



Research Article

Trace elements analysis in hair strand of cooks chronically exposed to indoor air pollution in restaurants of Lhasa, Tibet: preliminary results

Bigyan Neupane^{1,2} · Shichang Kang^{1,2,3} · Chaoliu Li^{3,4} · Pengfei Chen¹

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Abstract

Considering the effect of environmental exposure and contamination, six trace elements including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) in scalp hair samples of cooks at Lhasa city, southern Tibetan Plateau were analyzed by inductively coupled plasma-mass spectrometry. Potential of human hair in indicating the exposure and contamination has been assessed. Concentrations of these elements were found in the rank order of $Zn > Cu > Cr > Pb > As > Cd$, with concentrations of Zn and Cu exceeding $10 \mu\text{g/g}$ ($Zn = 208.01 \mu\text{g/g}$; $Cu = 23.60 \mu\text{g/g}$). All the elements, especially Cu and Cr concentration in the hair samples were higher than those of the control, indicating higher indoor air pollution posing higher health risk. Cu, Cr, and Zn concentrations were higher than those of other areas (e.g. Turkey, Poland and Italy), implying that these metals might accumulate in the body and affect the health of cooks. No significant difference between genders was observed. Significantly positive correlations for several elements: Cr and As, Cr and Cd, Cu and Pb, As and Pb were obtained, which were different from the control, indicating heavy exposures to these metals through cooking activities. Our observations suggested that human scalp hair could be a useful biomarker to assess the intensity of heavy metals exposure as well as the indoor air pollution to cooks in Tibet.

Keywords Hair · Heavy metals · Restaurant · Indoor air pollution · Tibet

1 Introduction

Indoor air pollution caused by cooking and biomass burning has strong association with human health [1–4]. Recent studies have revealed the connection between the indoor air pollution and health-related problems in hospitals [5, 6], schools [7], factories [8], and residences [9, 10]. In addition, the verification is preferred to be done in the Tibetan plateau which is considered as one of the cleanest regions in the world [9, 11]. Particulate matter and carbon monoxide which are generally considered as the direct indicator of indoor air pollution have been measured extensively [12, 13]. But they cannot reflect the

direct influence of the indoor air pollution on the human health status. With the widespread recognition of Chinese food and increasing number of restaurants, the indoor air pollution caused by cooking has gained more attention considering the health risk. Because cooks spent long time working within kitchen every day, it is meaningful to study cooks especially in the Tibetan plateau with the most severe occupational exposure of indoor air pollution caused by cooking.

Biomonitoring which is to measure the human exposure to background levels of trace elements in the environment has gained critical importance as a tool to reflect the nutritional and health status [14–16]. Metals are

✉ Pengfei Chen, chenpengfei@lzb.ac.cn | ¹State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences (CAS), Lanzhou 730000, China. ²University of Chinese Academy of Sciences, Beijing 100049, China. ³CAS Center for Excellence in Tibetan Plateau Earth Sciences, Beijing 100101, China. ⁴Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, CAS, Beijing 100101, China.



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ubiquitous elements and present in both environment and all living organisms. Essential elements required by an organism to maintain its normal physiological function are key components of metalloenzymes or are involved in crucial biological functions, such as oxygen transport, free radical scavenging, or hormonal activity [17]. For example, zinc (Zn) is the most abundant intracellular component involved in genetic stability, gene expression, and DNA repair. Deficiency of Zn is associated with growth retardation and increased cancer risk, and excess of Zn is neurotoxic [18, 19]. Copper (Cu) is a component of various enzymes involved in not only the collagen synthesis but also the normal development of connective tissues, nerves and immune system. In excess, Cu is extremely toxic due to its pro-oxidant activity, causing DNA damage and even neurodegenerative changes such as Alzheimer's disease [19]. The trivalent form of chromium (Cr) is an essential nutrient for human and required for the maintenance of normal glucose tolerance [20]. However, its hexavalent form is toxic leading to severe skin, nasal, pulmonary or gastrointestinal injury as well as hepatic or renal failure. Other nonessential elements which result in impairment of biological functions are toxic at even trace doses. For example, cadmium (Cd) and arsenic (As) are carcinogenic and lead (Pb) is neurotoxic. Even in small amounts, Cd and Pb may interact with Ca and replace it in the skeleton or Zn in the heme enzymes and metallothioneins [21].

Concerns about these effects have driven the scientific community to find reliable tools and methods for assessing the impact of trace metal emissions on human health from anthropogenic sources [22]. So far, various biological materials have been used to measure exposure of toxic substances. Among them, human scalp hair has been widely used for research of bio-monitoring environmental and occupational exposures of heavy metals in various areas [15, 23–30]. Generally, human scalp hair is less invasive, convenience to store and transport and less hazardous while handling. Additionally, hair sample is also an effective assessment tool reflecting contaminant exposure of long-term period (weeks to years) compared with other materials such as blood and urine [31]. Heavy metal concentrations in hair sample have been widely studied [11, 27, 32]. For example, concentrations of heavy metals (e.g. Cu, Pb, and Cd) of hair samples at electronic waste recycling area were significantly higher than those from control areas [27], indicating human scalp hair was a useful biomarker to assess the extent of heavy metal exposure. Besides working and living environment, other factors such as gender and age also greatly affect the elemental concentrations of hair. For example, Chojnacka et al. [32] examined the inter-relationship between elements of hair and genders. They found elemental concentrations varied between two gender groups, indicating that gender also

played an important role to influence elemental concentrations of hair. Additionally, significant correlations can be found in hair samples due to their similar behavior within human body. For instance, close relationships were found between Cd and Pb, Cd and As in hair samples of residents living in villages around a polymetallic mine [11].

Cooks of Lhasa, the Tibetan Plateau, without industry and modernization are exposed to the prolonged indoor air pollution within kitchen every day. The objective of this study was to examine the concentrations of heavy metals (Zn, Cu, Cr, Cd, As, and Pb) in the scalp hair samples of cooks in Lhasa city by inductively coupled plasma-mass spectrometry (ICP-MS). In addition, concentrations of these elements were compared with levels in other regions of the world. Besides, mutual correlations among these metals were examined. To our knowledge, this study is one of the very few studies conducted within restaurants on human exposure to heavy elements, which will provide useful data on understanding the health status of these cooks at Lhasa. Meanwhile, these values can also be utilized for making related occupational policy.

2 Materials and methods

2.1 Description of sampling sites

Lhasa (91°60'E, 29°36'N, 3650 m a.s.l) located in the valley of the middle reach of the Lhasa River, southern Tibetan Plateau (Fig. 1). The amount of oxygen in Lhasa air is approximately 60–70% of the normal concentration at sea level because of its high elevation. Economy and tourism of Lhasa have developed rapidly during last decades, especially after the construction of Qinghai–Tibet railway. Consequently, lots of restaurants have been setup in Lhasa. Generally, these restaurants can be divided into two types: Han style restaurant and Tibetan style restaurant. Liquid gas and coal are two most commonly used fuels in these restaurants. Although all the restaurants are equipped with exhaust fans, air quality within the kitchen is still poor due to relatively small space and intensive cooking activities. Furthermore, lack of oxygen aggravates incomplete combustion and emission of particles [33].

2.2 Sample collection

Five Han style restaurants and four Tibetan style restaurants were chosen for study in August 2011. A total of eighteen scalp hair samples of cooks were collected with stainless steel scissors under agreement of participants. Cooks with dyed hair were excluded. Information collected included age, gender and work experience. Meanwhile, ten scalp hair samples of local residents with occupation



Fig. 1 Map showing the study area and sampling sites at Lhasa

other than cooking and seldom entering kitchens were selected as the control. Collected samples were stored in plastic bags and transported to laboratory for analysis.

2.3 Sample pre-treatment and analysis

Hair samples were cut into small pieces and washed by acetone (Beijing Institute of Chemical Reagent Research, P. R. China) and Milli-Q water [14]. Briefly, cut samples were immersed in 20 mL acetone for 10 min, the liquid was then decanted and the procedure was repeated twice with 5 mL of water, and finally rinsed once again with water. The washed samples were dried for 24 h at a relatively low temperature of 40 °C. Then the weighted samples were digested by a microwave digestion unit (CEM Mars-X 500, USA) [27]. In short, about 0.1 g of the sample was transferred into a Teflon digestion vessel and predigested with 6 mL concentrated HNO₃ (69%, BVIII, Beijing Institute of Chemical Reagent Research, P. R. China) for 30 min. Afterwards, 2 mL of 30% H₂O₂ (analytical reagent, Beijing Institute of Chemical Reagent Research, P. R. China) was added and put into digestion unit. After initially increasing to 160 °C in 10 min, and maintaining at 160 °C for 30 min, the digestion temperature increased from 160 to 180 °C in 10 min, and finally maintained at 180 °C for 30 min. After cooling to room temperature, the digest was diluted to approximate 120 mL with Milli-Q water. The samples were analyzed by ICP-MS (X-7 Thermo Elemental, USA) at Key Laboratory of Tibetan

Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research for the determination of heavy metals of Zn, Cu, Cr, Cd, As, and Pb.

Three blanks were made and concentrations of all elements were much lower than those of hair samples. The detection limits of Cr, Cu, Zn, As, Cd and Pb were 0.444 ng/g, 0.155 ng/g, 0.224 ng/g, 0.22 ng/g, 0.0049 ng/g and 0.004 ng/g. And procedural replicates showed relative standard deviation (RSD) < 10% for all analyzed elements (n = 5).

Statistical analysis was carried out with the SPSS 17.0 software and was expressed as Mean ± standard deviation (SD). Pearson's correlation coefficient was employed to provide a technical description of the correlations between different elements. ANOVA test was used to assess the differences among various groups. The significance was set to $P < 0.05$. However, only 18 hair samples and 10 control samples were collected in this study; this may have caused uncertainties in analyzing the results and comparing that with data from other locations. Nevertheless, this study provides preliminary results and seeks further work precisely in the future.

3 Results and discussion

3.1 Trace metal concentrations in hair

The selected heavy metals in hair samples of cooks and controls is listed in Table 1, where a/b ratio (Table 1) is the

element concentration ratio of cooks to controls. Concentrations of all elements in cook group were higher and with broader ranges than those of control group. For example, Cu and Cd of cook group were about 2.4 and 2.8 times of those of control group, respectively. The rank order of these measured elements of both groups were similar: Zn > Cu > Cr > Pb > As > Cd. The most abundant heavy elements were Zn and Cu (Zn = 208.01 µg/g, Cu = 23.60 µg/g) followed by Cr (5.58 µg/g). Pb, As, and Cd had relatively low concentrations. In view of low uncertainties in measurement precision, the coefficient of variations (CVs) corresponds to the intrinsic biological variations due to gender, lifestyle, and small-scale environmental factors [34]. In this study, CVs of all tested elements of cooks are larger than those of controls, indicating their greater variability.

The elevated concentrations of Cu, Zn, and Cd in cook hair could be the result of high fine particle (PM_{2.5}) concentration of kitchen air, which is enriched with heavy metals [35, 36]. For instance, mean concentrations of Cu, Zn, and Cd of kitchen air are 3.52 µg/m³, 0.25 µg/m³ and 0.004 µg/m³ respectively, much higher than those of ambient air of Lhasa city [36]. Therefore, cooks are at risk of being exposed to high levels of these metals through inhalation. Furthermore, coal has high concentrations of trace elements compared with geological materials. During coal combustion, particles that enriched of trace elements are produced [37, 38].

Additionally the effect of gender on trace metals was studied between hair samples from the same type of restaurant considering the similar natural environment. Eight cooks from four restaurants (two Han style and two Tibetan style) with similar age were chosen. Although concentrations for all elements except Zn of female hair were a little higher than those in males (Fig. 2), no significant differences were observed, indicating that gender has little influence on the metal concentrations of cook hair at Lhasa.

Some differences were found between two types of restaurants. For example, Pb concentration of cooks hair from Tibetan style restaurant was 10 times higher than those

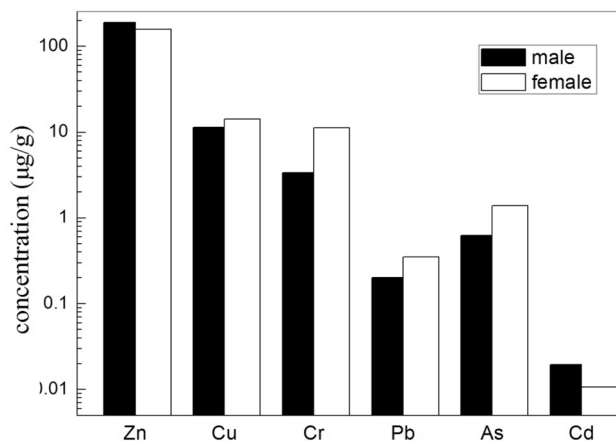


Fig. 2 Comparison of selected elements between hair of male and female cooks

from Han style restaurant, reflecting cooks of Tibetan style restaurant are considerably influenced by the Pb exposures. Correspondingly our previous study have shown Pb concentration in air of Tibetan style restaurant was higher than that of Han restaurant [36] due to larger amount of coal used as fuel in the past, reflecting close relationship between environment concentration of Pb and its level in hair samples. Similar phenomenon has also been found at electronic waste recycling area of China [27].

3.2 Correlation between elements in hair

The analysis of element correlations assists the interpretation of meaningful hair measurements. Meanwhile, it also helps to identify common factors inducing the observed elemental relationships. Pearson’s product moment correlation for the investigated elements in cook hair is presented in Table 2. Significantly positive correlations for several elements were obtained: Cr and As, Cr and Cd, Cu and Pb, as well as As and Cd, indicating different patterns from those of the control, which revealed negative correlation between Pb and Cu, and positive correlation between As and Pb, Zn

Table 1 Heavy metal concentrations (µg/g) of hair samples at Lhasa and the ratio of element concentration for cook to control (a/b)

Elements	Cook ^a				Control ^b				a/b ratio
	Average	Range	STD	CV%	Average	Range	STD	CV%	
Zn	208.01	110.30–417.92	80.43	39	164.57	94.13–201.34	42.39	26	1.26
Cu	23.60	10.05–101.49	27.79	117	9.73	6.92–12.50	2.46	25	2.43
Cr	5.58	3.38–11.15	2.14	38	4.55	2.42–5.58	1.24	27	1.23
Pb	0.97	0.20–2.55	0.84	87	0.59	0.23–0.96	0.28	48	1.66
As	0.48	0.14–1.39	0.43	90	0.30	0.16–0.51	0.15	50	1.63
Cd	0.05	0.11–0.10	0.04	80	0.02	0.02–0.03	0.01	28	2.84

STD, arithmetic standard deviation; CV, coefficients of variation; range, min–max
The superscript letters a and b is the ratio of controls to cooks

and Cu. Furthermore, significant positive correlations among heavy metals have been found in air particle. For instance, As and Cd are in close relation in the PM_{2.5} samples of kitchen [36], which might cause the interaction between these two elements in cook hair. Similarly, significant correlations between Cu and Pb were observed previously [27] for the whole population correlations, resulting from similar environmental exposure to these two heavy metals. Besides, correlation between Cr and As might be explained by the coal combustion [39].

Through multivariate analysis, Cr, Cd and As were found highly correlated in hair of cook, indicating that cooking activities are likely the main source. These significant pair-wise correlations can be used to determine whether cooks are affected by the serious indoor air pollution. Hence cooks who are in charge of most cooking activities were at risk for adverse health effects. Therefore, efficient measures against indoor air pollution of kitchen such as adopting effective exhaust fans, using clean fuel (such as liquefied petroleum gas—LPG) should be taken for the sake of cook's health.

3.3 Comparisons with other regions

Data from other areas (population exposed to other environment) in the world were selected to compare with our results in Table 3. Generally, Zn and Cu are harmful if consumed in large quantities. For example, increased level of Cu can be found in the hair of hair loss patients [40]. Mean Zn concentration of cook group at Lhasa was higher than those of other areas [23, 41–43], probably due to high Zn exposure within kitchen (0.25 µg/m³, [36]). Although mean Cu concentration of the cook group was lower than those of electronic waste recycling area [28] in China, it was higher than all the other areas [23, 41, 43]. Therefore, High concentrations of Zn and Cu in cook hair were likely to be a valid indication of the body burden, indicating significant influence of intensive cooking activities on cooks.

Intoxications of Cr compounds are life threatening and often lethal. It may cause severe skin, nasal, pulmonary, or gastrointestinal injury [20]. Chromium concentration (5.58 µg/g) of cook group in Tibet was significantly higher than those of other studies [23, 27, 42, 43]; was found to be 50 and 13 fold higher than the reference values of Italy [42] and Poland [23], probably due to direct exposure of high Cr concentration in kitchen air emitted by fuel burning [39].

Table 2 Pearson correlation matrix of data set for heavy metals of cook hair at Lhasa

	Zn	Cu	Cr	Pb	As	Cd
Zn	1					
Cu	−0.23	1				
Cr	−0.19	−0.08	1			
Pb	0.43	0.60*	−0.12	1		
As	−0.20	−0.13	0.77**	−0.32	1	
Cd	0.29	−0.14	0.54*	−0.04	0.81**	1

**Correlation is significant at the 0.01 concentration (two-tailed)

*Correlation is significant at the 0.05 concentration (two-tailed)

Table 3 Heavy metal concentrations (µg/g) of cook hair at Lhasa compared with other areas

Elements	Cook group	Turkey ^a	Taizhou ^b	Poland ^c	India ^d	Italy ^e
Zn	208.01	109.763	NA	129	152.42	189.2
Cu	23.60	15.753	53	7.96	14.76	22.87
Cr	5.58	0.934	1.591	0.6	NA	0.11
Pb	0.97	0.114	85.3	4.99	8.03	1.01
As	0.48	0.558	0.423	NA	3.43	0.00
Cd	0.05	0.316	0.94	0.61	0.4	0.04

NA not available

^a74 samples of male with an age of 42–72 years [43]

^b139 samples of male and female with all age group [27]

^c266 samples of male and female with all age group [23]

^d44 samples of male and female with all age group [41]

^e137 samples of children with an age of 11–13 years [42]

Lead is also a potent toxicological agent posing serious health risks on every organ system [44]. Lead concentration in hair is considerably influenced by the environmental exposures. Mean Pb concentrations of cook group were similar to that of Italy [43], but lower than other areas [23, 41], especially electronic waste recycling area of China due to exposure of e-waste recycling activities [27]. Arsenic causes serious health problems in human beings and is a defined human carcinogen causing skin, lung, and bladder cancer after high exposure. The concentrations of As were comparable with those of other regions except India, where the high concentration of As in India might come from the exposure through drinking water and food [41]. Cadmium is known to be nephro-toxic and may have adverse neuro-developmental consequences [45]. In this study Cd concentrations in cook group were similar to those of Italy [42] and lower than other regions [23, 27, 41, 43].

In short, Cr concentrations reported in this study were higher than all reference values; Zn and Cu concentrations were higher than those of most of other areas except for Taizhou—a seriously polluted area caused by electronic waste recycling. Therefore, it is natural to assume that intensive cooking activities caused serious indoor air pollution and consequently, high metal concentrations in cook hair in Lhasa city. Other elements were similar or even lower than those of other areas, indicating that effect of cooking on these elements were insignificant.

4 Conclusions

Concentrations of six heavy metals in hair from cooks and controls in Lhasa City of the Tibetan Plateau were determined by ICP-MS. All of these six elements, especially Cu and Cd in cook group were higher and with broader ranges compared with those of control group, due to intensive cooking activities. No significant change exists in elemental concentrations between male and female. Cu, Cr and Zn concentrations in hair of cooks were higher than those of most other areas, indicating these metals accumulated obviously and may affect the health of cooks. Concentrations of other elements such as Pb, As, and Cd were similar or lower than other areas. The interrelationships between elements were studied and significant correlations between Cr and As, Cr and Cd, Cu and Pb, and As and Cd were found in hair, which can be used as tracers to determine whether cooks were affected by high indoor air heavy metals. Our study suggested that noninvasive and cost-effective hair sample could provide preliminary information on the exposure of heavy metals due to intensive cooking activities.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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