Heavy metal pollution characteristics and health evaluation of farmland soil in a gold mine slag area of Luoyang in China

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Abstract: The characteristics of eight heavy metals (lead, zinc, copper, nickel, chromium, cadmium, mercury and arsenic) in the surface soil of the historical slag area of the Au ore dressing plant in the South-West of Luoyang City were investigated and evaluated in terms of a pollution index, potential ecological hazards and health risks. The results showed that the average amounts of the heavy metals Pb, Zn and As in the soils of plots S3, S5, S7, S12 and S18 exceeded the soil pollution risk screening values. The Mero comprehensive pollution index in plots S7, S12 and S18 was greater than 3, indicating severe pollution. The severe pollution plot integrated the potential ecological risk index (RI) of each sampling point, which was in the order of $RI_{S12}>RI_{S18}>RI_{S7}>RI_{S5}>RI_{S3}$. Among the heavy metals, Cd poses the greatest threat to ecological and human health. The effects of heavy metals in soil on the single non-carcinogenic health risk index (HQ) and the non-carcinogenic total risk index through three exposure pathways were in the order of $HQ_{Hg}<HQ_{Cu}<HQ_{Ni}<HQ_{Zn}<HQ_{Cd}<HQ_{Cr}<HQ_{Pb}<HQ_{As}<1$, which meant that the adult and child total carcinogenic risk (TCR) and individual carcinogenic health risk indices CR_{As} and CR_{Cd} were above the maximum acceptable human health level recommended by the USEPA (10^{-6}). TCR_{As} and TCR_{Cd} accounted for 75.65% and 23.94% of the adult TCR, respectively. TCR_{As} and TCR_{Cd} accounted for 75.93% and 23.97% of the child TCR, respectively. Overall, the TCR of children was greater than that of adults. In summary, the soil in the historical slag area of the Au ore dressing plant constitutes a serious threat to the surrounding ecological environment and to residents.

Keywords: historical slag area, heavy metals, pollution assessment, health assessment, farmland soil, ecological hazard
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1 Introduction

Luoyang City is one of the most important heavy metal mining areas in China, with many high-quality heavy metal mines. The area contains over 800 heavy metal-rich resources and co-associated minerals that have served as the foundation for the stable development of China's economy[1]. However, owing to the lack of awareness of environmental protection and poor management, the process of long-term mining of heavy metal areas has seriously affected the surrounding environment, which has led to a series of ecological and environmental problems[2,3]. A large amount of beneficiation waste generated in the process of ore smelting is one of the most important sources of heavy metal pollution[4,5]. However, due to the insufficient environmental awareness of enterprises in the past, a large amount of waste rocks and tailings and other solid wastes generated in the mining and smelting process are randomly stacked, which not only takes up a lot of land resources, but also causes serious damage to the mine and the surrounding environment. Ecological destruction and environmental pollution have resulted in the accumulation of large amounts of heavy metals in the soil around mining areas and solid waste storage areas such as waste rocks and tailings[6-8]. In recent years, with regard to heavy metal pollution in the soil near mining areas, predecessors have used different analysis methods to carry out a lot of research work in terms of content characteristics, source analysis and spatial distribution characteristics. Chen et al.[9] found that the mining and smelting process of gold mines will cause different levels of heavy metal pollution in the surrounding soil. Among them, the average concentration of lead, mercury and copper far exceeds the local soil background value. Cao et al.[10] sampled and analyzed heavy metals in the soil near the Jiaojia Gold Mine in Shandong Province. The average Hg, As, Cd and Pb concentrations in all samples exceeded the local background value. Feng et al.[11] studied the Hg pollution in the air, water, sediment, soil and crops near the Tongguan Au mine in China and found that the average concentration of total gaseous mercury in the ambient air in the Au mine reached 1.8×10^{-2} mg/m^3, exceeding China's limit of 10^{-3} mg/m^3.

Humans can be exposed to toxic pollutants in a variety of ways, and these pollutants can easily enter the body through skin contact, respiratory absorption and soil intake[12]. In addition, heavy metals in soil are prone to accumulate in the human body owing to their non-biodegradable properties and long half-life[13]. Therefore, Cr, Cd and Pb are considered potential carcinogens and are related to the pathology of many diseases[14]. Trace amounts of heavy metals are essential for normal human physiological processes, but excessive intake can adversely affect the human body. Therefore, the health risk assessment of soil heavy metal

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pollution is an important research field of environmental science. The assessment provides a scientific basis for linking soil environmental pollution with human health, describes the risks of heavy metal pollution in soil to human health and identifies priorities for controlling pollution elements and potential health risks[15].

Karim and Qureshi[16] found that children with different exposure routes had a combined risk index (HI) of 8.9 times that of adults. Sun et al.[17] used the Geological Accumulation Index to study heavily polluted Au mining activity areas and the remediation of heavy metal pollution in soils to provide information on pollution levels and ecological risks in residential areas. Gržetić and Ghariani[18] adopted a specific approach to determine human exposure to soils in urban residential areas, paying particular attention to the different exposure rates for children and adults. Tao et al.[19] evaluated the pollution characteristics and health risks of heavy metals Cu, Cd, Cr, Pb, Zn in the soil of a copper mine wasteland in Shangrao City and showed that the risk of Cr pollution to human health cannot be ignored. Nie et al.[20] evaluated the distribution characteristics and health risk of heavy metals in vegetable soils in the Xihuashan tungsten mining area and showed that Cr has the most serious non-carcinogenic risk, far exceeding the health limit set by the US Environmental Protection Agency (US EPA). Therefore, when evaluating heavy metal pollution in the soil of a certain area, a variety of evaluation methods should be used to analyze the potential risks of heavy metal pollution from multiple aspects and perspectives[21-23]. At the same time, these evaluation methods link soil environmental pollution with human health and describe soil pollution. The risks of heavy metal pollution to human health have determined the priority control of pollutant elements and potential health risks, as well as the subsequent risk control to provide a scientific basis. These methods can provide scientific guidance and comprehensive protection for the health of residents.

The research area is a historical residue slag area generated by the typical cyanidation process. To date, there are few reports on the characteristics of soil heavy metal pollution in the historical legacy slag generated by the cyanidation process in the Luoyang area; however, few studies have systematically described the potential health risks of humans studying the region's historical slag heap area through three contact routes. Therefore, this study analysed the changes in the heavy metal contents in the soil of the historical slag area of the Au ore dressing plant and illustrated the paths of Pb, Zn, Cu, Ni, Cr, Cd, Hg and As through atmospheric deposition, precipitation runoff and slag percolation. This study analysed the distribution characteristics of heavy metal pollution in the soil and the application of pollution index methods and potential ecological risk assessment methods and introduced a toxicity coefficient to make a more objective and accurate determination of the status of contaminated land. The above analysis was combined with the health risk assessment model developed by the United States, Environmental Protection Agency (USEPA) to assess the health of different populations near the contaminated soil. The risks were evaluated to provide a scientific basis for the rational use and restoration of the study area to protect the health of residents[24,25].

2 Materials and methods

2.1 Overview of the study area

Songxian County is located in the southwest of Luoyang City, Henan Province, between the northern foot of Funiu Mountain and its branches outside Fangshan and Xiong'er Mountain. The county is located between 111°24′-112°22′E, 33°35′-34°21′N and it is approximately 62 km wide at the widest point and approximately 86 km long. The terrain gradually rises from northeast to southwest with an elevation of 245.0-2211.6 m and a vertical height difference of 1966.6 m. It is located in the transition zone from a warm temperate zone to a subtropical zone. The annual rainfall is 500-800 mm and the annual average temperature is 14 ℃. Summer experiences mostly an easterly and southeasterly wind, whereas winter experiences mostly a westerly and northwesterly wind with maximum wind power of 10.8-20.7 m/s. The survey area is rich in mineral resources. As of June 2013, there were 35 types of proven minerals in Xongxian County, among which the metal minerals are Au, Ag, Mo, Pb, Cu, Mn and more than 10 types of U[1]. The county contains large Au mineral reserves, and it is one of the six major Au-producing counties in the country. Xongxian County is known as a location of high-purity Au both within and outside of China.

The total study area covers 0.14 km^2. According to the investigation, there is no other production enterprise within approximately 1 km around the study site and only one Au ore dressing plant on the south side. Before 1993, the land in the study area was low-lying tidal flats, and during 1993-1995, slag continued to be discharged into the area. It is understood that the emissions at that time were approximately 10^6 kg/a. In recent years, local villagers levelled the land in the study area and planted crops for their own use.

2.2 Sample collection and processing

Using a 100 m×100 m grid layout, the cultivated land in the study area was divided into 18 plots (Figure 1). Three surface soil samples were collected for each plot (approximately 0-20 cm), with soil samples of 1 kg per point. The soil samples were air-dried indoors, and the gravel and plant roots were removed, ground and passed through a 200 mesh (0.074 mm) sieve for use. Each sample was weighed to be 0.3000 g to a scale of one ten-thousandth of a gram using the HCl-HNO_3-$HClO_4$-HF digestion method. For quality control, each digestion batch included reagent blanks and representative reference standards. Analytical blanks and replicate samples each accounted for 10% of the total sample to assess the accuracy and precision of the analysis. The analytical procedures were verified using the Chinese National Reference Materials Research Center standard references GBW-07403 (soil). Repeated analysis of these reference materials showed that the method had high accuracy, the element recovery rate was 90%-110% and the reagents used in the analysis were analytically pure. The samples were digested with soil samples using a Beijing Kewei Yongxing Instrument Co., Ltd. adjustable electric heating plate (ML2A-4), and heavy metals were detected using a combination of a Beijing Amplifier General Instrument Co., Ltd. flame atomic absorption spectrophotometer (TAS-990AFG) and atomic fluorescence photometer (Model AFS-930).

2.3 Risk assessment method

The pollution status of the soil in the historical slag area of the Au mining plant was evaluated using the single pollution index method, the Mero comprehensive pollution index (P_N) and the potential ecological risk index (RI). The health risk assessment model generated by the USEPA was used to evaluate the health risks posed by heavy metals to adults and children.

Figure 1 Schematic diagram of the sampling points in the study area

2.4 Soil pollution assessment method

2.4.1 Pollution index method

The pollution level of surface soil by a given heavy metal was evaluated using the pollution index (PI)[26], which is calculated as:

$$\mathrm{PI}=C_i/S_i \tag{1}$$

where, C_i is the measured concentration of the pollutant, mg/kg; S_i is the evaluation standard of the pollutant, mg/kg.

The level of pollution caused by multiple heavy metal species was evaluated using the Mero integrated pollution index (P_N)[27], which is calculated as:

$$\mathrm{P_N}=\sqrt{\frac{P_{\mathrm{ave}}^2+P_{\max}^2}{2}} \tag{2}$$

where, P_{ave}^2 is the average pollution index of the pollutant in the soil; $P_{\max}^2$ is the maximum index of a single pollutant in the soil.

The single pollution index method and the PN evaluation criteria are listed in Table 1[26,27].

Table 1 Classification criteria of the pollution index methods

Single pollution index	Mero Comprehensive Pollution Index Act	Pollution level
PI	P_N	
PI≤1.0	P_N≤1.0	Clean
1.0<PI≤2.0	1.0<P_N≤2.0	Light pollution
2.0<PI≤3.0	2.0<P_N≤3.0	Medium pollution
PI>3.0	P_N>3.0	Heavy pollution

2.4.2 Potential ecological risk index

EI is the single risk index for heavy metal i and can be calculated from the measured PI, The RI of heavy metals is commonly expressed as follows:

$$\mathrm{EI}=T_i\,\mathrm{PI} \tag{3}$$

The potential ecological risk posed by heavy metal pollution in the surface soils of the Gold Mine Slag area was evaluated with the ecological risk index (RI) introduced by Hakanson et al.[28], It was calculated as the sum of risk index of the individual heavy metals:

$$\mathrm{RI}=\sum_{i=1}^{n}\mathrm{EI} \tag{4}$$

where, PI is the single factor pollution index for contaminated elements in the soil; T_i is the different metal biological toxicity response factors and RI is a potential ecological hazard index for a variety of heavy metals. The toxicity coefficients of the Pb, Zn, Cu, Cr, Ni, As, Hg and Cd pollutants involved in this study are 5, 1, 5, 2, 5, 15, 40 and 30[29], respectively. The specific classification is shown in Table 2[28,29].

Table 2 Potential ecological risk indicators and classification relationships

Single heavy metal ecological risk index	Multiple heavy metals ecological risk index	Ecological risk level
EI	RI	
EI<40	RI<150	Slight
40≤EI<80	150≤RI<300	Medium
80≤EI<160	300≤RI<600	Strong
160≤EI<320	600≤RI	Very strong
320≤EI		Extremely strong

2.4.3 Health risk assessment of heavy metals in soil

This study used the health risk assessment model developed by the US EPA, which includes a carcinogenic health risk model and a non-carcinogenic health risk model, to conduct health risk assessments for residents near the historical slag area of the Au mining plant. The model calculation equations are listed in Table 3.

Table 3 Calculation formula of the health risk assessment model

Exposure pathway	Risk calculation	
Ingestion of soil	$\mathrm{ADD}_{ingestion-soil}=\frac{\mathrm{C}_i\times\mathrm{IR}_{soil}\times\mathrm{CF}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}}$	(5)
Skin contact	$\mathrm{ADD}_{dermal-soil}=\frac{\mathrm{C}_i\times\mathrm{CF}\times\mathrm{SA}\times\mathrm{AF}\times\mathrm{ABS}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}}$	(6)
Respiratory intake	$\mathrm{ADD}_{inhale-soil}=\frac{\mathrm{C}_i\times\mathrm{IR}_{air}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{PEF}\times\mathrm{BW}\times\mathrm{AT}}$	(7)
Carcinogenic risk	$\mathrm{CR}_i=\sum\mathrm{ADD}\times\mathrm{SF}$	(8)
	$\mathrm{TCR}=\sum\mathrm{CR}_i$	(9)
Non-carcinogenic risk	$\mathrm{HQ}_i=\sum\frac{\mathrm{ADD}}{\mathrm{RfD}}$	(10)
	$\mathrm{HI}=\sum\mathrm{HQ}_i$	(11)

CR_i is the individual carcinogenic heavy metal health risk index, SF is the slope coefficient of the first exposure pathway for carcinogenic heavy metals and TCR is the total carcinogenic risk index of carcinogenic heavy metals through three pathways. In general, CR and TCR values of less than 10^{-6} can be considered safe and do not require soil remediation. HQ_i is a single health risk index for non-carcinogenic heavy metals, RfD is the reference dose for non-carcinogenic heavy metal exposure pathways and HI is the non-carcinogenic total risk index of eight heavy metals through three pathways. When the HQ value is less than 1, it can be considered that there is no risk to sensitive populations. If the value of HI is less than 1, there is no chronic non-carcinogenic risk. If the HI value is greater than 1, it exceeds the human health acceptable threshold, indicating that the soil needs to be repaired. The meaning and values of each parameter are shown in Tables 4 and 5[24,25,30].

Table 4 RfD and SF values of model parameters

Pathway	Parameter	Cu	Zn	Pb	Cd	Cr
Skin contact	RfD	1.90×10^{-3}	6.00×10^{-2}	3.52×10^{-3}	1.00×10^{-3}	2.50×10^{-4}
	SF				6.1	
Oral intake	RfD	3.70×10^{-2}	3.00×10^{-1}	3.50×10^{-3}	1.00×10^{-3}	5.00×10^{-3}
	SF				6.1	
Respiratory intake	RfD	4.02×10^{-2}	3.00×10^{-1}	5.25×10^{-3}	1.00×10^{-3}	2.86×10^{-5}
	SF				3.80×10^{-3}	0.5

Note: Since the non-toxic parameters of Ni, Hg, and As among the eight characteristic pollutants can be used for reference, this study only conducts health risk assessment for Zn, As, Cd, Hg, and Pb.

Table 5 Health risk assessment exposure parameters

Exposure parameter	Parameter meaning	Adult reference value	Child reference value	Reference
BW/kg	Receptor weight	56.8	19.2	[30]
IR_{soil}/mg d^{-1}	Soil uptake rate	100	200	[30]
IR_{air}/m^3 d^{-1}	Air intake rate	20	10	[30]
ED/a	Exposure time	25	6	[24]
EF/d a^{-1}	Exposure frequency	350	350	[24]
AF/mg cm^{-2}	Soil adhesion coefficient to skin	0.07	0.20	[24]
CF/kg mg^{-1}	Conversion factor	10^{-6}	10^{-6}	[24]
SA/cm^2 d^{-1}	Skin area that may be in contact with soil	5700	2800	[30]
PEF/m^3 kg^{-1}	Soil dust diffusion factor	1.13×10^9	1.13×10^9	[30]
ABS	Skin absorption coefficient	0.001	0.001	[30]
At cancer/d	Average contact time	70×365	70×365	[24]
At non-carcinogenic /d	Average contact time	ED×365	ED×365	[24]

3 Results and analysis

3.1 Soil heavy metal characteristics

The statistical results of the analysis of the heavy metal content of soils in the historical slag area of the Au ore dressing plant are shown in Table 6. The average soil pH in the survey area was greater than 7.5, which meant that the soil was weakly alkaline. The contents of Cd, Cr, Ni, Pb, Cu, Zn, Hg and As in the soils of different plots were 0.02-7.70 mg/kg, 51.00-94.00 mg/kg, 33.00-123.00 mg/kg, 0.001-583.00 mg/kg, 23.00-56.00 mg/kg, 65.10-892.00 mg/kg, 0.038-0.73 mg/kg and 13.40-112.00 mg/kg, respectively. In general, the average levels of the heavy metals Pb, Zn and As in some parts of the historical slag area of the Au mining plant exceeded the risk control standard for soil contamination of agricultural land (Trial) (GB 15618-2018)[31]. The average levels of Ni, Pb, Cu, Zn, Hg and As in the soil of the historical slag area of the Au mining plant exceeded the background soil levels in Henan Province. The values indicated that some areas of the soil in the study area had been exposed to significant exogenous heavy metal pollution[32].

The coefficients of variation of heavy metals in the soil were in the order of Cd>Pb>Hg>Zn>As>Ni>Cu>Cr, which was different from the coefficients of variation with a low pH. The difference in heavy metal contents in different sampling areas was significant, and the dispersion was even more significant. The magnitude of (Cd, Pb, Hg, Zn, As, Ni, Cu and Cr) indicated that the levels of the eight heavy metals were greatly affected by exogenous heavy metals, and the spatial distribution was significantly different. The spatial distribution of heavy metals in the surface soil is strongly influenced by human activities such as mineralization and slag[33].

A common source of multiple heavy metals was suggested by the correlation between the heavy metal elements[34]. The Pearson correlation coefficients shown in Table 7 indicate that pH was negatively correlated with the heavy metals, except for Cr. Among them, Cd and Cu, Zn, Hg and As showed strong positive correlations ($p<0.01$), with correlation coefficients greater than 0.7, indicating that these five heavy metal elements might have had the same source. The correlation coefficients of heavy metal elements Cu and Hg, and Cu and As in the soil are 0.698 and 0.714, respectively, which have a very strong positive correlation ($p<0.01$); the correlation coefficient of Hg and As is greater than 0.8, which also shows a significant positive correlation. Since Cd, Cu, Zn, Hg, and As have a significant positive correlation, it can be preliminarily determined that the above-mentioned metal elements have high homology and may have the same occurrence form or environmental effect, which is likely to be affected by The influence of the historical accumulation of slag in the gold concentrator, which is consistent with the results of previous studies[35].

Table 6 Descriptive analysis of heavy metal parameters in the soil

Sampling point (number of samples)	pH	Cd	Cr	Pb	Cu	Ni	Zn	Hg	As
S1 (3)/mg kg^{-1}	8.17	0.13	51.00	29.50	23.00	33.00	73.80	0.091	13.40
S2 (3)/mg kg^{-1}	7.56	0.13	61.00	39.30	26.00	38.00	87.00	0.044	15.60
S3 (3)/mg kg^{-1}	8.17	0.16	58.00	38.40	28.00	46.00	686.00	0.090	16.60
S4 (3)/mg kg^{-1}	8.01	0.17	85.00	36.90	28.00	51.00	98.30	0.063	15.00
S5 (3)/mg kg^{-1}	8.18	1.20	73.00	237.00	36.00	40.00	302.00	0.059	29.30
S6 (3)/mg kg^{-1}	8.46	0.16	59.00	42.00	38.00	40.00	118.00	0.065	17.00
S7 (3)/mg kg^{-1}	8.05	2.48	56.00	909.00	38.00	36.00	465.00	0.280	48.80
S8 (3)/mg kg^{-1}	8.25	0.12	62.00	67.40	40.00	56.00	92.30	0.073	17.40

Sampling point (number of samples)	pH	Cd	Cr	Pb	Cu	Ni	Zn	Hg	As
S9 (3)/mg kg^{-1}	7.96	0.14	56.00	35.30	48.00	123.00	91.20	0.075	15.10
S10 (3)/mg kg^{-1}	8.16	0.12	62.00	39.60	33.00	40.00	92.10	0.053	14.80
S11 (3)/mg kg^{-1}	8.28	0.22	59.00	66.90	33.00	35.00	65.10	0.078	16.50
S12 (3)/mg kg^{-1}	7.83	11.30	59.00	584.00	56.00	100.00	592.00	0.729	97.10
S13 (3)/mg kg^{-1}	8.26	0.16	75.00	48.10	37.00	37.00	126.00	0.076	15.20
S14 (3)/mg kg^{-1}	8.09	0.58	80.00	55.10	37.00	42.00	178.00	0.076	17.70
S15 (3)/mg kg^{-1}	8.25	0.25	69.00	58.90	36.00	40.00	112.00	0.047	16.00
S16 (3)/mg kg^{-1}	8.04	0.18	67.00	51.70	39.00	42.00	115.00	0.299	15.90
S17 (3)/mg kg^{-1}	8.28	0.02	94.00	44.40	39.00	47.00	107.00	0.038	15.40
S18 (3)/mg kg^{-1}	7.89	7.70	69.00	0.001	51.00	18.00	892.00	0.411	102.00
Maximum value/mg kg^{-1}	8.46	7.70	94.00	584.00	56.00	123.00	892.00	0.729	102.00
Minimum value/mg kg^{-1}	7.56	0.02	51.00	0.001	23.00	33.00	65.10	0.038	13.40
Average value/mg kg^{-1}	8.11	1.40	66.39	132.42	37.00	48.00	238.49	0.150	27.71
Standard deviation	0.20	2.98	11.01	228.55	8.20	24.03	241.67	0.17	26.64
Coefficient of variation/%	2.46	213.00	16.58	173.00	22.16	50.00	101.00	113.00	93.13
Henan background value (surface layer)/mg kg^{-1}	7.70	0.06	63.20	22.30	20.00	27.40	62.50	0.025	9.80
(GB15618-2018) Risk screening values (pH>7.5) /mg kg^{-1}		0.60	250.00	170.00	100.00	190.00	300.00	3.40	25.00

Table 7 Correlation analysis of the soil heavy metal content

	pH	Cd	Cr	Pb	Cu	Ni	Zn	Hg	As
pH	1.000								
Cd	–0.439	1.000							
Cr	0.130	–0.130	1.000						
Pb	–0.194	0.483*	–0.255	1.000					
Cu	–0.157	0.724**	0.170	0.314	1.000				
Ni	–0.248	0.242	–0.186	0.169	0.506*	1.000			
Zn	–0.300	0.729**	–0.140	0.365	0.447	0.509	1.000		
Hg	–0.436	0.930**	–0.215	0.558*	0.698**	0.275	0.650**	1.000	
As	–0.425	0.966**	–0.116	0.478*	0.714**	0.097	0.811**	0.879**	1.000

Note: * is significantly correlated at $p<0.05$ and ** is significantly correlated at $p<0.01$.

3.2 Pollution index evaluation of the soil heavy metal content

According to the risk screening value of the Soil Environmental Quality Agricultural Pollution Risk Control Standards (Trial) (GB 15618-2018), the single factor pollution index (PI) and PN are evaluated in Figure 2. The land analysis of the historical dumping area of the Au mining plant indicated that in plots S5 (PI_{Cd}, PI_{Pb}, PI_{Zn}, and PI_{As}), S7 (PI_{Zn} and PI_{As}) and S12 (PI_{Zn}), the PI was between $1<RI\leq2$, which indicated mild pollution. In the soil of plots S3 (PI_{Zn}) and S18 (PI_{Zn}), the PI was between 2 and 3, indicating moderate pollution. In plots S7 (PI_{Cd} and PI_{Pb}), S12 (PI_{Cd}, PI_{Pb} and PI_{As}) and S18 (PI_{Cd} and PI_{As}), the PI was greater than 3, indicating severe pollution.

In the study area, the PN in plots S7, S12 and S18 was greater than 3, indicating heavy pollution. The PN in plots S3 and S5 was between 1 and 2, indicating slight pollution. The comprehensive pollution index was in the order of $PN_{S12}>PN_{S18}>PN_{S7}>PN_{S3}>PN_{S5}>PN_{S14}>N_{S8}>PN_{S6}>PN_{S9}>PN_{S11}>PN_{S15}>PN_{S16}>PN_{S17}>PN_{S13}>PN_{S2}>N_{S10}>PN_{S4}>PN_{S1}$. As shown in Figure 2, the heavy metal pollution in plots S7, S12, S18, S3 and S5 was greatly affected by the historical slag of the Au ore dressing plant, thereby increasing the health hazards posed by heavy metals to residents of the surrounding area.

3.3 Potential ecological risk assessment of heavy metals in soil

The potential ecological risk assessment results of the heavy metals at each sampling point in the slag area of the Au mine are shown in Figure 3. In the soil of plots S5 (EI_{Cd}), S12 and S18, the RI was $40\leq EI_{Cd}<80$, indicating a medium potential ecological hazard. In the soil of plot S7 (EI_{As}), the RI was $80\leq EI_{Cd}<160$, indicating a moderate potential ecological hazard. In the soil of plots S12 and S18 (EI_{Cd}), the RI was greater than 320, indicating a strong potential ecological hazard.

The RI of each plot in the study area was in the order of $RI_{S12}>RI_{S18}>RI_{S7}>RI_{S5}>RI_{S14}>RI_{S15}>RI_{S16}>RI_{S11}>RI_{S3}>RI_{S6}>RI_{S9}>RI_{S8}>RI_{S13}>RI_{S4}>RI_{S2}>RI_{S10}>RI_{S1}>RI_{S17}$. The RI of the soil in plot S7 was $150\leq RI_{Cd}<300$, indicating a medium potential ecological hazard. The RI of plot S18 was $300\leq EI_{Cd}<600$, indicating a strong potential ecological hazard. The RI of plot S12 was greater than 320, indicating a strong potential ecological risk. The soil risks of the S7, S12 and S18 plots mainly originated from Cd, which accounted for 65.93%, 86.03% and 84.14% of the RI, respectively. This shows that the ecological risk level of Cd is not only severely affected by the historical piles of slag in the gold concentrator, but also is related to the high toxicity response coefficient of Cd（The toxicity coefficient of Cd contaminant is 30）. Heavy metals in the soil of the historical slag area of the Au ore dressing plant may cause different levels of heavy metal pollution owing to precipitation runoff, percolation and human farming activities, thus increasing the potential ecological hazards of these heavy metals[36].

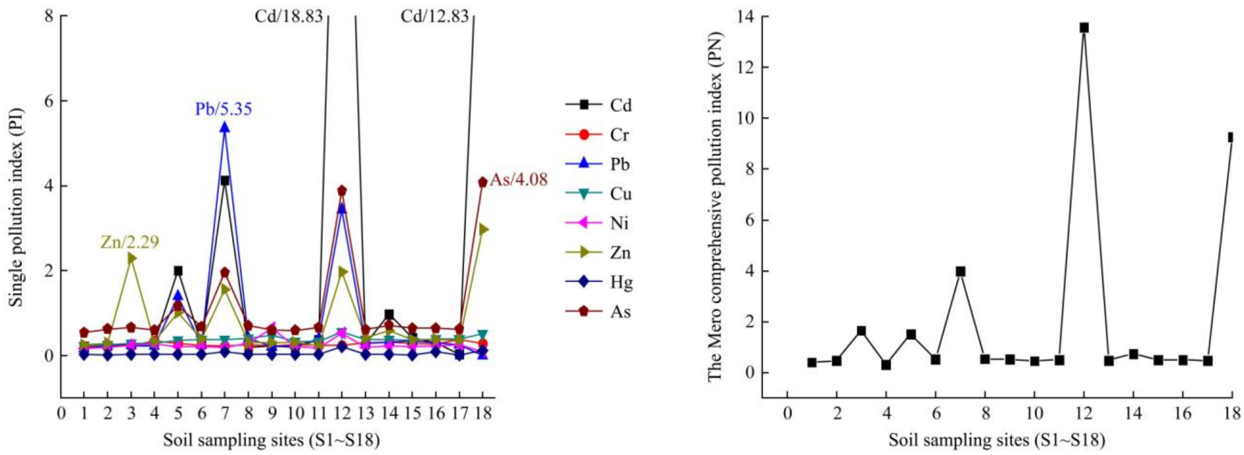
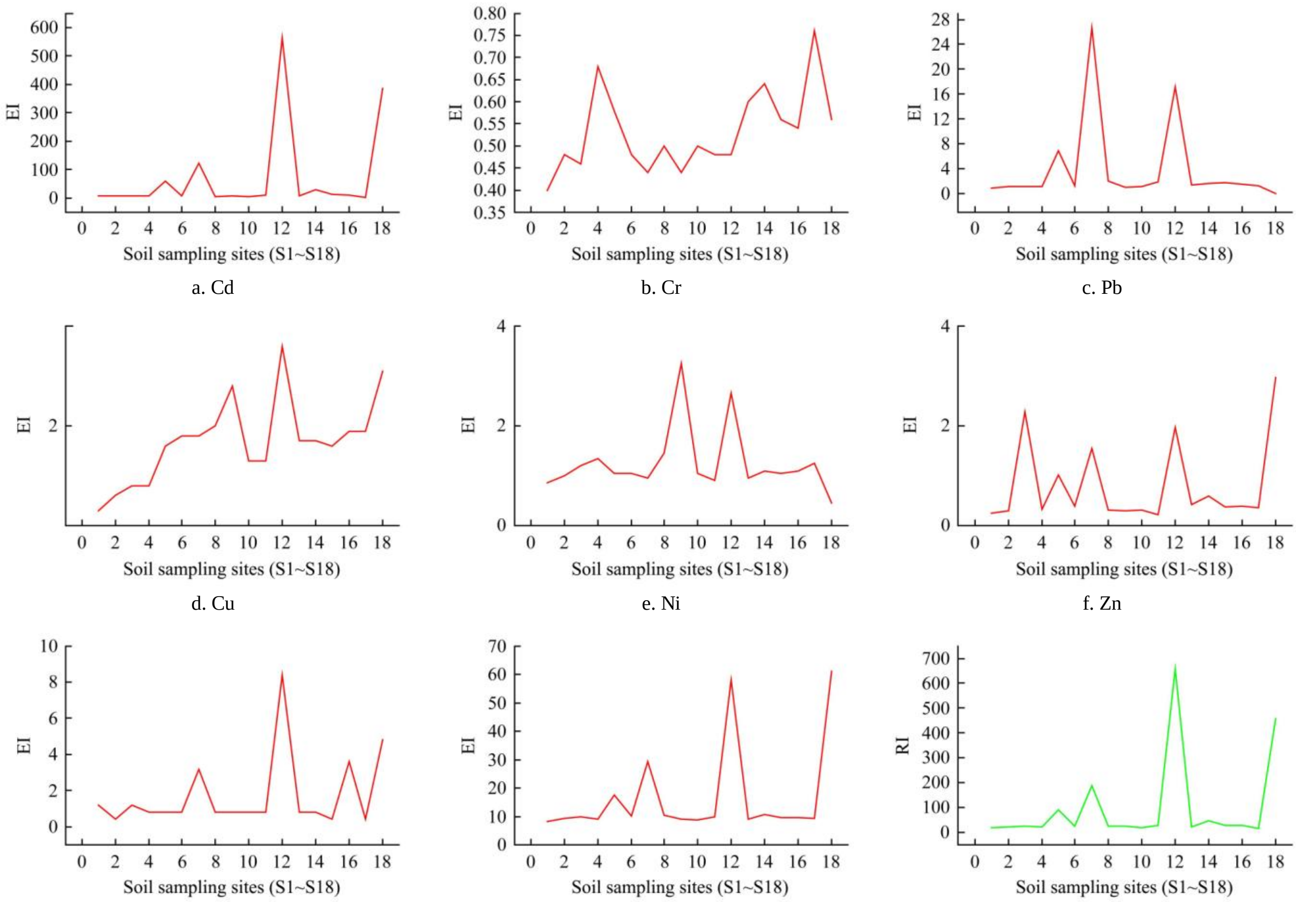


Figure 2 Pollution assessment index of heavy metals in soil



a. Cd b. Cr c. Pb

d. Cu e. Ni f. Zn

g. Hg h.As i. Multiple heavy metals

Notes: EI: Single heavy metal ecological risk index; RI: Multiple heavy metals ecological risk index.

Figure 3 Potential ecological risk assessment results of heavy metals

3.4 Health risk assessment

3.4.1 Non-carcinogenic health risk assessment of heavy metals in soil

The pollution index of the heavy metal content in the soil and the RI showed that the levels of heavy metal pollution in plots S7, S12, S18, S3 and S5 were affected by the historical slag area of the Au ore plant and were close to the nearby residential area. The four heavy metals mentioned in Section (S7, S12, S18, S3 and S5) were selected for analysis of the health risks posed to surrounding residents. The HQ and non-carcinogenic risk of the three exposure pathways of adults and children in the study area, namely oral intake, skin contact and respiratory intake, were analysed. The HI is shown in Table 8. The action of heavy metals in the soil of the study area on the HQ through the three exposure pathways was in the order of $HQ_{Hg}<HQ_{Cu}<HQ_{Ni}<HQ_{Zn}<HQ_{Cd}<HQ_{Cr}<HQ_{Pb}<HQ_{As}<1$. Table 8 shows that the heavy metals Pb and As are important constituent elements of the soil non-carcinogenic risk in the study area. The HQ and HI for children were greater than those for adults, but lower than the maximum acceptable level recommended by US EPA.

3.4.2 Soil health risk assessment of heavy metals

The individual carcinogenic health risk index (CR) and total carcinogenic risk index (TCR) of heavy metals in the soil of the study area for adults and children are shown in Figure 4. The risk analysis of carcinogenic heavy metal elements and population health hazards was conducted in the study area. The adult and child TCR, CR_{As} and CR_{Cd} were all above the maximum acceptable levels recommended for human safety by the US EPA (10^{-6}). The CR and TCR for children were greater than those for adults, as shown in Figures 4a and 4b. TCR_{As} and TCR_{Cd} accounted for 75.65% and 23.94% of the adult TCR, respectively. TCR_{As} and TCR_{Cd} accounted for 75.93% and 23.97% of the child TCR, respectively. The soil in the study area is threatened by serious heavy metal pollution and poses an unacceptable cancer risk.

Table 8 Risk of non-carcinogenic exposure to heavy metals in different pathways

Index Heavy metal	HQ								HI
	Cu	Ni	Zn	Pb	Cd	Cr	Hg	As	
Adult	7.34×10^{-4}	1.45×10^{-3}	1.20×10^{-3}	6.12×10^{-2}	2.77×10^{-3}	8.44×10^{-3}	6.62×10^{-4}	1.19×10^{-1}	1.95×10^{-1}
Child	1.02×10^{-3}	2.06×10^{-3}	1.70×10^{-3}	8.68×10^{-2}	3.92×10^{-3}	1.15×10^{-2}	9.27×10^{-4}	1.68×10^{-1}	2.76×10^{-1}

Remarks Remarks	CR				TCR
	Cd	As	Cr	Ni	
Adult	1.69×10^{-5}	5.34×10^{-5}	2.82×10^{-7}	4.30×10^{-9}	7.05×10^{-5}
Child	2.39×10^{-5}	7.57×10^{-5}	1.00×10^{-7}	1.53×10^{-9}	9.97×10^{-5}

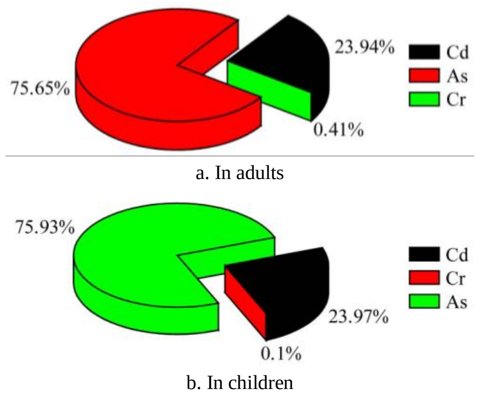


Figure 4 Total cancer risk from heavy metal exposure in adults and children

The data from the assessment of heavy metal health risks to residents in the vicinity of the plots in the study area showed that residents have a significantly increased risk of cancer due to exposure to high concentrations of heavy metals in the soil. Similar observations have been previously reported[37-40]. Therefore, the agricultural practices on the land in the vicinity of the study area should be adjusted and the heavy metal contents and health risks of the soil in the area should be monitored and evaluated regularly. Residents are currently strictly prohibited from polluting key plots for various production activities, which is conducive to preventing environmental health risks and avoiding and slowing heavy metal poisoning.

4 Discussion

Some of the land in the study area is seriously affected by the historical slag area of the Au ore plant, and the Pb, Zn and As contents exceeded the soil pollution risk screening value of agricultural land. This indicates that the soil in the area is subject to significant exogenous heavy metal pollution. The combination of the pollution index method, potential ecological risk assessment method that introduces the toxicity coefficient and soil health risk assessment model developed by the US EPA accurately identifies the contaminated land in the study area and its threat to nearby residents. The health risk assessment provides a scientific basis for rational use and restoration of soil in the study area. The pollution index and the potential ecological risk assessment identified the soil in plots S3, S5, S7, S12 and S18 as being seriously polluted by heavy metals and posing potential ecological risks. Deng et al.[41] found heavy pollution of the heavy metals Pb and Cd in a Pb-Zn smelter waste dump and surrounding soil, and the pollution in the overall area was serious. Jiang et al.[42] found that Cd exposure from the surrounding soil was common in residents. The heavy metals Cd and Cr in the soil of the historical slag research area of the Au ore plant pose the most serious threats to human health. Zhao et al.[43] studied the effects of metallurgical slag on the environment and human health, and found that Pb and Cd are impactful pollutants. Yang et al.[44] found that the health impacts caused by heavy metals in soils and crops around the mining area of Chenzhou City were mainly caused by Cd pollution[45]. This study supports the above research conclusions, indicating that the historical slag of the Au mining plant will lead to heavy metal pollution in the surrounding soil and result in a significant increase in the health risks to nearby residents.

Each of the three evaluation methods has its own emphasis and rationality. The RI method that introduces the toxicity coefficient focuses on the potential risk of heavy metal toxicity to the environment. The pollution index method reflects the degree of pollution by individual elements and also analyses multiple concurrent effects of elements on soil. However, the pollution status of heavy metals in soil is only evaluated by the pollution index method and RI, and it is impossible to comprehensively and quantitatively evaluate the adverse health effects caused by harmful environmental factors. Environmental pollution is linked to human health using the carcinogenic health risk and non-carcinogenic health risk model developed by the US EPA. Comprehensive qualitative and quantitative analysis of the Au ore dressing plant indicated that the heavy metal pollution in the historical slag area is harmful to the surrounding ecological environment and residents, thereby providing a scientific basis for the rational use and restoration of the soil in the study area.

There are three main reasons for the heavy metal content in the farmland soil in the study area to be higher than the screening value of “Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standards (Trial) (GB 15618-2018)”. One is because the historical selection and accumulation of slag will continue to harm the nearby farmland soil with the erosion of precipitation and runoff; Second, affected by the wind direction, the toxic heavy metal slag particles were deposited in the farmland soil by atmospheric deposition. Third, man-made farming activities, such as the use of slag backfill to level the terrain, slag waste soil piling up in production activities and mining vehicles to transport ore residue and other reasons, will cause the heavy metal content of farmland soil in the study area seriously exceed the standard[46]. Therefore, according to the investigation and analysis, soil heavy metal content was sampled from the agricultural land near the mining area, and excessive pollutants were evaluated and screened out. Combined with the Technical Guide for Classification of Soil Environmental Quality on Agricultural Land and Standards for Control of Soil Pollution Risk on Agricultural Land on Soil Environmental Quality[47], the soil environmental quality of agricultural land was classified. The soil pollution of agricultural land was classified into priority protection, safe utilization and strict control. According to the classification of farmland soil pollution condition by source control, agricultural control, soil improvement, plant repair, measures such as reducing cultivated land input, the total amount of pollutants in the soil or reduce its activity, thereby reducing pollutants exceed the risk of agricultural products, to improve the polluted farmland soil environment quality, greatly reducing the soil heavy metal enters the body through the food chain, To reduce the threat to the health and living environment of the residents near the mining area, and to provide a scientific basis for the rational utilization, remediation and treatment of the soil in the study area and the health of residents in the later period.

5 Conclusions

Plots S3, S5, S7, S12 and S18 in the historical slag research area of the Au mining plant were seriously polluted by heavy metals. The Pb, Zn and As contents exceeded the soil pollution risk screening value of agricultural land, leading to a strong potential ecological risk. The effects of residents on the 8 heavy metals HQ through 3 exposure routes is in the order of $HQ_{Hg}<HQ_{Cu}<HQ_{Ni}<HQ_{Zn}<HQ_{Cd}<HQ_{Cr}<HQ_{Pb}<HQ_{As}<1$. The adult and child TCR, CR_{As} and CR_{Cd} were all above the maximum acceptable levels recommended for human safety by the US EPA (10^{-6}). The sums of TCR_{As} and TCR_{Cd} accounted for 75.65% and 23.94% of the TCR of adults and 75.93% and 23.97% of the TCR of children, and the harm to children was greater than that to adults. This shows that the soil in the study area is seriously polluted by heavy metals and carries an unacceptable risk of cancer and illness. This suggests that certain approaches may be conducive to avoiding environmental risks and avoiding or reducing heavy metal poisoning, such as adjusting the agricultural planting structure in nearby plots and regularly monitoring and assessing health risks such as the heavy metal content of the soil in the area.

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