Pol. J. Environ. Stud. Vol. XX, No. X (XXXX), 1–10
DOI:*10.15244/pjoes/194580* ONLINE PUBLICATION DATE:

Original Research

Pollution Characteristics and Ecological Risks of Heavy Metals in Soil Near a Pb-Zn Mine in Northeast China

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Received: 6 June 2024
Accepted: 13 October 2024

Abstract

The heavy metal pollution in the surrounding environment of the Chaihe Pb-Zn Mine in Liaoning Province has become quite severe, yet our understanding of the chemical speciation and potential ecological risks of metals in the soil of its adjacent areas remains inadequate. Consequently, this study collected 28 soil samples from the vicinity of the Pb-Zn mine and analyzed the concentrations and speciation of Cr, As, Cu, Pb, Zn, Ni, and Cd in the soil. The results indicated that compared to background values, Cd was the metal with the highest level of exceedance, followed by Pb and Zn, with over-standard multiples of 62.33, 39.11, and 13.69, respectively. Notably, the average percentage of exchangeable Cd fractions reached 24.95%, suggesting a high bioavailability of this metal. This finding is echoed by the risk assessment code results, which indicated that Cd posed a high risk at 53.57% of the sampling sites and a medium risk at 39.29% of the sites. Furthermore, the risk index calculations revealed that the potential ecological risk in the study area was extremely severe, with cadmium and lead being the primary sources of risk. In conclusion, the contamination of Cd, Pb, and Zn in the soil surrounding the Chaihe Pb-Zn Mine is severe and requires urgent remediation measures.

Keywords: heavy metals, Pb-Zn mine, ecological risk, risk assessment code, pollution characteristics

Introduction

Soil heavy metal pollution has emerged as a severe environmental issue in many countries [1, 2]. In China, soil heavy metal contamination caused by human activities such as mining, ore dressing, and smelting has become increasingly alarming [3, 4]. Heavy metals in soil are non-degradable, impacting soil properties, leading to the degradation of soil ecological functions, penetrating the food chain, and posing a threat to human health [5, 6]. Directly correlated with food safety issues, soil heavy metal pollution has garnered mounting concern.

The Chaihe Pb-Zn mine, located upstream of Chaihe Reservoir in Tieling City, Liaoning Province, holds a significant position among Pb-Zn mines in Northeast China. Mining activities at this mine date back to the Tang

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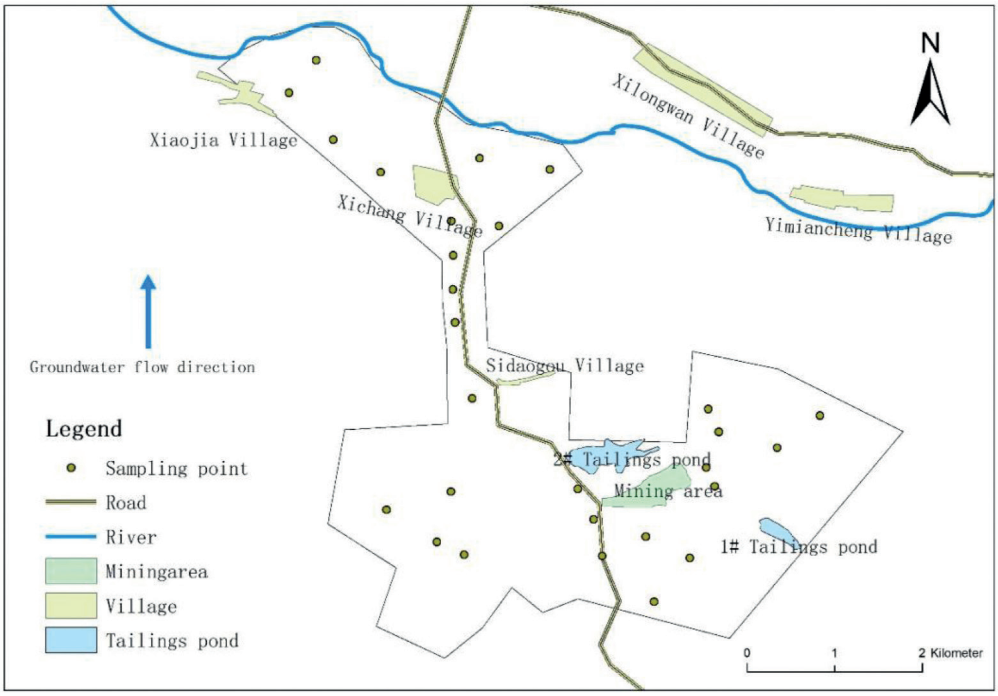

Fig. 1. Sampling locations in surface soil near the Chaihe Pb-Zn mine, Northeast China.

Dynasty, an astonishing 1200 years ago. However, large-scale mining only commenced in 1966. Due to the depletion of underground resources, the mine was closed in 1992 [7], but two large tailings ponds storing tailings and piles of low-grade ores surrounding the mining pits remain. Over time, metals have gradually entered the environment and Chaihe Reservoir through drainage, rainwater infiltration, surface runoff, and underground leakage. Prior studies have revealed shocking figures: from 1966 to 1992, approximately 265 tons of heavy metals were discharged into the environment through mining wastewater. Furthermore, it is estimated that around 150 tons of heavy metals in Chaihe Reservoir sediments may originate from the Chaihe Pb-Zn mine [8], emphasizing the importance of monitoring and managing the environmental impact of such mines to safeguard ecological balance and human health.

A series of studies conducted on heavy metals in the environment surrounding the Chaihe Pb-Zn mine have shown severe contamination, posing a significant threat to the ecological environment and human health [9–11]. For instance, Li and Li discovered that the Chaihe Pb-Zn mine had a significant impact on the metal content in fish from the Chaihe reservoir [12]. Liu et al. revealed that the concentrations of Cd, Pb, and Zn in the soil of the Pb-Zn mine tailing pond were significantly higher than the average concentrations in Liaoning Province [13]. Ma et al. found that Cd and Pb levels in the hair of residents in the mining area were much higher than the basin average [14]. Wu et al. observed that the metal content in rice and corn grown around or downstream of the Chaihe Pb-Zn mine was higher than in other areas of Tieling City [15]. Xie et al. noted that Cd concentrations in agricultural soil and sediment in the Liaoning Chaihe River Basin were substantially higher than the background values and the national average [16]. Nevertheless, studies on the chemical speciation and potential ecological risks of metals in the soil at and around this mine are rarely reported, which is crucial for understanding and assessing heavy metal pollution risks and formulating targeted remediation strategies.

Therefore, this study collected 28 soil samples from around the Chaihe Pb-Zn mine in Liaoning Province, Northeast China, analyzed the concentrations and chemical speciation of seven metals (Cr, As, Cu, Pb, Zn, Ni, and Cd), calculated the risk assessment code (RAC), and evaluated the potential ecological risk index (RI) in the study area. The aim is to provide quantitative data for future soil pollution management efforts and technical guidance for the formulation of targeted remediation strategies.

Materials and Methods

Sample Collection and Analysis

Within the study area depicted in Fig. 1, soil samples were gathered from 28 sites. At each of these sites, approximately 1–1.5 kilograms of soil were collected from five distinct sub-locations, ensuring triplicate samples for each sampling site. Prior to collection, a stainless steel shovel was thoroughly washed with deionized water to eliminate any lingering effects from previous samples, following procedures outlined by previous research [17–19]. The collected samples were securely stored in polyethylene packaging and maintained at room temperature (25°C) until laboratory analysis. Once in the lab, the soil samples underwent an initial screening through a 2-mm sieve to remove coarse elements and foreign debris, such as rocks, plastic waste, and leaves. The samples were then dried at room temperature before being ground with a grinder and further sieved through a 150-μm mesh to ensure consistency and homogeneity.

A portion of the soil samples was utilized to measure the concentrations of Cr, Cu, Pb, Zn, and Ni through atomic absorption spectrophotometry (Varian, Spectr AA 220, American) following digestion with $HF/HNO_3/HClO_4$, as described by Tang et al. [20]. Additionally, another section of the samples was analyzed for As and Cr concentrations, employing cold vapor atomic fluorescence spectrometry (Tekran 2500, CVAFS) and ultraviolet spectrophotometry (UVS, Hitachi, U 3900-H), following digestion with V2O5/H2SO4/HNO3, as reported by Wang et al. [21, 22].

For every 12 samples, standard solutions and reagent blanks were randomly inserted for precision analysis and quality assurance. Additionally, duplicates were also used randomly for every 12 samples, and whenever a deviation exceeding 5% was observed, the instruments underwent recalibration. The recovery rates ranged from 90–105%, and the average concentrations, along with their standard deviations, were ascertained through triplicate samples for each site. The detection thresholds for various elements were as follows: Cu at 1 mg/kg, Pb at 2 mg/kg, Zn at 2 mg/kg, Ni at 2 mg/kg, Cd at 0.002 mg/kg, As at 0.2 mg/kg, and Cr at 2 mg/kg. All solvents employed in this investigation were sourced from Sinopharm Chemical Reagent Co., LTD, located in Shanghai, China.

Chemical Speciation of Metals

Prior research conducted by Davidson et al. and Wang et al. underscores the close correlation between the chemical activity and bioavailability of metals with their chemical speciation [23, 24]. In the current study, we applied the Tessier sequential extraction method, as described by Tessier et al., to ascertain the chemical speciation of the metals [25]. This analysis encompassed five distinct fractions: the exchangeable fraction (F1), carbonate-bound fraction (F2), Fe-Mn oxides-bound fraction (F3), organic matter-bound fraction (F4), and the residual fraction (F5).

Risk Assessment Code

The chemical speciation of metals serves as a valuable tool for evaluating their potential risk based on the relative comparison of different fractions, as highlighted by Lu et al. [26]. Furthermore, there exists a close correlation between the bioavailability of metals and their chemical speciation, as observed by Hu et al. [27]. Specifically, the exchangeable fraction can be directly absorbed and utilized by plants, as noted by Zhang et al. [28], while the carbonate-bound form of metal is prone to easy release from the soil, as stated by Wu and Pan [29]. Therefore, the exchangeable fraction and carbonate-bound fraction serve as indicators of the bioavailability of metals.

A risk assessment code (RAC) was employed to evaluate the potential hazard, following the methodology of previous research [30, 31]. This code utilizes a scale based on the percentage of the exchangeable (F1) and carbonate-bound (F2) metal fractions to assess metal availability, as advocated by Sundaray et al. [32]. Specifically, the total proportion of these two fractions in relation to the total metal content is used to quantify the risk level. A total proportion below 1% suggests no risk, 1–10% indicates low risk, 11–30% signifies medium risk, 31–50% points to high risk, and anything above 50% suggests very high risk, as outlined by Sundaray et al. and Lu et al. [26, 32].

Potential Ecological Risk Index

Excessive metals often exert toxic effects on ecological systems. To evaluate the degree of metal contamination, the potential ecological risk index (RI) was introduced, which considers both the toxicity of metals and the environmental response [26]. This index utilizes Equations proposed by Hakanson to assess the contamination level of metals [33].

$$f_{\mathrm{i}} = \frac{C_{\mathrm{i}}}{B_{\mathrm{i}}} \tag{1}$$

$$E_{\mathrm{r}}^{\mathrm{i}} = T_{\mathrm{r}}^{\mathrm{i}} f_{\mathrm{i}} \tag{2}$$

$$\mathrm{RI} = \sum_{i=1}^{n} E_{\mathrm{r}}^{\mathrm{i}} \tag{3}$$

Here, f_{i} represents the pollution factor of a single metal, measured without units. It is calculated based on the concentration (C_{i}) of metal i in soil samples near the Chaihe Pb-Zn mine (expressed in mg/kg) and a reference value (B_{i}) for that metal (mg/kg). In this study, B_{i} represents the background value of metal i in the local region. $E_{\mathrm{r}}^{\mathrm{i}}$ stands for the potential ecological risk factor of a single metal i, also without units. It is determined by multiplying the pollution factor (f_{i}) by the toxic factor ($T_{\mathrm{r}}^{\mathrm{i}}$) of metal i. The toxic factors for Zn, Cr, Cu, Pb, Ni, As, and Cd are standardized to 1, 2, 5, 5, 5, 10, and 30, respectively, as proposed by Xu et al. and Huang et al. in this research [34, 35]. The overall potential ecological risk index (RI) is the sum of all $E_{\mathrm{r}}^{\mathrm{i}}$ values for the individual metals and represents the collective ecological risk posed by the metals present. n represents the total number of metals considered. The level of potential ecological risk can be determined by comparing the values of $E_{\mathrm{r}}^{\mathrm{i}}$ and RI with established grade standards. The specific grade standards for $E_{\mathrm{r}}^{\mathrm{i}}$ and RI are detailed in Table 1.

Statistical Analysis

For the statistical analyses and figure generation in this study, we utilized Microsoft Excel 2016 (Microsoft, Redmond, WA, USA) and SPSS Statistics for Windows (Version 22.0, SPSS, USA). The reported results for all

Table 1. The grade standards for E_r^i and RI.

E_i	Grade of potential ecological risk	RI	Grade of potential ecological risk
$E_i \leq 40$	low	RI < 150	low
$40 \leq E_i < 80$	moderate	150 ≤ RI < 300	moderate
$80 \leq E_i < 160$	considerable	300 ≤ RI < 600	considerable
$160 < E_i \leq 320$	high	600 ≤ RI	very high
$320 \leq E_i$	very high		

Table 2. The total metal concentrations in soil samples (mg/kg).

	Cu	As	Pb	Zn	Cr	Cd	Ni
Min	14.20	0.30	2.00	16.00	0.08	0.14	2.00
0.1	40.70	4.21	34.40	98.40	18.85	0.35	15.70
0.25	43.28	5.11	58.25	140.1	20.50	0.93	16.88
Medium	49.60	7.55	143.0	300.5	24.00	2.38	19.50
0.75	53.00	9.59	483.9	838.0	26.50	6.17	25.13
0.9	82.32	15.49	2003	3388	31.45	23.63	29.30
Max	97.95	28.60	9840	4780	47.00	37.75	38.00
Mean	53.11	8.85	858.5	932.8	24.32	6.84	20.88
SD	17.25	5.97	1969	1393	8.15	10.30	6.66
CV (%)	0.32	0.67	2.29	1.49	0.33	1.51	0.32
Background	19.8	8.8	21.4	63.5	57.9	0.108	25.6

indices are representative of the mean values obtained from triplicate samples. A T-test was employed to compare the data from different sites, with a significance level of $p < 0.05$ indicating statistical significance.

Results and Discussion

Characteristics of Metals

A comprehensive statistical analysis, encompassing range, mean, standard deviation (SD), and coefficient of variation (CV) of Cu, Pb, Zn, Ni, Cd, As, and Cr in soils near the Chaihe Pb-Zn mine in China, was conducted and tabulated in Table 2. The table also provides the local soil background values [36]. Notably, the mean Zn and Pb concentrations in the study area were significantly elevated due to emissions from the tailing pond and mining area. Zn concentrations ranged from 16.00 to 4780 mg/kg (mean 932.8 mg/kg), while Pb concentrations spanned from 2.00 to 9840 mg/kg (mean 858.5 mg/kg). Cu concentrations, albeit lower, varied between 14.20 and 97.95 mg/kg (mean 53.11 mg/kg). Meanwhile, Cr and Ni concentrations ranged from 0.08–47.00 mg/kg (mean 24.32 mg/kg) and 2.00–38.00 mg/kg (mean 20.88 mg/kg), respectively. As and Cd concentrations were the lowest, ranging from 0.30–28.60 mg/kg (mean 8.85 mg/kg) and 0.14–37.75 mg/kg (mean 6.84 mg/kg), respectively. In comparison to the local background values, Cd displayed the highest exceeding ratios, exceeding the background value in all sites. Cu, Pb, and Zn followed, with exceeding ratios of 96.63%. Ni exceeded the background value in 78.57% of the sites, while As exceeded it in 32.14% of the sites. In contrast, Cr concentrations remained below the local background value at all sites. Regarding the mean exceeding multiple metals compared to the background value, Cd stood the highest at 62.33, followed by Pb at 39.11. Other metals followed the order Zn (13.69) > Cu (1.68) > As (0.01) > Ni (-0.18) > Cr (-0.58).

Extensive research has demonstrated that cadmium (Cd) is a significant contaminant associated with lead and zinc ore mining and smelting processes [37, 38]. Consequently, environments near Pb-Zn mining sites often suffer from Cd contamination [39, 40]. Cd is considered a poisonous and harmful heavy metal, capable of severely damaging the human respiratory, immune, nervous, and reproductive systems. Moreover, it can lead to deformities and various forms of cancer

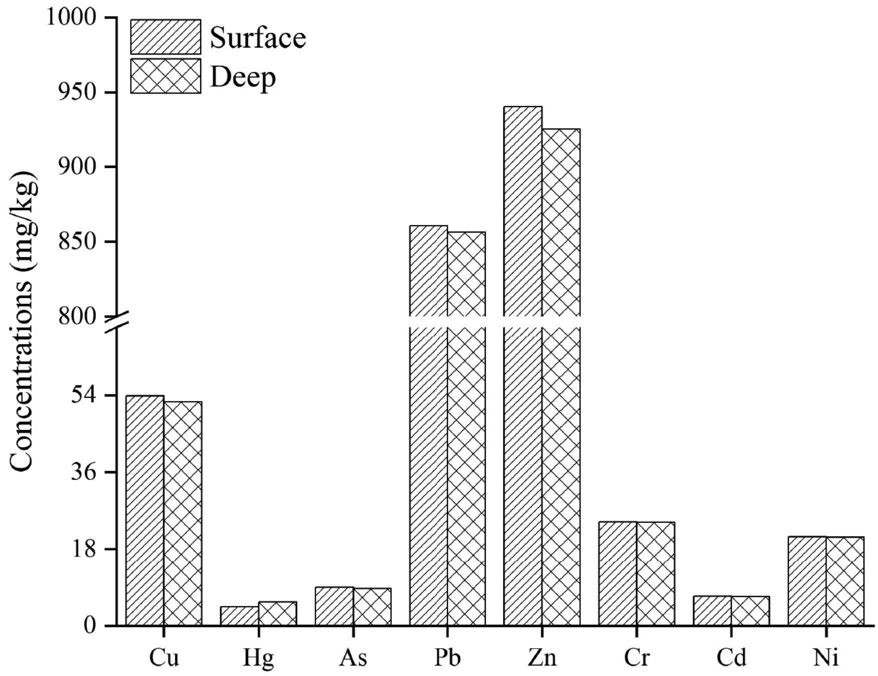

Fig. 2. Mean concentrations of metals in surface and deep soil in the study area.

Table 3. The paired T-test results of metals between surface (0–20 cm) and deep (20–60 cm) soil.

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Cu	Surface -Deep	1.35357	5.83904	1.10348	-0.91057	3.61772	1.227	27	0.231
As	Surface -Deep	0.35714	1.79205	0.33866	-0.33774	1.05203	1.055	27	0.301
Zn	Surface -Deep	15.60714	84.28011	15.92744	-17.07327	48.28756	.980	27	0.336
Pb	Surface -Deep	4.21429	89.83910	16.97799	-30.62168	39.05025	.248	27	0.806
Cr	Surface -Deep	0.07679	1.35889	0.25681	-0.45014	0.60371	.299	27	0.767
Cd	Surface -Deep	0.06143	0.89251	0.16867	-0.28465	0.40751	0.364	27	0.719
Ni	Surface -Deep	0.10714	2.58685	0.48887	-0.89593	1.11022	0.219	27	0.828

if ingested or inhaled in high concentrations [41]. Therefore, the potential impact of Pb, Zn, and Cd on the soil environment in the study areas is more significant than other metals, necessitating further investigation into the pollution characteristics of these elements in the soil.

In this study, we examined the impact of sampling depth on metal concentrations. The comparative analysis and T-test results for metal concentrations in surface (0–20 cm) and deep (20–60 cm) soil layers are presented in Fig. 2 and Table 3. Our findings revealed that the average concentrations of Cu, Pb, and Zn were slightly elevated in surface soil compared to deep soil, while the differences for the other four metals were minimal (Fig. 2). Furthermore, statistical analysis indicated that the differences in concentrations for all seven metals between surface and deep soil were not significant ($p>0.05$) (Table 3). Consequently, it can be concluded that sampling depth had little to no influence on metal concentrations in the studied area.

Table. 4 Percentages of chemical speciation of metals in surface soils of the study area (%).

		F1	F2	F3	F4	F5
Cd	Range	7.74–48.81	0.00–14.45	7.96–54.05	3.34–36.53	2.40–58.07
	Average	24.95	6.36	33.10	16.90	18.70
	SD	11.15	3.96	9.80	8.17	11.83
Pb	Range	0.07–21.89	0.00–3.39	6.72–61.47	1.15–40.92	22.71–89.06
	Average	2.73	0.83	26.34	6.84	63.26
	SD	3.97	0.89	12.49	7.03	15.13
Zn	Range	0.25–18.58	0.00–8.31	3.15–49.34	2.84–49.34	18.69–90.87
	Average	2.48	0.56	22.67	20.00	54.28
	SD	2.95	1.12	11.68	13.30	20.91

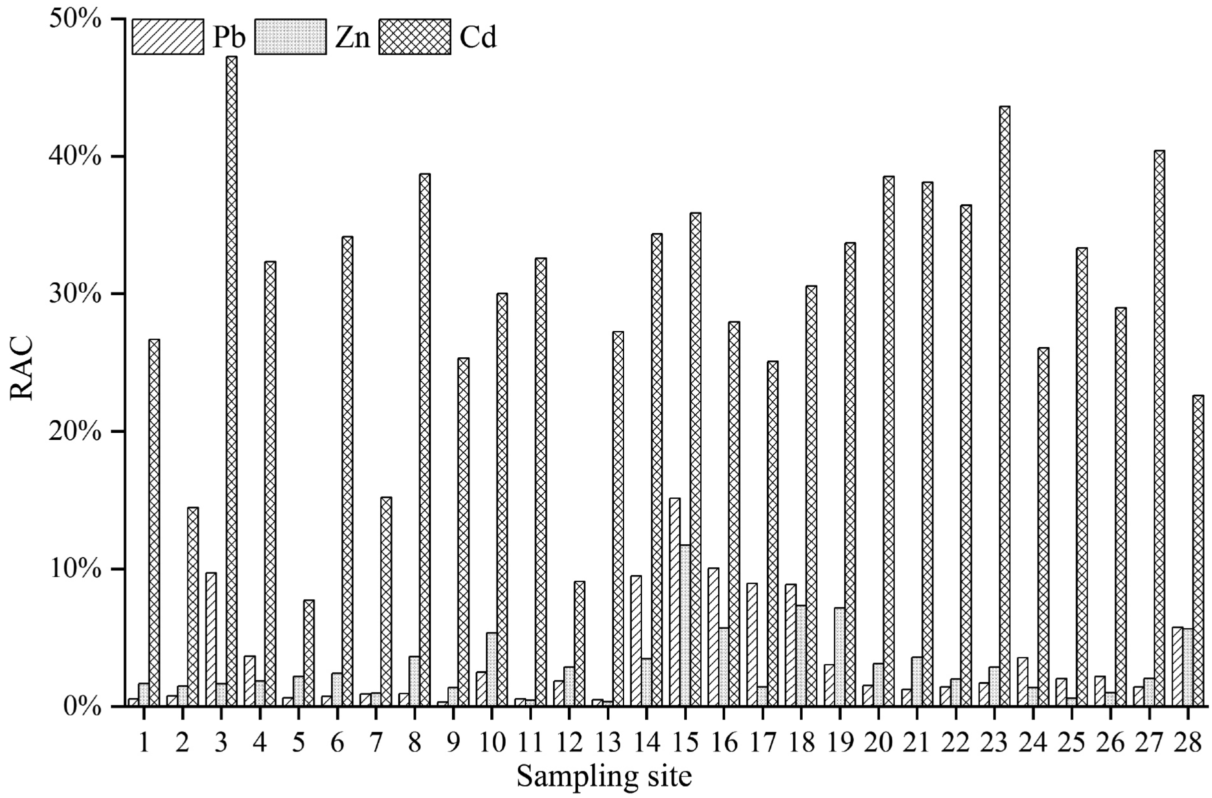

Fig. 3. Risk assessment code (RAC) of metals in soil.

Metals Speciation

The chemical activity, mobilization potential, and bioavailability of metals are heavily influenced by their chemical speciation [23, 24]. In fact, metal speciation has emerged as a pivotal research focus in understanding metal characteristics in soil, as evidenced in several prior studies [22, 26, 42, 43]. Given the significant potential impact of metals on the soil environment, Pb, Zn, and Cd were chosen for chemical speciation analysis using sequential extraction techniques [25]. The resulting distributions of these metals across various chemical fractions are presented in Table 4.

The findings revealed that the major speciation of Pb and Zn predominantly resided in the residual fraction (F5), accounting for average percentages of 63.26% and 54.28%, respectively, with a range of 22.71% to 89.06% for Pb and 18.69% to 90.87% for Zn. The lower percentages of the exchangeable fraction (F1) and a carbonate-bound fraction (F2) for Pb and Zn, specifically 2.73% and 2.48%

Table. 5. Ecological risk assessment for metals in soils of the study area.

	f_i							f
	Cu	As	Pb	Zn	Cr	Cd	Ni	
Average	2.682	1.006	40.12	14.69	0.42	63.33	0.815	123.1
SD	0.871	0.679	91.99	21.93	0.141	95.39	0.26	199.6
Range	0.717–4.947	0.034–3.25	0.093–459.813	0.252–75.28	0.001–0.812	1.250–349.6	0.078–1.484	2.426–831.6
	E_r^i							RI
	Cu	As	Pb	Zn	Cr	Cd	Ni	
Average	13.41	10.06	200.6	14.69	0.84	1900	4.077	2144
SD	4.356	6.786	459.9	21.93	0.281	2862	1.3	3267
Range	3.586–24.74	0.341–32.5	0.467–2299.1	0.252–75.28	0.003–1.623	37.5–10486	0.391–7.422	42.54–11612

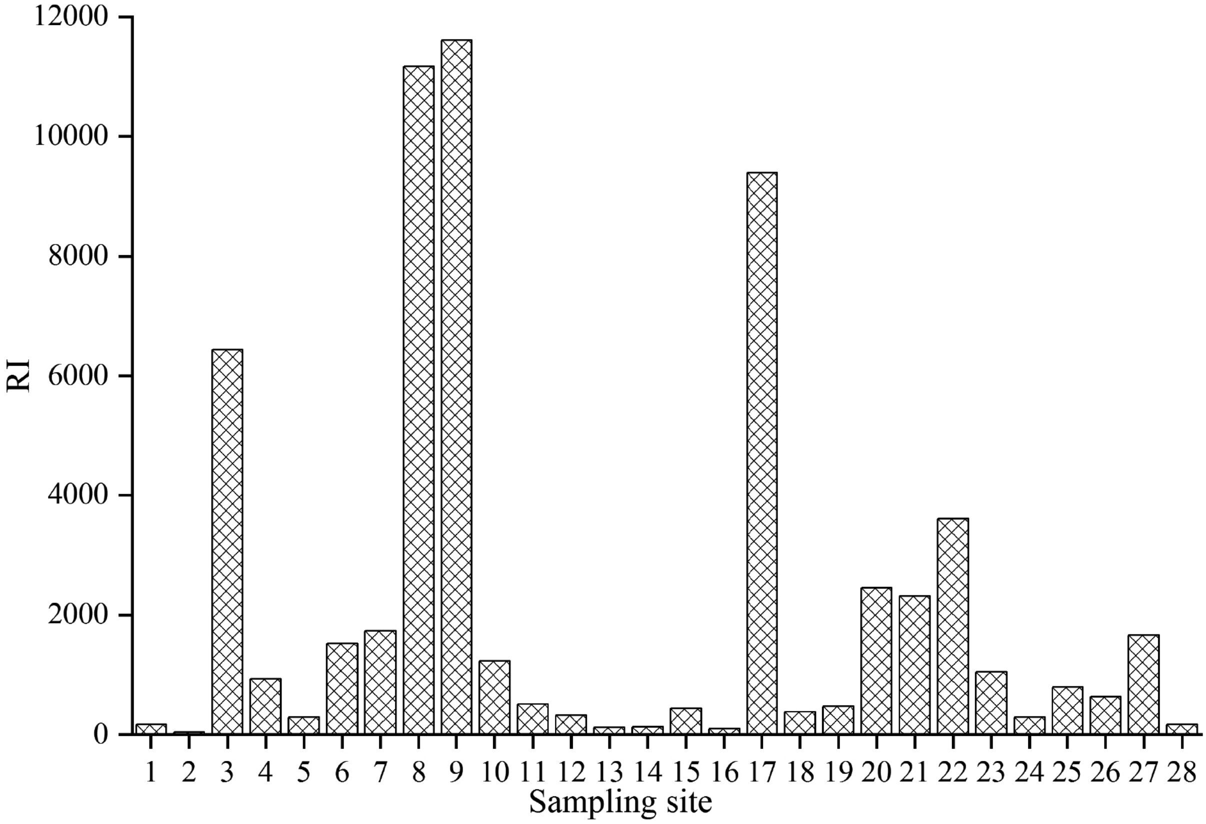

Fig. 4. The potential ecological risk (RI) in different sampling sites of the study area.

for F1, and 0.83% and 0.56% for F2 contributed significantly to their lower mobilization capacity and bioavailability.

The speciation of Cd exhibited a distinct pattern from Pb and Zn, with the Fe-Mn oxides-bound fraction (F3) dominating, ranging from 7.96% to 54.05% (averaging 33.10%). Closely following was F1, with percentages spanning from 7.74% to 48.84% (averaging 24.95%). These high percentages of F1 contributed significantly to the elevated mobilization capacity and bioavailability of Cd, aligning with previous research on metal pollution in Pd-Zn mining areas [26, 44, 45]. The significant F1 proportion and low residual fraction (F5) of 18.70% suggest that Cd possesses a greater bioavailability, posing a greater risk of entering the food chain and threatening ecosystems and human health due to its high toxicity [26, 45].

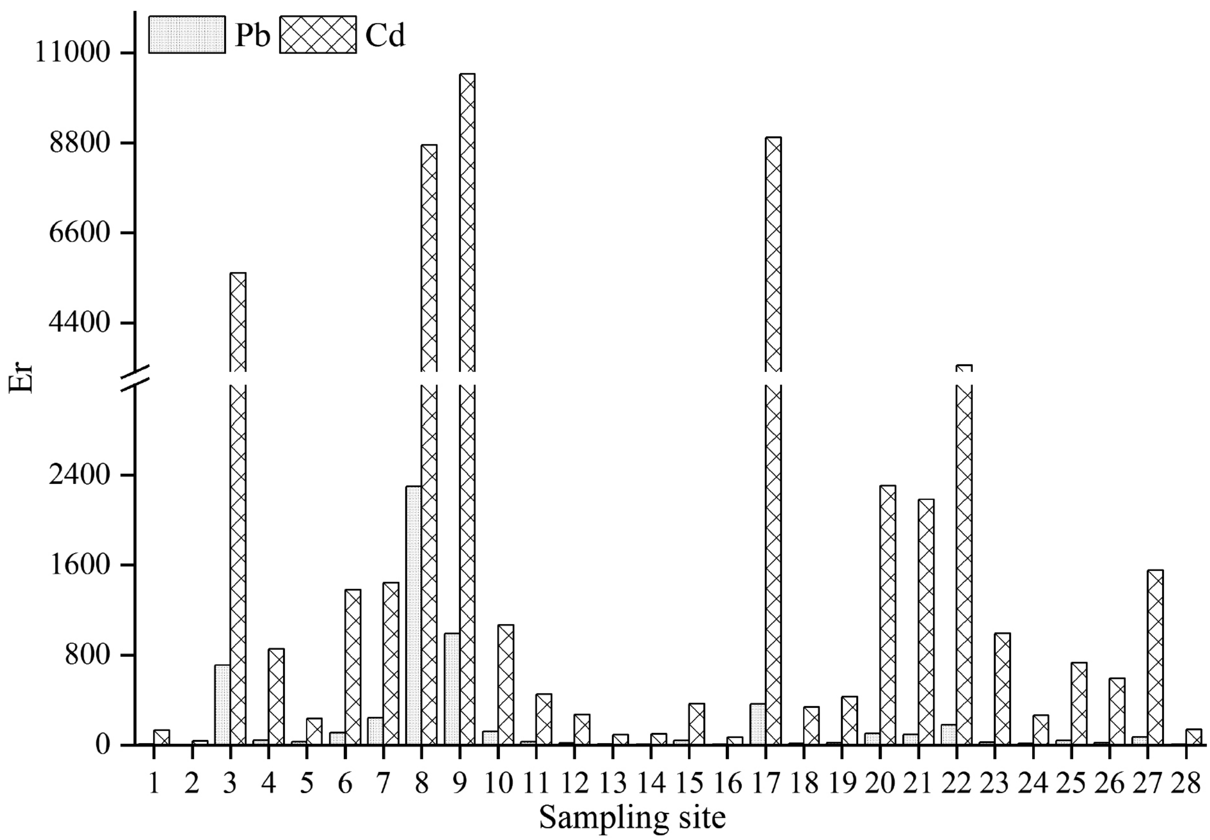

Fig. 5. Er of Pb and Cd in different sampling sites of the study area.

Risk Assessment Code

Upon calculating the RAC values for the metals, the findings are presented in Fig. 3. The analysis revealed that Cd posed a significant risk, with 53.57% of sites classified as high risk, 39.29% as medium risk; and only 7.14% as low risk. In contrast, Pb and Zn exhibited much lower risks, with RAC values below 30% across all sites. Specifically, for Pb, 7.14% of RACs fell in the 11–30% range, indicating a medium risk; 60.71% were within the 1–10% range indicating a low risk; and 32.14% posed no risk. For Zn, 3.57% of RAC values were in the 11–30% range, suggesting a medium risk; 78.57% fell within the 1–10% range, indicating a low risk; and 17.86% posed no risk. Furthermore, the results indicate that the potential hazards of these metals followed the order of Cd > Pd > Zn, with the risks being particularly high in soils near the Pb-Zn mine due to the elevated ratios of exchangeable (F1) and carbonate-bound (F2) fractions of Cd. This underscores the need to prioritize the management of Cd contamination in the soils of the study area.

Assessment of Ecological Risk of Metals

In this study, the Hakanson method was employed to quantify the potential ecological risk posed by metals [33]. The findings are presented in Table 5 and Fig. 4, revealing that 14.29% of the RI values fell below 150, 10.71% ranged between 150 and 300, 17.86% were between 300 and 600, and a significant 57.14% exceeded or equaled 600. These results indicate a significant potential ecological risk in the soil of the studied area, particularly with 57.14% of sites exhibiting a very high grade of such risk.

The average Er of metals in the study area's soils followed the sequence: Cd > Pb > Zn > Cu > As > Ni > Cr. Notably, the Er values for Cu, As, Cr, and Ni across all sites remained below 40, indicating a low potential ecological risk from these metals. Zinc exhibited a moderate Er, with only 14.29% exceeding 40 but remaining below 80, suggesting a non-serious ecological risk. However, the mean Er values for Pb and Cd were notably higher, at 200.6 and 1900, respectively, suggesting a high ecological risk from Pb and an extremely high risk from Cd. While 53.57% of sites displayed a low ecological risk for Pb, a substantial 21.43% faced a high to very high risk (Fig. 5). Conversely, for Cd, only six sites had an Er below 160, and a staggering 78.57% of sites faced a high to very high ecological risk (Fig. 5). Consequently, the study area faces significant ecological risks, primarily stemming from Cd contamination, followed closely by Pb.

Conclusions

Zn and Pb are the heavy metals with the highest concentrations in the soils surrounding the Chaihe

Pb-Zn mine in Liaoning Province, Northeast China, with average concentrations of 932.8 mg/kg and 858.5 mg/kg, respectively. Cd, on the other hand, has the lowest concentration but exhibits the highest exceed ratios and mean exceed multiples when compared to background levels, with Cd exceeding the local background value at all sampling sites. In the soil, Pb and Zn primarily exist in residual fractions, while Cd is predominantly associated with Fe-Mn oxide-bound fractions, indicating a higher bioavailability and potential to enter the food chain. The RAC indicates that Cd poses a medium to high risk at 92.86% of the sampling sites, while Pb and Zn pose lower risks at 92.85% and 96.43% of the sites, respectively. The RI results reveal that 57.14% of the sampling sites exhibit a very high potential ecological risk, primarily due to Cd and Pb contamination. This study provides essential baseline data on heavy metal contamination in the soils surrounding the Chaihe Pb-Zn mine and identifies the priority heavy metals for remediation, thereby offering significant scientific and practical value.

Acknowledgements

This work was funded by the Liaoning Revitalization Talents Program (XLYC2203141), the Applied Basic Research Program of Liaoning Province (2023JH2/101300015) and the Young and Middle-aged Scientific and Technological Innovation Talents Project of Shenyang (No. RC220128).

Conflict of Interest

The authors declare no conflict of interest.

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