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# Levels of Cd, Pb, As, Hg, and Se in Hair of Residents Living in Villages Around Fenghuang Polymetallic Mine, Southwestern China

**Yonghua Li · Xiuwu Zhang · Linsheng Yang · Hairong Li**

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**Abstract** Heavy metal levels in hair of residents living in villages around Fenghuang mine were investigated. Samples belonging to mine areas showed the highest values, with mean concentrations (mg $kg^{-1}$) of 0.17 for Cd, 8.67 for Pb, 0.11 for As, 2.19 for Hg, and 0.64 for Se. Significant correlations ($p < 0.01$) were found between Cd–Pb, Cd–As, Pb–As, and Se–Hg. There is no significant difference in any of the elements among age groups. However, significant differences in Cd and Pb levels were found between genders. Results revealed that children and females were more susceptible to Cd and Pb exposure.

**Keywords** Hair · Heavy metals · Mining activities · Environmental exposure

Effects of environmental exposure to metals on human health have been discussed in recent decades, especially with respect to exposure to heavy metals from mining activities (Pereira et al. 2004; Sharma and Kumar 2005; Yang et al. 2011). Hair samples have been widely used in the biomonitoring of heavy metals exposure in large cohorts (Rodrigues et al. 2008). Moreover, determination of heavy metal concentrations in hair of residents from villages adjacent to mining has also proven useful in assessing their health status (Carvalho et al. 2009). Li et al. (2004) found that the average Hg concentration in the hair of workers from the Wanshan Hg mine, China, was 837 mg $kg^{-1}$, which is much higher than those from other areas in the world. Similar results were found among the residents on Canteiro Island, Brazil, whose hair Hg and Pb contents were higher than the average level due to the gold mining activities (Carvalho et al. 2009).

Fenghuang polymetallic mine, located in Hunan province, southwestern China, can be regarded as one of the largest known of low temperature hydrothermal mercury and lead mines in China. Mining activities in the area goes back to the Qin Dynasty (221 BC). Existing research has shown that the mining activities lead to contamination of soil, surface water, vegetable, and rice, and cause a series of health problems among the local residents (Sun et al. 2010). Therefore, it is important and necessary to evaluate the health status of residents living near the mining areas. In the present work, Fenghuang polymetallic mine is divided into two regions according to its mine type, namely, Chatian mercury mining area (CMM) and Ciyan lead mining area (CLM). An agricultural village (Liaojiaqiao, LC) situated in the same county about 20 km north of the Fenghuang polymetallic mine, was selected as control area. The objective of this study is to examine the heavy metal (Cd, Pb, As, Hg, and Se) concentrations and behaviors in the scalp hair of residents from villages adjacent to Fenghuang polymetallic mine. The effects of gender and age on element concentrations were also considered.

## Materials and Methods

95 scalp hair samples (40 males and 55 females) were collected from residents living in the study sites in May 2008. Hair that was dyed or marcelled was not collected.

Y. Li (✉) · L. Yang · H. Li
Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China
e-mail: yhli@igsnrr.ac.cn

X. Zhang
Dongying Environmental Protection Bureau, Dongying 257091, China

During the process of collecting samples, each participant was asked to answer a questionnaire for basic information on age, sex, address, occupation, and whether he/she smokes. In order to eliminate external contamination, each sample was washed in a sequence of non–ionic detergent solution, tap–water, and Milli–Q water. The washed samples were air–dried at room temperature in a dust–free area and then cut into pieces less than 1 cm long ready for storage or digesting. About 0.1 g of the dried hair from each participant was subjected to a digestion in $HNO_3$–$H_2O_2$ solution (3:1 in v/v) at 120°C and diluted to 10 mL with Milli–Q water. The final solution for the determination contained 5 % nitric acid. The concentrations of Cd, Pb, As, Hg, and Se in the digestion solution were determined by inductively coupled plasma mass spectrometry (ICP-MS, Model 9000, PerkinElmer, USA). For quality assurance and quality control (QA/QC), method blanks, blank spikes, certified reference material (GBW9101b), and blind duplicates were used during analyses. The analytical results of Cd, Pb, As, Hg, and Se in the certified reference material were in good agreement with the certified values, with RSDs around 2.32 %–12.58 %. The percentage of recoveries on spiked samples ranged from 87 % to 110 % for the five elements in hair samples, and the relative percentage difference was <10 % for the elements in hair duplicate samples. The detection limits for Cd, Pb, As, Hg, and Se on ICP-MS were 15, 5, 40, 2, 34 ng $L^{-1}$, respectively.

Differences in metal concentrations in hair between groups were examined by the nonparametric test (such as Kruskal–Wallis H test, Mann–Whitney U test, etc.) and were considered to be significant when $p < 0.05$. Meanwhile, the Spearman's rank correlation was tested among all the analyzed metals existed in hair. All statistical analyses were performed using SPSS 16.0 (SPSS Inc.).

## Results and Discussion

The average concentrations of Cd, Pb, As, Hg, and Se in scalp hair of the 83 residents living in the mining areas (CMM and CLM) and their standard deviation are presented in Table 1. As can be seen, the average concentrations of the elements including Cd, Pb, As and Se were within the normal range of the general Chinese population, except for Hg. However, the average concentrations of all elements in hair of residents living around the mining areas were significantly higher than those of the 12 residents living in the control area. Table 2 summarizes the inter-element correlation in all the 95 hair samples. The coefficient between Cd–Pb, Cd–As, Pb–As, Se–As, and Se–Hg was positive and statistically significant. These correlations may be due to the natural geochemical background: both the CMM and CLM are typical low temperature hydrothermal combined Pb–Hg ore deposit with the presence of Cd, As, and Se as impurity elements (Li et al. 2009). Previous studies also observed there were significant correlations between Pb–Cd, As–Cd, and Hg–Se in local soil, water and crops (Sun et al. 2010). The inter-element correlation in hair was mainly affected by the geochemical background through a similar mechanism to that which affected inhabitants of the Azores, Portugal (Amaral et al. 2008).

It has been reported that several factors such as gender, age and geographic location affect trace elements levels in human hair. In this study, the participants were categorized by location (namely, CMM, CLM and LC) and tested for differences by using the Kruskal–Wallis test (Tables 3, 4). The results show that the average hair concentrations of Cd, As, Hg, and Se decreased in the order of CMM, CLM and LC, and Pb in the order of CLM, CMM and LC. Furthermore, significant differences ($p < 0.01$) were found in hair As, Hg, and Se concentrations in the three areas. The proportion of residents' hair elements burden exceeded the upper limit of the normal content in China (Qin 2004):

**Table 2** Spearman's rank correlation coefficients between the five trace elements

| | Cd | Pb | As | Hg |
|---|---|---|---|---|
| Pb | 0.73* | | | |
| As | 0.34* | 0.31* | | |
| Hg | −0.09 | −0.18 | 0.10 | |
| Se | 0.16 | 0.17 | 0.20** | 0.48* |

* Correlation significant at $p < 0.01$ level; ** Correlation significant at $p < 0.05$ level

**Table 1** Hair element levels in this study and normal range for Chinese people

| | No. of samples | Cd (mg $kg^{-1}$) | Pb (mg $kg^{-1}$) | As (mg $kg^{-1}$) | Hg (mg $kg^{-1}$) | Se (mg $kg^{-1}$) |
|---|---|---|---|---|---|---|
| LC | 12 | 0.11 ± 0.07 | 3.16 ± 2.12 | 0.05 ± 0.06 | 0.99 ± 0.42 | 0.47 ± 0.05 |
| CMM and CLM | 83 | 0.17 ± 0.18 | 8.67 ± 13.83 | 0.11 ± 0.37 | 2.19 ± 1.58 | 0.64 ± 0.35 |
| Value[a] | NA | 0.5 | 10.0 | 1.0 | 1.5 | NA |

*NA* not available

[a] The upper limit normal value in China (Qin 2004)

**Table 3** Characteristics of hair trace element concentrations in the three areas (mg $kg^{-1}$)

| Location | Element | Min | Max | Mean | SD | No. of samples |
|---|---|---|---|---|---|---|
| CMM | Cd | 0.02 | 1.01 | 0.19 | 0.20 | 31 |
| | Pb | 0.51 | 26.00 | 5.96 | 5.45 | 31 |
| | As | 0.02 | 3.38 | 0.19 | 0.60 | 31 |
| | Hg | 0.30 | 7.62 | 3.04 | 1.85 | 31 |
| | Se | 0.41 | 2.05 | 0.91 | 0.43 | 31 |
| CLM | Cd | 0.010 | 1.03 | 0.16 | 0.16 | 52 |
| | Pb | 0.55 | 113.00 | 10.29 | 16.82 | 52 |
| | As | 0.01 | 0.44 | 0.05 | 0.06 | 52 |
| | Hg | 0.43 | 6.58 | 1.67 | 1.14 | 52 |
| | Se | 0.26 | 0.83 | 0.48 | 0.11 | 52 |
| LC | Cd | 0.04 | 0.29 | 0.11 | 0.07 | 12 |
| | Pb | 0.87 | 8.69 | 3.16 | 2.12 | 12 |
| | As | 0.03 | 0.08 | 0.05 | 0.02 | 12 |
| | Hg | 0.44 | 2.08 | 0.99 | 0.42 | 12 |
| | Se | 0.40 | 0.55 | 0.47 | 0.05 | 12 |

**Table 4** Kruskal–Wallis H test for hair trace element concentrations in the three different areas

| | Cd | Pb | As | Hg | Se |
|---|---|---|---|---|---|
| *p* | 0.375 | 0.127 | 0.001 | 0.000 | 0.000 |

Cd, 9.7 % in CMM and 3.8 % in CLM; Pb, 16.1 % in CMM and 26.9 % in CLM; Hg, 80.6 % in CMM and 42.3 % in CLM. The highest concentrations of hair As, Hg, and Se in CMM matched the soil background in CMM, where the soil had a significantly higher concentration of As, Hg, and Se than the control area (Li et al. 2009). When the hair element concentrations in our study are compared with the results from other research, the hair Hg level in CMM is lower than Wanshan (Li et al. 2004) and Wuchuan (Li et al. 2008) Hg mining areas in Guizhou, China, but the concentrations of hair Hg in CLM are higher than Chaihe (Wu et al. 2007) lead/zinc mine area in Liaoning, China, and the hair burden of Cd, Pb, and As in CLM are at a lower range.

Recent studies from other research have found that the levels of toxic metal in hair, especially the levels of bio-accumulated Pb, Cd, and Hg, are increasing with age under normal conditions (Amaral et al. 2008; Barbieri and Gardon 2009). In this research, the participants were divided into three groups based on their age: (a) ≤14 years old (N = 18); (b) 15–60 years old (N = 65); (c) ≥61 years old (N = 11). No significant difference in element concentrations was found in all tested elements among the three age groups either in the whole study area or in the subdivided sites of CMM, CLM and LC, respectively (Table 5). That is to say, children showed the same level of metal exposure as the adults in the mining villages. Similar results were found by Li et al. (2008) showing that there is no appreciable change in hair Hg levels among different age groups in Wuchuan Hg mining area, China. Nevertheless, there is also research to support that an age difference exists in toxic metals concentrations. For example, Xu et al. (2008) found that the hair Hg level of adults was significantly higher than the level of children in Xiaoqinling gold mine area in Shaanxi province, China.

Table 5 shows that across all the samples (40 males and 55 females), hair Cd and hair Pb levels were significantly different for males and females. In CMM, the significant difference only exists for the Pb level and in CLM, the significant difference exists for Cd, Pb, and Hg. In all the 95 samples, the average hair Cd and Pb levels in females (Cd 1.76 mg $kg^{-1}$ and Pb 11.43 mg $kg^{-1}$) were higher than those in males (Pb 3.23 and Cd 1.39 mg $kg^{-1}$). In CMM, the average hair Pb in females was 8.35 mg $kg^{-1}$, which was higher than that of males (3.07 mg $kg^{-1}$). In CLM, the average hair Cd and Pb levels in females (Cd 0.19 mg $kg^{-1}$ and Pb 14.07 mg $kg^{-1}$) were higher than those in males (Cd 0.10 mg $kg^{-1}$ and Pb 3.73 mg $kg^{-1}$), but the average hair Hg was higher in males (1.98 mg $kg^{-1)}$ than in females (1.49 mg $kg^{-1}$). The variable levels of hair Cd, Pb, and Hg in males and females is possibly due to different environmental backgrounds

**Table 5** Mann–Whitney U test for the effect of age, gender, and mining activities on element concentrations

| Age | *p* | | | | |
|---|---|---|---|---|---|
| | Cd | Pb | As | Hg | Se |
| CMM + CLM + LC | 0.434 | 0.587 | 0.580 | 0.687 | 0.148 |
| CMM | 0.377 | 0.179 | 0.554 | 0.825 | 0.139 |
| CLM | 0.913 | 0.823 | 0.601 | 0.242 | 0.293 |
| CK | 0.355 | 0.407 | 0.489 | 0.366 | 0.237 |
| Gender | *p* | | | | |
| | Cd | Pb | As | Hg | Se |
| CMM + CLM + LC | 0.008 | 0.000 | 0.271 | 0.053 | 0.690 |
| CMM | 0.475 | 0.002 | 0.153 | 0.451 | 0.321 |
| CLM | 0.016 | 0.001 | 0.157 | 0.015 | 0.887 |
| LC | 0.372 | 0.168 | 0.223 | 0.291 | 0.372 |
| Mining activities | *p* | | | | |
| | Cd | Pb | As | Hg | Se |
| CMM + CLM | 0.470 | 0.528 | 0.554 | 0.095 | 0.627 |
| CMM | 0.922 | 0.628 | 0.961 | 0.005 | 0.354 |
| CLM | 0.328 | 0.287 | 0.373 | 0.550 | 0.737 |

(Strumylaite et al. 2004; Khalique et al. 2005). As a result, in the mining areas such as CMM and CLM, females were more vulnerable to exposure to Cd and Pb than males, even though males were more likely to expose to Cd and Pb from smoking than females (Satarug et al. 2004).

Results from the questionnaires show that 54.5 % of study participants in CMM and 64.7 % of those in CLM used to or continue to work in mining activities. The Mann–Whitney U test was used to determine the effect of mining activities on element concentrations, and the results in Table 5 suggest that the effect was negligible because the concentrations of most elements including Cd, Pb, As and Se in hair show no statistically significant differences between the residents who engaged in mining activities and those who did not. Only the concentration of hair Hg in CMM is statistically significant: the average concentration of Hg in hair of residents engaging in mining ($3.83 \pm 1.83$ mg kg$^{-1}$) was higher than that of those who were not in mining industry ($2.20 \pm 1.10$ mg kg$^{-1}$). Similar results were found in the Wanshan and Wuchang Hg mines in Guizhou, China (Li et al. 2004, 2008), the gold mine area in Shaanxi, China, and Canteiro Island, Brazil (Wu et al. 2007; Carvalho et al. 2009). In terms of the Hg burden in CMM, mining activities had no direct impact on the hair metals burden of residents living in CLM. This may be because of the differences in exposure routes and the environmental behaviors of various metals. Hg exists as liquid at normal room temperature and evaporates easily. Therefore, it is likely to be absorbed through skin or inhaled though the respiratory system. But other elements such as Pb, Cd, As, and Se are solid at standard conditions for temperature and pressure and so are less likely to enter the human body by dermal and/or respiratory intake.

Based on analyses of the hair samples collected from Fenghuang polymetallic mine area and a control area in this study, the results provide a better understanding of the human burden of exposure to heavy metals. To summarize, the hair of residents from the mining areas contained high concentrations of Hg, which exceeded the upper limit of the normal value of Hg in China. Affected by the geochemical background, significant correlations were found in hair inter-elements between Pb–Cd, As–Cd, As–Pb, and Se–Hg. There were high Pb and Hg burdens in the hair of residents living in CMM and CLM. Hair concentrations of elements in residents were significantly affected by gender but not by age. Children showed the same metal exposure levels as the adults in the mining villages. Females were more easily exposed to Cd and Pb pollution than males, and Hg mining activities might have made a significant contribution to the elevated hair Hg burden. Moreover, our study suggested that children and women in the mining areas were more susceptible to Cd and Pb pollution, and therefore, should be paid more attention to.

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