A review of human hair heavy metal concentration characteristics from mines in China

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Abstract. This paper summarized the human hair sampling, treatment and determination methods for heavy metal testing, also organized the researches and analyzed the spatial distribution characteristics of 11 heavy metals (Hg, As, Pb, Mn, Se, Zn, Cu, Cr, Cd, Sb, ΣREEs) contents from human hair pollution caused by the mining activities in China.

1. Introduction

Mine resources play an important role in China’s national economy, but the environmental problems caused by the mining activities cannot be ignored. Mining activities include mining and ore transportation products that release large amounts of heavy metal pollutants into the surrounding environment of river water, sediments, soil, plants and animals, and ultimately cause concern for human health. Environmental monitoring methods are essential for exposure to heavy metal pollution, including soil, water, air, food (plant and animal) and human biomonitoring. Blood, urine, and hair monitoring are commonly used to study the accumulation of toxic environmental pollutants in the human body. As a stable substrate, human hair provides many advantages for human biological monitoring, such as easy collection, low cost, easy transportation and storage, and information on short-term and long-term exposure. [1-4]

The use of human hair analysis as one of the heavy metal monitoring methods dates back to 1983 in China. [5] In recent years, with the extensive research on the concentration of heavy metals in human hair, hair analysis technology has developed rapidly. Hair analysis technology has now become an effective monitoring method for heavy metal exposure in mining areas in China. [6-15]

This paper focuses on the important research on the human hair heavy metal pollution caused by mining activities in China, summarizes the sampling, processing and determination methods, and carrying out the spatial distribution characteristics of each element (Hg, As, Pb, Mn, Se, Zn, Cu, Cr, Cd, Sb).
2. The summary of sampling, treatment and determination methods

There are some challenges the heavy metal monitoring in human hair aspect needs to face. Due to the sample diversity of age, sex, length, color, position, season and the adopted sampling and treatment methods, the heavy metal contents are difficult to compare from different research fields. Thus, building a standard for sampling, treatment and determination of human hair as a heavy metal monitoring method is urgent. The sampling and treatment methods for detecting the heavy metal contents could be divided into 4 steps: sampling, washing, dissolution and determination.

2.1 Sampling

Different locations of the hair sample contain different heavy metal contents, varying from roots to top, so the study should control the position and length of the different bodies. It is recommended to cut the sample (2g) from the occipital region of the scalp with quartz or stainless-steel scissors. It is 1-2cm long and weighs 2g. It is bundled with a file, placed and sealed in polyethylene bags or envelope for proper identification. Before cutting the sample, the information such as age, gender, address, hair color, drinking water source (well, spring water, tap water), occupation, treatment and drug using conditions, smoking habits, capacity need to record alcohol and swimming frequency.

2.2 Washing

Weighting the sample before cleaning could avoid the pollution during weighting. The clean method still lacks a unified standard all over the world. The common detergent has EDTA, SDS (sodium dodecyl sulfate) 1%Na₂CO₃, 0.1NHCl, acetone, ethyl alcohol. Currently, two main clean methods were widely used in the investigation: washing the samples with organic solvent firstly, detergent secondly, deionized water finally; washing the samples with detergent firstly and deionized water secondly. [16-17]

2.3 Dissolution

The mixed nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) could dissolve samples. The reagents need to be stored in glassware or plastic bottles, which require to be cleaned by soaking in 10% (v/v) HNO₃ for 24 h, rinsed five times with Milli-Q water and dried in class 100 laminar flow hoods before use. [18] Dissolution means can be divided into incineration, wet and high-pressure digestion. Incineration digestion has advantages such as low reagent usage, low blank value and large sample treatment, but the volatile elements are not suitable. Wet digestion is simple, fast and sample loss is low, but the high blank value and small sample handling are unavoidable. High pressure digestion can cause air pollution, which takes time and money and is not suitable for large-scale sample processing.

2.4 Determination

Human hair has low heavy metal content and requires an elemental analysis instrument with high sensitivity and high precision. The main methods of measurement are atomic absorption spectrometry (AAS), plasma emission spectrum (ICP), anodic stripping voltammetry, neutron activation analysis, ICP-MS and atomic fluorescence spectrometry (HG-AFS).

The AAS is suitable for the single element and multi element analysis. ICP is suitable for multi-element microanalysis. A few milligrams of the sample can be used for quantitative analysis of certain elements, but show low sensitivity in As, Pb, Be, Cd, Hg analysis. Anodic stripping voltammetry can simultaneously analyze 3-4 elements and has high sensitivity to Cu, Se, Pb, Cd. Neutron activation analysis has many advantages: it is easy, fast, sensitive and has no blank values, but
the instrument is too expensive to generalize. ICP-MS is the fastest growing inorganic ultra-trace analysis in the past 10 years and is often used to test the heavy metal content in human hair in China. [19-23] The AFS is mainly used for metal elements testing and is also widely used for the investigation of human hair mark elements, especially in China. [24-26]

3. The heavy metal contents in the human hair research situation

Recently, many reports about human hair exposure around the mining area were carried out by Chinese and foreign researchers.

The methylmercury (Me-Hg) and total mercury (T-Hg) contents from 98 local inhabitants in the Wanshan Hg mining area South China were studied, the results showed mean T-Hg content as 4.4 ±0.1 μg/g and mean Me-Hg content as 3.5 ±0.1 μg/g. The relationships between the estimated rice Me-Hg intake and hair Me-Hg levels (r = 0.65, p < 0.001) confirmed rice with high Me-Hg levels indeed was the main route of Me-Hg exposure for the residents in the Wanshan Hg mining area. [27] The Concentrations of total mercury (T-Hg) and methylmercury (Me-Hg) in human hair were also measured in a mercury mining area in central China, the results indicated that T-Hg concentrations in hair samples ranged from 1.57 to 12.61 μg/g, with a mean value of 4.29 ± 3.25 μg/g and Me-Hg ranged from 0.04 to 0.94 μg/g, with a mean value of 0.35 ± 0.33μg/g. [28] The hair samples from 91 urban, town and fishing village residents were collected and analyzed in Pearl River Delta (PRD) is located in the Guangdong Province, the results showed that the average total mercury (T-Hg) and methylmercury (Me-Hg) concentrations in hair were 1.08 ± 0.94 and 0.58 ± 0.59 μg/g. [29] The concentration levels of mercury in human hair was studied from Xikuangshan antimony mining area located in Guiyang city by Liu, the content of Sb, As and Hg are 15.9, 4.21, 1.79 μg/g in the samples from Xikuangshan antimony mining area. [30] Mercury (Hg) exposure in the population from Wuchuan mercury mining area (WMMA), Guizhou, China, was evaluated by human hair Hg investigation by Li, the results showed the means of hair T-Hg concentrations were 33.9 μg/g and 21.5 μg/g in two different sites, the mean concentration of this mining area considered as 27.7μg/g. [31] Mercury (Hg) concentrations were determined in human hair samples from the artisanal mercury mining areas, Guizhou, China, the results showed that the means of hair Me-Hg concentrations were 4.26μg/g (1.87–10.6 μg/g). [32] The mercury concentrations in hair samples from 177 coastal residents in Hainan, South China Sea were investigated, the average T-Hg concentrations in hair of adults (1.02±0.92 μg/g). [33]

Also, the total and bio-available REEs contents in human hair from the vicinity of a large-scale mining area located in Hetian Town of Changting County, Fujian Province, Southeast China were investigated, concentrations of total REEs ranged from 0.06 to 1.59μg/g with an average of 0.48 ± 0.59 μg/g. [34] The scalp hair of residents living near the smelting and mining areas in Hezhang County, China were collected and REEs were analyzed, the results showed that ΣREEs for hair in mining and smelting were 1.13 and 1.55 μg/g. [35]

Moreover, many pieces of research focused on more than one element. The contents of arsenic (As), antimony (Sb) and bismuth (Bi) in human hair were investigated from two typical antimony mines (Xikuangshan antimony mine and Qinglong antimony mine, Southwest China). The results showed that Arsenic (As) concentrations for Xikuangshan, Qinglong and Guiyang ranged 0.236–48.4 (mean 4.21), 0.130–16.1 (mean 2.96), and 0.104–0.796 (mean 0.280) μg/g; Antimony concentrations for Xikuangshan, Qinglong, and Guiyang ranged 0.250–82.4 (mean 15.9), 0.060–45.9 (mean 5.15);
Bismuth contents were found to be greater than the limit of detection (LOD > 0.016 μg/g) in all the human hair samples collected from residents from Qinglong antimony mine, 95.5% samples from Xikuangshan mine. [36] A human hair investigation was conducted by Qu in a Lead-Zinc mining area located in Jiangsu Province, the samples from the residents in one of the investigated village contained Pb (8.14 μg/g) and Hg (0.86 μg/g). [37] The human hair samples from the residents living in the Dabaoshan mine area located in Guangxi Province, contained average Cd (0.27–0.57 μg/g) and Pb (12.5–23.9 μg/g). [38] Heavy metal levels in hair of residents living in villages around Fenghuang polymetallic mine located in southwestern China were investigated, the results showed that the mean concentrations (μg/g) of 0.17 for Cd, 8.67 for Pb, 0.11 for As, 2.19 for Hg, and 0.64 for Se. [39] The heavy metal concentrations in human hair from local people living around the Huodehong lead-zinc mining area in Yunnan, Southwest China were determined, the contents of Cd, Cr, Cu, Pb and Zn in local area samples varied from 0.021 to 1.1, 0.0500–1.07, 4.81–11.3, 2.49–12.6 and 59–360 μg/g. [40] Levels of seven metals (Mn, Cu, Zn, Pb, Cr, Cd, and Se) in the scalp hair of Daicun and Xiangtian inhabitants living around Dexing Copper Mine, Jiangxi Province, China, were determined by ICP-MS/AFS, the results showed that the mean contents (μg/g) from Daicun are Se for 0.16, Cd for 0.12, Cr for 0.35, Cu for 9.05, Mn for 4.86, Pb for 6.46, Zn for 114.11; Xiangtian are Se for 0.22, Cd for 0.07, Cr for 0.29, Cu for 8.4, Mn for 7.91, Pb for 3.24, Zn for 113.34, the mean contents for both village are Se for 0.19, Cd for 0.095, Cr for 0.32, Cu for 8.725, Mn for 6.385, Pb for 4.865, Zn for 113.725. [26]

4. The spatial distribution characteristics of each element

4.1 Hg

The regular total Hg (T-Hg) content from human hair was considered as 10 μg/g, symptomatic content as 150 μg/g and lethal content as 500 μg/g by Eyl [41]. The normal total content (T-Hg) also considered as 2μg/g -6μg/g, symptomatic content as 50 μg/g and lethal content as 500μg/g by Joselow [42]. The high methylmercury (Me-Hg) content in human hair was found highly related to the Me-Hg polluted fishes consuming.

The Hg content spatial distribution characteristics could be seen in Figure 1. Comparing to the lowest regular T-Hg content (2μg/g), four studies showed the greater contents, which all distributed in the south-east China. The highest content distributed in middle China. The highest Me-Hg content was showed in south China.
4.2 As
The conventional As content in human hair can be less than 2 μg/g, and more than 3 μg/g can be regarded as abnormal exposure, and 12 μg/g can be defined as arsenicism. [43] As can be seen from Figure 2, all studies are concentrated in southern China, and only one study has shown pollution.

4.3 Pb
The regular Pb content was considered as less than 30μg/g in hair for normal citizens and 30-100μg/g for occupational exposure workers. [44] As we could see from Figure 3, no research possessed greater content than 30μg/g and the contents showed similarity.
4.4 Mn
The regular Mn content was reported less than 5μg/g for normal citizens by Sun Yat-sen university Zhongshan school of Medicine. As we could see from Figure 4, only one research here, the content is greater than 5μg/g, considered as pollution.

4.5 Se
Some Chinese researchers have found that the lack of selenium can cause keshan disease, and taking sodium selenite for the treatment of Keshan disease may increase the selenium content in human hair. Se in the hair is typically in the lower micrograms per gram (μg/g) and is near or below the detection limit of inductively coupled plasma atomic emission spectrometry (ICP-AES). [2] As can be seen from Figure 5, the sampling positions of the two studies are close, the contents are very good, showing similarity.
4.6 Zn
The close relationship between zinc content in hair and acceptable daily intake (ADI) in many animal and human experiments. Nano and anemia may be associated with zinc deficiency (ZD). The Zn content of men is usually 167.0±5.09μg/g and of women is 172.1±9.32μg/g. Figure 6 shows the results of two studies, one of which is lower than the normal value in southeastern China and the other higher than normal.

4.7 Cu
It has been found that low and medium Cu content in human hair is associated with kwashiorkor and pellagra. [45] The copper content of men is usually 16.1±1.19μg/g, and that of women is 55.6±10.27μg/g. [46] The content shown in Figure 7 is relatively lower than the normal content. The results of the two sampling positions show similarities.
4.8 Cr

The Cr content in human tissue decreasing as aging was found by Tipton, 1963, which normally recognized as 0.69±0.063 μg/g for male and 0.96±0.049 μg/g for female. [46] Hambidge, 1982 found that the Cr in human hair could reveal the Cr accumulation in the human body. [47, 48] As we can see from Figure 8, the Cr contents from two sampling locations were relatively lower than the normal content and showed similarity.

4.9 Cd

Cd is known to damage organs such as the kidneys, liver and lungs. [49] The content normally considered as 2.76±0.483 μg/g for male and 1.77±0.239 μg/g for female. The data showed in Figure 9 from three sampling locations were lower than the normal content, two of them showed similarity.
4.10 Sb

The Sb content in human hair samples is very low and usually only contains a few ng/g. [50] As we can see in Figure 10, the Sb contents from 3 locations all much greater than the normally content, which may be caused by sampling, processing and determination methods. It is recommended to repeat the test for accurate data.

4.11 REEs

Rare earth elements (REEs) refer to the elements spanning atomic numbers 57 (lanthanum) to 71 (lutetium). In recent decades, the increasing applications of REEs and mining of rare earth mineral may release more REEs into the environment. Due to the lack of the normal content of ΣREEs, the data is not easy to evaluate, but the contents from 2 different sampling locations in Figure 11 showed
relative similarity.

Figure 11. The ΣREEs content spatial distribution characteristics in human hair

According to the concentration of 11 elements in the hair of Chinese mining areas, it can be concluded that Hg, As and Pb are the most popular research elements in human hair, Hg also has the most serious exposure, As and Pb showed slightly pollution. The data of Sb and ΣREEs need to be further discussed for pollution characteristics, and the research on Mn, Se, Zn, Cu, Cr, Cd shows slight pollution and has not been developed in China.

5. Conclusions

According to the concentration of 11 elements in the hair of Chinese mining areas, it can be concluded that Hg, As and Pb are the most popular research elements in human hair, Hg also has the most serious exposure, As and Pb showed slightly pollution. The data of Sb and ΣREEs need be further discussed for pollution characteristics, and the research on Mn, Se, Zn, Cu, Cr, Cd shows slight pollution and has not been developed in China. The data could provide support for further human hair research in China.

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