

Original Research

Distribution Characteristics and Ecological Risk Assessment of Heavy Metals in Typical Farmland Soils from Baijiazui Village of Ningyuanbu Town, China

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Abstract

In the process of industrial production, the flue gas discharged from the chimneys adjacent to the farmland often contains some heavy metal elements, which enter the soil by atmospheric deposition, resulting in long-term accumulation of some heavy metal elements in the soil exceeding the standard. The paper reports the spatial distribution and risk assessment of soil heavy metals in suburban soil from the interior area of Ningyuanbu Town in Jinchuan District, China. Forty-one soil samples were obtained from a depth of 0-40 cm or 0-100 cm using a wooden shovel to analyze the concentrations of heavy metals (Zinc, Copper, Nickel, Lead, Cadmium, Chromium, Arsenic and Mercury) by ICP-MS. The results showed that the Zn, Cu, Pb, Ni, As, Hg and Cd were mainly distributed in the soil layers of 0-60 cm, and there was a point of inflection at a depth of 60 cm, it basically showed a uniform distribution below the inflection point, but the Cr in the soil layers of 0-100 cm was distributed uniformly. Based on the assessment of the risk screening values and geo-accumulation index, it was found that Cu and Ni surpassed the standard value. According to the index of potential ecological risk (RI), the average value of RI was 323.71 in the soil layers of 0-20 cm and it belong to severe contamination, and the average value of RI was 236.36 in the soil layers of 20-40 cm and it belonged to moderate contamination, and more attention must be paid to Cu and Ni in farmland soils in these areas. Therefore, the study area should be divided into safe utilization category and priority protection category. The input of pollution sources should be strictly controlled for the priority protection category, for instance, alternative planting, fallow and rotating should be implemented to reduce the transfer of heavy metals to crops and reduce the risk of food safety and health.

Keywords: Jinchuan district, heavy metal pollution, risk screening values, geo-accumulation index, potential ecological risk index

Introduction

Heavy metal pollution in soils is one of the serious environmental problems in the world [1]. At present, with the rapid development of industrialization and urbanization, all kinds of industrial wastewater discharge, livestock and poultry manure, agricultural fertilizer, irrigation water and so on can become the pollution sources of heavy metals (Zinc, Copper, Nickel, Lead, Cadmium, Chromium, Arsenic and Mercury) in soils [2,3]. Because heavy metal pollution has the characteristics of concealment, hysteresis, accumulation and morphological diversity, it poses a major risk to the health of plants, animals and humans [4-8]. It is estimated that the annual emissions of Cd, Pb, Hg, Cu and Ni to the environment are about 1.0×10^6 t, 5.0×10^6 t, 1.5×10^3 t, 3.4×10^6 t and 1.0×10^6 t, respectively [9, 10]. In China, about 12 million tons of grain are polluted by heavy metals every year, and the grain reduction exceeded 10 million tons due to heavy metal pollution, resulting in a total economic loss of at least 20 billion yuan [11]. Long term consumption of foods with excessive heavy metals will cause damage to human liver and other organs [12]. Moreover, soil heavy metal pollution will significantly reduce the number of individuals and species of rare groups of soil animals [13]. Therefore, it is urgent to find out the overall situation of heavy metal pollution in farmland soils in this area.

Jinchang City is the largest nickel, cobalt and copper production base in China, which is known as China's "nickel capital", such as nickel, accounting for nearly 90% of China's total production [14]. Ningyuanbu Town, Jinchuan District, Jinchang City is located in the north of the eastern Hexi Corridor and is a typical suburban township. It is known as the "Hometown of Malachite" because of the discovery of the world's second largest nickel sulfide deposit, the establishment of a national nickel industrial base and the birth of the "Nickel Capital of the Motherland". There are 445 enterprises of various types. In the process of industrial production, the flue gas discharged from the chimneys adjacent to the farmland often contains some heavy metal elements, which enter the soil by atmospheric deposition, resulting in long-term accumulation of some heavy metal elements in the soil exceeding the standard. In addition, sewage irrigation, sludge and the application of chemical fertilizers and pesticides can also increase the content of heavy metals in soils. In recent years, Ningyuanbu Town has been listed as one of the first national soil pollution control and remediation pilot projects, reflecting its typicality, representativeness and demonstration.

From a recent literature review, the few existing studies have been reported that the heavy metal concentrations in the study area's soil. For instance, Liao et al. [15] reported that the soils were severely contaminated by Ni and Cu, 70% and 57% of which in

samples exceeded the limit values (GB15618-1995III). Huang [16] suggested the average concentrations of Cu, Ni, Cd, Pb and Zn were more than the local background levels, especially Ni 361 mg/kg and Cu 430 mg/kg. Gao [17] found that the contents of Cu, Ni, Zn, Pb, Mn and Co all exceeded the background values in the local soil, especially Ni and Cu polluted seriously. Xu et al. [18] discovered that the average level of As, Hg, Cr, Ni, Cu, Zn, Cd and Pb in Jinchuan District exceeded the background values of Gansu province and the content of Ni was above the national soil quality secondary standard. However, most of the aforementioned studies have focused on surface (0-20 cm) soils, and the distribution characteristics of heavy metals in the soil profile of 0-100 cm are unclear. The vertical migration of heavy metals in soils may lead to groundwater pollution, so the research on the vertical distribution characteristics should not be ignored. Moreover, some studies have focused on a single evaluation method. Scientific evaluation methods can better evaluate the degree or spatial distribution of heavy metal pollution in soil, which is the basis of ensuring food security and ecological health. This is because determining the degree of heavy metal pollution can evaluate soil heavy metal pollution, which is more helpful to understand its harm to the ecological environment.

At present, there are many methods to evaluate soil heavy metal pollution, among which the index method is the most common, such as nemero comprehensive pollution index [19], enrichment factor [20], meta-analysis [21], geoaccumulation index [22-24] and potential ecological hazard index [25-27]. Thus, a comprehensive evaluation method is urgently needed. Therefore, the purpose of this study is to assess on heavy metal content and characteristic of farmland soil in Jinchuan suburban. The objectives of this research are elucidate the horizontal and vertical distribution characteristics of soil heavy metals, and to assess the soil heavy metal pollution levels of typical farmland in Jinchuan District.

Materials and Methods

Study Area

The study area is located in Baijiazui Village, Ningyuanbu Town, Jinchuan District, Jinchang City, China, which is a typical suburban area. This study area belongs to temperate continental climate, with wide sunshine temperature difference and dry climate. The annual sunshine hours are 2884 hours, the annual average temperature is 10°C, the average annual rainfall is 139 mm, the average annual evaporation is 2094 mm, the frost-free period is 156 d, and the average altitude is 1500 mm. The soil type is gray-brown desert soils, and the soil texture is loamy clay.

Soil Sampling

It is considered that the downwind direction of the mining enterprise chimneys is the most polluted area through the investigation of visiting farmers and relevant research institutions. Heavy metal contaminated soils of this region were divided into three areas (A, B and C), five sampling points are selected in area A, three sampling points are selected in area B, five sampling points are selected in area C (Fig. 1). 16 soil samples were obtained from the layers of 0-20 cm and 20-40 cm, and 25 soil samples were obtained from 5 typical soil profiles (in the layers of 0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm and 80-100 cm) in August 2019. The collected soil samples were air-dried under shade and thoroughly mixed ground to pass through a 100-mesh nylon sieve, and store it in a plastic bag for determination of heavy metal content in soils [28].

Soil Chemical Analysis

Zn, Pb, Cd, Cr, Cu and Ni are digested by tetracarboxylic acid (hydrochloric acid + nitric acid + hydrofluoric acid + perchloric acid) [29] electric heating plate, and detected by ICP-MS (Thermo Fisher Scientific, X-SERIES2). As and Hg are digested by aqua regia water bath, and detected by atomic fluorescence spectrometry (Beijing Haiguang Instrument Co., Ltd, AFS-3100) [28, 30].

Data Processing

Analysis of the horizontal distribution characteristics of heavy metals in soil was conducted using Surfer 8.0 software (Golden Software Company, Inc.), and IBM SPSS Statistics software (version 28.0.1) was used for correlation analysis and principal component analysis.

Evaluation of Heavy Metal Pollution in Soils

The geo-accumulation index [31] and potential ecological risk index [32] were used to evaluate the soil heavy metal pollution in this area.

Geo-accumulation index formula:

$$I_{geo} = \log_2 \left(\frac{C_n}{K \times B_n} \right) \tag{1}$$

In the formula (1), I_{geo} is the ground-accumulation index; C_n is the measured value of heavy metal elements in soil, unit $mg \cdot kg^{-1}$. K is conversion factors (1.5). B_n is the background values of surface chemical elements. According to the value of I_{geo} , the pollution degree of heavy metals in soil can be divided into seven grades: no pollution ($I_{geo} \leq 0$), light pollution ($0 < I_{geo} \leq 1$), moderate pollution ($1 < I_{geo} \leq 2$), moderate pollution ($2 < I_{geo} \leq 3$), heavy pollution ($3 < I_{geo} \leq 4$), heavy pollution ($4 < I_{geo} \leq 5$), and serious pollution ($I_{geo} > 5$) [33, 34].



Fig. 1. Distribution of sampling points in the study area.

the index of single factor potential ecological risk:

$$E_r^i = T_r^i \times \frac{C_f^i}{C_n^i} \quad (2)$$

the index of potential ecological risk:

$$RI = \sum_{i=1}^n T_r^i \times \frac{C_f^i}{C_n^i} \quad (3)$$

In the formula (2) and (3), T_r^i is the toxicity coefficients of a certain heavy metal, the coefficients are Zn = 1, Cr = 2, Cu = Pb = Ni = 5, As = 10, Hg = Cd = 30 [32, 35], C_f^i is the actual content of a certain heavy metal. The background value of heavy metal in soils in Gansu Province [36] is Zn 69.3 mg·kg⁻¹, Cr 70.0 mg·kg⁻¹, Cu 24.1 mg·kg⁻¹, Pb 18.8 mg·kg⁻¹, Ni 35.2 mg·kg⁻¹, As 12.6 mg·kg⁻¹, Hg 0.02 mg·kg⁻¹ and Cd 0.116 mg·kg⁻¹.

E_r^i is a single factor potential ecological risk index of heavy metals, light pollution ($E_r^i < 40$), moderate pollution ($40 \leq E_r^i < 80$), intense pollution ($80 \leq E_r^i < 160$), very intense pollution ($160 \leq E_r^i < 320$), extremely intense pollution ($E_r^i \geq 320$). RI is the potential ecological hazard index [37]. According to the value of RI, the classification of potential ecological risk is determined (RI < 150, belonging to low degree; 150 ≤ RI < 300, belonging to moderate; 300 ≤ RI < 600, belonging to severe; RI ≥ 600, belonging to serious) [34].

Results and Discussion

Horizontal Distribution Characteristics of Heavy Metals in Soils

The study showed that (Fig. 2) the content of Zn and Cr in the topsoil were higher at the southwest corner, and with the increase of radius, the trend of decrease is basically shown. These are mainly due to the southwest corner at the foot of the mine, where Zn and Cr are enriched and leached and migrated under the action of rainfall. The distribution of Cu, Ni, As, Hg and Cd is similar, and the concentration of Cu, Ni, As, Hg and Cd in the northeast corner is higher. Taking the northeast corner as the center of the circle, it basically presents a decreasing trend with the increase of the radius, which may be due to the atmospheric deposition of the tail gas from mining enterprises. Pb accumulated in the northwest corner, which was mainly due to the fact that the northwest corner was adjacent to the highway, and the concentration of Pb in the soil increased due to the influence of anthropogenic activities (e.g. industries, road traffic, demolition and construction) [38, 39]. The results are basically consistent with Liao reported that the over-standard rates of Ni, Cu and As in Jinchang area were 70%, 57% and 13%, respectively [15].

Vertical Distribution Characteristics of Heavy Metals in Soils

The study found that Zn, Cu, Pb, Ni, As, Hg, and Cd were mainly distributed in the 0-60 cm soil layer (Fig. 3), and there was an obvious inflection point at a depth of 60cm, and basically presented uniform distribution below the inflection point, indicating that Zn, Cu, Pb, Ni, As, Hg, and Cd occur leaching migration in the soil profile, and the migration depth was 60 cm. However, Cr was basically evenly distributed in the 0-100 cm soil layer, which indicated that Cr has no obvious vertical migration. Judging from the coefficient of variation, the coefficients of variation were ranked as follows: Cu > Hg > Cd > Ni > As > Zn > Pb > Cr, and the coefficients of variation were 80.3%, 69.5%, 48.8%, 47.3%, 23.4%, 19.7%, 18.3%, 13.2%, respectively. According to Wilding's classification of coefficient of variation [40], the Cu, Hg, Cd, and Ni were all highly variable (CV > 36%), while the As, Zn, and Pb were moderately variable (15% < CV < 36%), indicating that the Cu, Hg, Cd and Ni were greatly affected by human activities.

Evaluation of Heavy Metals Pollution in Soils

Evaluation of the Risk Value Screening

According to the "Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standard (Trial)" [41], the contents of Cu, Hg, Cd, Ni, As, Zn, Pb, and Cr in soils in the study area were evaluated (Table 1). In the 0-20 cm soil layer, it was found that the over-standard rates of As, Cu and Ni were 38.5%, 30.8% and 15.4%, respectively, and in the 20-40 cm soil layer, the over-standard rates of As, Cu and Ni were all 7.7%, and the contents of Hg, Cd, Zn, Pb, and Cr did not exceed the risk screening value. The results are basically consistent with Pan et al. reported that the over-standard rates of Cu, Ni and As in Jinchuan area were 100%, 91.7% and 4.2%, respectively [42]. Therefore, the pollution of Cu, Ni and As in soils existed in the study area.

Evaluation of the Geo-Accumulation Index

The geo-accumulation index was ranked as follows: Cu > Ni > Cd > Hg > Pb > Cr > As > Zn, and the geo-accumulation index decreased with the increase of soil depth (Table 2). The result was exactly the same as those reported by Xu et al. [18], and the different conclusions reported by Li [43]. In the 0-20 cm soil layer, the geo-accumulation index of Cu, Ni, Cd, Hg, Pb, Cr, As and Zn were 2.31, 1.70, 1.42, 1.32, 0.16, 0.03, -0.03 and -0.19, respectively. According to the pollution classification of the I_{geo} values, Zn and As were not polluted, Cr and Pb were light pollution, Ni, Cd and Hg belonged to partial moderate pollution, and

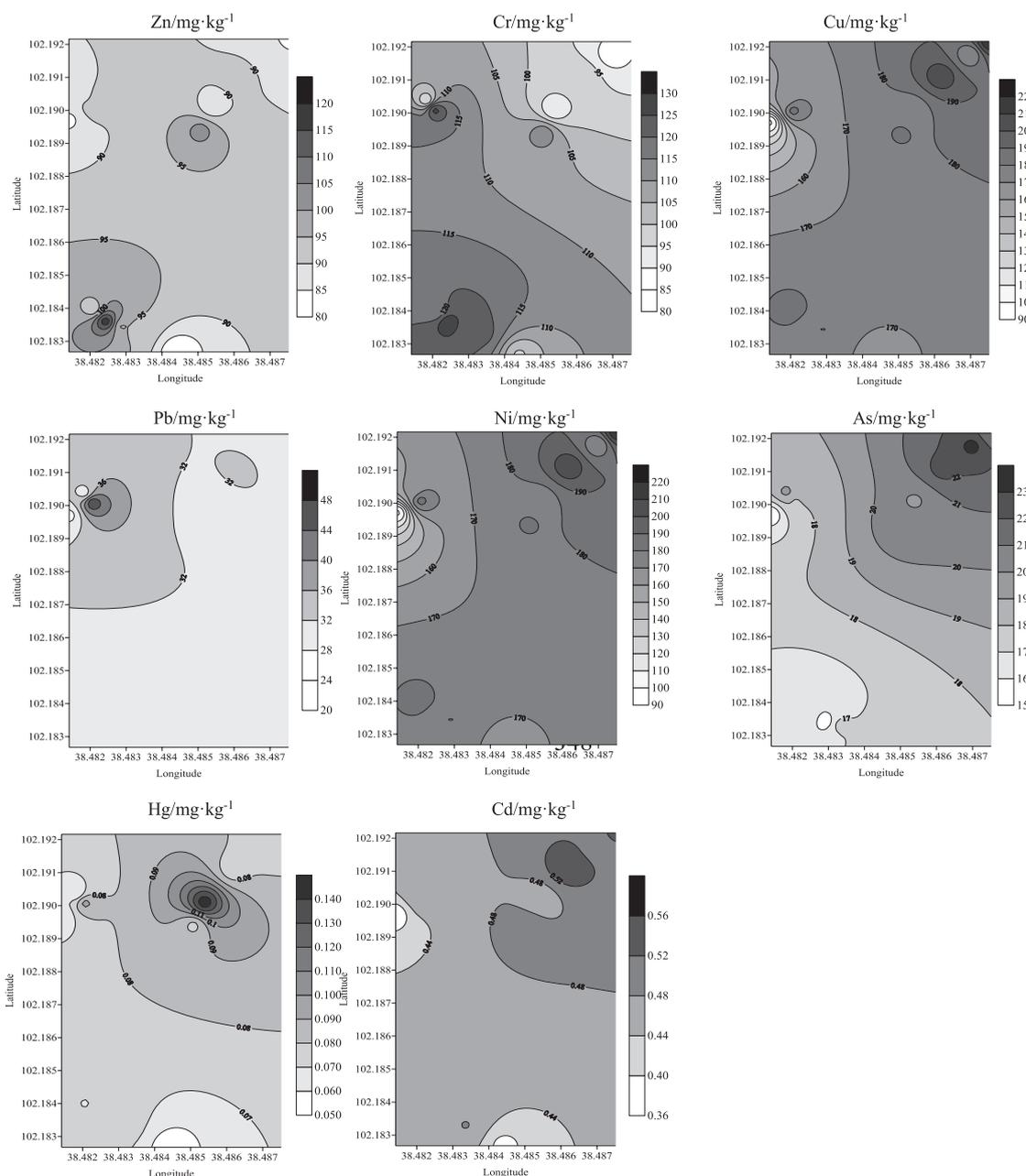


Fig. 2. Horizontal distribution characteristics of heavy metals in soils.

Cu belonged to moderate pollution. In the 20-40 cm soil layer, the geo-accumulation index of Cu, Ni, Cd, Hg, Pb, Cr, As, and Zn were 1.65, 1.24, 0.94, 0.86, -0.06, -0.02, -0.16, and -0.31, respectively. Zn, As and Cr were no pollution, Cd and Hg were light pollution, Cu and Ni belonged to partial moderate pollution.

Evaluation of the Potential Ecological Risk Index

The index of single factor potential ecological risk (E_r^i) was ranked as follows: Cd>Hg>Cu>Ni>As>Pb>Cr>Zn (Table 3). The Cd and Hg belonged to intensive pollution, and the E_r^i of Cu, Ni, As, Pb, Cr, and Zn were all less than 40, which was light pollution. This

indicated that Cd and Hg had a great contribution rate to the environmental quality of heavy metals in soil in the study area, and were the main controlling factors of heavy metal pollution in this area. In the 0-20 cm soil layer, the comprehensive potential ecological risk index (RI) was 323.71, which belonged to severe pollution, and in the 20-40 cm soil layer, the RI was 236.36, which belonged to moderate pollution (Fig. 4). From RI spatial distribution, the RI were all greater than 300 and less than 600 in the sampling sites of the 1 #, 2 #, 3 #, 4 #, 6 #, 9 #, 10 #, 11 #, 12 # and 13 #, they belonged to severe risk areas. The RI were all greater than 150 and less than in the sampling sites of the 5 #, 7 # and 8#, they belonged to moderate risk areas. Therefore, from the distribution of sampling sites

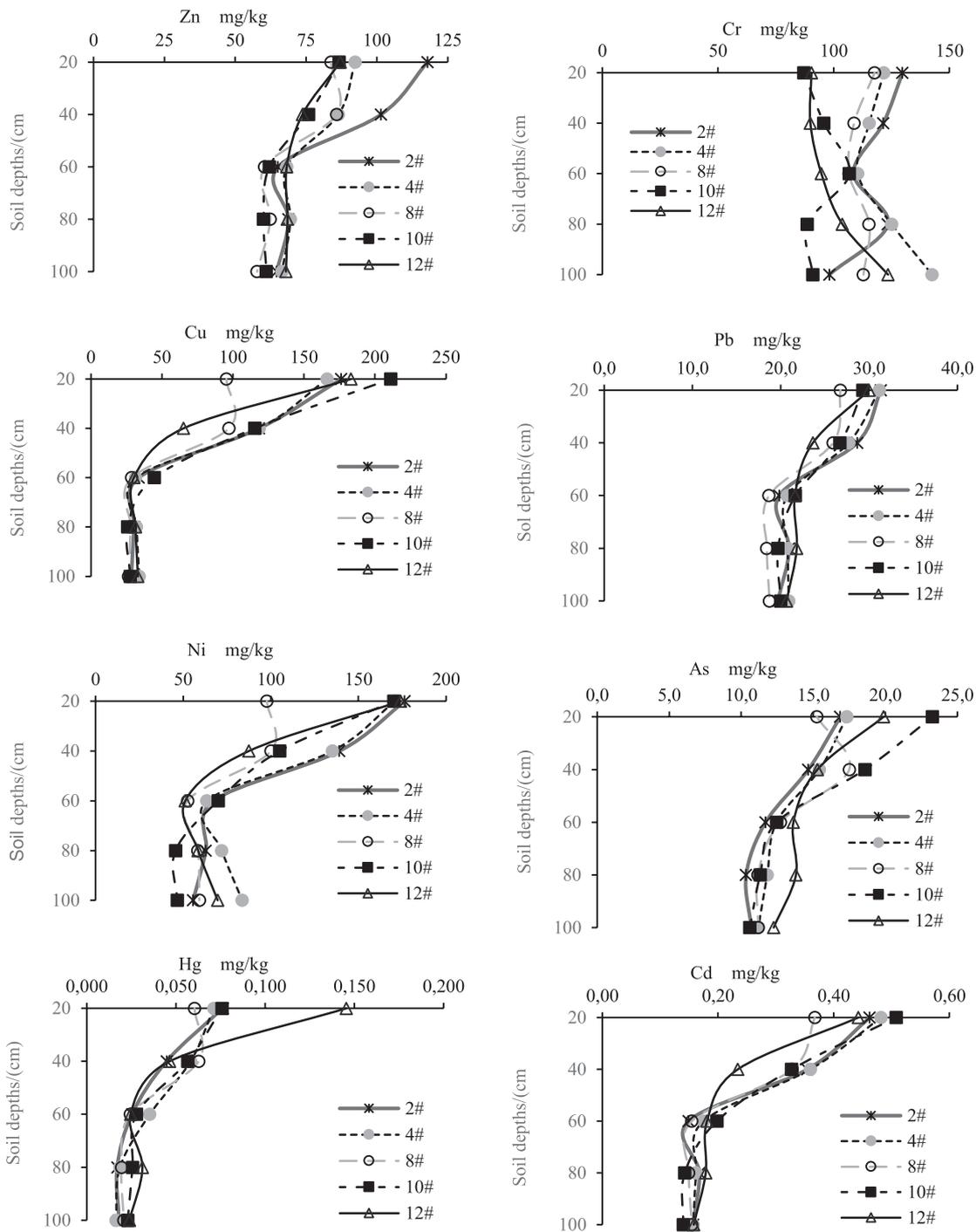


Fig. 3. Vertical distribution characteristics of heavy metals in soils.

on the map, the area A and C basically belonged to severe risk areas, while the area B belonged to moderate risk areas.

Analysis of Heavy Metal Pollution Sources

There is generally a certain correlation between pollutants from the same pollution source when the pollution source analysis, and the reflected information

has a certain overlap [43]. Therefore, in order to further verify the source of heavy metal elements in the study area, the principal component analysis was carried out (Table 4). The contribution rate of the first principal component reached 58.199%. The Cu, Cd and Ni have higher loads in the factor variables, the loads are 0.965, 0.964, and 0.947 in turn, which further shows that Cu, Cd and Ni have homology. This may be due to the obvious accumulation of Cu, Cd and Ni in soils caused by sewage irrigation and downwind atmospheric

Table 1. Heavy metals pollution survey in soil in the study area (n = 13, pH>8.0) unit: mg·kg⁻¹

Element	Risk value screening	Risk value controlling	0-20 cm		20-40 cm	
			Average±standard deviation	Over-standard rates (%)	Average±standard deviation	Over-standard rates (%)
Cr	350	1300	108.4±15.4	0.0	105.9±12.9	0.0
Ni	190	—	174.2±28.1	15.4	128.9±35.4	7.7
Cu	200	—	183.5±37.1	30.8	119.4±48.7	7.7
Zn	300	—	91.8±9.6	0.0	84.2±7.9	0.0
Cd	0.8	4.0	0.47±10.05	0.0	0.34±0.09	0.0
Pb	240	1000	31.7±4.9	0.0	27.1±2.5	0.0
As	20	100	18.7±2.6	38.5	16.8±2.6	7.7
Hg	1	6.0	0.078±0.023	0.0	0.056±0.012	0.0

Table 2. Geo-accumulation index (I_{geo}) of heavy metal in the study area.

Soil depths (cm)	Cr	Ni	Cu	Zn	Cd	Pb	As	Hg
0-20	0.03	1.70	2.31	-0.19	1.42	0.16	-0.03	1.32
20-40	-0.02	1.24	1.65	-0.31	0.94	-0.06	-0.16	0.86

Table 3. The average value of (E_r^i and RI).

Soil depths (cm)	E_r^i								RI
	Cr	Ni	Cu	Zn	Cd	Pb	As	Hg	
0-20	3.09	24.75	38.09	1.32	116.99	8.43	14.85	116.18	323.71
20-40	3.03	18.32	24.78	1.22	85.19	7.21	13.33	83.27	236.36

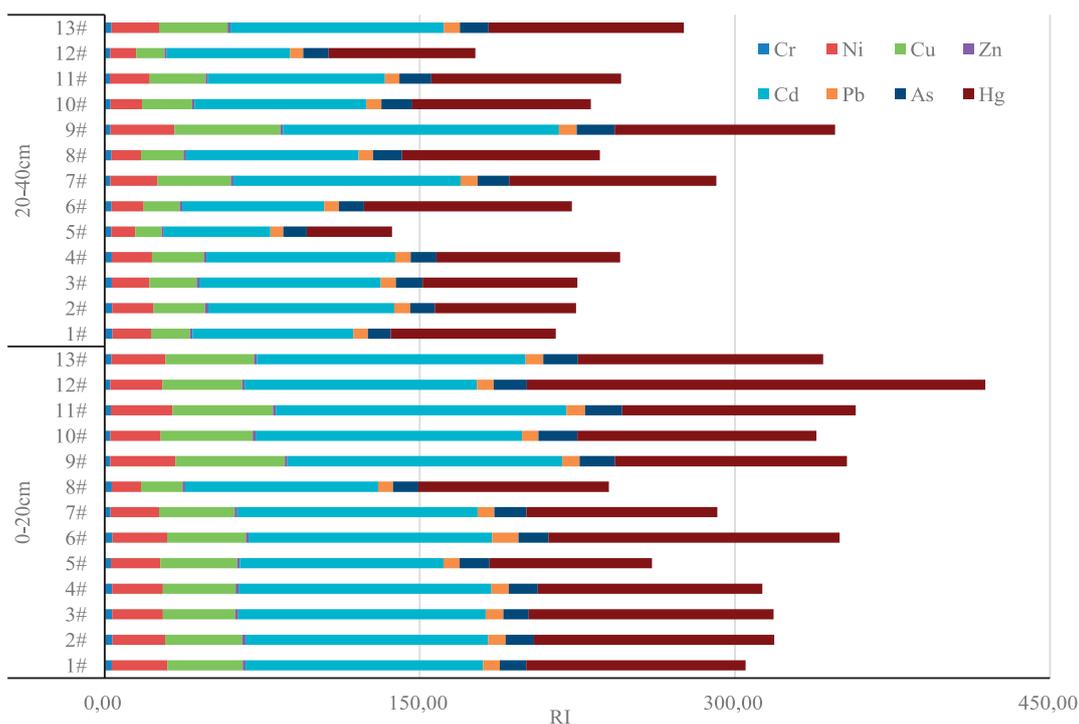


Fig. 4. Integrated potential ecological risk index (RI) at each sampling sites.

Table 4. Principal component analysis of heavy metals in soils in the study area.

Principal component	Eigenvalue	Proportion of cumulative variable (%)	Evaluation factors							
			Cr	Ni	Cu	Zn	Cd	Pb	As	Hg
PRIN1	4.656	58.199	-0.1	0.947	0.965	0.548	0.964	0.736	0.768	0.674
PRIN2	1.874	81.625	0.969	0.033	-0.154	0.681	0.030	0.352	-0.566	-0.017

settlement. But Chen et al. reported that the main anthropogenic pollution sources of Cu and Cd in soils are agricultural activities such as fertilization, whereas industrial activities contribute a large proportion in certain areas, Ni and Cr are mainly controlled by soil parent materials [45]. The contribution rate of the second principal component is 23.426%, and the Cr has a higher load in the factor variables, the loads is 0.969. Combined with the uniform distribution of Cr in soil profile, it is not difficult to infer that Cr mainly comes from soil background value. Because this area is adjacent to the mining area in the southern mountainous area, the content of the Cr is high in the soil background value. This is consistent with Deng's report that the Cr is an element obviously enriched in Jinchang nickel ore rock mass and has a high concentration in the ore, which leads to its accumulation near the mining area and around the tailings reservoir [46].

In this study, heavy metals pollution in soils were evaluated by three methods of the risk value screening, geo-accumulation index and potential ecological risk index. The advantage of the risk value screening evaluation method is to determine the risk value and control value of soil pollution of different elements according to different heavy metal elements, different agricultural land types and soil pH values, which makes up for some defects of the "Soil Environmental Quality Standard" promulgated in 1995, but at the same time, the influence of heavy metal morphology is ignored [47]. The geo-accumulation index evaluation method fully considers the environmental geochemical background value, man-made pollution factors and factors that may cause background value changes due to natural diagenesis [48]. However, the migration ability of heavy metals is closely related to the physical and chemical properties of soil, and there are certain differences compared with river sediments. There is no uniform standard at home and abroad on how to modify the coefficient to adapt to heavy metals in farmland soil [47]. The potential ecological risk index evaluation method not only considers the content and background value of heavy metals in soil, but also increases the toxicity coefficient, reflecting the bioavailability of heavy metals [49]. However, the interaction of toxicity of different heavy metals and the correction of toxicity coefficient need further study [50]. Compared with the three methods in this study, the risk value screening method is close to the actual conditions in the area, the ground accumulation index method has higher sensitivity, and the potential ecological risk index

method can reflect the comprehensive pollution of heavy metals in soils.

Conclusions

The concentration of Zn and Cr in the topsoil were higher at the southwest corner, and the trend of decrease was basically shown with the increase of radius. The distribution of Cu, Ni, As, Hg and Cd were similar, and the concentration of Cu, Ni, As, Hg and Cd in the northeast corner were higher, taking the northeast corner as the center of the circle, it basically presented a decreasing trend with the increase of the radius, and Pb accumulates in the northwest corner.

The study found that Zn, Cu, Pb, Ni, As, Hg, and Cd were mainly distributed in the 0-60 cm soil layer, and there was an obvious inflection point at a depth of 60cm, and basically presented uniform distribution below the inflection point, while the Cr was basically evenly distributed in the 0-100 cm soil layer.

It was found that the content of Cu and Ni in the soils of the study area exceeded the standard by the methods of the risk value screening and geo-accumulation index. The geo-accumulation index (I_{geo}) was ranked as follows: Cu>Ni>Cd>Hg>Pb>Cr>As>Zn, and the geo-accumulation index decreased with the increase of soil depth. The index of single factor potential ecological risk (E_r^i) was ranked as follows: Cd>Hg>Cu>Ni>As>Pb>Cr>Zn. Based on the comprehensive potential ecological risk index judgement, it belonged to severe pollution in the 0-20 cm soil layer and moderate pollution in the 20-40 cm soil layer. Therefore, the study area should be divided into safe utilization category and priority protection category. The input of pollution sources should be strictly controlled for the priority protection category, for instance, alternative planting, fallow and rotating should be implemented to reduce the transfer of heavy metals to crops and reduce the risk of food safety and health.

Acknowledgments

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Conflict of Interest

All the authors certify that all co-authors have read the manuscript and agreed with its submission.

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