Investigation and health risk assessment of heavy metals in soils from partial areas of Daye city, China

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Abstract. Heavy metals (Cu and Pb) in four sampling sites from parts areas of Daye city were collected. Concentrations of Cu and Pb in soils in sampling sites were detected, the enrichment degree was measured by geo-accumulation index, and the human health risks were calculated by applying the human health risk assessment model. The results show that the concentrations of Cu and Pb of soils in some areas are much more than Daye City, Hubei Province soil background value. The concentration of Cu and Pb in Xiaganwan soil sample has a higher value and the concentration of Cu (110.17 mg·kg⁻¹) exceeds the soil environmental quality standards. The values of Igeo of Cu and Pb in the soil in some areas of Daye city are 1 except Xiaganwan sample is 2. For human health risk assessment, the non-cancer risk of Cu in three routes of exposure is less than Pb. The non-cancer risk both adults and children are less than 1 and show a general trend of HQ in oral ingestion exposure pathway > HQ in inhalation exposure pathway > HQ in skin contact exposure pathway. It will not cause significant non-carcinogenic health effects on the human body.

1. Introduction

Heavy metals in soil can cause great harm to the ecological environment for their toxicity, poor-biodegradability and bioaccumulation [1-2]. Heavy metals in soil can be absorbed by plants and accumulated in the animals and human through the food chain [3]. Human will also be harmed when contact with soils containing heavy metals or breathe in dust with heavy metals [4].

With the rapid development of urbanization and industrialization, the pollution of heavy metals in soil has become an urgent problem to be solved [5]. The area of cultivated land polluted by heavy metals including Cd, Pb, Cu, Hg, and Zn reach 20,000,000 square kilometers, which accounts for 20 percent of the total area of China [6]. Heavy metals soil pollution events happened frequently in recent year, such as Cadmium-tainted rice events in 2009, which lead to human health hazards [7].

Daye city is an important mining area with 273 mines in Hubei Province, which is rich in mineral resources, one of the six largest copper ore production bases [8]. Largely mineral extraction in Daye has made a tremendous contribution to local economic development and national construction. But a lot of heavy metals were produced in the process of mineral mining and processing. However, there are quite a few studies on the heavy metals (such as Cu, Pb, Cd, Zn, and as) in soil of Daye, especially on the health risk assessment of human exposure to heavy metals in soil [9].
The objectives of this work were: (1) to measure the concentrations of heavy metals (Cu and Pb) in soils of Daye, (2) to determine the enrichment degree of Cu and Pb in soils, (3) to assess the health risk of human including adults and children exposed to heavy metals applying the health risk assessment model.

2. Methods and materials

2.1. Study area
Daye city is the hinterland of “Metallurgical Corridor” in Hubei, with an area from 29°40′N to 30°15′N, 113°07′E to 114°02′E, located in the hilly land of the north side of Mufu mountain. Daye is the birthplace of Chinese modern industry, one of the earliest mining areas and the cradle of world bronze culture. Tonglv Mountain is the biggest copper mining area in Daye, has a history of over 3000 years, which has been collected into the United Nation's mining heritage list.

2.2. Sampling and analysis
Soils in 4 sampling sites (S1: Yangqiaocun, S2: Xiaganwan, S3: Shangrila community and S4: Yingcai road) were collected from Daye during Aug. 2015, referring to the NY/T1121.1-2006. The soil samples were collected in polytetrafluoroethylene (PTFE) bags and then transferred rapidly to the laboratory in Wuhan. In the laboratory, surface sediments were put evenly on the plastic film to dry naturally in a cool ventilated place. Then, sediments were crushed into small pieces by using pestles and mortals. Next, sediment samples were sifted in 10 mesh nylon sieves to remove stones and plant residue. Finally, all the sediment samples were sifted in 100 mesh sieves and were kept in the plastic bottles prior to analyses.

The soil acidity was measured by pH Meter (Mettler Toledo FE20K FiveEasy, China), using the method in the Industry standard (NYT 1377-2007). For the determination of total heavy metal content, 0.25g treated samples were weighed by an electronic analytical balance (Mettler Toledo-EL204, China). After that, the samples were put into digestion vessels and digested with HCL, HNO₃, HF, and HClO₄ by the graphite furnace digestion instrument. Then the solutions were diluted into a final volume of 50 ml with 2% (v/v) HNO₃. The heavy metal contents of Cu and Pb were all detected by Atomic Absorption Spectroscopy (AAS, ZEEnit700, Germany).

To ensure reliability and accuracy of the analysis results, the quality assurance and quality control were assessed strictly by using blank samples, parallel samples and standard reference materials (GB07423). The analysis results were reliable when repeat sample analysis error was below 5%, and the analytical precision for replicate samples was within ± 10%. Accepted recoveries of standard samples ranged from 90% to 108%.

2.3. Geo-accumulation index
To assess the enrichment degree of heavy metals in the soils of Daye, the geo-accumulation index (Igeo) was used. Igeo can be calculated by the following formula [10]:

\[ I_{geo} = \log_2 \left( \frac{C_i}{B_i} \right) \]  

Where, \( C_i \) is the actually measured concentration of the heavy metal in the samples. K is corrected coefficient, which take account variation of background value caused by anthropogenic influences or lithology variations in the sediments (in general k=1.5). \( B_i \) is the reference value of heavy metal concentration in sediments.

Igeo is classified into seven levels and its corresponding contamination degrees of heavy metal are as follows: (1) \( I_{geo} \leq 0 \), uncontaminated. (2) 0 < \( I_{geo} \leq 1 \), uncontaminated to moderately contaminated. (3) 1 < \( I_{geo} \leq 2 \), moderately contaminated. (4) 2 < \( I_{geo} \leq 3 \), moderately contaminated to heavily contaminate. (5)
3 < $I_{geo}$≤4, heavily contaminated. (6) 4 < $I_{geo}$≤5, heavily to extremely contaminate. (7) $I_{geo}$ > 5, extremely contaminate.

### 2.4. Health risk assessment

#### 2.4.1. Exposure assessment

In this work, the exposure routes of human exposure to Cu and Pb in soil of Daye were ingestion, skin contact and inhalation. Exposure doses of human exposure to pollutants through these three exposure routes can be calculated as follows [11-12]:

1. **Ingestion**
   
   $$ ADD_1 = \frac{CS \times IR \times CF \times FI \times EF \times ED}{BW \times AT} $$
   
   Where, $ADD_1$ is average daily doses in ingestion exposure pathway, $CS$ is chemical concentration in soil (mg·kg$^{-1}$), $IR$ is ingestion rate (mg·d$^{-1}$), $CF$ is conversion factor ($10^{-6}$ kg·mg$^{-1}$), $EF$ is exposure frequency (d·year$^{-1}$), $ED$ is exposure duration (a), $BW$ is body weight (kg), and $AT$ is averaging time (d).

2. **Skin contact**
   
   $$ ADD_2 = \frac{CS \times AF \times CF \times SA \times ABS \times EF \times ED}{BW \times AT} $$
   
   Where, $ADD_2$ is average daily doses in skin contact exposure pathway, $CS$ is chemical concentration in soil (mg·kg$^{-1}$), $AF$ is soil to skin adherence factor (mg/cm$^2$), $CF$ is conversion factor ($10^{-6}$ kg·mg$^{-1}$), $SA$ is the skin area available for contact (cm$^2$), $ABS$ is absorption factor (unitless), $EF$ is exposure frequency (d·year$^{-1}$), $ED$ is exposure duration (a), $BW$ is body weight (kg), and $AT$ is averaging time (d).

3. **Inhalation**
   
   $$ ADD_3 = \frac{CS \times PM10 \times DAIR \times PIAF \times FSPO \times CF \times EF \times ED}{BW \times AT} $$
   
   Where, $ADD_3$ is average daily doses in inhalation exposure pathway, $CS$ is chemical concentration in soil (mg·kg$^{-1}$), $PM10$ is the concentration of PM10 (mg·m$^{-3}$), $DAIR$ is daily air inhalation rate (m$^3$·d$^{-1}$), $PIAF$ is retention fraction of inhaled particulates in body (unitless), $FSPO$ is fraction of soil-borne particulates in air (unitless), $CF$ is conversion factor ($10^{-6}$ kg·mg$^{-1}$), $EF$ is exposure frequency (d·year$^{-1}$), $ED$ is exposure duration (a), $BW$ is body weight (kg), and $AT$ is averaging time (d).

#### 2.4.2. Non-carcinogenic risk assessment

$$ HI = HQ_1 + HQ_2 + HQ_3 = ( ADD_1 / RfD_1 ) + ( ADD_2 / RfD_2 ) + ( ADD_3 / RfD_3 ) $$

Where, $HI$ is hazard index of non-carcinogens (unitless). $HQ_1$, $HQ_2$ and $HQ_3$ are hazard quotients of ingestion, skin attach and inhalation. $ADD$ is average daily dose (mg·kg$^{-1}$·d$^{-1}$), and $RfD$ is reference dose (mg·kg$^{-1}$·d$^{-1}$). $HQ$ is hazard quotient of non-carcinogens, according to the recommended value by USEPA, $HQ$≤1 indicates no risk, $HQ$ > 1 indicates that risks do exist [13].

### 3. Discussion

#### 3.1. Pollution assessment

1. **Concentrations of heavy metals in soils.** Table 1 shows concentrations of Cu and Pb in soils from 4 sampling sites in Daye. The concentrations of Cu and Pb from each sampling sites are both
decreased in the order of S2 > S4 > S1 > S3. The concentrations of Cu and Pb in all sampling sites are higher than background values of Hubei. Specifically, measured value of Cu in S2 are exceed Grade II standard (GB 15618-1995).

3.1.2. Enrichment degree of heavy metals in soils. The $I_{\text{geo}}$ values of Cu in each sampling sites are decreased in the order of S2, S4, S1, S3, which were 1.26, 0.76, 0.49 and 0.42, respectively. Like Cu, the $I_{\text{geo}}$ values of Pb in each sampling site are decreased in the order of S2, S4, S1, S3, which were 1.38, 0.58, 0.27, and 0.07. And for both Cu and Pb, $I_{\text{geo}}$ values in S2 are at “uncontaminated to moderately contaminated” level while other sampling sites are at “uncontaminated” level.

**Table 1.** Concentrations of heavy metals in 4 sampling sites

| Sampling sites | pH | Cu (mg/kg) | Pb (mg/kg) |
|----------------|----|------------|------------|
| S1             | 7.45 | 64.59      | 48.21      |
| S2             | 7.24 | 110.17     | 104.47     |
| S3             | 7.99 | 61.54      | 41.93      |
| S4             | 8.18 | 77.76      | 60.01      |
| Mean           | 7.72 | 78.52      | 63.65      |
| Background (Hubei) | None | 30.70     | 26.70      |

| Grand II | 6.5<pH<7.5 | 100 | 300 |
| >7.5     | 100         | 350 |

![Fig. 1 $I_{\text{geo}}$ values of Cu and Pb in 4 sampling sites](image)

3.2. Human health risk assessment

According to exposure factors handbook of USEPA, combining with the actual situation of local residents, the exposure factors mentioned above was determined as in the following Table 2.

According to the arithmetic calculation from (2) to (4) and values of exposure factors listed in Table 2, the calculation results of ADD of Cu and Pb in soils from four sampling sites are in Table 3. As can be seen from Table 3, the values of $ADD_1$ and $ADD_3$ of children exposure to Cu and Pb are higher than adults while values of $ADD_2$ are lower than adults. Overall, children are in the higher level of exposure dose. For both adults and children, the average exposure dose of Cu are higher than Pb.
and the average exposure dose of three exposure pathways are decreased in the order of \( \text{ADD}_1 > \text{ADD}_3 > \text{ADD}_2 \).

The RfD of human exposure to Cu and Pb in different exposure pathways can be seen in Table 4. And the results of human health risk assessment were shown in Table 5. The HI of Cu and Pb in soil of Daye were exceed 1, and the HQ were both decreased in the order of HQ$_1 > HQ_3 > HQ_2$.

For both adults and children, the HQ of Cu under each exposure pathway was lower than HQ of Pb under corresponding pathways. And the HI of Cu and Pb are lower than 1, which means that there were no risks for adults and children. The HI values of children are much higher than adults, and the HI of children exposure to Pb was relatively to 1. It shows that children are at the higher level of health risk and more likely to exposure to heavy metals.

For 4 sampling sites, the HI of both adults and children exposure to Cu and Pb under different routes are decreased in the order of S2, S4, S1, S3.

### Table 2. Exposure factors of health risk assessment

| Factors | Reference Values | Sources |
|---------|-----------------|---------|
| IR      | IR$_{adults} = 100$, IR$_{children} = 200$ | [14-15] |
| CF      | $10^4$ | USEPA [16] |
| FI      | 1 | Maximum limit |
| EF      | $365 \times 9/24 = 200$ | [14] |
| ED      | ED$_{adults} = 74$, ED$_{children} = 6$ | [14] |
| BW      | BW$_{adults} = 60$, BW$_{children} = 16$ | [14] |
| AT      | EF \times ED | USEPA |
| AF      | AF$_{adults} = 0.07$, AF$_{children} = 0.2$ | [14,15] |
| SA      | SA$_{adults} = 5700$, SA$_{children} = 2800$ | [14,17] |
| ABS     | 0.001 | USEPA |
| PM10    | 0.3 | USEPA |
| DAIR    | DAIR$_{adults} = 20$, DAIR$_{children} = 7.6$ | USEPA |
| PIAF    | 0.75 | USEPA |
| FSPO    | 0.5 | USEPA |

### Table 3. ADD of Cu and Pb in soils from Daye City

| Element | Exposure pathway | Age   | S1   | S2   | S3   | S4   |
|---------|-----------------|-------|------|------|------|------|
| Cu      | ADD$_1$         | adults| 1.08E-04 | 1.84E-04 | 1.03E-04 | 1.30E-04 |
|         |                 | children | 8.07E-04 | 1.38E-03 | 7.69E-04 | 9.72E-04 |
|         | ADD$_2$         | adults| 4.30E-07 | 7.33E-07 | 4.09E-07 | 5.17E-07 |
|         |                 | children | 2.26E-06 | 3.86E-06 | 2.15E-06 | 2.72E-06 |
|         | ADD$_3$         | adults| 2.99E-05 | 5.10E-05 | 2.85E-05 | 3.60E-05 |
|         |                 | children | 3.45E-06 | 5.89E-06 | 3.29E-06 | 4.16E-06 |
|         | ADD$_2$         | adults| 8.03E-05 | 1.74E-04 | 6.99E-05 | 1.00E-04 |
|         |                 | children | 6.03E-04 | 1.31E-03 | 5.24E-04 | 7.50E-04 |
| Pb      | ADD$_1$         | adults| 3.21E-07 | 6.95E-07 | 2.79E-07 | 3.99E-07 |
|         |                 | children | 1.69E-06 | 3.66E-06 | 1.47E-06 | 2.10E-06 |
|         | ADD$_2$         | adults| 2.23E-05 | 4.83E-05 | 1.94E-05 | 2.78E-05 |
|         |                 | children | 2.58E-06 | 5.58E-06 | 2.24E-06 | 3.21E-06 |
Table 4. RfD of human health risk assessment

| RfD  | Cu     | Pb     | Sources [16] |
|------|--------|--------|--------------|
| RfD1 | 4.00E-02 | 3.50E-03| USEPA        |
| RfD2 | 1.20E-02 | 5.25E-04| USEPA        |
| RfD3 | 4.00E-02 | 3.52E-03| USEPA        |

Table 5. Human health risks exposure to heavy metals through different routes

| Health risk | HQ | Age | S1     | S2     | S3     | S4     |
|-------------|----|-----|--------|--------|--------|--------|
| HQCu        |    | adults | 2.69E-03 | 4.59E-03 | 2.56E-03 | 3.24E-03 |
|             |    | children| 2.02E-02 | 3.44E-02 | 1.92E-02 | 2.43E-02 |
| HQ1         |    | adults | 3.58E-05 | 6.11E-05 | 3.41E-05 | 4.31E-05 |
|             |    | children| 1.88E-04 | 3.21E-04 | 1.79E-04 | 2.27E-04 |
| HQ2         |    | adults | 7.47E-04 | 1.27E-03 | 7.12E-04 | 8.99E-04 |
|             |    | children| 8.63E-05 | 1.47E-04 | 8.22E-05 | 1.04E-04 |
| HQ3         |    | adults | 3.47E-03 | 5.93E-03 | 3.31E-03 | 4.18E-03 |
|             |    | children| 2.05E-02 | 3.49E-02 | 1.95E-02 | 2.46E-02 |
| HIPb        |    | adults | 2.30E-02 | 4.97E-02 | 2.00E-02 | 2.86E-02 |
|             |    | children| 1.72E-01 | 3.73E-01 | 1.50E-01 | 2.14E-01 |
| HQ1         |    | adults | 6.11E-04 | 1.32E-03 | 5.31E-04 | 7.60E-04 |
|             |    | children| 3.21E-03 | 6.96E-03 | 2.80E-03 | 4.00E-03 |
| HQ2         |    | adults | 6.33E-03 | 1.37E-02 | 5.51E-03 | 7.88E-03 |
|             |    | children| 7.32E-04 | 1.59E-03 | 6.37E-04 | 9.11E-04 |
| HQ3         |    | adults | 2.99E-02 | 6.48E-02 | 2.60E-02 | 3.72E-02 |
|             |    | children| 1.76E-01 | 3.82E-01 | 1.53E-01 | 2.19E-01 |

4. Conclusion
The concentration of Cu and Pb in 4 sampling sites were much higher than the background values of Hubei Province, it was shown that soils in parts of Daye was polluted in different degree. The average values of concentration of Cu and Pb not exceeded the national Grade II standard. From the calculated results of geo- accumulation index, Cu and Pb in soils in each sampling sites were enriched in varying degree and S2 was at a higher degree of enrichment. For human health risk assessment, the hazard quotients of human exposure to Cu and Pb under three routes were all lower than 1, it means that there was no risks on human. But the hazard quotients of children were much higher than adults, which were relatively closed to 1. Therefore, children in parts of Daye are probably suffered from heavy metals in soil.

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