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Ecological risk assessment and early warning of heavy metal cumulation in the soils near the Luanchuan molybdenum polymetallic mine concentration area, Henan Province, central China

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ABSTRACT

The Luanchuan molybdenum polymetallic mine concentration area is rich in mineral resources and has a long history of mining. The environmental impact of long-term mining activities cannot be ignored. It is of great significance to study the ecological risk and the accumulation trends of heavy metals in the soil of mining areas for scientific prevention and control of heavy metal pollution. Taking the Taowanbeigou River Basin in the mine concentration area as the research object, the ecological pollution risk and cumulative effect of heavy metals in the soil of the basin were studied by using the comprehensive pollution index method, potential ecological risk assessment method and geoaccumulation index method. On this basis, the cumulative exceeding years of specific heavy metals were predicted by using the early warning model. The comprehensive potential ecological risk of heavy metals in the soil near the Luanchuan mine concentration area is moderate, and the single element Cd is the main ecological risk factor, with a contribution rate of 53.6%. The overall cumulative degrees of Cu and Pb in the soil are “none-moderate”, Zn and Cd are moderate, Mo has reached an extremely strong cumulative level, Hg, As and Cr risks are not obvious, and the overall cumulative risks order is Mo>Cd>Zn>Cu>Pb>Hg. According to the current accumulation rate and taking the risk screening values for soil contamination of agricultural land as the reference standard, the locations over standard rates of Cu, Zn and Cd will exceed 78% in 90 years, and the over standard rate of Pb will reach approximately 57% in 200 years. The cumulative exceeding standard periods of As, Cr and Hg are generally long, which basically indicates that these elements do not pose a significant potential threat to the ecological environment. Mining activities will accelerate the accumulation of heavy metals in soil. With the continuous development of mining activities, the potential pollution risk of heavy metals in the soil of mining areas will also increase.

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1. Introduction

Soil is a precious natural resource that is necessary for human survival and development, and its environmental quality is related to ecological security and human health. Unlike some typical soil pollutants, heavy metals, once entering the soil environment, cannot be degraded by

organisms and will continue to accumulate in the soil, thus changing the biogeochemical balance of heavy metals, by participating in the biogeochemical cycle with the help of groundwater, soil, plants and other media and entering the human body through food chain enrichment and other ways, thereby endangering human health (Chen T et al., 2016; Bao LR et al., 2020).

Mining activities are the main external source affecting the geological environment of mining areas (Zhang YK et al., 2017; Sun HY et al., 2021). In recent years, the heavy metal pollution of soils near mine concentration areas caused by long-term mining activities has increasingly attracted the attention of scholars at home and abroad (Nannoni F et al.,

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2016; Gao YF et al., 2018; Liu RP et al., 2020; Yu F et al., 2021). Some foreign scholars have evaluated the impact of toxic heavy metals in the soil around the Baikal tungsten-molybdenum mine and found that the heavy metals Cd, Cu, As, Pb and Mo around the tailings pond far exceeded the background value (Timofeev I et al., 2018). Some scholars have also conducted health risk assessments on urban soil samples near the Kajaran copper-molybdenum mine in Armenia and found that Mo, Cu and their accessory elements Pb and Zn were the main heavy metal pollutants (Tepanosyan G et al., 2018). China has carried out a large number of investigations and studies on the cumulative effect of heavy metals in mine concentration areas based on the status quo of environmental quality (Xu YN et al., 2007; Zhang JH et al., 2020); however, the long-term impact of heavy metal accumulation in soils caused by mining activities has rarely been discussed. From the perspective of geochemistry, the cumulative impact of heavy metals on the environment in mine concentration areas refer to the overall effect of the migration and precipitation of heavy metals in the specific environment before mining, during mine development and operation and after mine closure (Li W et al., 1995; Zhao YY et al., 2014).

Luanchuan County is rich in mineral resources and has a long history of mining. It is an important core area of the metal metallogenic belt and molybdenum-tungsten-lead-zinc polymetallic mineral area in China. At present, there are more than 50 kinds of proven metal, nonmetallic and other mineral resources (Xu ST et al., 2010), of which molybdenum

resource reserves rank first in Asia, and it is known as the molybdenum capital of China. At present, research on the Luanchuan mine concentration area has mainly been focused on the diagenesis and mineralization mechanism (Wang YP et al., 2018; Wang YS et al., 2018), and research on the environmental impact caused by mining activities has been limited. In the study presented in this paper, the Taowanbeigou River, a tributary of the Yellow River Basin in the Luanchuan molybdenum polymetallic mine concentration area, was selected as the research object to analyse and discuss the characteristics of heavy metal accumulation and potential ecological risks in the soil near this mining area. At the same time, with the help of heavy metal accumulation early warning model, the values of the number of years of heavy metal accumulation remaining until the soil exceeds the standard have been predicted to provide a theoretical basis for environmental protection and pollution prevention in mining areas.

2. Overview of the study area

The Luanchuan molybdenum polymetallic mine concentration area, which has convenient transportation, is located approximately 30 km northwest of Luoyang City, Luanchuan County and it is under the jurisdiction of Lengshui Town and Chitudian Town, Luanchuan County, Henan Province (Fig. 1). The mine concentration area is approximately 32.5 km², mainly composed of the Nannihu molybdenum-tungsten mining area, Shangfanggou molybdenum-iron ore area, Sandaozhuang molybdenum-

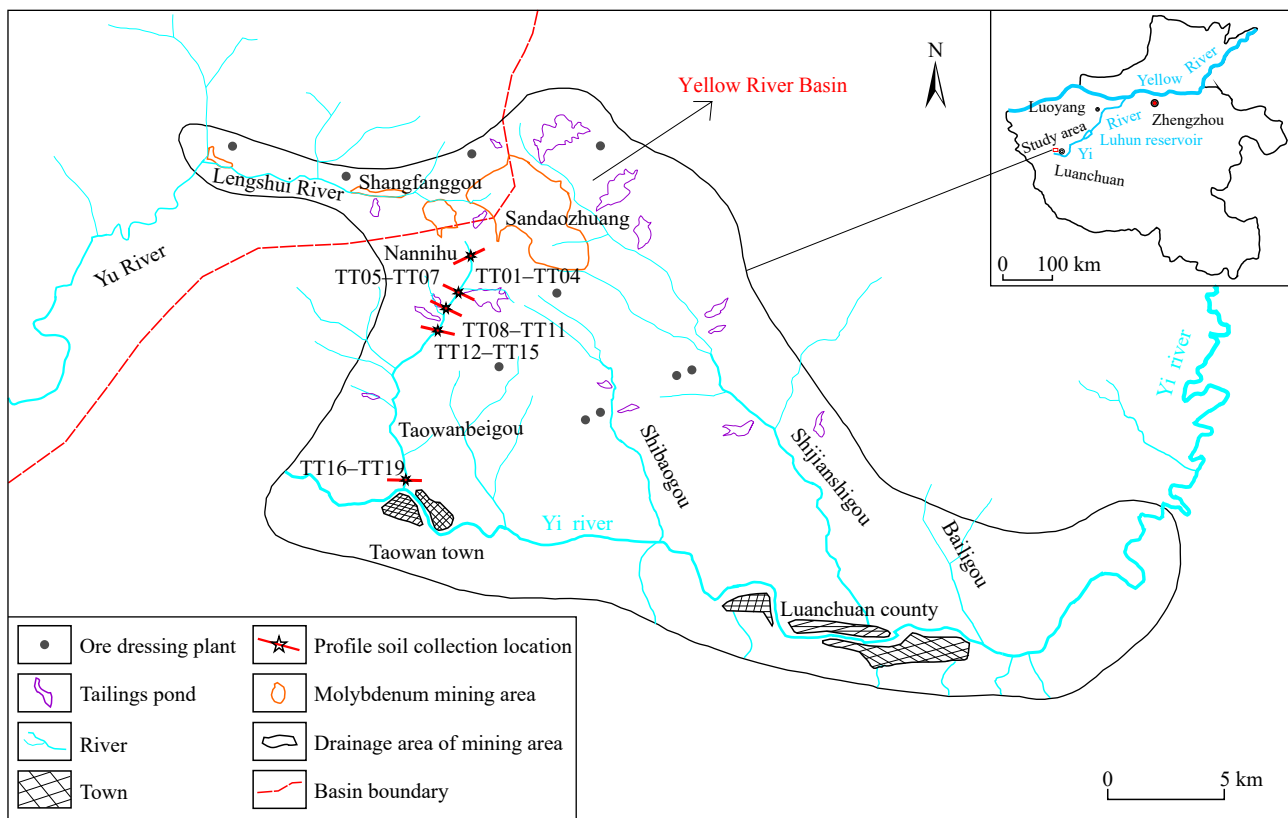


Fig. 1. Sampling location map near Luanchuan mine concentration area .

tungsten mining area, etc. Among them, the Sandaozhuang molybdenum-tungsten mine and Nannihu molybdenum-tungsten mine are in production, with large-scale operations and long production histories. The rest of the mines are currently idle. There are many ore dressing plants and tailings ponds in the mining area and low lying places along the river valley, and there are many lead-zinc ore stopes around the molybdenum mine concentration area.

The study area has a semiarid continental monsoon climate, with an average annual precipitation of approximately 809 mm and rainy seasons in July, August and September. The mine concentration area is located in the basins of the Yellow River and the Yangtze River between Xiong'er Mountain and Funiu Mountain in the eastern Qinling Mountains. The terrain is high in the north and low in the south. It belongs to the middle high mountain area. The hydrogeological conditions are relatively simple, and the surface runoff is relatively developed. The water filling sources of the mine pits are mainly atmospheric precipitation and surface runoff. There are two major river systems distributed in the study area. The southeastern part belongs to the Yellow River Basin, which is deeply incised. The tributary is the Yihe River, which flows into the Luohe River and then flows into the Yellow River. The northwestern part belongs to the Yangtze River Basin, and its tributary is the Yu River, which flows into the Laoguan River, Danjiang River, Hanshui River, and finally the Yangtze River. The mine concentration area is dominated by the Yellow River system, and the tributaries of the Yihe River section are developed. The tributaries of the Yihe River flowing through the mining area mainly include the Taowanbeigou, Shibaogou and Shijianshigou rivers. These three streams flow intermittently. The water volume increases in the rainy season, and the valley is often cut off during the dry season. The Taowanbeigou River is distributed in a near north-south direction, and Taowan Town is downstream.

3. Methods of sample collection and analysis

3.1. Sample collection

In this study, the Taowanbeigou River, the upstream tributary of the Yihe River, the main water system near the mine concentration area, was selected as the research object. In August 2019, the soil on both banks of the Taowanbeigou River was systematically sampled (Fig. 1), and a total of 19 soil samples were collected (TT01–TT19). According to the flow velocity and flow direction of the river and the landforms on both banks, the Taowanbeigou River was divided into three sections, namely, the upper, middle and lower reaches. During the collection of the soil samples, five transverse soil profiles were arranged in the upper, middle and lower reaches of the river according to the actual conditions, such as topography, ore dressing plant and tailings pond locations, including profile I (TT01–TT04), profile II (TT05–TT07), profile III (TT08–TT11), profile IV (TT12–TT15) and profile V (TT16–TT19). The soil samples

from the 0–20 cm deep tillage layer was collected from both banks of the river for each profile, and then they were naturally dried in a cloth bag. During sampling, a plastic shovel was used to scrape away soils contacting metal tools during profile excavation, and remove gravel, grass roots and other debris, and then a plastic shovel was used for the sampling.

3.2. Test methods

The analysis and testing of samples were entrusted to the testing centre of the Henan Provincial Bureau of Geo-exploration and Mineral Development. According to the technical standard for geological survey of China Geological Survey–“Technical Requirements for Analysis of Eco-geochemical Evaluation Samples (Trial) (DD2005–3)” and the “Specification for Quality Management of Geological and Mineral Laboratory Testing (DZ/T0130.6–2006)” issued by the Ministry of Natural Resources of the People’s Republic of China, inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS), and digital ion acidity metre (PHS) were used to determine the concentrations of Mo, Cu, Pb, Zn, As, Cd, Cr (+6 valence), and Hg in the samples in addition to the pH value.

3.2.1. Geoaccumulation index method

The geoaccumulation index method was first proposed by Muller, a German scientist, in the 1960s. This method introduced the background values of heavy metals in soil into the evaluation system. Taking into account the impact of natural diagenesis and mineralization on the background values of the soil, it can be used to comprehensively characterize the accumulation level of single or multiple heavy metals in soil (Muller G, 1969). Its expression is (Eq. 1):

$$I_{geo} = \log_2 [C_i / (KB_i)] \quad (1)$$

where C_i is the measured content of the i th element in the tested sample; B_i is the background value of the i th element. In this study, the background values were comprehensively determined according to the background values of heavy metals in the soil of the Henan section of the Yellow River Basin and 1 : 200000 regional geochemical survey data of Luanchuan River sediment (Zhao ZH, 1989; Sheng Q et al., 2009); and K is the correction coefficient of B_i , which is generally 1.5.

3.2.2. Nemeru comprehensive pollution index method

The comprehensive pollution index is a comprehensive method of assessing heavy metal pollution that is widely used by scholars at home and abroad (Guo JG et al., 2021). It represents the comprehensive impact of multiple pollutants in the environment. It is based on a single pollution index and obtained through a certain mathematical relationship. Its expression is (Eqs. 2, 3):

$$P = \sqrt{\frac{P_{imax}^2 + \bar{P}^2}{2}} \quad (2)$$

$$\bar{P} = \frac{1}{n} \sum_{i=1}^n P_i \quad (3)$$

In this expression, P is a comprehensive pollution index; $P_{i\max}$ is the maximum value of each pollutant singly; and \bar{P} is the average value of the single pollutant indices.

3.2.3. Potential ecological risk index method

The potential risk index was first proposed by the Swedish chemist Håkanson in 1980. It comprehensively considers the pollution content, ecological effects, environmental effects and toxicological effects and is widely used in the assessment of heavy metal pollution (Håkanson L., 1980). This index can quantitatively analyse the potential harm to the environment of a single heavy metal in soil and comprehensively evaluate the impact of specific pollutants and multiple pollutants on the external environment. Most domestic scholars use this method to evaluate the harm due to the heavy metals in the soils of mining areas (Feng QW et al., 2020). The calculation formula is as follows (Eqs. 4, 5):

$$E_r^i = T_r^i \frac{C_i}{S_i} \quad (4)$$

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

In this expression, E_r^i is the potential ecological risk index of a single heavy metal i ; C_i/S_i is the pollution parameter of heavy metal i , where C_i is the measured value and S_i is the reference value. Generally, the regional geochemical background values are taken as the reference values; T_r^i is the toxicity response coefficient of heavy metal i ; RI is a comprehensive potential risk index of several heavy metals. Previous studies have shown that the toxicity coefficient of each heavy metal is $Zn=1<Cr=2<Cu=5<As=10<Cd=30<Hg=40$ (Lin J et al., 2021). According to the E_r^i and RI values, potential ecological risks are divided into five grades.

4. Results and analysis

4.1. Heavy metal content characteristics

The soil in the Taowanbeigou River basin is generally weakly alkaline, with most of the pH values between 7.35 and

8.49, and some are weakly acidic. The degree of heavy metals exceeding the standard is generally high. Cu, Pb, Zn and Cd all exceeded the standard to different degrees (Table 1), among which Cd exceeded the standard most seriously; 13 of the 19 samples exceeded the risk screening values for soil contamination of agricultural land, the rate of exceeding the standard reached 68.42%, the highest content was 2.29×10^{-6} , which is approximately 3.8 times the screening value, and the comprehensive pollution index was 2.83, reaching the moderate pollution level (Table 2). The exceeding standard rates of Cu and Zn were 15.79%, of which the highest content of Cu was 135.9×10^{-6} , which is approximately 1.36 times the screening value, and the highest content of Zn was 529.0×10^{-6} , which is approximately 1.76 times the screening value. The comprehensive pollution index was within the warning range. The Pb content of one sample exceeded the screening value, with an over standard rate of 5.3% and a comprehensive pollution index of 1.39, which is in the alert range. The contents of As, Cr and Hg were lower than the national risk screening values for soil contamination of agricultural land and the comprehensive pollution indices were lower than 0.8, which is in a safe range and has little impact on the soil environment.

The coefficient of variation can eliminate the influence of different dimensions of heavy metal content (Zhan YZ et al., 2011), reflecting the average change degree of heavy metal content between sampling points and the degree of influence by human activities. The smaller the value is, the greater the element content is controlled by natural factors such as the soil parent material. The larger the value is, the more uneven the spatial distribution of heavy metal concentration and the greater the possibility of having been disturbed by human activities. There is a possibility of point source pollution, which is caused by the entry of foreign substances (Fan BX et al., 2020). Generally, a coefficient of variation less than 15% is considered to be a weak variation, 15% to 35% is considered to be a moderate variation, and more than 35% is considered to be a strong variation (Guo YH et al., 2017; Li X et al., 2017).

In the soil samples of the Taowanbeigou River Basin, the variation coefficients of Mo and the other five heavy metals were more than 40%, indicating a strong degree of spatial variability, except that the variation coefficients of As and Cr

Table 1. Statistical result of soil heavy metals content (10^{-6}) in Taowanbeigou Basin.

Test items	Minimum	Maximum	Average	Standard deviation	Coefficient of variation/%	Exceedance number of samples	Exceedance rate of samples/%	Risk screening values for soil contamination of agricultural land—GB15618–2018(other)	
								pH>7.5	6.5<pH≤7.5
Cu	30.80	135.90	66.26	26.77	41.5	3	15.79	100	100
Pb	23.30	226.80	64.73	44.80	71.1	1	5.3	170	120
Zn	118.9	529.0	221.7	105.17	48.7	3	15.79	300	250
As	2.87	16.76	10.33	3.26	32.4	0	0	25	30
Cd	0.26	2.29	0.73	0.44	61.7	13	68.42	0.6	0.3
Cr	50.10	87.0	69.43	10.82	16.0	0	0	250	200
Hg	0.02	0.20	0.06	0.05	83.4	0	0	3.4	2.4
pH	6.16	8.49	7.89	0.55	6.9	\	\	\	\

Table 2. Evaluation result of Nemeiluo comprehensive pollution index.

Heavy metal elements	Cu	Pb	Zn	As	Cd	Cr	Hg
<i>P</i>	1.07	1.39	1.62	0.56	2.83	0.31	0.04

were low. Among them, the spatial variation of Mo was the highest, with the coefficient of variation reaching 135.7%, indicating that the contents of Mo, Cu, Pb, Zn and Cd in the soil of the Taowanbeigou River basin have been largely affected by human factors, based on a comparison with the soil parent materials. Of these, Mo was the most obvious. Although Hg has a strong degree of variation, its content was far lower than the national screening value of agricultural land soil pollution risk. Most scholars have found that Hg in soil generally has a high degree of variation, but its content is in a safe range (Song JQ et al., 2017; Cao SW et al., 2022). It is speculated that this may have been due to the strong migration activity of Hg in nature, which exists in a series of oxidation–reduction and desorption processes in the soil and will be released into the atmosphere while being accumulated, leading to an increase in its spatial variation (Jiang F et al., 2019).

Skewness and kurtosis are two important indicators to describe whether the data conform to a normal distribution. In the absence of obvious human activities, the content of a soil element in nature usually follows a normal distribution (Huang Y et al., 2022). The skewness value can indicate the concentrated distribution of an element in the soil. The content distributions of Mo and the seven heavy metals in the soil of the Taowanbeigou River basin did not have standard normal distributions, which are a right-skewed type (Fig. 2). The samples were mainly concentrated in the safe range with small contents. Among them, Cu, Pb, Zn, Cd, Hg and Mo all had large skewness and kurtosis, and all exceeded their standards except Hg. The frequency distributions of As and Cr very close to the normal distribution, and their skewness values were 0.05 and 0.004, respectively. Their contents were far lower than the risk screening values of these elements for soil contamination of agricultural land, and both had small coefficients of variation, indicating that the contents of these two elements are less affected by the outside world and were mainly controlled by natural factors.

4.2. Potential ecological risk assessment

In general, the potential ecological risks of a single heavy metal in the soil of the Taowanbeigou River basin were generally low, and the potential ecological risk indices of Cu, Pb, Zn, As, Cr, and Hg were basically below the low risk criteria (Fig. 3). The value of Pb in one sample was 44.07, reaching a moderate potential ecological risk, while Hg fluctuated greatly, one sample reached a moderate risk, and two samples reached a high risk, with an average risk degree of $Cr < Zn < Pb < As < Cu < Hg$ (Table 3). It is worth paying attention to Cd. The potential ecological risk index values of the 19 samples reached a moderate level, of which “higher risk” accounted for 68.4%, “high risk” accounted for 10.5%,

and “extremely high risk” accounted for 5.3%. The average potential ecological risk index for Cd was 128.27, also reaching the “higher” level. Cd is the main heavy metal pollutant in the nonferrous metal mining area, and the phenomenon that Cd exceeds the standard generally exists in the soil of the mining area. Some scholars have studied the heavy metals in the soil of the abandoned land of a lead-zinc mining area in Changhua Town, Changjiang County, Hainan Province. The soil around this mining area has been polluted by Cu, Pb, Zn and Cd to varying degrees, of which Cd is the most serious pollutant, the content of which is 6.8 times higher than the risk intervention values for soil contamination of agricultural land, reaching the level of severe pollution (Yang N et al., 2021). Some scholars also studied the contents of heavy metals in the topsoil around a mining area in Longyan City and found that the contents of Pb and Cd in 64 soil samples generally exceeded the risk screening values for soil contamination of agricultural land, of which the rate of Cd samples exceeding the standard reached 79.7% (Wang R et al., 2021). Cd is the main potential ecological risk factor in the soil of nonferrous metal mining areas and should be given sufficient attention. In general, the comprehensive potential ecological risk indices of heavy metals of 19 soil samples in the Taowanbeigou River basin were between 107.34 and 514.11, with 73.7% above moderate risk, of which 15.8% of the locations had high risk, although the average risk level was moderate. Cd was the main potential ecological risk factor, with a contribution rate of 53.6%.

4.3. Accumulation effect of heavy metals in soil

The metal deposits form a large polymetallic situation. With the increasing intensification of mining activities such as mining, ore smelting and processing and other factors, the heavy metal exposure paths and migration rates will also increase under the influence. A large number of heavy metals, such as Cu, Pb, Zn, and Cd, will be released into the environment surrounding the mining area to varying degrees through surface runoff, rainwater leaching and atmospheric deposition. Heavy metals in various chemical states or chemical forms will migrate and transform in different environmental media, such as water, sediment and soil, after entering the environment and ecosystem and will accumulate in the sediment and soil environment as mining activities continue, thus posing a certain potential hazard to the ecological environment (Cao QY et al., 2017; Chen ZY et al., 2020). In the past 30 years, the mining scale of the Luanchuan mine concentration area has been expanding continuously. Since 2000, daily ore processing has reached the level of tens of thousands of tons. The environmental problems caused by perennial mining activities cannot be ignored. In this study, Mo and seven typical heavy metals, Cu, Pb, Zn, As, Cd, Cr and Hg, were selected to investigate the accumulation effect of heavy metals in soil.

4.3.1. Cumulative degree

The evaluation results of the geoaccumulation index show

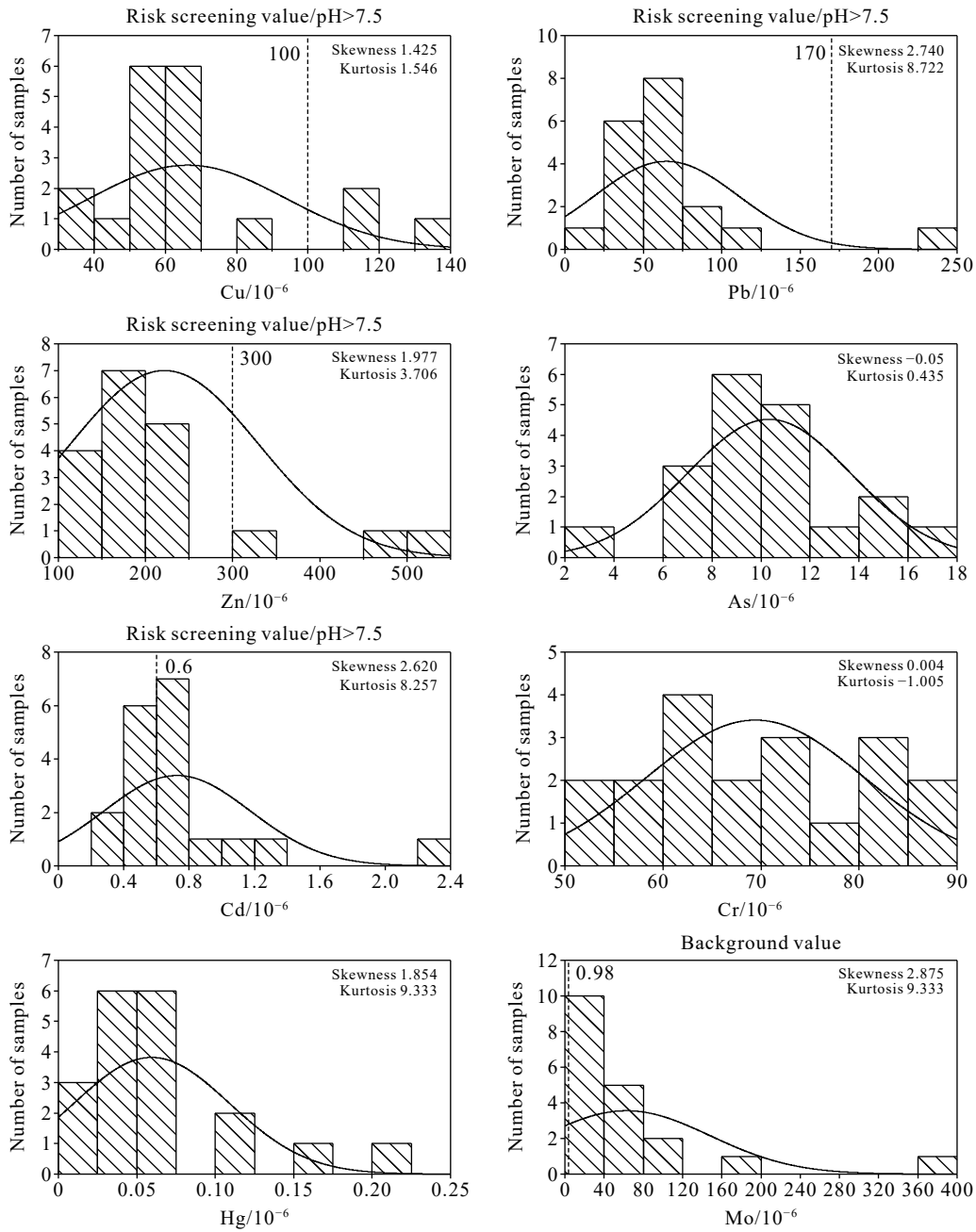


Fig. 2. Frequency distribution histogram of soil heavy metals content in Taowanbeigou Basin.

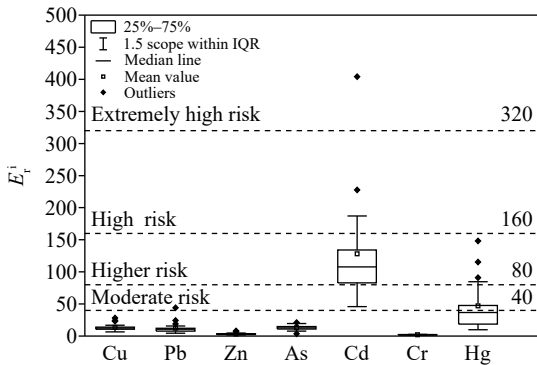


Fig. 3. Box diagram of potential ecological risk index distribution of soil heavy metals in Taowanbeigou Basin.

that the accumulation degree of the heavy metals in the soil of the Taowanbeigou River basin is generally high, and Mo, Cu, Pb, Zn, As, Cd and Hg have accumulated to varying degrees (Table 4). Mo and heavy metals Zn and Cd had the highest accumulation degree, and the sample accumulation rate reached 100% (Fig. 4). Among them, Mo has the strongest accumulation effect, and the accumulation degree values were above the “moderate–strong” level. Nine samples have reached the “extremely strong” accumulation degree value, and the geo-accumulation indices reached as high as 8.49, which is approximately 1.7 times the extreme strong accumulation limit value, and the average accumulation degree values also reached the “extremely strong” level. The second group of elements included Cd and Zn, whose cumulative degree values were above “none–moderate”. The

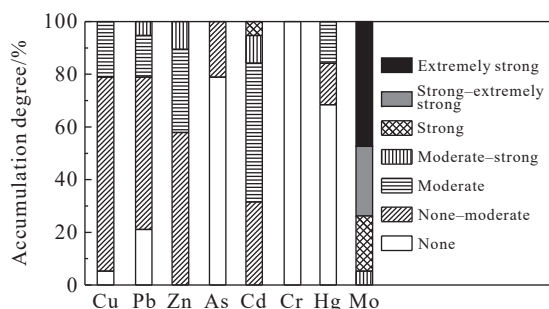
Table 3. Statistics of potential ecological risk index of soil heavy metals in Taowanbeigou Basin (N = 19).

Potential ecological risk index	Element	Value range	Distribution of ecological risk levels					Average risk level	
			Low	Moderate	Higher	High	Extremely high		
E_r^i	Cu	6.37–28.10	19	\	\	\	\	13.70	Low
	Pb	4.53–44.07	18	1	\	\	\	12.58	Low
	Zn	1.77–7.85	19	\	\	\	\	3.29	Low
	As	3.62–21.16	19	\	\	\	\	13.04	Low
	Cd	45.88–404.12	0	3	13	2	1	128.27	Higher
	Cr	1.45–2.52	19	\	\	\	\	2.01	Low
RI	Hg	13.33–133.33	13	4	2	\	\	66.08	Low
		98.45–520.35	5	11	\	3	\	212.54	Moderate

Table 4. Statistical results of soil heavy metals accumulation index in Taowanbeigou basin (N = 19).

Elements	Geoaccumulation index	Number of samples with corresponding cumulative degree							Average cumulative degree	Sample accumulation rate /%
		None	None–moderate	Moderate	Moderate–strong	Strong	Strong–extremely strong	Extremely strong		
Cu	−0.24–1.91	1	14	4	0	0	0	0	None–moderate	95%
Pb	−0.73–2.55	4	11	3	1	0	0	0	None–moderate	79%
Zn	0.23–2.39	0	11	6	2	0	0	0	Moderate	100%
As	−2.05–0.05	15	4	0	0	0	0	0	None	21%
Cd	0.03–3.17	0	6	10	2	1	0	0	Moderate	100%
Cr	−1.05–0.25	19	0	0	0	0	0	0	None	0%
Hg	−1.43–1.89	13	3	3	0	0	0	0	None	32%
Mo	2.75–8.49	0	0	0	1	4	5	9	Extremely strong	100%

Note: Sample accumulation rate is the ratio of the number of samples of “none–moderate” grade and above to the total number of samples.

**Fig. 4.** Soil heavy metals accumulation degree in Taowanbeigou Basin.

maximum Cd and Zn values of I_{geo} were 3.17 and 2.39, respectively, reaching the “strong” and “moderate–strong” cumulative levels. On the whole, the values of their average cumulative degrees reached the “moderate” cumulative level. The cumulative rates of Cu and Pb reached 95% and 79%, respectively, and their maximum values were 1.91 and 2.55, reaching the “moderate” and “moderate–strong” cumulative levels, and the average cumulative level was “none–moderate”. The accumulation rate of Hg was 32%, and the maximum value was 1.89, reaching the “moderate” accumulation level. The accumulation rate of the As samples was 21%, both Hg and As were at the “none–moderate” accumulation level. Overall, accumulations of Hg and As were not obvious. The geoaccumulation index of Cr was below zero, that is, without accumulation. It was within the safety range, and generally did not pose a potential impact on the environment. In general, the accumulation degrees of the eight heavy metals were in the order of Mo>Cd>Zn>Cu>

Pb>Hg>As>Cr.

4.3.2. Cumulative rate

Previous studies have shown that although the changes in heavy metals in some environmental media (ice cores, lakes and shallow sea sediments) show an exponential relationship on a scale of more than 100 years, the accumulation of both heavy metals and persistent residual organic pollutants in the soil environment for less than 100 years still conforms to the linear relationship (Ursula G et al., 1991; Liu JP et al., 2014; Zhao YY et al., 2017); therefore, the accumulation rate of heavy metals in the soil of the Luanchuan molybdenum mining area can be expressed by the following formula (Eq. 6):

$$V = (CnBEn)/n \quad (6)$$

where V is the cumulative rate; Cn is the current content of heavy metals; BEn is the background value of heavy metals in the mining area; and n is the number of years. In this study, the period from the large-scale mining of the Sandaozhuang molybdenum mine since records (1969) to the sample collection year (2019) was taken as the N value, for a total of 50 years.

The accumulation rates of Mo, Cu, Pb, Zn, As and Cd in the soil of the Taowanbeigou River Basin were found to be basically above the line of zero accumulation, showing a more obvious positive accumulation trend (Fig. 5). The upstream and middle reaches close to the mining area have strong scouring and leaching effects due to the rapid velocity of the river water and more confluent tributaries, and their cumulative rate was generally higher than that of the downstream location, which had relatively stable flow. Under

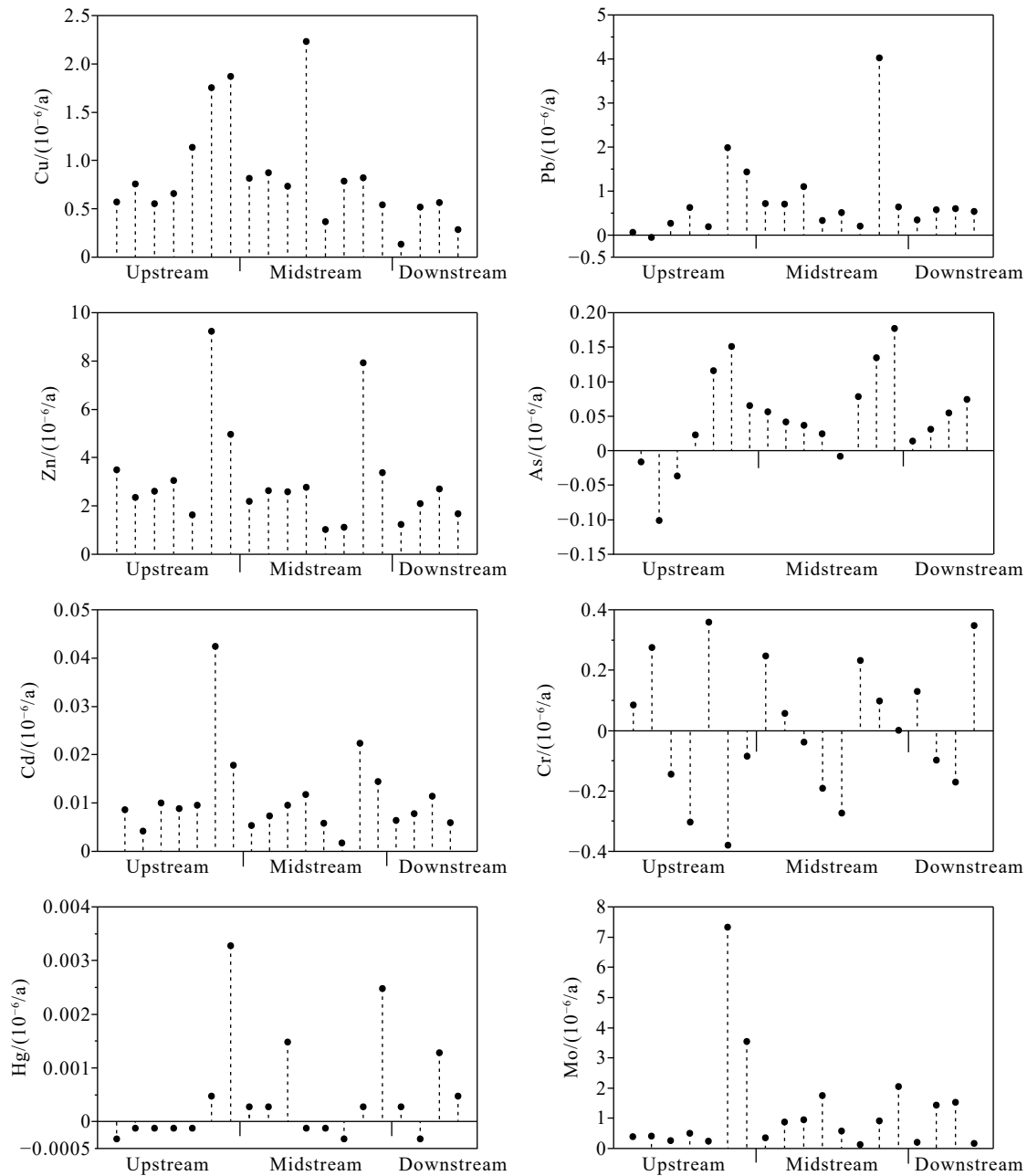


Fig. 5. Accumulation rate of soil heavy metals in Taowanbeigou Basin.

the comprehensive influence of mining activities such as the upstream molybdenum ore area and the surrounding lead-zinc ore stopes, Mo, Cu, Pb and Zn had high accumulation rates. The accumulation rate of Zn was the highest, reaching 9.23×10^{-6} per year, and the average cumulative rate is 3.09×10^{-6} per year. the second highest element was Mo, with an average cumulative rate of 1.83×10^{-6} per year, and the maximum accumulation rate upstream reaches 7.32×10^{-6} per year. The cumulative rates of Cu and Pb were basically between $(0.2-1.8) \times 10^{-6}$ per year, the average cumulative rates were 0.84×10^{-6} per year and 0.78×10^{-6} per year, and the cumulative rates were close. The overall accumulation rate of Cd was low; most of the values were in the range of $(0.004-0.02) \times 10^{-6}$ per year with an average cumulative rate of 0.011×10^{-6} per year, but Cd has a large cumulative base,

and many places exceeded the standard. The local accumulation rates of As were below the zero accumulation line, but mainly in the range of $(0.01-0.18) \times 10^{-6}$ per year, and the average cumulative rate was 0.048×10^{-6} per year.

The accumulation rates of Hg and Cr both fluctuated above and below the line of zero accumulation. The number and fluctuation amplitude of Cr samples with positive accumulation rates were close to those of negative accumulation, and the fluctuation amplitudes were within the range of $(-0.4-0.4) \times 10^{-6}$ per year. Overall, Cr had weak positive accumulation, and the accumulation rate was approximately 0.0079×10^{-6} per year. The Cr in the soil mainly came from the parent material of soil formation (Wu GH et al., 2020; Qin YL et al., 2020), and it naturally accumulates during the process of soil formation, resulting in

relatively stable values of its content. Therefore, this can be considered that the natural accumulation rate of Cr in the soil near the mining area is approximately 0.0079×10^{-6} per year. Different from Cr, although the numbers of positive and negative cumulative samples of Hg were similar, and its cumulative rate was low, its positive and negative cumulative rates had large differences. The positive cumulative rates were generally greater than the negative cumulative rates, and there was a local high rate accumulation of anomalies relative to other regions, with an average cumulative rate of approximately 0.0005×10^{-6} per year. Hg is highly volatile, and the release of mercury from soil is one of the most important sources of atmospheric mercury (Lu BQ et al., 2021). As the elemental mercury in soil is easily volatilized into the atmosphere, the Hg in local surface soil has a weak negative accumulation, thus showing a large degree of spatial variation. However, the volatilization amount was lower than the accumulation amount, still showing a certain positive accumulation trend. In general, the accumulation rates of Mo and seven heavy metals in the soil near the mining area were in the order of $Zn > Mo > Cu > Pb > As > Cd > Cr > Hg$.

5. Discussion

5.1. Prediction model for years of heavy metals exceeding the standard in soil

Previous studies have systematically studied mathematical models for predicting the years of accumulative exceedance of heavy metals in soil (Yan JY et al., 2007), which can be divided into two types: Accelerated accumulation models and uniform accumulation models. In the accelerated accumulation model, it is mainly due to the accumulation in the process from flood inundation to flood recession. It has the characteristics of a short accumulation time and fast accumulation speed, so the natural accumulation speed can be ignored. The river flow in the study area is not very large, and the accelerated accumulation of flooding rarely occurs. The accumulation of heavy metals in soil is mainly carried out in the form of natural uniform accumulation. Combined with the actual situation of the Luanchuan mine concentration area, the prediction model of the natural accumulation of heavy metals in soil can be expressed by the following mathematical expression (Yan JY et al., 2007; Eqs. 7, 8):

$$V_0 = \frac{\sum_{i=1}^n (C_i - C_b)}{nt} \quad (7)$$

$$T = \frac{Q}{V_0} = nt \frac{C_s - C_i}{\sum_{i=1}^n (C_i - C_b)} = 950 \frac{C_s - C_i}{\sum_{i=1}^n (C_i - C_b)} \quad (8)$$

In the formula, V_0 is the average value of the current natural accumulation rate of heavy metals; t is the mine development time, $t=50$ in this study; n is the number of samples collected, in this study, $n=19$; T is the predicted exceeding standard period; Q is the predicted cumulative quantity; C_i is the measured concentration of heavy metals; C_b

is the background value of heavy metals; and C_s is the risk screening value for soil contamination of agricultural land. When $C_i > C_s$, it means that the current heavy metals have exceeded the standard. At this time, if $C_i < C_b$, it means that the heavy metals present a negative accumulation trend. According to the current accumulation rate, the heavy metal will reach the safety range in a number of years, and this period is expressed as a negative number. Theoretically, once heavy metals enter the soil environment, they cannot be degraded and are difficult to remove. This situation may generally occur in the high geological background area of heavy metals. As heavy metals migrate to deep soil or other media, the contents of the heavy metals in the surface soil gradually decrease. If $C_i > C_b$ at this time, the heavy metals in the soil have positive accumulation trends, and the degree of exceeding the standard will increase year by year. The number of years exceeding the standard is expressed as 0. When $C_i < C_s$ and $C_i < C_b$, the content of heavy metals in the current soil does not exceed the standard and shows a negative cumulative trend. The heavy metals will not have pollution risk after several years, which is represented by “?”.

5.2. Early warning of heavy metal accumulation in soil

The Luanchuan molybdenum polymetallic mine concentration area has a large mining scale and a long mining time, and the mining method is mostly open-pit mining in which there are many exposed pits on the surface, resulting in mining waste rocks being exposed to the surface year-round. In addition, along the Taowanbeigou River from upstream to downstream, there are also many slag tailings ponds and lead-zinc ore stopes, which to some extent accelerate the release and accumulation of Cu, Pb, Zn, Cd and other heavy metals in the soil near the mining area. Assuming that the regional environment will not change in the future and the mining level will be the same as the current one, the prediction results of the overlimit years show that (Table 5), taking the risk screening values for soil contamination of agricultural land as the reference standard, according to the current cumulative rate, the cumulative pollution overlimit rate of Cd in the soil near the Luanchuan mine concentration area will reach more than 94% in the next 30 years. The second highest element is Zn, whose cumulative pollution exceeding the standard rate will reach approximately 79% in the next 60 years. The cumulative overstandard period of Cu is relatively long, and the cumulative overstandard pollution rate will reach approximately 79% in the next 90 years. After 200 years, the cumulative pollution rate of Pb will exceed 57%. The cumulative exceedance period of As is generally long, and its cumulative pollution rate exceeded the standard by only approximately 26% after 200 years. Cr is mainly carried out at the natural accumulation rate, and its cumulative exceeding standard period is more than 500 years. The accumulative trend of Hg in the surface soil is not obvious, and its accumulative exceeding standard years are more than 1000 years, which basically does not pose a potential threat to the

Table 5. Prediction of the accumulative exceedance years of heavy metals in soil near Luanchuan mine concentration area.

Sample numbers	Predicted exceeding standard years/a						
	Cu	Pb	Zn	As	Cd	Cr	Hg
TT01	83	2156	17	/	0	2069	/
TT02	50	\	28	/	0	426	/
TT03	86	478	39	/	0	/	/
TT04	65	181	26	693	0	/	/
TT05	17	432	62	140	0	314	/
TT06	0	23	0	63	0	/	6958
TT07	0	51	0	212	0	/	976
TT08	43	150	56	254	30	681	11964
TT09	37	156	39	363	8	3103	11964
TT10	54	81	40	409	0	/	2223
TT11	0	391	34	644	0	/	/
TT12	158	229	176	/	24	/	/
TT13	46	652	159	168	189	732	/
TT14	42	0	0	114	0	1295	8393
TT15	89	176	19	47	0	129214	1306
TT16	523	363	140	1206	17	1349	11964
TT17	96	115	37	658	0	/	/
TT18	84	190	36	264	0	/	2578
TT19	215	125	59	248	0	327	4875

soil ecological environment.

6. Conclusions

(i) Cu, Pb, Zn, and Cd in the soil near the Luanchuan mine area exceeded the risk screening values for soil contamination of agricultural land to varying degrees, of which the Cd exceeding the standard rate reached 68.4%, and the comprehensive pollution degree was moderate. The exceeding standard rate of Cu and Zn were 15.8%, that of Pb was 5.3%, and their comprehensive pollution degrees are within the warning range. The comprehensive pollution levels of As, Cr and Hg are within the safe range. The comprehensive potential ecological risk of heavy metals is moderate, and the single element Cd is the main ecological risk factor, with a contribution rate of 53.6%.

(ii) Mo and six heavy metals, Cu, Pb, Zn, As, Cd and Hg, in the soil near the Luanchuan mine concentration area have accumulated to varying degrees. Mo, Zn and Cd have the highest accumulation degrees, and the sample accumulation rate reached 100%. Among them, Mo had the strongest accumulation effect, and its average accumulation degree reached the “extremely strong” level, followed by Cd and Zn, and their average accumulation degree reached the “moderate” level. The sample accumulation rates of Cu and Pb reached 95% and 79%, respectively, and their average accumulation degree were “none–moderate”. The sample accumulation rates of As and Hg were 21% and 32%, respectively, but the overall accumulation degrees were not obvious. Cr is close to natural accumulation, and its accumulation rate is 0.0079×10^{-6} per year.

(iii) Cu, Pb, Zn and Cd are the main pollution risk elements. According to the current cumulative rate, in the next

30 years, the cumulative pollution rate of Cd in the soil near the Luanchuan mine concentration area will reach more than 94%. In the next 60 years and 90 years, the cumulative pollution rates of Zn and Cu, respectively, will exceed the standard by more than 78%. After 200 years, Pb and As will reach 57% and 26%, respectively. The accumulated exceeding standard years of Hg and Cr are relatively long and will not pose a potential threat to the ecological environment.

CRediT authorship contribution statement

Zhen-yu Chen and Yuan-yi Zhao conceived of the presented idea. Zhen-yu Chen wrote and revised the paper with support from all authors and drew all the figures. Dan-li Chen and Hai-tao Huang provided the raw data and technical supervision. Yu Zhao and Yu-jing Wu participated in the field work. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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