02E-05	3.97E-02
Ni	5.80E-04	1.45E-01		1.45E-01	5.19E-04	3.66E-01	8.74E-05	3.67E-01
Cr	3.95E-04	2.74E-02	2.51E-05	2.78E-02	2.59E-04	3.04E-02	3.98E-05	3.07E-02
Pb	1.58E-06	7.86E-05		8.02E-05	5.83E-04	5.05E-03	4.08E-07	5.63E-03
Total metals	1.11E-03	2.09E-01	2.93E-05	2.10E-01	2.73E-03	4.40E-01	1.48E-04	4.43E-01

The values in bold in the table mean the potential health risks were much higher than the acceptable levels for the heavy metals through studied exposure pathways

Vegetable consumption is considered as an important pathway for heavy metal absorption (Fu et al. 2015), as it is the inhalation of metal dusts from the soil, which affects children in particular, due to their regular hand-to-mouth activity (Li 2013).

Risk characteristics

Ten heavy metals (As, Co, Ni, Cu, Cr, Cd, Sb, Pb, Be, and Zn) were taken in consideration to evaluate health risk assessment. The results of non-carcinogenic and carcinogenic health risks posed by studied heavy metals in smelting and mining areas are shown in Table 6. Blank values in the table are due to the missing of corresponding RFD and SF values.

The HQ values were 3.32E+02 and 1.16E+02 for mining and smelting areas, respectively. Values were greater than 1 indicating that the residents may have a higher potential concern for potential non-carcinogenic effect. Mining tended to have a higher probability than

smelting areas. The order of HQ values in smelting areas for different heavy metals increased in this order As > Cr > Co > Ni > Pb > Cd > Cu > Zn > Sb > Be. Among these values, As, Cr, Co, Ni, and Pb exceed 1. The order in mining area was different from smelting areas and increased in this order Pb > As > Sb > Cr > Ni > Co > Cd > Zn > Cu > Be. All these elements exceed 1 except Cu and Be. Vegetable ingestion was the major exposure pathway for all studied areas. Furthermore, Pb, Sb, and As in soil from mining area also appeared predominant elements. The Pb contribution in our study to non-cancer health risks was higher in vegetable and soil ingestion. However, Tao et al. (2014) found that Pb in ingested ash was the main contributor (> 80%). The HI order was vegetable ingestion > soil ingestion > drinking water.

Every pathway of most all elements in mining area has higher non-carcinogenic risks than smelting areas, showing that mining area are more sensible to environmental contamination (Jiang et al. 2016). This may be due to the nearness of human activities and exposed

duration of vegetables and soil. The Cao et al. (2010) study in Jiangsu China demonstrated that the rice and self-planted vegetables are highly ingested so the ingestion of self-planted vegetables is the main way to determine which heavy metal generates a harmful effect to human health on local people. Because Co, Cu, Cd, Sb, Bi, Be, and Zn were not included in carcinogenic category (USEPA 2016), thus four elements (As, Ni, Cr, and Pb) were estimated.

The R values for mining and smelting areas were 4.43×10^{-1} and 2.10×10^{-1} , respectively (Table 6). Mining area showed higher carcinogenic risks compared to smelting areas. However, the carcinogenic risks for both mining and smelting areas were higher than the acceptable risk (1×10^{-4} ; Cao et al. 2016). The R values for both mining and smelting areas have similar trend for different heavy metals and decreased in this order $Ni > As > Cr > Pb$. In smelting areas, Pb was in the range of acceptable level (1×10^{-6} to 1×10^{-4}). By comparing the different pathways, vegetables were the main pathway to carcinogenic risk in all studied areas, and it influences the total pathway. Food in rural area is renewed to be self-planted and harvested (Jiang et al. 2016). According to this study and earlier study in the same areas (Briki et al. 2015), it is important to note that there is a big relation among the exposures pathways from soil, plant, to human, and this relation should not be neglected. However, further measure should be taken to analyze more kinds of vegetables and reduce the carcinogenic risk.

Conclusion

The present study found elevated contents of Pb, Be, Bi, Co, Cr, Ni, Sb, and Zn in hair and urine samples of residents in smelting and mining areas. Lead levels were higher than those of other metals. The mining area exhibited higher total mean concentrations than the smelting areas. In addition, metals were not distributed evenly between different genders and age groups. Higher values were found in the hair of males aged 18–40 and in the urine of participants aged ≥ 66 . Higher values were also found in the hair of females aged 41–65 in the mining area and 18–40 in the smelting areas, while in urine samples, the higher values were found in those aged 6–18 in the smelting areas and ≥ 66 in the mining area. Significant positive correlations were found between Ni U-Cr H and Cd U-Co H in urine

and hair samples from mining area. The average daily intake of vegetation was approximately more than 70% for all heavy metals, thereafter comes the soil. However, drinking water does not represent an important daily source of exposure. The estimated ADD was mainly caused by the ingestion of vegetation than by inhalation of soil. According to the calculation, hazard quotient and hazard index values of total metals in soil and vegetables in mining and smelting areas were all higher than 1. And carcinogenic risks of total pathway are higher than accepted level, indicating that the studied areas may be facing the threat of cancer risk. On the other hand, water's HQ, HI, and R are all within the accepted levels. Moreover, the health risk posed by heavy metals via ingestion is higher, so further study is required to assess health risks associated with heavy metal exposure in this population and to formulate mitigation strategies.

Acknowledgements We thank Dr. Li Daojing for her assistance with field sampling, and we thank Prof. Dipti Halder for his help to answer our queries. Furthermore, we are indebted to Prof. Li Zifu for discussion and suggestions about this study. This work was jointly supported from the National Natural Science Foundation of China (Nos. 41173113 and 41473122) and the Hundred Talents Programs of Chinese Academy of Science.

References

- Afridi, H. I., Kazi, T. G., Jamali, M. K., Kazi, G. H., Arain, M. B., Nusrat, J., et al. (2006). Evaluation of toxic metals in biological samples (scalp hair, blood and urine) of steel mill workers by electrothermal atomic absorption spectrometry. *Toxicology and Industrial Health*, 22, 381–393.
- Angerer, J., Aylward, L. L., & Hays, S. M. (2011). Human biomonitoring assessment values: approaches and data requirements. *International Journal of Hygiene and Environmental Health*, 214(5), 348–360.
- Bader, M., Dietz, M. C., Ihrig, A., & Triebig, G. (1999). Biomonitoring of manganese in blood, urine and axillary hair following low-dose exposure during the manufacture of dry cell batteries. *International Archives of Occupational and Environmental Health*, 72, 521–527.
- Barbosa Jr., F., Corrêa-Rodrigues, M. H., Buzalaf, M. R., Krug, F. J., Gerlach, R. F., & Tanus-Santos, J. E. (2006). Evaluation of the use of salivary lead levels as a surrogate of blood lead or plasma lead levels in lead exposed subjects. *Archives of Toxicology*, 80, 633–637.
- Baselt, R. C. (2000). *Disposition of toxic drugs and chemicals in man* (5th ed.). Foster City: Chemical Toxicology Institute ISBN 0-9626523-3-4.

- Bencko, V. (1995). Use of human hair as a biomarker in the assessment of exposure to pollutants in occupational and environmental settings. *Toxicology*, *101*, 29–39.
- Bernard, A., & Lauwerys, R. (1984). Cadmium in human population. *Experientia*, *40*, 143–152.
- BerzasNevado, J. J., Guzmán Bernardo, F. J., Jiménez, M. M., Herculano, A. M., Nascimento, J. L., & Crespo-López, M. E. (2010). Mercury in the Tapajós river basin, Brazilian amazon: a review. *Environment International*, *36*, 593–608.
- Bhattacharya, A. K., Das, S. K., & Mandal, S. N. (2004). Removal of zinc from waste water. *Research Journal of Chemistry and Environment*, *8*(4), 77–79.
- Bi, X., Feng, X., Yang, Y., Li, X., Shin, G. P. Y., Li, F., et al. (2009). Allocation and source attribution of lead and cadmium in maize (*Zea mays*, L.) impacted by smelting emissions. *Environmental Pollution*, *157*(3), 834–839.
- Bi, X., Feng, X., Yang, Y., Li, X., Sin, G. P. Y., Qiu, G., et al. (2007). Heavy metals in an impacted wetland system: a typical case from southwestern China. *Science Total Environmental*, *387*(1–3), 257–268.
- Bi, X., Feng, X., Yang, Y., Qiu, G., Li, G., Bi, X., et al. (2006a). Quantitative assessment of cadmium emission from zinc smelting and its influences on the surface soils and mosses in Hezhang County, southwestern China. *Atmospheric Environment*, *40*(22), 4228–4233.
- Bi, X., Feng, X., Yang, Y., Qiu, G., Li, G., Li, F., et al. (2006b). Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China. *Environment International*, *32*(7), 883–890.
- Briki, M., Ji, H. B., Li, C., Ding, H. J., & Gao, Y. (2015). Characterization, distribution, and risk assessment of heavy metals in agricultural soil and products around mining and smelting areas of Hezhang, China. *Environmental Monitoring and Assessment*, *187*(12), 767 1-21.
- Buchet, J. P., Lauwerys, R., & Roels, H. (1981). Comparison of the urinary excretion of arsenic metabolites after a single oral dose of sodium arsenite, monomethyl arsenate, or dimethyl arsenate in man. *International Archives of Occupational and Environmental Health*, *48*, 71–79.
- Callan, A. C., Hinwood, A. L., Heyworth, J., Phi, D. T., & Odland, J. Ø. (2016). Sex specific influence on the relationship between maternal exposures to persistent chemicals and birth outcomes. *International Journal of Hygiene and Environmental Health*, *219*, 734–741.
- Campbell, L., Dixon, D. G., & Hecky, R. E. (2003). A review of mercury in Lake Victoria, East Africa: implications for human and ecosystem health. *Journal of Toxicology Environmental Health, Part B: Critical Reviews*, *6*, 325–356.
- Cao, H., Chen, J., Zhang, J., Zhang, H., Qiao, L., & Men, Y. (2010). Heavy metals in rice and garden vegetables and their potential health risks to inhabitants in the vicinity of an industrial zone in Jiangsu, China. *Journal of Environmental Sciences*, *22*(11), 1792–1799.
- Cao, S., Duan, X., Zhao, X., Chen, Y., Wang, B., Sun, C., et al. (2016). Health risks of children's cumulative and aggregative exposure to metals and metalloids in a typical urban environment in China. *Chemosphere*, *147*, 404.
- Cao, S., Duan, X., Zhao, X., Ma, J., Dong, T., Huang, N., et al. (2014). Health risks from the exposure of children to As, Se, Pb and other heavy metals near the largest coking plant in China. *Science Of the Total Environment*, *472*, 1001–1009.
- Cao, S., Duan, X., Zhao, X., Wang, B., Jin, M., Fan, D., et al. (2015). Health risk assessment of various metal (loid)s via multiple exposure pathways on children living near a typical lead-acid battery plant, China. *Environmental Pollution*, *200*, 16–23.
- Cao, S., Duan, X., Zhao, X., Wang, B., Ma, J., Fan, D., et al. (2014). Isotopic ratio based source apportionment of children's blood lead around coking plant area. *Environment International*, *73*, 158–166.
- Castaño, A., Cañas, A., Esteban, M., Navarro, C., Arribas, M., & Díaz, G. (2012). Mercury, lead and cadmium levels in the urine of 170 Spanish adults: a pilot human biomonitoring study. *International Journal of Hygiene and Environmental Health*, *215*, 191–195.
- Chuang, H. Y., Cheng, W. C., Chen, C. Y., Yang, Y. H., Sung, F. C., Yang, C. Y., & Wu, T. N. (2008). A follow-up comparison of blood lead levels between foreign and native workers of battery manufacturing in Taiwan. *Science of the Total Environment*, *394*, 52–56.
- (CNEMC) China National Environmental Monitoring Centre (1990). *Soil element background values of China*. Beijing: China Environmental Science Press [Chinese paper].
- Cullen, W. R., & Reimer, K. J. (1989). Arsenic speciation in the environment. *Chemical Reviews*, *89*, 713–764.
- Donati, G. L., Pharr, K. E., Calloway, C. P., Nóbrega, J. A., & Jones, B. T. (2008). Determination of Cd in urine by cloud point extraction—tungsten coil atomic absorption spectrometry. *Talanta*, *76*(5), 1252–1255.
- Dutkiewicz, T., Sokolowska, D., & Kulka, E. (1993). Health risk assessment in children exposed to lead compounds in the vicinity of mine-smelter plant “Orzel Bialy”. *Polish Journal of Occupational Medicine and Environmental Health*, *6*, 71–78.
- Ellingsen, D. G., Horn, N., Aaseth, J., 2007. *Copper (third edition)—chapter 26. Handbook on the toxicology of metals* (pp. 529–546). Academic press. doi: [10.1016/B978-012369413-3/50081-1](https://doi.org/10.1016/B978-012369413-3/50081-1).
- Esteban, M., & Castaño, A. (2009). Non-invasive matrices in human biomonitoring: a review. *Environment International*, *35*, 438–449.
- Feldmann, J., Lai, V. W. M., Cullen, R. W., Ma, M. S., Lu, X. L., & Le, C. (1999). Sample preparation and storage can change arsenic speciation in human urine. *Clinical Chemistry*, *45*, 1988–1997.
- Feng, X., Li, G., & Qiu, G. (2004). A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous method in Hezhang County, Guizhou, China: part 1. Mercury emission from zinc smelting and its influences on the surface waters. *Atmospheric Environment*, *38*, 6223–6230.
- Feng, X., Li, G., & Qiu, G. (2006). A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China: part 2. Mercury contaminations to soil and crop. *Science of the Total Environment*, *368*(1), 47–55.
- Feng, X., Li, P., Qiu, G., Wang, S., Li, G., Shang, L., et al. (2008). Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou Province, China. *Environmental Science & Technology*, *42*, 326–332.
- Filon, F. L., D'Agostina, F., Crosera, M., Adami, G., Bovenzi, M., & Maina, G. (2009). In vitro absorption of metal powders

- through intact and damaged human skin. *Toxicology In vitro. An International Journal Published in Association with Bibra.*, 23, 574–579.
- Foo, S. C., Khoo, N. Y., Heng, A., Chua, L. H., Chia, S. E., Ong, C. N., et al. (1993). Metals in hair as biological indices for exposure. *International Archives of Occupational and Environmental Health*, 65(1), S83–S86.
- Fowler, B.A., & Sexton, M. J. (2007). Chapter 22—bismuth. *Handbook on the toxicology of metals* (433–443).
- Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W., & Giesy, J. P. (2015). Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China. *Science of the Total Environment*, 539, 97–104.
- Gao, Y., Guo, X., Ji, H., Li, C., Ding, H., Briki, M., et al. (2016). Potential threat of heavy metals and PAHs in PM 2.5 in different urban functional areas of Beijing. *Atmospheric Research*, 178–179, 6–16.
- Gil, F., Hernández, A. F., Márquez, C., Femia, P., Olmedo, P., López-Guarnido, O., & Pla, A. (2011). Biomonitorization of cadmium, chromium, manganese, nickel and lead in whole blood, urine, axillary hair and saliva in an occupationally exposed population. *Science of the Total Environment*, 409, 1172–1180.
- Goullé, J. P., Mahieu, L., Castermant, J., Neveu, N., Bonneau, L., Laine, G., Bouige, D., & Lacroix, C. (2005). Metal and metalloid multi-elementary ICP-MS validation in whole blood, plasma, urine and hair: reference values. *Forensic Science International*, 153, 39–44.
- Gray, J. E., Crock, J. G., & Lasorsa, B. K. (2002). Mercury methylation mines in the Humboldt River Basin, Nevada, USA. *Geochemistry: Exploration, Environment, Analysis*, 2, 143–149.
- Halder, D., Bhowmick, S., Biswas, A., Chatterjee, D., Nriagu, J., Mazumder, D. N. G., Slejkovec, Z., et al. (2013). Risk of arsenic exposure from drinking water and dietary components: implications for risk management in rural Bengal. *Environmental Science & Technology*, 47, 1120–1127.
- Heitland, P., & Koster, H. D. (2004). Fast, simple and reliable routine determination of 23 elements in urine by ICP-MS. *Journal of Analytical Atomic Spectrometry*, 19, 1552–1558.
- Hightower, J. M., & Moore, D. (2003). Mercury levels in high-end consumers of fish. *Environmental Health Perspectives*, 111, 604.
- Infante, P. F., & Newman, L. S. (2004). Beryllium exposure and chronic beryllium disease. *Lancet*, 363, 415–416.
- Islam, M. S., Ahmed, M. K., & Al-Mamun, M. H. (2014). Heavy metals in cereals and pulses: health implications in Bangladesh. *Journal of Agricultural and Food Chemistry*, 62.
- Jakubowski, M., Palczynski, C., 2007. Beryllium. *Handbook on the toxicology of metals* (third edition)—chapter 21. *Handbook on the toxicology of metals* (415–431).
- Ji, A., Wang, F., Luo, W. J., Yang, R. H., Chen, J. Y., & Cai, T. J. (2011). Lead poisoning in China: a nightmare from industrialization. *Lancet*, 377, 1474–1476.
- Ji, H. B., Wang, S., Ouyang, Z., Zhang, S., Sun, C. X., Liu, X. M., & Zhou, D. Q. (2004). Geochemistry of red residua underlying dolomites in karst terrains of Yunnan-Guizhou Plateau I. The formation of the Pingba profile. *Chemical Geology*, 203, 1–27.
- Jiang, Y., Chao, S., Liu, J., Yang, Y., Chen, Y., Zhang, A., & Cao, H. (2016). Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu province, China. *Chemosphere*, 168, 1658–1668.
- Kazi, T. G., Arain, M. B., Baig, J. A., Jamali, M. K., Afridi, H. I., Jalbani, N., et al. (2009). The correlation of arsenic levels in drinking water with the biological samples of skin disorders. *Science of the Total Environment*, 407(3), 1019–1026.
- Ke, C. M., Li, X. J., & He, D. J. (1985). Investigation on the effect of cadmium on human health in the environment of open lead zinc mine. *Journal of Environment and Health*, 2(5), 9–18 Chinese paper.
- Khalique, A., Ahmad, S., Anjum, T., Jaffar, M., Shah, M. H., Shaheen, N., et al. (2005). A comparative study based on gender and age dependence of selected metals in scalp hair. *Environmental Monitoring and Assessment*, 104(1–3), 45–57.
- Khlifi, R., Olmedo, P., Gil, F., Feki-Tounsi, M., Hammami, B., Rebai, A., et al. (2014). Biomonitoring of cadmium, chromium, nickel and arsenic in general population living near mining and active industrial areas in southern Tunisia. *Environmental Monitoring and Assessment*, 61–779.
- Kono, K., Yoshida, Y., Watanabe, M., Watanabe, H., Inoue, S., Murao, M., et al. (1990). Elemental analysis of hair among hydrofluoric acid exposed workers. *International Archives of Occupational and Environmental Health*, 62, 85–88.
- Kuo, C. C., Weaver, V., Fadrowski, J. J., Lin, Y. S., Guallar, E., & Navas-Acien, A. (2015). Arsenic exposure, hyperuricemia, and gout in US adults. *Environment International*, 76, 32–40.
- Langard, S., & Costa, M., (2007). Chromium. *Handbook on the toxicology of metals* (third edition)—chapter 24. *Handbook on the toxicology of metals*, 487–510.
- Li, Y. (2013). Environmental contamination and risk assessment of mercury from historic mercury mine located in southwestern China. *Environmental Geochemistry and Health*, 35, 27–36.
- Li, X. F., Chen, Z. B., & Chen, Z. Q. (2014). Distribution and fractionation of rare earth elements in soil–water system and human blood and hair from a mining area in southwest Fujian Province, China. *Environment and Earth Science*, 72, 3599–3608.
- Li, P., Du, B., Chan, H. M., & Feng, X. (2015). Human inorganic mercury exposure, renal effects and possible pathways in Wanshan mercury mining area, China. *Environmental Research*, 140, 198–204.
- Li, G., Feng, X., Qiu, G., Bi, X., Li, Z., Zhang, C., et al. (2008). Environmental mercury contamination of an artisanal zinc smelting area in Weining County, Guizhou, China. *Environmental Pollution*, 154(1), 21–31.
- Li, P., Feng, X. B., Qiu, G. L., Shang, L. H., & Li, G. H. (2009). Human hair mercury levels in the Wanshan mercury mining area, Guizhou Province, China. *Environmental Geochemistry and Health*, 31, 683–691.
- Li, P., Feng, X., Qiu, G., Shang, L., & Wang, S. (2008). Mercury exposure in the population from Wuchuan mercury mining area, Guizhou, China. *Science of the Total Environment*, 395, 72–79.
- Li, P., Feng, X. B., Shang, L. H., Qiu, G. L., Meng, B., & Zhang, H. (2011). Human co-exposure to mercury vapor and methylmercury in artisanal mercury mining areas, Guizhou, China. *Ecotoxicology and Environmental Safety*, 74, 473–479.

- Lim, H. S., Lee, J. S., Chon, H. T., & Sager, M. (2008). Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. *Journal of Geochemical Exploration*, *96*, 223–230.
- Lison, D. (2007). Cobalt. Handbook on the toxicology of metals (third edition)—chapter 25. *Handbook on the toxicology of metals*. 511–528.
- LLerena, F., Maynar, M., Barrientos, G., Palomo, R., Robles, M. C., & Caballero, M. J. (2012). Comparison of urine toxic metals concentrations in athletes and in sedentary subjects living in the same area of Extremadura (Spain). *European Journal of Applied Physiology*, *112*, 3027–3031.
- Mandal, B. K., Ogra, Y., Anzai, K., & Suzuki, K. T. (2004). Speciation of arsenic in biological samples. *Toxicology and Applied Pharmacology*, *189*, 307–318.
- Massadeh, A., Gharibeh, A., Omari, K., Al-Momani, I., Alomary, A., Alomari, A., et al. (2010). Simultaneous determination of Cd, Pb, Cu, Zn, and Se in human blood of Jordanian smokers by ICP-OES. *Biological Trace Element Research*, *133*, 1–11.
- Massaquoi, L. D., Hui, M., Xue, H. L., Han, P. Y., Zuo, S. M., Hua, Z. X., & Liu, D. W. (2015). Heavy metal accumulation in soils, plants, and hair samples: an assessment of heavy metal exposure risks from the consumption of vegetables grown on soils previously irrigated with wastewater. *Environmental Science and Pollution Research*, *22*(23), 18456–18468.
- McDowell, M. A., Dillon, C. F., Osterloh, J., Bolger, P. M., Pellizzari, E., Fernando, R., et al. (2004). Hair mercury levels in US children and women of childbearing age: reference range data from NHANES 1999–2000. *Environmental Health Perspectives*, *112*, 1165–1171.
- Molina-Villalba, I., Lacasaña, M., Rodríguez-Barranco, M., Hernández, A. F., Gonzalez-Alzaga, B., Aguilar-Garduño, C., et al. (2014). Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas. *Chemosphere*, *124*, 83–91.
- Moon, J., Smith, T. J., Tamaro, S., Enarson, D., Fadl, S., Davison, A. J., et al. (1986). Trace metals in scalp hair of children and adults in three Alberta Indian villages. *Science Total Environment*, *54*, 107–125.
- Moreno, M. E., Acosta-Saavedra, L. C., Meza-Figueroa, D., Vera, E., Cebrian, M. E., Ostrosky-Wegman, P., et al. (2010). Biomonitoring of metal in children living in a mine tailings zone in southern Mexico: a pilot study. *International Journal of Hygiene and Environmental Health*, *213*(4), 252–258.
- Mortada, W. I., Sobh, M. A., El-Defrawy, M. M., & Farahat, S. E. (2002). Reference intervals of cadmium, lead, and mercury in blood, urine, hair, and nails among residents in Mansoura city, Nile delta, Egypt. *Environmental Research*, *90*, 104–110.
- Nam, S. H., Kim, J. J., & Han, S. S. (2003). Direct determination of total arsenic and arsenic species by ion chromatography coupled with inductively coupled plasma mass spectrometry. *Bulletin of the Korean Chemical Society*, *24*, 1805–1808.
- Natural Healing Site (2010). *Heavy metal toxicity*. Accessed 15 Aug 2010.
- Qin, J. F. (2004). The upper limit of normal value of hair Pb, Cd, As, Hg in Chinese resident. *Guangdong Trace Elements Science*, *1*(4), 29–37 Chinese paper.
- Rivai, I. F. (2001). Heavy metals in human hair related to age groups and automotive pollution levels of Bandarlampung city, Indonesia. *Bulletin of Environmental Contamination and Toxicology*, *66*, 443–448.
- Sandstead, H. H., Au, W. (2007). Zinc (third edition). Handbook on the toxicology of metals—chapter 47. 925–947.
- Shimomura, S., Kimura, A., Nakagawa, H., & Takao, M. (1980). Mercury levels in human hair and sex factors. *Environmental Research*, *22*, 22–30.
- Skerfving, S., Bergdhal, A. A. (2007). Lead. Handbook on the toxicology of metals (third edition)—chapter 31. (599–643).
- Sonne, C., Aspholm, O., Dietz, R., Anderson, S., Berntssen, M. H. G., & Hylland, K. (2009). A study of metal concentrations and metallothionein binding capacity in liver, kidney and brain tissues of three Arctic seal species. *Science of the Total Environment*, *407*, 6166–6172.
- Stadlbauer, C., Prohaska, T., Reiter, C., Knaus, A., & Stingeder, A. (2005). Time-resolved monitoring of heavy-metal intoxication in single hair by laser ablation ICP–DRCMS. *Analytical and Bioanalytical Chemistry*, *383*, 500–508.
- Strumylaite, L., Ryselis, S., & Kregzdyte, R. (2004). Content of lead in human hair from people with various exposure levels in Lithuania. *International Journal of Hygiene and Environmental Health*, *207*(207), 345–351.
- Tang, J., Xiao, T., Wang, S., et al. (2009). High cadmium concentrations in areas with endemic fluorosis: a serious hidden toxin? *Chemosphere*, *76*(3), 300–305.
- Tao, X. Q., Shen, D. S., Shentu, J. L., Long, Y. Y., Feng, Y. J., & Shen, C. C. (2014). Bioaccessibility and health risk of heavy metals in ash from the incineration of different e-waste residues. *Environmental Science and Pollution Research*, *22*, 3558–3569.
- Tylenda, C.A., & Fowler, B.A. (2007). Antimony. Handbook on the toxicology of metals (third edition)—chapter 18, 83, 353–365.
- Umbangtalad, S., Parkpian, P., Visvanathan, C., Delaune, R. D., & Jugsujinda, A. (2007). Assessment of Hg contamination and exposure to miners and schoolchildren at a small-scale gold mining and recovery operation in Thailand. *Journal of Environmental Science Health Part A*, *42*, 2071–2079.
- USEPA (United States Environmental Protection Agency) (1989). *Risk assessment guidance for superfund. Vol. I: human health evaluation manual. EPA/540/1-89/002*. Office of Solid Waste and Emergency Response.
- USEPA (United States Environmental Protection Agency) (1997). *Exposure factors handbook*. Washington, DC: US Environmental Protection Agency, EPA/600/P-95/002Fa.
- USEPA (United States Environmental Protection Agency) (2011). *Risk assessment guidance for superfund. Volume I: (part A: human health evaluation manual; part E, supplemental guidance for dermal risk assessment; part F, supplemental guidance for inhalation risk assessment); [EPA/540/1-29/002]*.
- USEPA (United States Environmental Protection Agency) (2016). *Integrated risk information system (IRIS)*. Available at: <https://cfpub.epa.gov/ncea/iris/search/index.cfm?keyword=>
- Vahter, M., Åkesson, A., Lidén, C., Ceccatelli, S., & Berglund, M. (2007). Gender differences in the disposition and toxicity of metals. *Environmental Research*, *104*(1), 85.
- Vimercati, L., Baldassare, A., Gatti, M. F., Gagliardi, T., Serinelli, M., De, M. L., et al. (2016). Non-occupational exposure to heavy metals of the residents of an industrial area and bio-monitoring. *Environmental Monitoring and Assessment*, *188*(12), 673.

- Wang, Y., Qiao, M., Liu, Y., & Zhu, Y. (2012). Health risk assessment of heavy metals in soils and vegetables from wastewater irrigated area, Beijing-Tianjin city cluster, China. *Journal of Environmental Sciences*, 24(4), 690–698.
- Wang, Z., Yu, X., Geng, M., Wang, Z., Wang, Q., & Zeng, X. (2017). Accumulation of heavy metal in scalp hair of people exposed in Beijing sewage discharge channel sewage irrigation area in Tianjin, China. *Environmental Science and Pollution Research*, 24, 13741–13748.
- WHO. (1991). *Environmental health criteria 118: inorganic mercury*. Geneva: World Health Organization.
- WHO (2010). *Preventing disease through healthy environments: exposure to lead: a major public health concern*.
- WHO (2011). *Guidelines for drinking-water quality*. Fourth edition. http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf.
- Wongsasuluk, P., Chotpantarat, S., Siriwong, W., & Robson, M. (2014). Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. *Environmental Geochemistry and Health*, 36(1), 169.
- Wu, B., & Chen, T. B. (2010). Changes in hair arsenic concentration in a population exposed to heavy pollution: follow-up investigation in Chenzhou city, Hunan province, southern China. *Journal of Environmental Sciences*, 22(2), 283–289.
- Yasutake, A., Matsumoto, M., Yamaguchi, M., & Hachiya, N. (2004). Current hair mercury levels in Japanese for estimation of methylmercury exposure. *Journal of Health Science*, 50, 120–125.
- Ying, Z. J., Qin, Z. (2001). Investigation and analysis on environmental pollution due to a small antimony smeltery in southwest Guizhou province. *Journal of Environment & Health*.
- Zhang, L., & Wong, M. H. (2007). Environmental mercury contamination in China: sources and impacts. *Environment International*, 33, 108–121.
- Zidek, A., Macey, K., Mackinnon, L., Patel, M., Poddalgoda, D., & Zhang, Y. (2016). A review of human biomonitoring data used in regulatory risk assessment under Canada's Chemicals Management Program. *International Journal of Hygiene and Environmental Health*. doi:10.1016/j.ijheh.2016.10.007.