Risk Assessment of Heavy Metals in Soils of a Lead-Zinc Mining Area in Hunan Province (China)

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Abstract

Eighty-two soil samples were collected, and As, Pb, Cd, Zn, Cu and Ni were analysed for their concentrations, potential ecological risks and human health risks. The average concentrations of As, Pb, Cd and Zn exceeded their corresponding limits prescribed by the Chinese National Soil Environmental Quality Standard III, while Cu and Ni were far less than prescribed. The potential ecological risk index results indicated that Cd showed severe potential ecological risk. The human health risk assessment indicated that 80.49 % of the soil samples expressed acceptable non-carcinogenic risks, while 19.51 % of the soil samples expressed unacceptable non-carcinogenic risks. The research area represents unacceptable carcinogenic risks, the major contributor of the risk being As. Of the soil samples, 34.15 % posed acceptable carcinogenic risks, and 65.85 % posed unacceptable carcinogenic risks.

Keywords

Heavy metals, mining area, ecological risk, human health risk, non-carcinogenic risk, carcinogenic risk

1 Introduction

Heavy metals are persistent, irreversible, and toxic pollutants of great environmental concern.1–3 They are released by natural weathering of minerals and human activities. Mining and smelting operations are significant sources of heavy metal contamination in soil.4 Heavy metal pollution of soil can have adverse effects on the agricultural production and inhabitants’ health around mining areas.5–7

Hunan Province is regarded as the heartland of Chinese non-ferrous mining.8 Qingjiang town, located in the Chenzhou city of Hunan Province, is very rich in Pb-Zn mineral resources. It has a long history of Pb-Zn mining activities since the Qing dynasty. Thus, investigation of heavy metal content in soils and evaluation of the potential risks and human health risks from heavy metals in this mining area are of vital importance to better understanding the long-term impact of Pb-Zn mining activities on the environment around the mining areas and the inhabitants’ health.

It has been known that Pb-Zn mining and smelting leads to considerable heavy metal pollution in the soil of the surrounding area.9,10 Some studies have focused on the heavy metal pollution in Pb-Zn mining areas. F. Douay et al.11 studied the long-term effects of the smelter after its shutdown by combining data on the degree of soil contamination and the quality of the crops grown in these soils for a better assessment of the local population’s exposure to Cd, Pb, and Zn. They found that the high contamination level of the soils studied continues to be a risk for the environment and the population’s health. F. J. Xu et al.12 reviewed studies on the environmental and human health consequences of Pb-Zn mineral exploitation, and drew a conclusion that most of the reviewed cases of water, soil, and crop pollution and human health risk were caused by Pb and Zn. B. Li et al.13 conducted a field survey to investigate the present situation and health risk from heavy metals in the soil near a zinc smelter, and the results showed that the smelting had caused significant Cd and Zn contamination and is imposing a health risk to local residents via vegetable consumption. S. C. Obiora et al.14 determined the heavy metals concentration in arable soils and associated food crops around the Pb-Zn mines in Enyigbigha and found that Pb had a high health risk index. However, more comprehensive investigations including heavy metal concentrations, potential ecological risk assessment, and human health risk assessment of heavy metals in Pb-Zn mining area have been rarely documented.

In this study, the Qingjiang Pb-Zn mining area was chosen as the study area. The concentrations of As, Pb, Cd, Zn, Cu and Ni were determined to study the heavy metal pollution levels. To further study the ecological risk posed by heavy metals in the mining area, the potential ecological risk index method (PERI) suggested by Hakanson15 was applied. Moreover, the carcinogenic and non-carcinogenic risks of As, Pb, Cd, Zn, Cu and Ni were analysed in the study area using the exposure assessment model from China’s Technical Guidelines for Risk Assessment of Contaminated Sites16 and the human health risk assessment model from the United States Environmental Protection Agency (USEPA). The study can provide basic information on heavy metal pollution control and human health risk assessment management in the study region.
2 Materials and methods

2.1 Sample collection

The geographic coordinates of the study area is longitude 113°17′17.76″ E ~ 113°17′36.07″ E, latitude 25°45′39.29″ N ~ 25°46′1.13″ N, located in the Qingjiang County, Chenzhou City, Hunan Province. Eighty-two soil samples were collected according to regulations and standards (GB/T 15618-1995). The top 5 cm of soil were discarded, the 5–20 cm tillage layer was sampled in the surface soil, and the impurities were removed. Each sample was picked out from a mixture of 3–5 subsamples for 1 kg or so by quarter method. Soil samples were pretreated and processed according to the book “Modern analytical methods of soil elements” and the relevant national standards (GB/T 17141-1997, GB/T 17138-1997, GB/T 17139-1997, GB/T 22105.2-2008), in order to reach the requirements of laboratory analysis.

2.2 Assessment method

To determine the environmental heavy metal pollution and the ecological damage caused by heavy metals in the soil around the mining area, the potential ecological risk index method proposed by Swedish scholar Hakanson was employed. This method not only considers the heavy metal pollution level in soil, but also links their ecological, environmental and toxicological effects, and quantitatively determines the level of potential ecological risk. The assessment procedure followed the Eq. (1). 18

\[
RI = \sum_{i=1}^{6} E_i \cdot C_i
\]

where \( C_i \) is the contamination factor, \( RI \) is the potential ecological risk index, \( E_i \) is the ecological risk factor, \( T_{ci} \) is the toxic-response factor of heavy metal (i): \( T_{cPb} = T_{cAs} = T_{cCu} = 5, T_{cCd} = 30, T_{cZn} = 10, T_{cAs} = 1 \).

Indices and grades for dividing the potential ecological risk level — \( E_i \) < 10, low; 10 ≤ \( E_i \) < 50, moderate; 50 ≤ \( E_i \) < 100, considerable; \( E_i \) ≥ 100, very high. Indices and grades for dividing ecological risk level of heavy metal pollution — \( RI \) < 150, low; 150 ≤ \( RI \) < 300, moderate; \( RI \) ≥ 300, very high.

2.3 Human health risk assessment

In this study, Zn, Pb, Cd, As, Cu and Ni were identified as potential contaminants with regard to human health. Considering the residents’ living habits and daily activities, they are exposed to soil heavy metals through soil ingestion, dermal contact, and air inhalation. Average daily dose values (ADD) of contaminants were calculated using Eqs. 2, 3, and 4 in different exposure pathways. Cancer and non-cancer health risks were determined using Eqs. 6 and 8. The meaning of the parameters in these equations and their values are given in Table 1.

\[
ADD_{ingest} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times CF
\]

\[
ADD_{dermal} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF
\]

\[
ADD_{inhale} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \times CF
\]

\[
HQ = \sum_{i} \frac{ADD_i}{RID_i}
\]

\[
HI = \sum_{i} HQ_i
\]

\[
CR = \sum_{i} ADD_i \times SF_i
\]

\[
TCR = \sum_{i} CR_i
\]

where, \( C \) is heavy metal concentration (mass fraction) in soil; \( HQ \) is hazard quotient of heavy metal; \( HI \) is hazard index of heavy metal, indicating the cumulative non-cancer risks; \( CR \) is cancer risk of heavy metal; \( TCR \) is the total carcinogenic risk index. \( RID \) is the corresponding reference dose (mg kg\(^{-1}\) d\(^{-1}\)); \( SF \) is the corresponding slope factor (per mg kg\(^{-1}\) d\(^{-1}\)); and the \( RID \) and \( SF \) values for certain heavy metals are given in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>IngR, soil ingestion rate</td>
<td>100 mg d(^{-1})</td>
</tr>
<tr>
<td>EF, exposure frequency</td>
<td>350 d a(^{-1})</td>
</tr>
<tr>
<td>ED, exposure duration</td>
<td>24 d</td>
</tr>
<tr>
<td>CF, exposure frequency</td>
<td>10(^{-6}) d a(^{-1})</td>
</tr>
<tr>
<td>BW, body weight</td>
<td>56.8 kg</td>
</tr>
<tr>
<td>AT, average time</td>
<td>365 × ED</td>
</tr>
<tr>
<td>SA, skin area exposed to soil contact</td>
<td>5700 cm(^2)</td>
</tr>
<tr>
<td>AF, soil-to-skin adherence factor</td>
<td>0.07 kg cm(^{-2}) d(^{-1})</td>
</tr>
<tr>
<td>ABS, absorption factor</td>
<td>0.001</td>
</tr>
<tr>
<td>InhR, inhalation rate</td>
<td>14.5 m(^3) d(^{-1})</td>
</tr>
<tr>
<td>PEF, particle emission factor</td>
<td>1.36 × 10(^9) m(^3) kg(^{-1})</td>
</tr>
</tbody>
</table>

a – the general symbol for year (fr. année, lat. annum)

3 Results and discussion

3.1 Concentrations of heavy metals

Heavy metal concentrations of the soil samples are presented in Table 3. Results of statistical analysis indicated that the average concentrations of heavy metals As, Pb, Cd and Zn in the samples exceeded the limits prescribed by the Chinese National Soil Environmental Quality Standard III, with exceeding multiples As (1.11), Pb (0.57), Cd (6.32), Zn (0.88). The exceeding ratios of the four heavy
metals ranged in the sequence: Cd > As > Pb > Zn, slightly different from the exceeding multiples sequence. The Cu and Ni in the soils were close to the corresponding background value of soils in Hunan Province, China (BG), and far less than prescribed by the Chinese National Soil Environmental Quality Standard III. The standard deviations of heavy metals were relatively high compared to the concentrations, manifesting a large varied amplitude of heavy metal concentrations in soil samples.

3.2 Potential ecological risk assessment

Table 4 shows the ecological risk factors and potential ecological risk index. According to Table 4, the average ecological risk factors of As, Pb, Cd, Zn, Cu and Ni were 21.07, 7.84, 219.58, 1.88, 0.30, and 0.64 respectively. The ecological risk sequence of the heavy metals was Cd > As > Pb > Zn > Ni > Cu. The ecological risk factors of As, Pb, Zn, Cu and Ni were much less than 40, indicating low risk. However, the average ecological risk factor of Cd was 219.58, which was greater than 160 and less than 320, indicating that it posed a severe potential ecological risk.

Table 4 also shows that the index range of potential ecological risk ranges from 163.94 to 385.05, and the average index of potential ecological risk factors (RI) was 251.31, which was greater than 150 and less than 300, indicating a moderate potential ecological risk. However, the maximum potential ecological risk index of soil in the study area was as high as 385.05, which was greater than 320, indicating a very high potential ecological risk, which should be given rise to widespread concern.

3.3 Human health risk assessment

The non-carcinogenic and carcinogenic risks posed by As, Pb, Cd, Zn, Cu and Ni in soils of the research Pb-Zn mining area for humans, through different exposure pathways (soil and dust ingestion, dermal contact and air inhalation),
were evaluated. Table 5 shows the average health risks posed by heavy metals in the research soils through different pathways.

### 3.3.1 Non-carcinogenic risk

Table 5 suggests that people living around the research area are exposed to acceptable non-carcinogenic risk, since the total average non-carcinogenic risk index of six kinds of heavy metals (As, Pb, Cd, Zn, Cu, Ni) under three different pathways was $9.01 \times 10^{-1}$, which was less than 1 (threshold value), indicating that people can be exposed to such circumstances for a long time with no evident non-carcinogenic risk impact on human health. The sequence of the non-carcinogenic risk for heavy metals was: As > Pb > Cd > Zn > Ni > Cu. And the non-carcinogenic risk for exposure pathways ranged: ingestion > dermal contact > inhalation. Fig. 1 shows the non-carcinogenic risks distribution characteristics of the sampled 82 soil samples. It illustrates that 80.49 % of the soil samples expressed acceptable non-carcinogenic risks, and the rest 19.51 % of the soil samples posed unacceptable non-carcinogenic risk. These sample spots should be paid attention to and long-term contact should be avoided.

### 3.3.2 Carcinogenic risk

According to Fryer et al., carcinogenic risks exceeding $1 \times 10^{-4}$ are considered unacceptable, risks between $1 \times 10^{-6}$ and $1 \times 10^{-4}$ are viewed as acceptable, whereas risks below $1 \times 10^{-6}$ are viewed as no significant health effects. As shown in Table 5, the average carcinogenic risk index of As, Pb, Cd, Ni under three exposure pathways exceeded $1 \times 10^{-4}$, indicating that the research area posed an unacceptable carcinogenic risk. To be specific, As is the major contributor of the risk, and the heavy metal carcinogenic risks ranged: As > Pb > Cd > Ni. In addition, the risks for pathways were: ingestion > dermal contact > inhalation. Fig. 2 shows the carcinogenic risks distribution in 82 soil samples. It reveals that 34.15 % of the soil samples posed acceptable carcinogenic risks, 65.85 % of the soil samples posed unacceptable carcinogenic risks, which means that corresponding methods that can reduce risks should be brought out.

### 4 Conclusions

(1) The average concentrations of As, Pb, Cd and Zn in the samples exceeded their corresponding limits prescribed...
(2) The sequence of the potential ecological risks was Cd > As > Pb > Zn > Ni > Cu. Cd posed severe risk for the ecological environment. The average index of potential ecological risk factors (RI) was 251.31, indicating a moderate potential ecological risk. The maximum potential ecological risk index of soil in the study area was as high as 385.05, indicating a very high potential ecological risk, which should be given rise to widespread concern.

(3) The sequence of the non-carcinogenic risk of heavy metals was: As > Pb > Cd > Zn > Ni > Cu. The non-carcinogenic risk for exposure pathways ranged: ingestion > dermal contact >> inhalation. Of the soil samples, 80.49% expressed acceptable non-carcinogenic risks and 19.51% of the soil samples expressed unacceptable non-carcinogenic risks. The research area represents unacceptable carcinogenic risks. The carcinogenic risks caused by heavy metals ranged: As > Pb > Cd > Ni, and the risk for pathways was: ingestion > dermal contact >> inhalation. Of the soil samples, 34.15% posed acceptable carcinogenic risks, 65.85% posed unacceptable carcinogenic risks, which means that corresponding methods that can reduce risks should be brought out.

ACKNOWLEDGEMENTS

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List of abbreviations and symbols

PERI – potential ecological risk index
ADD – average daily dose
RI – potential ecological risk index
C – heavy metal mass fraction in soil, mg kg⁻¹
HQ – heavy metal hazard quotient
HI – heavy metal hazard index
CR – cancer risk of heavy metal
TCR – total carcinogenic risk index
RD – corresponding reference dose, mg kg⁻¹
SF – corresponding slope factor, mg kg⁻¹
Cᵣ – contamination factor
Eᵣ – ecological risk factor
Tᵣ – heavy metal toxic-response factor

References

14. S. C. Obiora, A. Chukwu, T. C. Davies, Heavy metals and health risk assessment of arable soils and food crops around...


SAŽETAK
Procjena rizika za zdravlje zbog teških metala u tlu na području rudarenja olova i cinka u provinciji Hunan (Kina)
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Koncentracija As, Pb, Cd, Zn, Cu i Ni te određena je u 82 uzorka tla te procijenjen potencijalni ekološki rizik i rizik za ljudsko zdravlje. Prosječna koncentracija As, Pb, Cd i Zn prelazi granicu zadanu standardima GB15618-1995 III, dok je bakra i nikla bilo znatno manje. Za kadmij je utvrđen velik indeks potencijalnog ekološkog rizika. Prema procjeni rizika za ljudsko zdravlje 80,49 % uzoraka tla pokazuje prihvatljiv nekarcinogeni rizik. Istraživano područje predstavlja neprihvatljiv karcinogeni rizik, čemu najviše doprinosi arsen. Neprihvatljiv karcinogeni rizik pokazuje 65,85 % uzoraka tla.

Ključne riječi
Teški metali, rudarsko područje, ekološki rizik, rizik za ljudsko zdravlje, nekarcinogeni rizik, karcinogeni rizik

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