Ecological risk assessment and carcinogen health risk assessment of arsenic in soils from part area of the Daye City, China

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Abstract. Soils in four sampling sites from part area of the Daye City were collected. Concentrations of arsenic (As) in soils in sampling sites were detected by Atomic Fluorescence Spectrometry, ecological risk was calculated by potential ecological risk index (RI) and human health risk was measured by human health risk assessment model established by USEPA. The results showed that, the total content of As in soils in Daye was decreased in the order of S4 (66.58 mg/kg)>S2 (44.73 mg/kg)>S3 (34.86 mg/kg)>S1 (21.84 mg/kg), concentrations in all sampling sites were higher than background values of Hubei Province. The potential risk and human health risk were decreased in the order of S4>S2>S3>S1 and S4>S3>S2>S1, respectively. Specially, S1, S2 and S3 were at low potential ecological risk while S4 was at moderate ecological risk. But there was no carcinogenic risk for human exposure to As in soil in Daye.

1. Introduction
Arsenic (As) is one of the constituent elements of human bodies, which is one of the most important elements for human health [1-2]. A small amount of intake of As promotes metabolism, but too much arsenic can cause poison [3]. Skin, respiratory system, gastrointestinal tract, cardiovascular system, nervous system and hematopoietic system of human will be damaged to varying degrees in long-term exposure to high arsenic environment [4]. The As was classified as carcinogen in class A by United States Environmental Protection Agency (USEPA) [5].

The As in soils consist mainly of natural source and anthropogenic source. Industrial and agricultural activities raise arsenic concentration in the soil, such as mining, smelting, burning of fossil fuels, using of pesticides and fertilizers [6-7]. In recent years, the investigation found that Hunan, Yunnan, Hubei and other areas are facing serious problems of arsenic pollution [8]. Daye is one of the key areas of heavy metal pollution in Hubei province, the heavy metal pollution has become a major obstacle for the sustainable development of the city [9].

As early as 3500 years ago, advanced mining and metallurgy industry was developed in Daye [10]. The economic development of Daye has been achieved at the cost of mineral resources. With the development of mining economy, the scale and intensity of mining have increased. Daye City was
polluted by heavy metals such as Cd, Pb, Cu, As and Hg which contained in the wastes produced in the process of mining and smelting. Particularly, during the process of mining and smelting nonferrous metals, a large number of wastes containing As enter the soil and water sources, and become an important source of environmental pollution [11-12].

The objects of this study were (1) to measure the concentration of As in soils from part area of the Daye City, (2) to investigate the potential ecological risk caused by As in soils, (3) to assess the health risk of human exposure to As using health risk assessment model.

2. Methods and materials

2.1. Study area

Daye city is located in the southeast of Hubei province, which is close to the South Bank of the middle reaches of the Yangtze river, with an area of 1566.3 km² (29°40′N to 30°15′N, 113°07′E to 114°02′E). Daye city is the hinterland of “Metallurgical Corridor” in Hubei, which is the birthplace of bronze culture in China and all over the world. The exploitation of mine has lasted for more than 2000 years. It is a resource-based city with mining and metallurgy as its leading industries.

2.2. Sampling and analysis

Soils in 4 sampling sites (including S1: Shangrila community, S2: Xiaganwan, S3: Yingcai road and S4: Yijing Garden) 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 mortars. 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, 0.15 g 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 and HNO₃ by the microwave digestion instrument. Then the solutions were diluted into a final volume of 50 ml with 1% (v/v) HCl. The heavy metal content of As detected by Atomic Fluorescence Spectrometry (AFS-9730, Haiguang, China) under appropriate analytical conditions. 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. Potential ecological risk

To further study degree of eco-risk of heavy metal pollution in soils, the potential ecological risk index method was introduced. The potential ecological risk index (RI) was established by Hakanson in 1980, which was based on the principles of sedimentology. It is widely used by scholars to assess the pollution and ecological risk of heavy metal in sediment. The toxicity of heavy metals and response of environment were adequately considered [13-14].

\[ E_r^i = T_r^i \cdot C_r^i \]  
\[ C_f^i = C_a^i / C_0 \] (2)
Where, $E_r^i$ is the potential risk of individual heavy metal, $T_r^i$ is the toxic-response factor for a given heavy metal, and it reflects toxic level and environmental sensitivity of the heavy metal. $C_f^i$ is the contamination factor, $C_a^i$ is the actually measured concentration of the heavy metal, and $C_0$ is the reference value of heavy metal concentration. For $T_r^i$, the values of As suggested by Hanson was 10. Soil background values for Hubei province were used as reference, and the values of As were 12.3 mg/kg. Five levels of $E_r^i$ is recommended by Hanson as in Table 1.

| Level | $E_r^i$ value | Extent of ecological risk of single metal |
|-------|---------------|------------------------------------------|
| I     | $E_r^i < 40$  | Low potential ecological risk            |
| II    | $40 \leq E_r^i < 80$ | Moderate ecological risk                    |
| III   | $80 \leq E_r^i < 160$ | Considerable ecological risk               |
| IV    | $160 \leq E_r^i < 320$ | High ecological risk                     |
| V     | $E_r^i \geq 320$ | Very high ecological risk                 |

2.4. Health risk assessment
In this study, the health risk of As was evaluated by human health risk assessment model established by the US Environmental Protection Agency (USEPA). According health risk assessment model recommended by USEPA, the human health risk was classified into carcinogen risk and non-carcinogen risk, and As has the carcinogen risk. Carcinogen risks reflect the probability of an individual exposed to the potential carcinogen developing cancer over a lifetime. Carcinogen risk assessment models have generally been based on the premise that risk is proportional to cumulative lifetime dose [15].

$$CR = LADD \times CSF$$

Where, CR is carcinogen risk, LADD is lifetime average daily dosed in inhalation exposure pathway; CSF is carcinogen slope factor (per mg/(kg·d)). Carcinogen risk exceed $10^{-4}$ was viewed as unacceptable, risk below $10^{-6}$ was viewed at no significant health effects, and risks at between $10^{-6}$ and $10^{-4}$ are generally considered an acceptable range. The LADD is typically an estimate of the daily intake of a carcinogenic agent throughout the entire life of an individual, which typically used in conjunction with the corresponding slope factor to calculate individual excess cancer risk. The carcinogen slope factor is an upper-bound estimate of risk per increment of dose that can be used to estimate risk probabilities for different exposure levels.

According to the local investigation, the main exposure routes of human exposure to As in soils of Daye was ingestion. Exposure doses of human exposure to pollutants through inhalation route can be calculated as follows [16]:

$$LADD_{inh} = \frac{C \cdot EF}{PEF \cdot AT} \left( \frac{R_{inh,child} \cdot ED_{child}}{BW_{child}} + \frac{R_{inh,adult} \cdot ED_{adult}}{BW_{adult}} \right)$$

Where, $LADD_{inh}$ is lifetime average daily doses in inhalation exposure pathway; C is concentration of heavy metal in soils (mg/(kg·d)); EF is exposure frequency (d/a), PEF is particle emission factor
(m³/kg); AT is average exposure time (d); \( R_{\text{inh,child}} \) and \( R_{\text{inh,adult}} \) are inhalation rate of child and adult, respectively (m³/d); \( E_{\text{D,child}} \) and \( E_{\text{D,adult}} \) are exposure durations (a) of children and adult, respectively; \( BW_{\text{child}} \) and \( BW_{\text{adult}} \) are body weights (kg) of children and adult, repectively.

3. Results and discussion

3.1. Concentrations of arsenic in soils

The average concentrations of As in soils from 4 sampling sites in Daye City were shown in Table 1. The concentration of As from each sampling sites were decreased in the sequence of S4 (66.58 mg/kg) > S2 (44.73 mg/kg) > S3 (34.86 mg/kg) > S1 (21.84 mg/kg). The concentrations of As in all sampling sites are higher than background values of Hubei. The concentration of As in S2, S3 and S4 exceeded Grand II standard (GB 15618-1995) while S1 was lower than Grand II standard.

| Table 2. Concentrations of As from 4 sampling sites in the Daye City. |
|------------------|-----------------|------------------|
| Sampling site    | pH              | Concentration(mg/kg) |
| S1               | 7.99            | 21.84            |
| S2               | 7.24            | 42.73            |
| S3               | 8.18            | 34.86            |
| S4               | 7.42            | 66.58            |
| Background (Hubei)| None            | 12.3             |
| Grand II         | 6.5<pH<7.5      | 30               |
|                  | >7.5            | 25               |

3.2. Potential ecological risk assessment

According to the arithmetic calculation from (1) to (2), calculated results of potential ecological risk assessment for As were shown in Fig. 1. The \( E'_{i} \) values for As were decreased in the order of S4 > S2 > S3 > S1, which were 54.13, 34.74, 28.34 and 17.76, respectively. \( E'_{i} \) values for As in S1, S2 and S3 were under low potential ecological risk while in S4 was under moderate ecological risk.

![Figure 1. \( E'_{i} \) values of As in 4 sampling sites.](image)

3.3. Health risk assessment

Based on exposure factors handbook of USEPA, combining with the academic research and report published by USEPA, the exposure factors mentioned above was determined as in the following Table 3. According to the arithmetic calculation from (2) to (4) and values of exposure factors listed in Table 3, the calculation results of human health risk assessment exposure to As in soils from four sampling sites were shown in Table 4.
The carcinogenic risk of human exposure to As in soils from four sampling sites in Daye City were decreased in the order of S4>S3>S2>S1, which were 5.55E-08, 3.74E-08, 3.56E-08 and 1.82E-08, respectively. And risk of S4 was much higher than other sites due to its higher concentration of heavy metal in soil. Human health risks in all sampling sites were lower than 1E-06. It proved that there was no carcinogenic risk for human exposure to As in soil in Daye.

Table 3. Exposure factors of health risk assessment.

| Factors | Reference Values (Children) | Reference Values (Adults) |
|---------|----------------------------|---------------------------|
| EF (d/a) | 180                        | 180                       |
| PEF (m³/kg) | 1.36E+09                   | 1.36E+09                  |
| AT (d)   | 74×365                     | 74×365                    |
| ED (a)   | 6                          | 24                        |
| R inh (m³/d) | 7.63                     | 20                        |
| BW (kg)  | 15.9                       | 56.8                      |
| CSF (mg/(kg·d)) | 1.5E+01                  | 1.5E+01                   |

Table 4. Human health risk assessment of As in soils in Daye City.

| Sampling site | LADD inh | CR   |
|---------------|----------|------|
| S1            | 1.21E-09 | 1.82E-08 |
| S2            | 2.37E-09 | 3.56E-08 |
| S3            | 2.49E-09 | 3.74E-08 |
| S4            | 3.70E-09 | 5.55E-08 |

4. Conclusion
Concentration of As in soils from the Daye City was detected. The concentration of As in S2, S3 and S4 were exceed Grand II standard (GB 15618-1995) while S1 was lower than Grand II standard. It was shown that soils from the Daye may be polluted by As in different degree. The results of potential ecological risk assessment showed that, the ecological risk for As were decreased in the order of S4>S2>S3>S1. Specially, S1, S2 and S3 were at low potential ecological risk while S4 was at moderate ecological risk. The health risk of human exposure to As in each sampling sites were decreased in the order of S4>S3>S2>S1. The result of human health risk assessment agrees with the result of the potential ecological with some departure. More human health risks in all sampling sites were lower than 1E-06 which means that there was no carcinogenic risk for human exposure to As in soil in Daye.

Acknowledgments
This study was financially supported by the Humanities and Social Sciences Foundation of Ministry of Education of China (17YJCZH081), the Science and Technology Research Project of Hubei Provincial Education Department (B2017601) and the Open Fund from Institute of Wuhan Studies (IWHS20172005).

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