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Pollution assessment and health risk of metals in surface soil near a Pb–Zn mine, northeast China

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The Chaihe Pb-Zn mine, one of the largest Pb-Zn mines in northeast China, began to be exploited aggressively in 1966, but the degree of environmental impact is not well understood. Therefore, this study conducts a systematic study on the farmland areas upstream, downstream and around the lead-zinc mine, and metals, such as chromium (Cr), nickel (Ni), mercury (Hg), zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu), and arsenic (As), were detected. The coefficient of variation (CV) indicated that, with the exception of Cu, Ni, and Cr, the metals in the surface soil were markedly affected by human activities. Enrichment factors further demonstrated that Hg, Cd, Pb, and Zn primarily originated from anthropogenic sources, while As, Ni, and Cr mainly stemmed from natural sources. Geoaccumulation index (I_{geo}) values disclosed that the contamination of Cd and Hg in the areas was particularly severe. The USEPA health risk model was employed to calculate the non - carcinogenic risk (HI) and carcinogenic risk (CR). In terms of health risk, the order of mean HI is as follows: Pb > As > Hg > Cd > Cr > Zn > Cu > Ni, and the order of mean CR is As > Pb > Cr > Cd > Ni. The results also illustrated that oral ingestion was the most important during the three exposure pathways, and children were shown to be prone to metal pollution. The CR for children, adolescents, adults, and total lifetime were acceptable, but HI for children, and total lifetime were unacceptable. Therefore, the results indicated significant contamination of Pb, Zn, Cd, and Hg in the surface soil around the Pb–Zn mine, offering valuable insights for enhancing ecological restoration and environmental protection efforts.

KEYWORDS

metals, Pb-Zn mine, health risk assessment, enrichment factor, geoaccumulation index, China

1 Introduction

As indispensable basic materials, nonferrous metals, particularly lead (Pb) and zinc (Zn) play a crucial role in the national economy of China (Xue et al., 2022), and it lead to greatly increasing demand for Pb and Zn ores (Luo et al., 2023). Through the mining, beneficiation, and smelting process of Pb-Zn ore, some associated metals, particularly Cd, might be incorporated into the soil, water bodies, the atmosphere, and groundwater, which could lead to metal pollution issues (Fernández-Caliani et al., 2009). With the continuous exploitation of mineral resources, some researchers have noticed that potentially toxic metal environmental pollution around the mining area was becoming more and more serious, soil in particular (Cao et al., 2022; Nguyen et al., 2020). Mining activities have been the main source of heavy metal contamination in soil (Shi et al., 2022; Tran et al., 2022), and heavy metal pollution in soil has become a common phenomenon near uncontrolled mining sites (Cao et al., 2022; Zou et al., 2021). Once metals enter into soil, they are difficult to remove naturally, and they can migrate, bioaccumulate, and amplify through the food chain (Zhong et al., 2014). Huang et al. (2023) observed that the rice grains suffered from combined contamination of Cd and Pb, and mining activities have an adverse effect on health risks for residents in a paddy field near the Pb-Zn mine, in Guangxi Province, China (Huang et al., 2023). Heavy metals can affect the germination of seeds, reducing the germination rate and decreasing chlorophyll in plants, and that may lead to a reduction in the yield of crops (Xu and Tang, 2018). At the same time, the mining of lead-zinc mines can lead to an excessive amount of heavy metals that are harmful to human health. In particular, excessive levels of lead and cadmium can cause high blood lead levels in children, as well as the occurrence of a series of diseases such as rickets, kidney damage, and even cancer (Zhang et al., 2012). The previous study reported that the health of approximately 10 million people all over the world was affected by heavy metal pollution in mine soils (Ashraf et al., 2019). Therefore, metal contamination, resulting from the mining of Pb-Zn ore, has become a major threat to the ecological environment and human health, and it has become the focus of research.

The Chaihe Pb-Zn mine is located in Tieling City, Liaoning Province, Northeast China, and lies upstream of the Chaihe reservoir. The ore is simple in mineral composition, with the main minerals including sphalerite, galena, pyrite, etc. (Qin et al., 2014), and the Pb-Zn orebody was located in the banded dolomite of the fifth lithologic section of the Gaoyuzhuang Formation (Yang, 2010). Except for Pb and Zn, other associated elements (Cd, Ag, etc.) of the ore are also in high concentrations (Qin et al., 2014). The mining activities of the Chaihe Pb-Zn mine can be traced back to the Tang Dynasty (about 1,200 years ago), and the large-scale mineral processing plant was put into operation in 1966, and went out of production in 1992 (Qin et al., 2014). Meanwhile, two large-scale tailing storages, large amounts of tailings, and low-grade ore were left behind, and some research was carried out on the contamination of metals in the study area in the research area. Xie et al. (2018) found that Cd in agriculture soil and sediment in the Liaoning Chaihe River Basin was much higher than the background value and the average level of China. Ma et al. (2007) revealed that the levels of Cd and Pb in the rice of the Chaihe River Basin were significantly higher than in other areas of North Liaoning Province, and Cd and Pb in the hair of the residents in the mining area were well above the average of the basin. Recently, the excessive concentration of heavy metals in crops has also been monitored at some locations downstream of the mining area, and it is a potential health risk source to the surrounding residents. Previous studies mainly focused on the heavy metal pollution in the Chaihe River downstream of the lead-zinc mine and around the Chaihe Reservoir. However, the level of environmental impacts on the degree of heavy metal pollution in farmland soil near the Pb-Zn mine is not well-known systemic, and the health risks posed by the soil surrounding the Pb-Zn mine constitute a knowledge gap awaiting addressing.

To comprehensively understand the impact of the Chaihe lead-zinc mine on the soil of the surrounding farmlands and assess the harm to the health of the surrounding residents, this study conducts a systematic study on the farmland areas upstream, downstream, and around the lead-zinc mine. Seventy-eight monitoring sites were established in farmlands near the study area, and eight metals Cr, As, Cu, Pb, Zn, Ni, Hg, and Cd were analyzed. Metal pollution was illustrated with an enrichment factor and geoaccumulation index, and carcinogenic and non-carcinogenic risks of metals for nearby residents through ingestion, inhalation, and dermal contact were evaluated using USEPA human health risk models in this study. The results will provide useful information on the contamination and health risks of metals in farmland soil near the Chaihe lead-zinc mine. It is helpful to provide a basis for the safe utilization of soil resources and the prevention and restoration of soil pollution by local governments.

2 Materials and methods

2.1 Study area and sample collection

The Chaihe Pb-Zn mine is located in a valley terrain. The mining area, the storage area, and the tailings pond are situated halfway up the mountain and at the mountaintop. The surface runoff formed during the rainy season may carry pollutants and flow into the small streams at the bottom of the valley, and then flow into the Chai River. Meanwhile, there are a large number of farmlands distributed around the lead-zinc mine, and these farmlands may be polluted by means such as dust deposition and drainage from the mining area. Therefore, soil samples were sampled from seventy-eight farmlands sites around the Pb-Zn mine, including the upstream and downstream of the lead-zinc mine, and the areas near the surrounding villages in May 2020 (Figure 1). Surface soil (0–20 cm) is closely related to human health and agricultural production. At the same time, it is easily affected by external pollution. The surface soil is alkaline or weakly alkaline, and the pH ranges from 7.2 to 8.3. Organic matter content was 3.11% ± 1.55%, and the composition of the soil was 5.92% clay, 60.62% silt, and 33.46% sand.

The surface soil (0–20 cm) was obtained in each site by mixing five subsamples, which were uniformly distributed within 50 m of the sampling point. Stainless steel shovels, washed and rinsed with deionized water, were used to collect the soil, and the soil sample was kept in polyvinyl chloride packages. Soil samples were air-dried first, then, coarse material and foreign matter (stones and leaves, etc.) were removed using a 2 mm sieve, then an agate grinder was employed to grind the samples to achieve sample homogeneity for facilitating digestion, and a 150-μm mesh was used to sieve the samples after grounding in the laboratory.

2.2 Sample analysis

One g soil samples were subjected to acid digestion with 5 mL HF/5 mL HNO_3/3 mL $HClO_4$ to determine the contents of Cr, Cu, Pb, Zn, Cd, and Ni in samples in polytetrafluoroethylene crucible heating with a heating plate (Tang et al., 2016). Subsequently, the digestion solution was filtered through Whatman No. 42 filter paper and analyzed by atomic absorption spectrophotometry (Varian, Spector AA 220, Palo Alto, US). Another 1 g soil sample was digested using 5 mL HCl/10 mL HNO_3 to determine As, and Hg

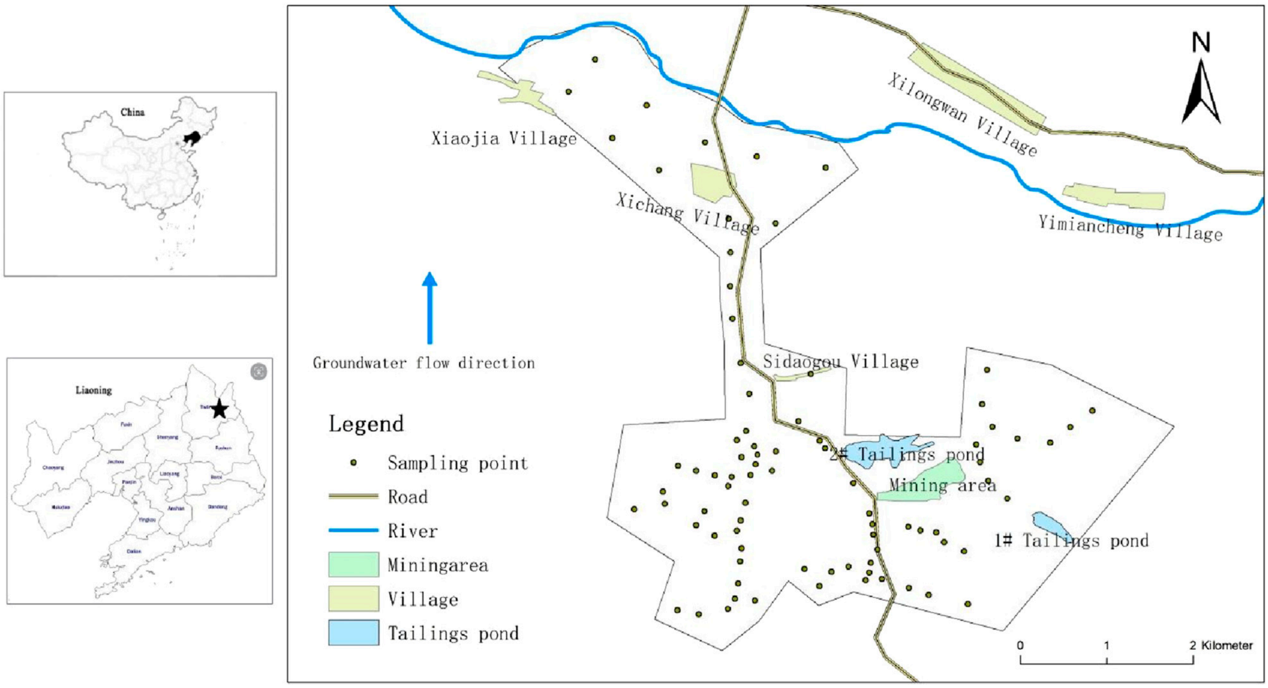

FIGURE 1
Sampling locations in surface soil nearby a Pb–Zn mine, Northeast China.

in a sealed polytetrafluoroethylene crucible (Bo et al., 2021). After filtering, As was detected by cold vapor atomic fluorescence spectrometry (Tekran 2,500, CVAFS, Toronto, Canada), and Hg was detected using ultraviolet spectrophotometry (UVS, Hitachi, U 3900-H, Tokyo Metropolis, Japan) (Wang et al., 2020).

The solvents, purchased from Sinopharm Chemical Reagent Co., LTD. (Shanghai, China), were used in this study. Detection levels of the eight elements (Cu, Pb, Zn, Ni, Cd, As, Cr, and Hg) were 1, 2, 2, 2, 0.002, 0.2, 2, and 0.005 mg/L, respectively, and standard solutions and reagent blank were randomly added every 10 samples for precision analysis and quality control. Duplicates were also run every 12 samples, and instruments were recalibrated when the deviation was >5%. The recovery rates of the method to eight metals were 90%–105%. At each site, three replicate samples were gathered to ascertain the average concentrations as well as the standard deviations (SD).

2.3 Soil heavy metal pollution assessment

2.3.1 Enrichment factor

According to previous studies, the degree of metal enrichment in soil was calculated using enrichment factor (EF), and could be estimated using Equation 1 (Bourliva et al., 2016; Pan et al., 2018):

$$\mathrm{EF} = \left(\frac{C_{\mathrm{n}}}{C_{\mathrm{ref}}}\right)_{\mathrm{sample}} \Big/ \left(\frac{B_{\mathrm{n}}}{B_{\mathrm{ref}}}\right)_{\mathrm{background}} \tag{1}$$

Where C_{n} and B_{n} are the sample concentration and background value of the metals in the soil (mg/kg); C_{ref} and B_{ref} are the sample concentration and background value of the reference metal in the soil (mg/kg). Due to low variability, manganese (Mn) was selected as the reference metal (Hu et al., 2013), and the background value of Cu, Pb, Zn, Ni, Cd, As, Cr, and Hg in the soil is shown in Table 1 (Wei et al., 1991).

According to Sutherland (2000), EF could be divided into five classifications and the classification of EF is shown in Supplementary Table S1. Meanwhile, it could preliminarily discuss the probable sources, and metal pollution mainly came from anthropogenic metal sources if EF >10, otherwise it mainly came from natural background sources (Christophoridis et al., 2009).

2.3.2 Geoaccumulation index

The geoaccumulation index (I_{geo}), proposed by Muller (1969) (Muller, 1969), was an index used to express the degree of metal contamination by comparison with the regional background value, and it could be calculated with the following Equation 2 (Abrahim and Paker, 2008).

$$I_{geo} = \log_2\left[\frac{C_i}{1.5C_n}\right] \tag{2}$$

Where I_{geo} is the geoaccumulation index of metals, C_i is the concentration of metals in the soil samples, and C_n is the background value. According to the previous research literature (Abrahim and Paker, 2008; Sultana et al., 2016), the degree of metal pollution in the surface soil could be divided into seven classifications based on the value of I_{geo} (Supplementary Table S2).

TABLE 1 Summary of metal concentrations (mg kg^{-1} dw) in surface soils near a Pb–Zn mine.

Metal	Maximum (mg/kg)	Minimum (mg/kg)	Mean ± Standard deviation (±SD) (mg/kg)	CV (%)	Background soil concentration (mg/kg) (Bo et al., 2021)
Cu	114.00	14.50	54.07 ± 18.80	34.77	19.8
Hg	36.60	0.05	3.45 ± 6.75	195.73	0.037
As	51.20	0.60	9.90 ± 8.03	81.05	8.8
Pb	9790.00	4.00	766.00 ± 1620.34	211.53	21.4
Zn	6830.00	16.00	921.59 ± 1502.82	163.07	63.5
Cr	47.00	0.15	23.95 ± 6.19	25.85	57.9
Cd	87.90	0.10	7.50 ± 14.63	194.98	0.108
Ni	56.00	2.00	20.87 ± 7.00	33.52	25.6

2.4 Health risk assessment

The health risk of potentially toxic metals could be assessed using USEPA models (Pan et al., 2018; USEPA, 1989; USEPA, 2002; USEPA, 2004), and it had been used to estimate the health risk of potentially toxic metals for humans in various environmental media in previous studies (Pan et al., 2018; Wang et al., 2021; Chabukdhara and Nema, 2013). The ingestion, inhalation, and dermal absorption meant that pollutants entered the human body by direct ingestion, inhalation through the mouth and nose, and dermal absorption in particles adhered to exposed skin (Chabukdhara and Nema, 2013), and they were selected as exposure pathways in this study. Depending on age, the human was divided into three groups: children (<6 years), adolescents (6–17), and adults (>17).

The daily intake via each exposure pathways were estimated using Equations 3–5 (Pan et al., 2018; USEPA, 1989; Chabukdhara and Nema, 2013):

$$ADI_{oral} = \frac{C \times IngR \times EFQ \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

$$ADI_{inh} = \frac{C \times InhR \times EFQ \times ED}{PEF \times BW \times AT} \quad (4)$$

$$ADI_{derm} = \frac{C \times SA \times AF \times ABS \times EFQ \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

Where C is the concentration of potentially toxic metal in the topsoil (mg kg^{-1}); IngR is the ingestion rate (mg day^{-1}); EFQ is the exposure frequency (day year^{-1}); ED is the exposure duration (year); InhR is the inhalation rate (m^3 day^{-1}); SA is the exposed skin area (cm^2); AF is the skin adherence factor (mg cm^{-2}); ABS is the dermal absorption factor; PET is the particle emission factor (m^3 kg^{-1}); BW is the body weight (kg); AT is the averaging time (days): for non-carcinogens, ED × 365 days and for carcinogens, 70 × 365 days.

The hazard quotient (HQ) was usually used to present for non-carcinogenic, and the total non-carcinogenic risk for more than one metal could be defined by the summation of all the hazard quotients, which is called the hazard index (HI) (USEPA, 1989). HI was calculated according to Equations (6 and 7) (USEPA, 2002):

$$HQ_i = \frac{ADI_i}{RfD_i} \quad (6)$$

$$HI = \sum HQ_i \quad (7)$$

Where HQ is the hazard quotient; the RfDi is the reference dose of the metal i (mg kg^{-1} per day). When HI <1, it indicates that no potential non-carcinogenic risks occurred for humans, otherwise, the potential non-carcinogenic risk exceeded the acceptability for non-carcinogenic risk, and a potential non-carcinogenic health effect may occur (USEPA, 1989).

Carcinogenic risks (CR) were calculated following Equation 8:

$$CR = ADI \times SF \quad (8)$$

Where SF is the carcinogenicity slope factor (mg kg^{-1}/day).

The parameters used are listed in Supplementary Tables S4, S5.

2.5 Statistical analysis

SPSS statistics for Windows (version 22.0 SPSS, USA) and EXCEL (Microsoft, Redmond, WA, USA) were used to analyze data and generate figures. One-way analysis of variance (ANOVA) was used to assess the significant difference between groups at $P <$ 0.05 (SPSS 13.0). Data are given as mean value ±standard deviation (SD). The CV of metals, a statistical measure of the degree of variation of each observation value in data, was calculated as the ratio of the standard deviation to the mean, eliminating the influence of measurement scales and dimensions, and can be used to compare the degree of dispersion of different metals.

3 Results and discussion

3.1 Metals concentrations

The characteristic, CV, and background values of the metal in the surface soils near a Pb–Zn mine, in China, are shown in Table 1. Concentrations of Zn and Pb were higher than those of other metals, and they were 16.00–6830.00 (mean 921.59 ± 1502.82) mg/kg and 4.00–9790.00 (mean 766.00 ± 1620.34) mg/kg in surface soil, respectively. Cu concentration was 14.50–114.00 (mean 54.07 ± 18.80) mg/kg, and Cr and Ni concentrations were following, which ranged from 0.15 to 47.00 (mean 23.95 ± 6.19) mg/kg and from 2.00 to 56.00 (mean 20.87 ± 7.00) mg/kg. As varied from 0.60 to

51.20 (mean 9.90 ± 8.03) mg/kg, and Cd ranged from 0.10 to 87.90 mg/kg, with a mean value of 7.50 ± 14.63 mg/kg. The mean Hg concentrations were the smallest and ranged from 0.05 to 36.60 (mean 3.45 ± 6.75) mg/kg. When compared with the background soil concentration, aside from Ni and Cr, the concentrations of the other six metals exceeded that of the background soil. Specifically, the multiples by which Cu, Hg, As, Pb, Zn, and Cd exceeded the background were 1.73, 92.25, 0.13, 34.79, 13.51, and 68.47, respectively. The concentration of Pb and Zn was higher, and they mainly came from the Pb-Zn mine mining process. Hg and Cd had the highest multiple exceeding in the surface soil near the Pb-Zn mine, and similar results were also obtained in previous research on metal pollution in other lead-zinc mines (Gao et al., 2020; Li et al., 2021). Compared with previous studies (shown in Supplementary Table S3) (Gao et al., 2020; Nikolaidis et al., 2013; Qu et al., 2012; Razo et al., 2004; Song et al., 2015), the concentration of the main heavy metal pollutants, namely, Pb, Zn, and Cd were low than Pb-Zn mines in Jiangsu, but they were significantly higher than other Pb-Zn mine. Therefore, the heavy metal pollution in this study is quite serious and must be given due attention.

In this study, the coefficient of variation (CV) was calculated to explore the impact of human activities on potentially toxic metals in the surface soil adjacent to the Pb - Zn mine. The CV is a useful metric for characterizing the accumulation of various metals (Manta et al., 2002; Rodríguez et al., 2009), and the results are presented in Table 1. The order of CV values for metals in the surface soil is Pb > Hg > Cd > Zn > As > Cu > Ni > Cr. Excluding Cu, Ni, and Cr, the CVs of the other five metals exceeded 60%. This indicates that metals in the surface soil near the mine are significantly influenced by human activities such as ore mining, transportation, and industrial operations.

Principal component analysis (PCA) is also used for the source analysis of heavy metals in this study, and the results are presented in Supplementary Tables S6, S7. The result of total variance explained (Supplementary Table S6) showed that the cumulative contribution rate of the first two principal components (PC1 and PC2) reached 81.26%, indicating that the original heavy metals data can be represented by these two principal components. PC1 was distinguished by the high positive loadings for Cu, As, Pb, Zn, and Cd. Industrial activities, such as metallurgy industry, metal mining, smelting industries, and mineral provessing are the important source of Cu, Zn, Cd, and Zn (Aminiyan et al., 2016; Yeung et al., 2003), and it means that PC1 mainly derived from anthropogenic sources. PC2 was distinguished by the high positive loadings for Cr and Ni, and they were came from local background. Thus, the results of PCA are consistent with the CV.

To examine the relationships among the eight metals in the surface soil around the Chaihe Pb - Zn mine, a correlation analysis was conducted, and the Pearson product-moment correlation coefficients are shown in Supplementary Figure S1. The results indicate that the correlation between Pb and Zn is highly significant. Moreover, there are significant pairwise correlations among Cu, As, Cd, Pb, and Zn. This finding is in line with the research of Fernández-Caliani et al. (2009), Yang (2010), who discovered that Cd and As are commonly associated with Pb - Zn ore. In contrast, Hg, Ni, and Cr, especially Cr, exhibit weak correlations with Pb and Zn. The correlation results further suggest that Cu, As, Cd, Pb, and Zn may share the same source and are likely to be strongly affected by the mining activities of the Chaihe Pb - Zn mine. In contrast, the lead-zinc ore mining and beneficiation processes have a relatively minor impact on Hg, Ni, and Cr, which may be influenced by the background values and other human-induced factors. As can be seen from the CV results, the CVs of Ni and Cr are relatively small compared to those of the other metals.

TABLE 2 Descriptive statistics for EFs of metals in surface soils near a Pb–Zn mine.

EF	Cu	Hg	As	Pb	Zn	Cr	Cd	Ni
Max	8.32	883.66	6.03	464.06	174.85	1.93	828.47	3.53
Min	1.10	0.90	0.11	0.30	0.41	0.00	1.12	0.13
Mean	3.10	93.84	1.28	39.58	16.99	0.47	78.47	0.93

Distribution patterns of heavy metals in the surface soil surrounding the Chaihe Pb-Zn mine are shown in Supplementary Figures S2, S3. The results showed that the distribution of the other five heavy metals except Pb, Zn, and Cd in the study area was relatively uniform, while Pb, Zn, and Cd were mainly distributed in the mining area, tailings pond and along the downstream road, and the detection rate in other areas was relatively low. This indicates that the pollution of Pb, Zn, and Cd in the study area primarily stems from the mining activities of lead-zinc mines. Meanwhile, as this region has a valley terrain, the drainage from the mining area will flow downstream along the drainage ditch adjacent to the highway and eventually merge into the downstream river. During the rainy season, the residual heavy metals in the mining area and tailings pond will also migrate downstream under the influence of rainwater and soil runoff. This has led to the heavy metal pollution in the study area being distributed in a band from the mining area and tailings pond to the downstream. The distributions and the patterns of metal pollution in the soil around the mining area are affected by historical mining activities, such as mined ores, mining methods, and times elapsed since mining ceased (Sutkowska et al., 2020; Sutkowska et al., 2013). Previous research on heavy metal distribution around the Pb-Zn mine also demonstrates that the drainage from the mining area is a significant source of heavy metal pollution in the mining area (Yeung et al., 2003). Moreover, the pollution is typically distributed in a band extending from upstream to downstream (Kovács et al., 2012; Omanović et al., 2015).

3.2 Metals pollution assessment

3.2.1 Enrichment factor

EF of metals was calculated on surface soils near the Pb–Zn mine (shown in Table 2). EFs of Hg were the highest in surface soils ($p<0.05$), ranging from 0.90 to 883.66, with a mean value of 93.84, and EFs of Cd were followed, ranging from 1.12 to 828.47 (mean 78.47). EF values of Pb and Zn were higher and varied from 0.30 to 464.06 (mean 39.57) in surface sediments and from 0.41 to 174.85 (mean 16.99), respectively. The mean value of Cu was 3.10, and they were 1.28, 0.93, and 0.47 for As, Ni, and Cr. According to the previous study (Sutherland, 2000), this suggested that the enrichments of Hg and Cd were extremely high, and it was very

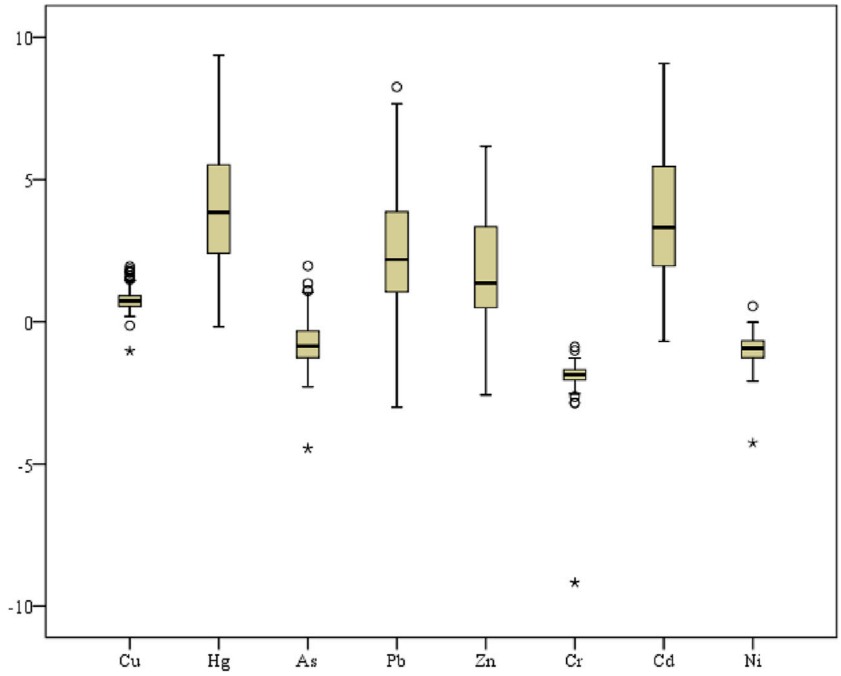

FIGURE 2
I_{geo} of metals in surface soils near a Pb–Zn mine.

high for Pb. Then, it was a significant enrichment for Zn and a moderate enrichment for Cu. Meanwhile, the enrichment degree was minimal for As, Ni, and Cr.

The mean Enrichment Factors (EFs) for Hg, Cd, Pb, and Zn were greater than 10. This indicates that these metals in the surface soils near the Pb - Zn mine predominantly originated from anthropogenic metal sources. In contrast, the mean EFs for Cu, As, Ni, and Cr were less than 10, suggesting that they were mainly controlled by the natural background metal sources. Typically, if the EFs range from 0.5 to 1.5, crustal materials or natural weathering are likely to be the main sources of the metals. Conversely, if the EFs are greater than 1.5, anthropogenic sources contribute to the metal sources (Chai et al., 2017). The mean EFs for As (1.28), Ni (0.93), and Cr (0.47) were all less than 1.5. Thus, As, Ni, and Cr mainly stemmed from crustal materials or natural weathering processes. For Cu, with an EF of 3.10, although it mainly originated from a natural background metal source, anthropogenic activities also exerted a certain influence. In conclusion, Hg, Cd, Pb, and Zn were mainly derived from anthropogenic sources, specifically the lead-zinc mine mining activities. On the other hand, As, Ni, and Cr were mainly sourced from natural origins, namely, crustal materials or natural weathering.

3.2.2 Geoaccumulation index (I_{geo})

Boxplots were employed to depict the Geoaccumulation Index (I_{geo}) of metals in each surface soil sample adjacent to the Pb - Zn mine, and the results are presented in Figure 2. According to the classification proposed by Abrahim and Paker (2008), the mean I_{geo} values of As (−0.73), Cr (−1.97), and Ni (−0.97) were less than 0. This implies that the surface soil in the vicinity of the Pb-Zn mine was not contaminated by As, Cr, and Ni. The mean I_{geo} values of Cu (0.79), Zn (1.90), and Pb (2.67) fell into classes 1, 2, and 3 respectively. This indicates that the surface soil was either uncontaminated to moderately contaminated by Cu, moderately contaminated by Zn, and moderately to strongly contaminated by Pb. Moreover, the surface soil was strongly contaminated (Class 4) by Cd, with a mean Igeo of 3.73, and extremely strongly contaminated (Class 5) by Hg, with a mean Igeo of 4.02. Consequently, the surface soils near the Pb - Zn mine were more severely contaminated by Cd and Hg. Thus, greater attention must be directed towards the Cd and Hg contamination in these surface soils. The local government should revise the land-use plan and adjust the types of crops. Additionally, the local government ought to formulate a monitoring plan for metals in the surface soil near the mine and regularly detect the metal levels in plants, especially in crops.

3.3 Health risk assessment of potentially toxic metals

The health risk of potentially toxic metals was assessed, and the results of the health risk assessment of metals in surface soils near a Pb–Zn mine in China were shown in Supplementary Tables S8–S10, and Figure 3.

CR and HI of children, adolescents, and adults were calculated (Figure 3). The CR for the children was 4.66×10^{-7}–5.35×10^{-5}, with a mean of 1.05×10^{-5}, 4.13×10^{-7} - 4.62×10^{-5} (mean 9.26×10^{-6}) for the adolescents, and 3.41×10^{-7} – 3.84×10^{-5} (mean 7.71×10^{-6}) for adults. Meanwhile, for HI, the mean value for children was 1.65 (0.044–17.3), 0.616 (0.016–6.43) for adolescents, and 0.240 (0.006–2.51) for adults. For the three age groups as well as total

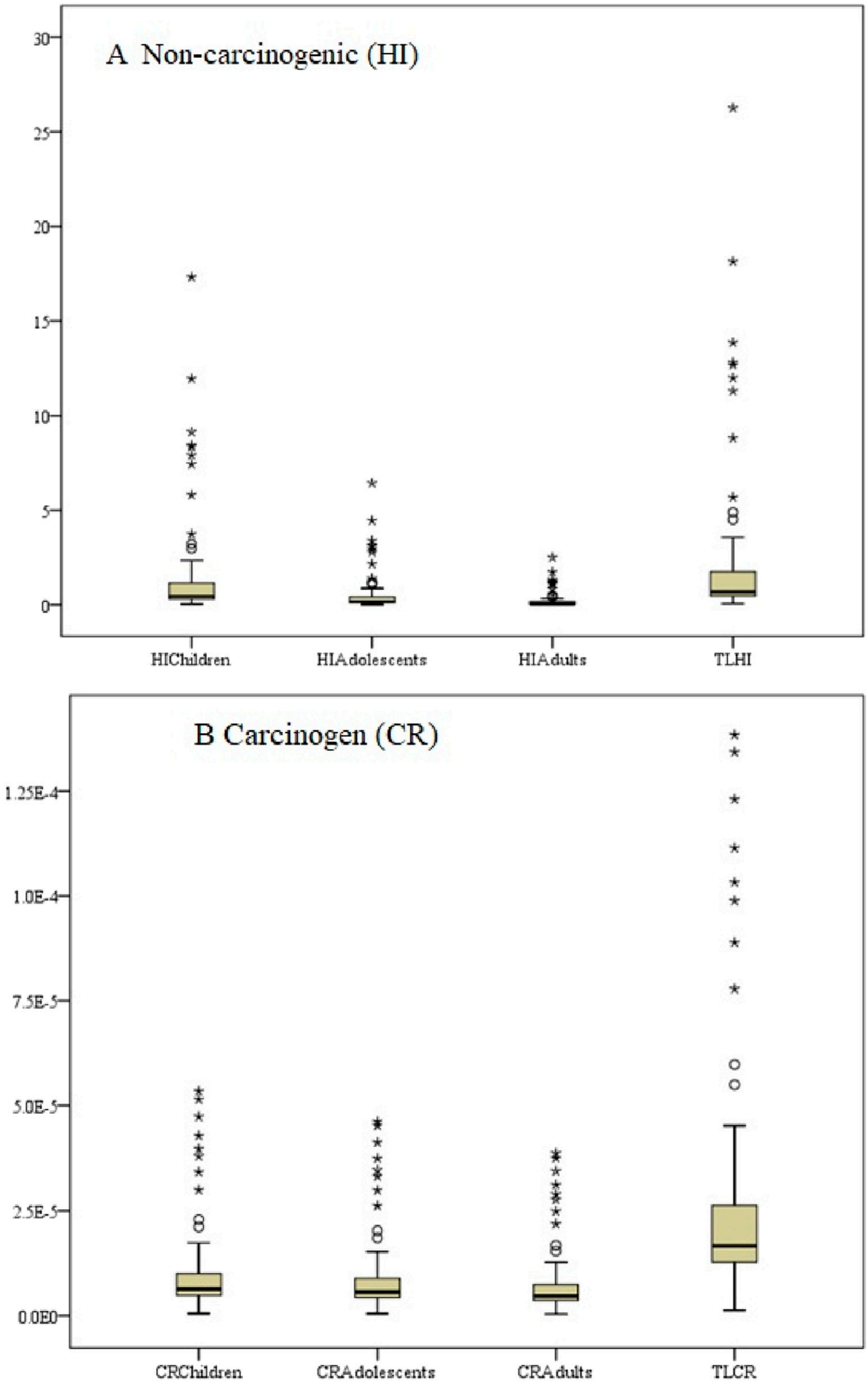

FIGURE 3
Non-carcinogenic (HI) **(A)** and Carcinogenic (CR) **(B)** health risks from metals in surface soils near a Pb–Zn mine for children, adolescents, adults, and total lifetime. Circles represent discrete values, and the star indicates extreme values in statistical data.

lifetime, their 95% cumulative probability CR and mean CR were all within the acceptable risk range for carcinogenic risks set by USEPA (2011) (USEPA, 2011) (10^{-6} to 10^{-4}). It suggested that carcinogenic risks existed, but were acceptable in surface soil. Meanwhile, the HI of children and total lifetime were >1, and this indicated that the HI had exceeded safe levels and was unacceptable to children and total lifetime. The results implied that children were more susceptible to the impact of metals in surface soil compared with adolescents and adults, and greater protections should be placed on strengthening the protection of children.

Significant differences ($p < 0.05$) were observed in HI and CR among the three groups. Children faced the highest risks among children, adolescents, and adults. Adolescents ranked second, while adults had the lowest health risks. On average, children accounted for 65.90% of the total lifetime non - carcinogenic risks, adolescents for 24.54%, and adults for 9.56%. In terms of total lifetime carcinogenic risks, children, adolescents, and adults contributed 38.30%, 33.66%, and 28.03% respectively.

The differences in CR and HI between males and females among children, adolescents, and adults were examined through three exposure pathways. The results are presented in Supplementary Tables S5, S6. When comparing CR and HI between genders, the HI for females was significantly higher than that for males across all three age groups ($P < 0.01$). However, in children and adolescents, the CR of females was lower than that of males, while in adults, female CR was greater than male CR ($P < 0.01$). The differences in CR and HI for the three age groups across different exposure pathways were highly significant ($P < 0.01$) (Supplementary Tables S5, S6). Among the three age groups, oral ingestion contributed the highest CR and HI values. Dermal absorption ranked second, and inhalation was the lowest ($P < 0.01$). For children, the mean HI percentages for oral ingestion, dermal absorption, and inhalation were 97.85%, 2.13%, and 0.02% respectively. For adolescents, these values were 96.36%, 3.60%, and 0.03% respectively. In the case of adults, they were 97.17%, 2.76%, and 0.07% respectively. Meanwhile, for children, the mean CR contributions from oral ingestion, dermal absorption, and inhalation were 96.19%, 3.51%, and 0.30% respectively; for adolescents, 93.66%, 5.88%, and 0.46% respectively; and for adults, 94.52%, 4.51%, and 0.96% respectively. Oral ingestion was the most crucial exposure pathway for all three age groups.

The HI and CR values varied among different metals. The mean HI followed the order of Pb > As > Hg > Cd > Cr > Zn > Cu > Ni. Pb contributed the most to HI, accounting for 76.34%, followed by As with 11.39%, while Ni had the lowest contribution at 0.36%. Regarding CR, the order was As > Pb > Cr > Cd > Ni. As contributed 70.61% to CR, and Pb contributed 28.92%. Thus, As and Pb had a more substantial impact on HI and CR compared to other metals. It is essential to implement additional environmental protection measures to reduce the As and Pb contamination in surface soil.

This research elucidated the influence of a Pb - Zn mine on the surface soil in its vicinity in Northeast China and uncovered the health risks associated with metals. The findings of this study are valuable for enhancing future soil pollution management. However, certain uncertainties remain. Firstly, the health risk assessment methods and some exposure parameters were drawn from the United States Environmental Protection Agency, which may deviate from the Chinese context. Secondly, apart from the eight potentially toxic metals investigated in this study, there could be other carcinogenic and non - carcinogenic substances present in the soil. As a result, the actual health risks posed by the Chaihe Pb-Zn mine are probably more substantial than the value estimated in this research. Furthermore, improper management in the past or natural processes either have already triggered or might trigger the migration of heavy metal pollution in the future, thus endangering the quality of the surrounding soil environment, as previously noted in reference (Sutkowska et al., 2015). Consequently, it is imperative to intensify research on the control of heavy-metal-contaminated soil. A variety of remediation technologies, such as the sorption method (Shen et al., 2019), the application of nanomaterials (Sergeeva et al., 2023), the use of carbonaceous compounds (Terekhova et al., 2021), electrochemical techniques (Xu et al., 2019), biological remediation (Khalid et al., 2016), soil replacement, stabilization, chemical reduction, and acid washing (Devi et al., 2023), should be applied to remediate heavy-metal -contaminated soil.

4 Conclusion

The information on contamination level, pollution degree, and human health risks of eight metals in surface soil near a Pb–Zn mine, in Northeast China was reported in this study, and it was useful to better understand the effect of metal contamination in China and globally. To investigate the impact of the Pb–Zn mine on surface soil, seventy-eight monitoring sites were set up in the vicinity of the Pb–Zn mine. The results showed that the mean concentrations of metals were all beyond background values, and the coefficients of variation of metals were greater than 60% except for Cu, Ni, and Cr. Consistent with previous findings, the human mining activities of lead-zinc mines had influenced the metal levels in surface soil, and the surface soil near the mine was contaminated by Pb–Zn metals. The results also showed that the pollution of Hg, Cd, Pb, and Zn was significant, and the HI for children and total lifetime was unacceptable. These findings indicate monitoring of heavy metal pollution in surface soil near the Pb–Zn mine should be strengthened, and corresponding control and remediation research should be carried out subsequently. More research on health risk assessment should be carried out, especially regarding its impact on children.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

HuW: Conceptualization, Funding acquisition, Investigation, Methodology, Resources, Writing – original draft, Writing – review and editing. SY: Data curation, Formal Analysis, Validation, Writing – original draft. LS: Conceptualization, Writing – original draft. YW: Data curation, Investigation, Writing – review and editing. HaW: Formal Analysis, Methodology, Writing – original draft. XW: Data curation, Investigation, Writing – review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2025.1585272/full#supplementary-material

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