Health risk assessment of heavy metal pollution in farmland downstream of Lead-zinc smelter

Jingjing Liu1, 2, Yanlong Ma1, Songlin Zhang1,*, Yiming Yao1, Xiaoping Wang2, Tao Chen2, Youxiang He2 and Jianhong Qi2

1Department of Environmental Engineering, Northwest Normal University, Lanzhou, 730070, China
2The Third Institute of Geology and Mineral Exploration and Development, Gansu Bureau of Geology and Mineral Exploration and Development, Lanzhou 730050, China

*The first author’s e-mail: 1603305057@qq.com
Corresponding author’s e-mail: zhangsonling65@163.com

Abstract. In order to investigate whether heavy metals in farmland soils downstream of the abandoned lead-zinc smelter are harmful to local human health, the Plum blossom and diagonal sampling methods were used to collect the soil samples of cultivation layer (0~25cm) from the farmland soils downstream of the abandoned lead-zinc smelter, Hui County, Gansu province, P. R. China at the end of December, 2019. The US EPA health risk assessment model was used to analyse the impact of the selected five heavy metals (Pb, As, Cr, Hg and Cd) on the physical health of local residents. The results showed that the average value of the total non-carcinogenic risk index of these five heavy metals in the soil of the three plots in the study area was 6.71 for children and 4.27 for adults, both of which were greater than 1, it meant that there were non-carcinogenic risk to both children and adults. The average cancer risk index of these five heavy metals for children was 4.49×10⁻⁴, and that for adults was 2.51×10⁻⁴, both of which are greater than 1×10⁻⁴, which is a notable cancer risk for local residents. The results provided a significant support for remediation and treatment of heavy metal contaminated farmland.

1. Introduction
In 2014, the Ministry of Environmental Protection conducted a spot check on hazardous heavy metals in 300,000 hectares of basic farmland soil, and found that the rate of heavy metals exceeding the standard was 12.1% [1]. The heavy metal pollution caused by mining and smelting was one of the biggest sources of soil heavy metal pollution [2]. The farmland soil polluted by heavy metals would do harm to the health of surrounding residents [3, 4]. In recent years, scholars [5-8] investigated the soil polluted by heavy metals all over the world and found that different mining areas [9, 10] caused different heavy metal pollution to the soil, and even the same mining area [11, 12] caused slightly different heavy metal pollution to the soil. Although there were many reports on the soil around the smelter in the existing literature [13], there were only a few literatures on the health risk assessment of heavy metal pollution in the farmland soil around the smelter. Hui county is located in the second largest lead-zinc ore belt in China, where the lead-zinc ore reserves are rich, derivative lead-zinc smelters are also numerous. Therefore, it is necessary to assess the risk of human health caused by
heavy metal pollution in the farmland around the lead-zinc smelter in Hui County, which is of great significance to maintain the health of residents around the local lead-zinc smelter.

This paper selected the farmland around an abandoned lead-zinc smelter in Hui County as the object of study, the US EPA health assessment model was used to evaluate the human health risks from the farmland soil contaminated with five heavy metals (Pb, As, Cr, Hg and Cd). It could provide important reference value for the rational utilization of local soil and the health protection of local residents, and is conducive to the later remediation of soil contaminated by heavy metals.

2. Materials and methods

2.1. Overview of the Research Area

The study area locates in Liulin Town, Hui County, Gansu province, P. R. China, its latitude and longitude is 106°10′06″~106°11′13″N, 33°51′46″~33°52′28″E (Figure 1). The terrain here is high in the east and low in the west. The lead-zinc smelter was founded in 1994 that located in the Jialing River tributary Yongning River upstream right bank east highland, and it ceased operations in 2008 and was closed in 2012, and finally eliminated the source of lead-zinc pollution. The farmland which is located in the west lower part of the terrain was greatly affected by the heavy metals from the smelter through the precipitation runoff, the atmospheric deposition, and the waste water irrigation.

2.2. Setting of sample plots

The types and boundaries of the sample plots were divided by the route of contamination of downstream farmland during the operation stage of the lead-zinc smelter. (1) The plot 1 polluted mainly by the emissions from the smelter and road transportation covered roughly 70,848 square meters. (2) The plot 2 polluted by the sewage irrigation and the atmospheric deposition covered roughly 25,694 square meters. (3) The plot 3 polluted mainly by irrigation with smelting sewage, covering roughly 99,044 square meters. The shapes of the plots were irregular (Figure 1).

Figure 1. location and sampling point distribution of the study area.

2.3. Sample collection and analysis

2.3.1. Sample collection. The soil samples of the tillage layer only 0–25cm thick in the study area were collected according to the "soil monitoring technical specifications" (HJ/T 166-2004) [14]. The Plum blossom and diagonal sampling methods were selected in order to ensure the sample representative. A 1kg soil sample was taken by a quartering method and put into the sample bag.
Meanwhile, the number of sample points, the sampling position, the sampling date, the soil colour, the vegetation and surrounding environment of the sample points were recorded.

2.3.2. Sample analysis. The five heavy metals Hg, Pb, Cd, As and Cr in the soil pollution risk control project of agricultural land were taken as the analysis objects and the human health risk assessment factors. The samples were dried naturally at room temperature, grounded, and passed through the 100 mesh sieve, and stored in the plastic bottles at low temperature for testing. In strict accordance with the "soil environmental quality of farmland soil pollution risk control standard (trial)" (GB 15618-2018) [15], the heavy metals in the soil samples were tested by the inductively coupled plasma mass spectrometer((ICP-MS, NexION300X, Perkin Elmer company), the atomic fluorescence photometer (AFS, AFS-830, Shanghai Shuangxu electronics company), and the inductively coupled plasma emission spectrometer ((ICP-OES, ICAP7400, Thermo Fisher science and technology company).

2.4. Data processing and analysis
The Excel 2010 was used to sort out the heavy metal content data of the collected samples, and the SPSS 21.0 was used for statistical analysis. The human health risks of the local population were assessed according to the following methods.

2.4.1. Sample collection. The US EPA Health Risk Assessment Model [16]: We referred the health risk model and recommended standards proposed by US EPA to the methods and standards for human health risk assessment of heavy metal pollution in farmland soil.

\[
ADD_{\text{ing}} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6}
\]

\[
ADD_{\text{inh}} = \frac{C \times InhR \times EF \times ED}{PF \times BW \times AT} \times 10^{-6}
\]

\[
ADD_{\text{derm}} = \frac{C \times SA \times SD \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}
\]

ADD<sub>ing</sub>, ADD<sub>inh</sub> and ADD<sub>derm</sub> are acceptable daily intake dosage ingested, inhaled and dermal in units of mg. (kg d)<sup>-1</sup>. C is the content of heavy metals in soil, in mg.kg<sup>-1</sup>.The parameter in formula (1), (2), (3) were selected from the data in Table 1, which came from the literature of Wang et al. [17].

| Parameter | Units | Child | Adult | Meaning |
|-----------|-------|-------|-------|---------|
| IngR      | mg·d<sup>-1</sup> | 200   | 100   | Ingested rate |
| InhR      | m<sup>3</sup>·d<sup>-1</sup> | 5     | 20    | Inhaled rate |
| EF        | d·a<sup>-1</sup> | 350   | 350   | Exposure frequency, |
| ED        | a     | 6     | 24    | Exposure duration |
| BW        | kg    | 15    | 55.9  | Body weight |
| AT        | d     | 30×365 (Non-carcinogenic), 70×365(Carcinogenic) | Average time |
| PF        | m<sup>3</sup>·kg<sup>-1</sup> | 1.36×10<sup>9</sup> | 1.36×10<sup>9</sup> | Particulate release factor, |
| SA        | cm<sup>2</sup> | 1800  | 5000  | Skin exposure area |
| SD        | mg·cm<sup>-2</sup> | 1     | 1     | Skin adhesion degrees |
| ABS       |       | 0.001 | 0.001 | Adsorption factor of skin |

The formula for calculating the carcinogenic and non-carcinogenic effects of heavy metals on human health [17] is as follows:
HI is the non-carcinogenic risk index of multiple substances or multiple exposure modes of a substance, which has no dimension. \( HQ_i \) is a Non-carcinogenic health risk index of Non-carcinogenic heavy metal \( i \), which has no dimension. \( ADD_{ij} \) and \( RfD_{ij} \) are the daily exposure and reference doses of non-carcinogenic heavy metal \( i \) in the \( j \) exposure pathway, respectively, in mg.\( \text{kg}^{-1} \). \( ADI_{ij} \) is the average daily exposure in the \( j \) exposure pathway of carcinogenic heavy metal \( i \), and its unit is mg. \( \text{kg}^{-1} \). \( SF_{ij} \) is a dimensionless slope coefficient of exposure pathway in \( j \) of carcinogenic heavy metal \( i \). The \( RfD \) and \( SF \) reference values of each heavy metal are shown in Table 2[18]. When the HI \( \leq 1 \), it indicates that there is no risk of non-carcinogenic influence. When HI > 1, it means there is a risk of non-carcinogenic influence, and the non-carcinogenic possibility increases with the increase of HI value. CR is a dimensionless carcinogenic risk of multiple substances or multiple exposure modes of a substance. According to the US EPA recommendation, if CR < 10\(^{-6} \) is considered to be secure, if 10\(^{-6} \) < CR < 10\(^{-4} \) is considered to be a cancer risk but receivable. If CR > 10\(^{-4} \) is considered to be a cancer risk.

### Table 2. Values of the \( RfD \) and \( SF \) of different heavy metal exposure pathways [18].

| Heavy metals | \( RfD \) (mg.(kg\( \cdot \text{d} \))-1) | SF/(kg\( \cdot \text{d}^{-1} \cdot \text{mg}^{-1} \)) |
|--------------|-----------------|-----------------|
|              | Ingested | Inhaled | Dermal | Ingested | Inhaled | Dermal |
| As           | 0.0003   | 0.000123 | 0.00301 | 1.5 | 0.00043 | 1.5 |
| Cd           | 0.001    | 0.001   | 0.001   | 0.38 | 0.0018  | 0.38 |
| Cr           | 0.003    | 0.00286 | 0.00006 | -  | 42      | 0.5 |
| Hg           | 0.0003   | 0.0003  | 0.000024 | - | -      | - |
| Pb           | 0.0035   | 0.00352 | 0.0352  | - | -      | 0.0085 |

Note: "-" indicates that no corresponding reference data is available.

### 3. Results and discussion

#### 3.1. Human health risk assessment

**3.1.1. Non-carcinogenic risk.** The calculation results of non-carcinogenic risks are shown in table 3. The total non-carcinogenic risks of Pb, As, Cr, Hg and Cd in the soils of the three plots in the study area: block 3 >1> and 2. Because the lead-zinc plant is located in the upper reaches of the contaminated land and the farmland is located in the lower reaches of the downstream land, the pollutants may accumulate in the lower reaches of the downstream farmland with wind migration, slope runoff, soil erosion and gravity settlement [19]. The plot 3 is located on both sides of the canal and is mainly irrigated by sewage. It is most polluted and there is the greatest non-carcinogenic risk to humans. The plot 1 which located on both sides of the road is mainly affected by automobile exhaust and friction powder particles of tires and brake skin during transportation. The non-carcinogenic risk in block 1 is less than that in block 3. The plot 2 which is neither on the road nor in the sewage irrigation area there is the least pollution and is relatively less affected by the lead-zinc smelter [20], so its non-carcinogenic risk to human health is minimal. In general, the non-carcinogenic risks of the three plots are higher among children than adults, which is consistent with the research results of Tao et al. [10]. From the perspective of single factor non-carcinogenic risk, Pb there is the most serious non-carcinogenic risk, followed by As, and Cd is the least. Wang et al. [13] found the most serious non-carcinogenic risk was Cd to human body researching the farmland around a lead-zinc smelter in Jiaozuo city. As far As adults are concerned, Pb and As in the soil in plot 1 and plot 3 there are a non-carcinogenic risk. As far As children are concerned, Pb in the soil in plots 1 and 3 and As in the soil in plots 1, 2 and 3 there are non-carcinogenic risks. Generally speaking, the average value of the total
The non-carcinogenic risk index of these five heavy metals in the soil of the three plots in the study area is 6.71 for children and 4.27 for adults, both of which are greater than 1, it meant that there are non-carcinogenic risk to both children and adults.

### Table 3. Statistical description of the non-carcinogenic risk of heavy metals in the soil of the study area.

| Plot | As   | Cd   | Cr   | Hg   | Pb   |
|------|------|------|------|------|------|
| Child |      |      |      |      |      |
| 1#   | 1.88 | 0.10 | 0.77 | 0.10 | 2.64 |
| 2#   | 1.60 | 0.03 | 0.84 | 0.03 | 0.77 |
| 3#   | 3.11 | 0.26 | 0.79 | 0.29 | 6.91 |
| Mean Value | 2.20 | 0.13 | 0.8  | 0.42 | 3.44 |

| Adult |      |      |      |      |      |
| 1# | 1.01 | 0.05 | 0.99 | 0.08 | 1.42 |
| 2# | 0.86 | 0.02 | 1.09 | 0.03 | 0.41 |
| 3# | 1.68 | 0.15 | 1.02 | 0.23 | 3.73 |
| Mean Value | 1.18 | 0.07 | 1.03 | 0.11 | 1.85 |

### 3.1.2. Cancer risk. The calculation results of human health carcinogenic risk are shown in Table 4. The mean value of the total carcinogenic risk index of these five heavy metals in the soil of the study area is \(4.49 \times 10^{-4}\) for children and \(2.51 \times 10^{-4}\) for adults, both of which are greater than \(1 \times 10^{-4}\) (the maximum acceptable limit set by HJ 25.3-2014), so there are carcinogenic risk to local children and adults. The magnitude of carcinogenic risk in human health is the same as that of non-carcinogenic risk in the three plots. In the soil of the 3 plots, only As there is carcinogenic risk to children and adults, Cd and Cr are within an acceptable range, Pb is very low and negligible. In general, the carcinogenic risk of heavy metals in the soil in the study area is higher for children than for adults. In terms of the single factor carcinogenic risk, the carcinogenic risk of As and Cd for children is higher than adults, Cr and Pb for adults is higher than that of children. However, the total risk of cancer mainly came from As. This is different from the conclusion of Wang et al. [13] that the carcinogenic risk of a lead-zinc smelter in Jiaozuo city mainly came from Cr.

### Table 4. Statistical description of the carcinogenic risk of heavy metals in soil of the study area.

| Plot | As       | Cd       | Cr       | Pb       | CR     | TCR     |
|------|----------|----------|----------|----------|--------|---------|
| Child |          |          |          |          |        |         |
| 1#   | 3.66×10^{-4} | 1.58×10^{-5} | 3.06×10^{-6} | 3.02×10^{-7} | 4.72×10^{-4} | 3.85×10^{-4} |
| 2#   | 3.11×10^{-4} | 5.26×10^{-6} | 3.37×10^{-6} | 8.79×10^{-8} | 3.19×10^{-4} |
| 3#   | 6.05×10^{-4} | 4.31×10^{-5} | 3.13×10^{-6} | 7.93×10^{-7} | 6.52×10^{-4} |
| Mean Value | 4.27×10^{-4} | 2.14×10^{-5} | 5.47×10^{-13} | 3.95×10^{-7} | 4.49×10^{-4} |
| Adult |          |          |          |          |        |         |
| 1#   | 2.04×10^{-4} | 8.83×10^{-6} | 9.11×10^{-6} | 9.01×10^{-7} | 2.23×10^{-4} |
| 2#   | 1.74×10^{-4} | 2.94×10^{-6} | 1.01×10^{-5} | 2.62×10^{-7} | 1.87×10^{-4} |
| 3#   | 3.38×10^{-4} | 2.41×10^{-5} | 9.35×10^{-6} | 2.36×10^{-6} | 3.74×10^{-4} |
| Mean Value | 2.39×10^{-4} | 1.20×10^{-5} | 2.35×10^{-12} | 1.17×10^{-6} | 2.51×10^{-4} |

### 4. Conclusion

The non-carcinogenic risk assessment analysis of As, Cr, Cd, Hg and Pb in the soil of the study area showed that the 1#, 2# and 3# plots had non-carcinogenic risk to children and adults, mainly caused by As and Pb. The carcinogenic risk assessment analysis showed that the 1#, 2# and 3# plots there were
carcinogenic risks for children and adults, mainly caused by As, Cd and Cr. The total non-carcinogenic and carcinogenic risks were higher for children than for adults. In general, the carcinogenic and non-carcinogenic risks were the most serious in 3# plots, followed by 1# plots, and relatively low carcinogenic and non-carcinogenic risks in 2# plots. Therefore, it is necessary to take corresponding control and management measures according to the different risk levels of the three plots.

Acknowledgments
This paper was financially supported by National Nature Fund of China (NO. 51068025)

References
[1] Ministry of Environmental Protection, Ministry of Land and Resources. Bulletin of the National Survey of Soil Pollution. (2014) http://www.gov.cn/foot/2014-04/17/content_2661768.htm.
[2] Xu W J, Song X Y, Gong Z J, et al. (2019) Study on pollution and assessment of heavy metals in soil of a lead-zinc mining area in Southwest China. J. Sichuan Environment, 38(5): 49-54.
[3] Chen S B, Wang M, Li S S, et al. (2019) Current status of discussion on farmland heavy metal pollution prevention in China. China. J. Earth Science Frontiers, 26(6): 35-41.
[4] Ma H H, Peng M, Liu F, et al. (2020) Bioavailability, translocation and accumulation characteristic of heavy metals in a soil-crop system from a typical carbonate rock area in Guangxi, China. China. J. Environmental Science, 41(1): 449-459.
[5] Huang J H, Peng S Y, Mao X M, et al. (2019) Source apportionment and spatial and quantitative ecological risk assessment of heavy metals in soils from a typical Chinese agricultural county. J. Process Safety and Environmental Protection, 126:339-347.
[6] Kowalska J, Mazurek R, Gaśliorek M, et al. (2016) Soil pollution indices conditioned by medieval metallurgical activity - A case study from Krakow (Poland). J. Environmental Pollution, 218:1023-1036.
[7] He X W, Wang Y X, Fang Z Q, et al. (2016) Pollution characteristics and pollution risk evaluation of heavy metals in soil of lead-zinc mining area. J. Journal of Environmental Engineering Technology, 6(5): 476-483.
[8] Zhang F G, Peng M, Wang H Y, et al. (2020) Ecological risk assessment of heavy metals at township scale in the high background of heavy metals, Southwestern, China. J. Environmental Science, 41(09): 4197-4209.
[9] Lu J, Zhao X Q. (2017) Soil heavy metal pollution characteristics and ecological risk assessment of Shizig-Montain mining area in Tongling. J. Environmental Chemistry, 36(09): 1958-1967.
[10] Tao M X, Hu H, Hu L W, et al. (2018) Characteristics and health risk assessment of heavy metals in polluted abandon soil of Shangrao, Jiangxi. J. Ecology and Environmental Sciences, 27(6): 1153-1159.
[11] Xu W J, Song X Y, Gong Z J, et al. (2019) Study on pollution and assessment of heavy metals in soil of a lead-zinc mining area in Southwest China. J. Sichuan Environment, 38(5): 49-54.
[12] Gao Y, Sun R G, Ye C, et al. (2020) Ecological risk assessment of heavy metal pollution in soil of a lead-zinc mine area in Danzhai County, Guizhou Province, China. J. Chinese Journal of Ecology, 39(3): 928-936.
[13] Wang Y Y, Li F F, Wang X Y, et al. (2019) Spatial distribution and risk assessment of heavy metal contamination in surface farmland soil around a lead and zinc smelter. J. Environmental Science, 40(1): 437-444.
[14] National Ministry of Environmental Protection. (2004) Technical Specification for Soil Monitoring (HJ/T 166-2004) . Standards Press of China, Beijing.
[15] Ministry of Ecology and Environment. (2018) Soil Environmental Quality Standard for Soil Pollution Risk Control of Agricultural Land (trial);GB 15618-2018. China Standard Press, Beijing.
[16] US Environmental Protection Agency. (1996) Soil screening guidance: technical background document. US environmental protection agency. (EPA/540/R-95/128).

[17] Wang H Z, Bu X B, Zhang K X, et al. (2018) Determination of heavy metal content in soils on both sides of Chengdu city expressway and evaluation on the healthy risk. J. Sichuan Environment, 37(1): 111-119.

[18] He B, Zhao H, Wang T Y, et al. (2020) Spatial distribution and risk assessment of heavy metals in soils from a typical urbanized area. J. Environmental Science, 40(6): 2869-2876.

[19] Xiong J, Han Z W, Wu P, et al. (2020) Spatial distribution characteristics, contamination evaluation and healthy risk assessment of arsenic and antimony in soil around an antimony smelter of Dushan County. J. Acta Scientiae Circumstantiae, 40(2): 655-664.

[20] Žibret G, Gosar M, Miler M, et al. (2018) Impacts of mining and smelting activities on environment and landscape degradation-Slvenian case studies. J. Land Degradation & Development, 29(12): 4457-4470.