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Original Research

Characteristics of Soil Heavy Metal Contents and Its Source Analysis in Affected Areas of Luning Coal Mine in Huaibei Coalfield

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Abstract

This study analyzed the content characteristics, ecological risks, vertical migration characteristics and sources of soil heavy metals (Cr, Ni, Cu, Zn, As, Cd and Pb) in affected areas of Luning Coal Mine. Results showed that the average contents of Cr, Pb, Cu, As and Cd exceeded the surface soil background values of Anhui Province, but the risk of soil ecological environment was low. Cd had the largest single factor pollution index, As followed, and Cd in 14 sampling points reached the warning limit, 95% of the samples were in moderate hazard, 5% of the samples were in strong hazard, but the potential ecological hazard index of many kind of heavy metals was 81.81~121.41, which was low ecological hazard. The difficulty of vertical migration of heavy metals in soil was from easy to difficult: Cr>Ni&Cu>As>Zn>Cd&Pb; Cu, Zn and Pb were related to automobile exhaust emissions and transportation dust, Cd and Ni were mainly caused by natural geological processes, leaching of coal gangue hill and the discharge of industrial pollutants, As was mainly caused by agricultural activities, and Cr was closely related to coal combustion.

Keywords: soil heavy metals, content characteristics, vertical migration, potential ecological risk evaluation method, principle component analysis

Introduction

China is rich in coal resources and is the world's largest coal producer and consumer. However, with the development and utilization of coal resources, a large number of wastes, such as coal gangue, mine water and fly ash, will be generated, causing pollution to the surrounding environment of the mining area [1-5]. In particular, under the action of spontaneous combustion, rainwater leaching and wind blowing, the trace heavy metal elements in the coal gangue and fly ash piled in the open air diffuse and migrate to the surrounding environment media, polluting the soil and leading to

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the increase of heavy metal contents in the soil [6-10]. Coal mine power plants will release toxic and harmful substances during coal combustion, especially heavy metal elements, will have a serious impact on the mining environment. Heavy metal pollution has the characteristics of concealment, lag and long-term. It is not easy to be biodegraded, but easy to be absorbed and accumulated by organisms, and finally harms human health through the food chain [11]. Soil is the most basic resource for all life on earth to survive and develop. Once polluted, it will be difficult to repair. Therefore, it is particularly important to analyze the ecological risk of soil heavy metal pollution in the areas affected by coal mining engineering.

In recent years, predecessors have made a lot of studies on the content characteristics, spatial distribution, migration rules, ecological risks and source analysis of heavy metals in the soil around coal mines by using various methods. For example, Xintian Yuan [12] et al. studied the pollution characteristics of heavy metals such as Cu, Zn, Cr, Cd, Pb, Hg and As in the topsoil of farmland around the coal mine area in Suzhou. Results showed that the surface soil of the farmland within 500m of the coal mine area except Cu, Zn and Pb, Cr, Cd, Hg and As exceeded the national soil environmental quality standards (Level I), where As, Cd were slightly polluted, Cr was moderately polluted, and Hg was heavily polluted. Jianmei Yuan [13] et al. measured the contents of heavy metals Cr, Ni, Cu, Zn, Cd, Pb, As and Hg in six coal mining areas in Chongqing. Results showed that except Cr, Ni, Cu, Zn and Cd were exceeding the standard in some soil samples in the study area, all other soil samples met the national soil environmental quality standards, the comprehensive pollution level was clean, and the potential ecological risk was mild or moderate. Haimin Su [14] et al. studied the potential ecological harm of heavy metal pollution in the soil around the Suzhou mining area by using Hakanson potential ecological risk index method. They thought that except Cd and Hg, the potential ecological risk coefficients of heavy metals were all mild risk hazards, Cd and Hg had a high contribution rate in the farmland ecological pollution of Suzhou mining area. Xiaodong Guo [15] et al. measured the contents of As, Hg, Cu, Pb, Zn, Cr, Ni and Cd in the farmland soils of Hunchun basin in order to understand the characteristics of heavy metal pollution. Results showed that the contents of Pb and Zn were lower than the background values of Jilin Province, and the contents of other heavy metals exceeded the background values, especially Hg. More than 20% of the samples were obviously polluted by Hg, while less than 10% of the other elements were polluted. Abdugheni Abliz [16] et al. studied the sources of heavy metals in soils of Northwest coal mining areas. Zn and Cu came from parent materials, Cr, As and Hg came from human activities such as coal combustion, chemical industry and transportation, and Pb was influenced by both natural factors and human activities.

Coal mining history, development scale and the use of coal resources are different, the impact on the surrounding environment is completely different. This paper choice the Luning coal mine, which has the longest mining history, the largest development scale and has the pithead power plant in the Sunan mining area, to analyze the contents and migration of Cr, Ni, Cu, Zn, As, Cd and Pb in the surrounding soil. On this basis, the evaluation of soil environmental quality and potential ecological risk in coal mine affected areas was carried out, and the possible sources of heavy metal pollution were discussed to provide a scientific basis for soil environmental protection and restoration management around the coal mine.

Materials and Methods

Overview of the Study Area

Huaibei coalfield is located in the southern part of Huanghuaihai plain and the northern part of Anhui Province. The territory is rich in coal resources, is an important coal energy base in east China. Luning coal mine is located in the Sunan mining of Huaibei coalfield, covering an area of 23 km^2. It was completed and put into operation in December 1969, and had a mining history of more than 50 years. The mine produces 2.2 million tons of coal a year. In July 2015, the mine had a installed capacity of 30,000 kw and an average daily power generation of 46,000 degrees. After years of coal mining and utilization, great changes had taken place in the surface environment of the mining area. In particular, coal gangue hill and collapsed lake constitute a potential threat to soil pollution around the mining area. Tuo river in the study area is a seasonal river. Terrain is flat, elevation in +24 m or so. Sand ginger black soil is the main soil type in the region. The soil is deep, the organic matter content is not high, the soil clay content is high, the texture is viscous, the structure and the porosity are poor. The main crops are corn and wheat. Summer warm and rainy, the dominant wind direction is southeast wind. Winter cold and dry, the dominant wind direction is northeast wind. The geographical location of the study area was shown in Fig. 1a-b).

Sample Collection and Processing

In July 2019, based on the full understanding of the land use status and geological background of the study area, taking coal gangue hill and pithead power plant as the center, along the southeast downwind direction, the fan-shaped distribution method was used to collect 19 surface soil samples. In addition, 2 surface soil samples were collected between coal gangue hill and pithead power plant, a total of 21 surface soil samples (B1~B21); 5 vertical stratified soil samples (P1~P5), the vertical stratified sampling depth was 60cm, divided into

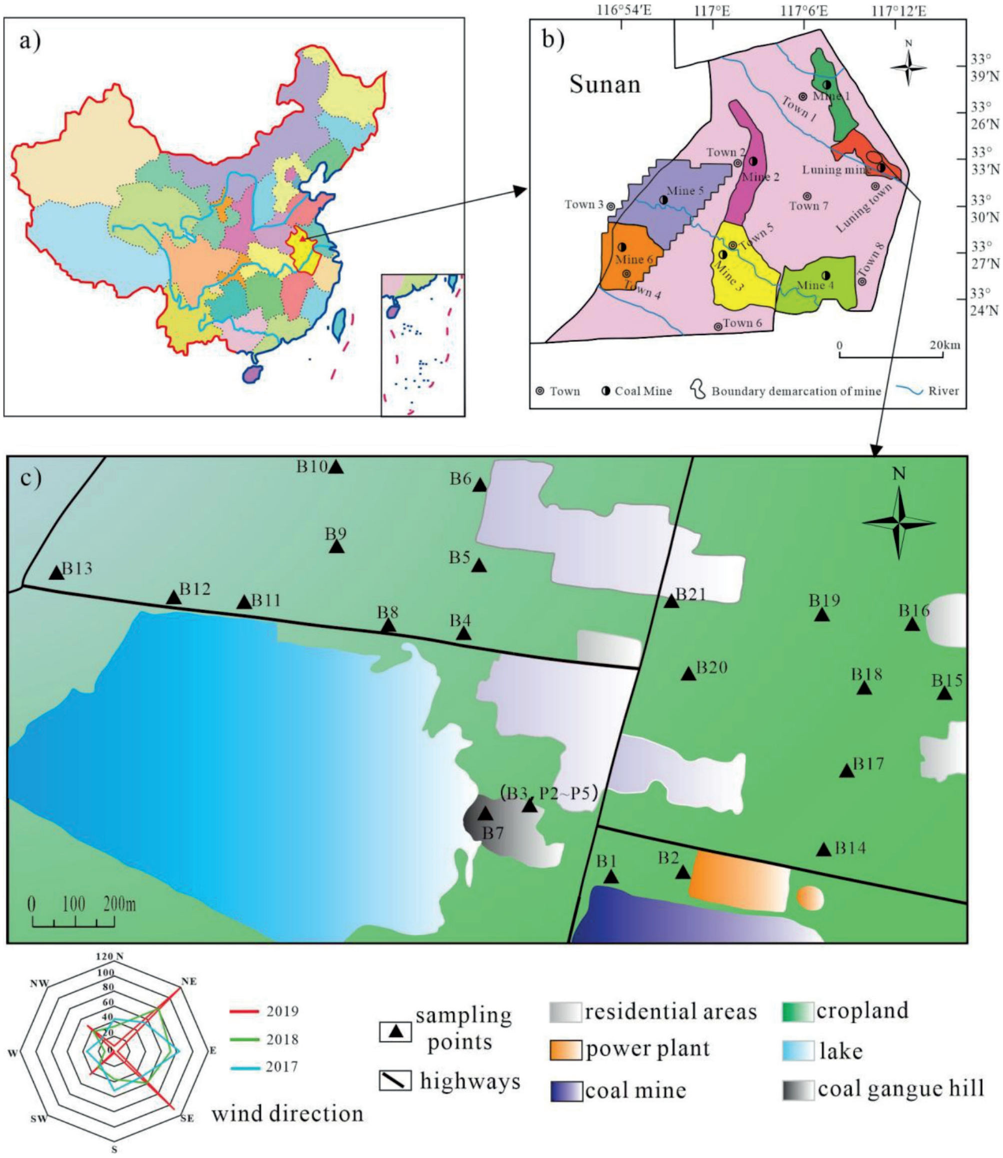

Fig. 1. Geographical location and distribution of sampling points of the study area.

six layers, which are 0~10 cm, 10~20 cm, 20~30 cm, 30~40 cm, 40~50 cm and 50~60 cm respectively. The sampling point distribution was shown in Fig. 1c).

Soil samples were taken within the area of 20cm×20cm square, and the collection depth was 0~10cm. The samples were put into a clean sealed bag, labeled well, and the sampling point was positioned by GPS. Meanwhile, the surrounding environment of the sampling point was recorded. After the samples were transported back to the laboratory, they were dried, ground, screened through 200 mesh, put into a sealed bag and labeled for testing.

Sample Test

The contents of Cr, Ni, Cu, Zn, As, Cd and Pb in the samples were determined by X-ray fluorescence (XRF) [17-19]. First, tablet with a special fluorescent boric acid abrasive and manual powder tablet press. A proper amount of soil samples after sieving was taken and put in the middle of the funnel. Then boric acid powder was put on the outside of the funnel, then quickly pulled out the funnel, then put the gasket and the upper pressure head in turn. The assembled mold was put into the tablet press, pressurized to about 10 Mpa and held the pressure for one minute. To invert the mould and remove the bottom of the mould, the mould was put into the tablet press again, and pushed out the pressed sample with the screw. After the tablet was made, the contents of heavy metals were measured by XRF, the standard used is GBW07430 (GSS-16).

Pollution Assessment Methods

Single Factor Index Method

Single factor index method reflects single pollution index in soil, which is one of the commonly used methods at present [20-21]. Its calculation formula is as follows:

$$P_i = \frac{C_i}{S_i} \quad (1)$$

In formula (1), P_i represents the pollution index of element i in soil. C_i is the actual measured value of element i (mg·kg^{-1}); S_i is the evaluation standard of element i (mg·kg^{-1}). In this paper, the pollution risk screening values in soil environmental quality--risk control standard for soil pollution in agricultural land (GB15618-2018) [22] and European standard guide maximum allowable limits [23] were taken as the evaluation standard. The single factor pollution index P_i were listed in Table 1.

Nemero Comprehensive Pollution Index Method

The nemero comprehensive pollution index method utilizes the average and maximum values of the single factor pollution index, which can highlight the impact of the maximum pollutant on the soil environment. It is an evaluation method that comprehensively reflects the soil pollution status polluted by various heavy metals [24-25], and its calculation formula is as follows:

$$P_n = \left[\frac{(P_{ave})^2 + (P_{max})^2}{2}\right]^{1/2} \quad (2)$$

In formula (2), P_n represents the comprehensive pollution index of heavy metal elements in soil; P_{ave} represents the average of all single factor pollution indexes; P_{max} represents the maximum value of all single factor pollution indexes. The classification criteria of nemero composite pollution index (P_n) were listed in Table 1.

Hakanson Potential Ecological Risk Evaluation Method

Hakanson [26] established a set of methods to evaluate the potential ecological hazards of heavy metals according to the compound effects of heavy metal pollution in soil and the ecotoxicity of different heavy metal elements [27], the calculation formulas are as follows:

$$E_r^i = T_r^i \times C_o^i / C_n^i \quad (3)$$

$$RI = \sum_{i=1}^{n} E_r^i \quad (4)$$

In formula (3), E_r^i represents the potential ecological hazard index of a single heavy metal; C_0^i represents the actual measured value of element i (mg·kg^{-1}); C_n^i represents the reference value of element i (mg·kg^{-1}), in this paper, the surface soil background values of Anhui Province was taken as the reference values. T_r^i represents the toxicity response coefficient of element i, reflecting the response relationship between heavy metals in aqueous phase, sedimentary phase and biological phase [28]. The toxicity response coefficients of Cr, Zn, Ni, Pb, Cu, As and Cd are 2, 1, 5, 5, 5, 10 and 30 respectively [29]. In formula (4), *RI* represents the potential ecological hazard index of multiple heavy metals. The classification criteria of the potential ecological hazard index of heavy metals were listed in Table 2.

Results and Discussion

Characteristics of Heavy Metal Contents in Surface Soil

According to the test results of heavy metal contents in the surface soil of the study area, it was compared the test results with the background values of heavy metal contents in the surface soil of Anhui Province, the soil pollution risk screening values of Chinese soil environmental quality [22] and the standard guide maximum allowable limits of Europe [23]. The statistical characteristics were shown in Table 3.

Visibly, in addition to the average content of Ni was lower than the background value, the average content of Zn closed basically to the background value, the average contents of 5 kinds of heavy metal Cr, Pb, Cu, As and Cd were 77.32, 36.89, 24.23, 17.97, 0.22 mg·kg^{-1}, which were 1.16, 1.39, 1.19, 2.00,

Table 1. Classification standards of single factor pollution index and comprehensive pollution index.

Hierarchy	Single factor pollution index	Composite pollution index	Pollution grade	Pollution level
1	$P_i \leq 0.7$	$P_n \leq 0.7$	Safety	Clean
2	$0.7 < P_i \leq 1.0$	$0.7 < P_n \leq 1.0$	Alert	Still clean
3	$1.0 < P_i \leq 2.0$	$1.0 < P_n \leq 2.0$	Slight pollution	Slight pollution
4	$2.0 < P_i \leq 3.0$	$2.0 < P_n \leq 3.0$	Moderate pollution	Moderate pollution
5	$P_i > 3.0$	$P_n > 3.0$	Serious pollution	Serious pollution

Table 2. Classification standard of heavy metal potential ecological hazard index.

Rank	E_r^i	*RI*	The degree of pollution
I	E_r^i<40	*RI*<150	Low hazard
II	40≤E_r^i<80	150≤*RI*<300	Moderate hazard
III	80≤E_r^i<160	300≤*RI*<600	Strong hazard
IV	160≤E_r^i<320	*RI*≥600	Very strong hazard
V	E_r^i≥320		Extremely dangerous

Table 3. Statistical analysis of heavy metal contents in surface soil.

Element	Mean/ ($mg\cdot kg^{-1}$)	Standard deviation/ ($mg\cdot kg^{-1}$)	Background values/ ($mg\cdot kg^{-1}$)	Chinese soil pollution risk screening values/($mg\cdot kg^{-1}$)	European maximum allowable limits/($mg\cdot kg^{-1}$)	Coefficient of variation/(%)
Cr	77.32	6.32	66.5	200	100	8
Zn	62.77	9.74	62	250	300	16
Ni	21.57	8.28	29.8	100	50	38
Pb	36.89	3.40	26.6	120	100	9
Cu	24.23	7.00	20.4	100	100	29
As	17.97	3.69	9	30	20	21
Cd	0.22	0.02	0.097	0.30	3	11

2.27 times the background soil values of Anhui Province respectively (Fig. 2), this indicated that the 5 heavy metals in the soil in the study area have produced different levels of pollution accumulation, among them, the contents of Cr and Cu were relatively low, the content of Cd was relatively high. Compared the average contents of heavy metals such as Cr, Zn, Ni, Pb, Cu, As and Cd in the surface soil of the study area with the soil pollution risk screening values of Chinese soil environmental quality [22] and the standard guide maximum allowable limits of Europe [23], the average

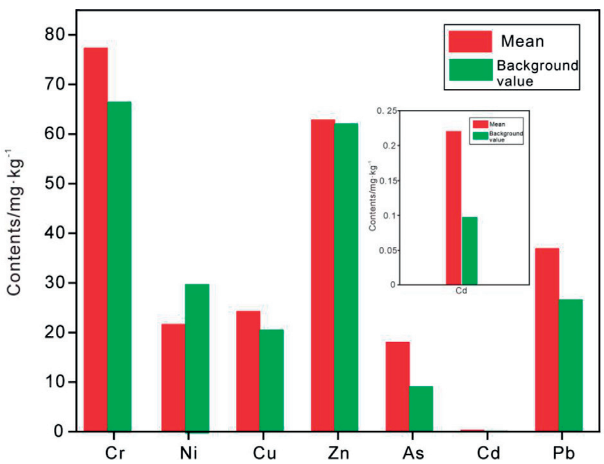

Fig. 2. Histogram of heavy metal contents in the study area and surface soil background values in Anhui Province.

contents of 7 heavy metals were less than these two safety limits. It indicated that the pollutants in the soil around the area have low risk to the quality and safety of agricultural products, crop growth or soil ecological environment, and can be ignored under normal circumstances.

Coefficient of variation is the ratio of standard deviation to mean, which reflects the degree of dispersion of data. According to Wilding's classification of variation degree, could know that Cr, Pb, Cd (8%, 9%, 11%) were low variation (<15%), Zn, Cu, As (16%, 29%, 21%) were medium variation (15%<CV<36%), and Ni (38%) were high variation (CV>36%). Therefore, Cu and Ni had the highest coefficient of variation and the highest degree of dispersion, indicating that these two elements were not evenly distributed and might be affected by human factors.

Evaluation of Heavy Metal Pollution in Surface Soil

According to formula (1), the calculation result of soil single factor pollution index in the study area was shown in Fig. 3a). Cd had the largest pollution index, 14 sampling points reached the alert limit, and had the largest accumulation degree. Secondly, the pollution index of As was relatively high, up to 0.84, indicating that As also had a certain degree of accumulation. Ni had the smallest pollution index, with the lowest being 0.11. Formula (2) was used to calculate the nemero comprehensive pollution index, as shown in Fig. 3b).

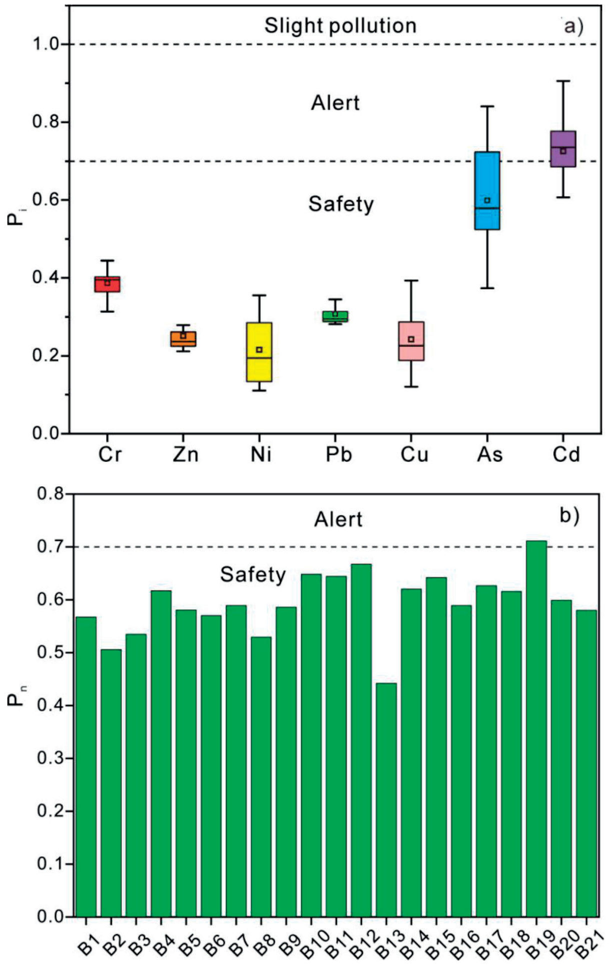

Fig. 3. Box diagram of single factor pollution assessment a) and integrated nemero pollution assessment b).

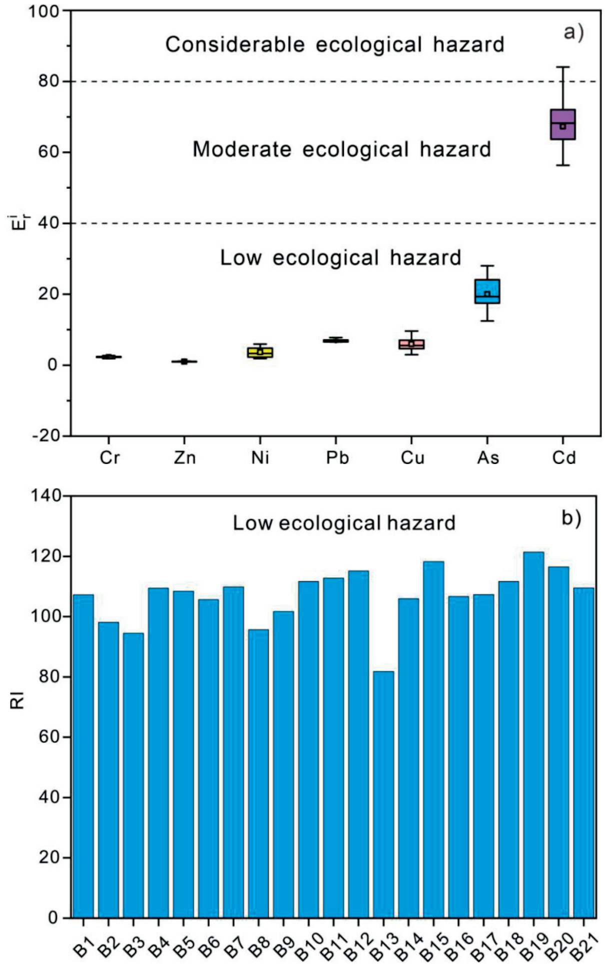

Fig. 4. Bar chart of potential ecological hazard assessment of single heavy metal a) and multiple heavy metal b).

P_n ranged from 0.43 to 0.70, and only one sampling site had a higher pollution index, reaching the alert limit.

The potential ecological hazard index for a single heavy metal calculated by formula (3) was shown in Fig. 4a), the ecological hazard index of Cd is the largest, 95% of the samples in a moderate hazard, 5% of the samples in a considerable hazard, between moderate and considerable ecological hazard level, except ecological hazard index of As was close to 40, the rest of the ecological hazard index of heavy metals were far less than 40, belonged a low ecological hazard, among them, Zn had the minimum ecological hazard. According to formula (4), the calculation results of the potential ecological hazard index of several heavy metals were shown in Fig. 4b). The *RI* ranged from 81.81 to 121.41, all of which were low ecological hazards.

Comparing the two pollution evaluation methods, it was found that Cd in the soil of the study area had a certain degree of pollution accumulation effect and ecological harm, which was related to its higher content. When evaluated by the single factor pollution index, 29% of As had a higher pollution index and reached the alert limit. Ni had the lowest pollution index, however, if evaluated by Hakanson's potential ecological risk assessment method, As is in a low ecological hazard, and Zn had the lowest ecological hazard index. The reason for this phenomenon may be that some heavy metals are highly enriched, but their pro granularity makes it adsorbed by other particulate matter into the soil for mineralization and burial, thus reducing their toxicity to organisms [30]. Therefore, only by combining the accumulation of heavy metals in the soil environment with the potential ecological hazard to the ecosystem can the pollution status of heavy metals in the soil be fully reflected [31]. When using the nemero comprehensive pollution index, 95% of the sampling points were within the safety limit, while when using the potential ecological risk evaluation method of Hakanson, all the sampling points were in low ecological hazard, and the results of the two methods were basically consistent.

Vertical Migration Characteristics of Heavy Metals in Soil

In order to study the vertical migration characteristics of heavy metals in the soil of the mining area, the soil in the study area was sampled vertically stratified, and the analysis results were shown in Fig. 5 and 6. The content ranges of Cr, Zn, Ni, Pb, Cu, As and Cd were 61.15~79.71, 58.89~69.31, 11.21~39.84, 36.80~37.75, 19.74~32.73, 10.35~15.69, and 0.17~0.23mg·kg^{-1}, the 7 heavy metal elements contents of the 6 vertical layered samples have reached the the soil pollution risk screening values of Chinese soil environmental quality [22], and European standard guide maximum allowable limits [23].

The Fig. 5 and Fig. 6 showed that, except the contents of Cd and Pb remained unchanged within the range of 0~60cm depth basically, the contents of the other 5 heavy metal elements (Cr, Ni, Cu, Zn, As) all fluctuate significantly within the range of 0~30 cm, indicating that these 5 heavy metal elements have relatively obvious migration within the range of 0~30 cm. From 0 to 30 cm, the variation trend of As content was first decreased and then increased, and the highest content was found at 20~30 cm, which may be related to natural precipitation and diversion irrigation; The change trends of Ni and Cu contents were reduced after rising first, both rose sharply at 10~20 cm, and decreased sharply at 20~30 cm, the maximum content appeared at 10~20 cm, the lowest value appeared at 20~30 cm, it may be because 10~20 cm was the depth of fertilization and the depth of plant root development, the application of organic fertilizer and the development of plant roots could cause heavy metals not easy to migrate downward [32], thereby appear the phenomenon that the contents of heavy metals rose sharply at 10~20 cm. The content of Cr and Zn decreased gradually within the range of 0~30 cm, and the highest content was found in the surface soil, indicating that these two elements were greatly disturbed by human factors. From 30 cm to 60 cm, the contents of Ni, Cu and Cr all showed a trend of gradual increase, which may be related to illivuation [33], the eluviation caused by natural rainfall or irrigation causes heavy metal elements to migrate downward and deposition occurred within the range of 30~60 cm, leading to the increase of heavy metal elements; The contents of As and Zn showed a gradually decreasing trend, indicating that these two elements also had the abilities of vertical migration, but the migration amount was small.

From the above analysis, it can be seen that the vertical migration characteristics of different heavy metal elements in the soil in the study area were different, the difficulty level was from easy to difficult was Cr>Ni&Cu>As>Zn>Cd&Pb (the two elements connected by & represented similar migration ability). The reasons for this difference were related to the contents of organic matter and lime in the soil, the types and quantities of clay minerals, the adsorption abilities of heavy metals to these negative charged surfaces, the adsorption capabilities of plant roots to heavy metals, and the evaporation of water in the soil [34-35].

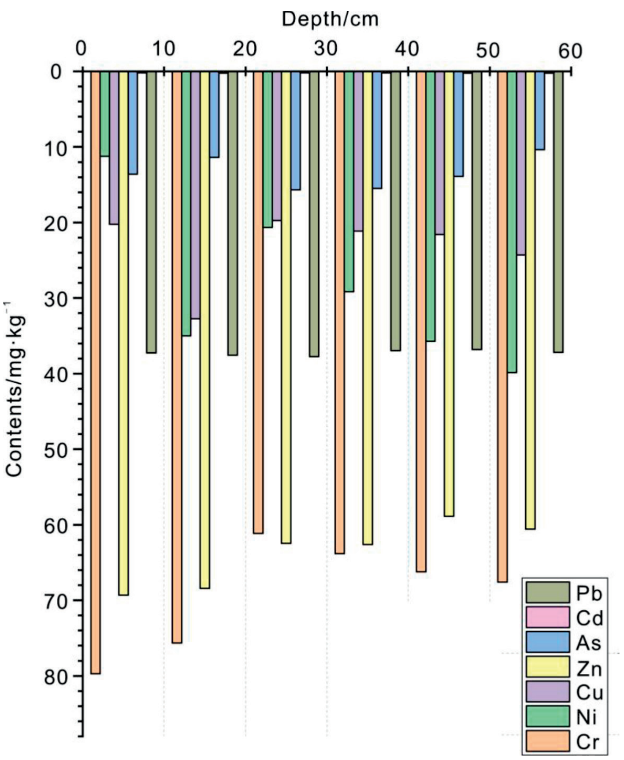

Fig. 5. Histogram of distribution characteristics of soil heavy metal profile.

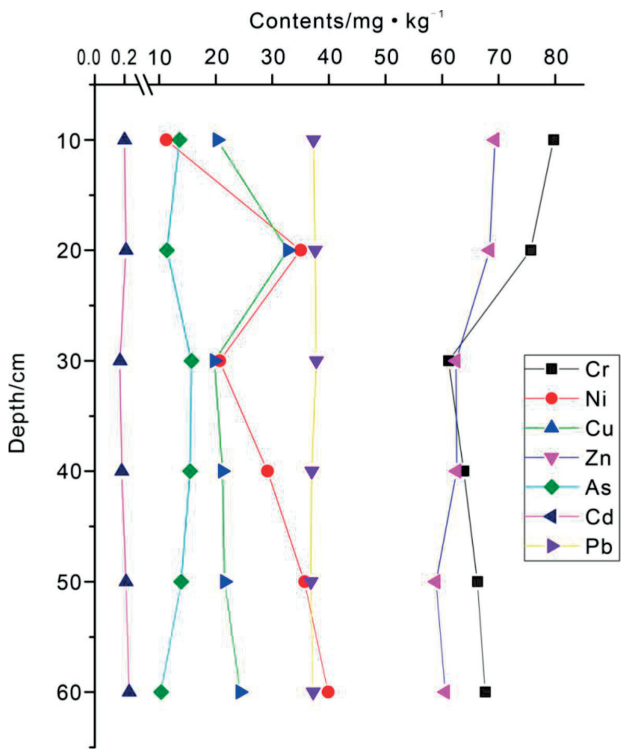

Fig. 6. Scatter diagram of distribution characteristics of soil heavy metal profile.

Table 4. Correlation analysis results of heavy metal contents.

Element	Cr	Ni	Cu	Zn	As	Cd	Pb
Cr	1.000						
Ni	0.032	1.000					
Cu	0.017	0.099	1.000				
Zn	0.186	-0.104	**0.469***	1.000			
As	-0.086	-0.169	0.072	-0.193	1.000		
Cd	-0.112	**0.563****	-0.007	-0.168	-0.030	1.000	
Pb	-0.142	-0.145	**0.518***	**0.375**	-0.294	**-0.397**	1.000

**correlation was significant at the level of 0.01 (bilateral) * correlation was significant at the level of 0.05 (bilateral)

Correlation Analysis

Studies had shown that the correlations between heavy metal elements can reflect whether each element has the same source [36]. It is generally believed that when the correlation coefficient of elements is greater than 0.3 [37], it shows a strong correlation, indicating that elements may have the same source. Pearson correlation analysis results of heavy metal contents were shown in Table 4. The absolute values of Pearson correlation coefficients of Cd-Ni, Zn-Cu, Pb-Cu, Pb-Zn and Pb-Cd were 0.563, 0.469, 0.518, 0.375 and 0.397 respectively, indicating that Cd-Ni, Cd-Pb, Zn-Cu-Pb were strongly correlated and may had the same source. The correlation coefficients between other elements were all less than 0.3, with weak correlation. Whether these elements came from the same source could be further determined by cluster analysis and principle component analysis.

Cluster Analysis and Principle Component Analysis

Cluster analysis and principle component analysis are the main methods to identify the source of heavy metals, and can also reflect whether all elements have the same source [38]. Clustering analysis of the sample point as shown in Fig. 7, when the distance between groups was 15, 21 sampling points could be divided into 4 groups with obvious differences, but 86% of the sampling points were concentrated in the first two groups, it is indicated that the sampling points were mainly affected by two pollution sources, while the sampling points of the first group were mostly distributed around the coal gangue hill, the sampling points of the second group were mostly distributed around the power plant, indicating that the coal gangue hill and power plant were two different sources of pollution. In order to further determine the sources of seven heavy metal elements in soil, principle component analysis was used.

The principle of principle component analysis is to transform multiple evaluation indicators into a few representative comprehensive indicators by using the idea of dimensionality reduction [39-40]. The loading amount of soil heavy metal principle component factors in the study area was shown in Table 5 and Fig. 8. The information contents of the 7 heavy metals could be reflected by four common factors, with less lost information, and the cumulative contribution rate of the total variance before and after rotation is the same.

According to the loading amount of the factor after rotation, the variance contribution rate of principle component 1 (PC1) was 26.687%, Cu, Zn and Pb all had large positive loading, while As and Cr had negative loading. Therefore, Cu, Zn and Pb may came from the same pollution source, which was consistent with the above correlation analysis result. As could be seen from Table 3, the variation coefficient of Cu was relatively large, and the contents of a few samples were relatively high. Although Pb was a low variation, its average content was 1.39 times of the soil background value of Anhui Province, which had caused pollution accumulation. In most cases, the contribution of human sources to trace element input is greater than that of natural sources [41], so Cu, Zn and Pb could be

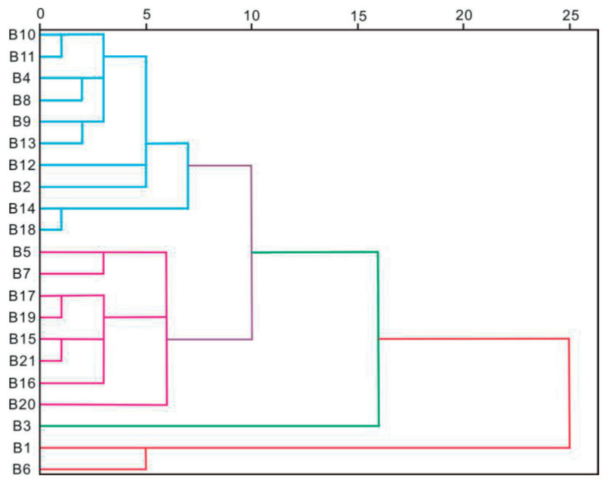

Fig. 7. Clustering analysis results of heavy metal element contents.

Table 5. Principle component analysis of heavy metals in soil.

Element	Before rotation				After rotation			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
Cr	0.089	0.050	-0.847	0.434	0.039	-0.032	-0.044	0.955
Ni	-0.371	0.805	-0.001	0.001	0.046	0.871	-0.158	0.029
Cu	0.631	0.450	0.333	0.414	0.912	0.132	0.174	-0.050
Zn	0.711	0.278	-0.190	0.230	0.730	-0.124	-0.163	0.312
As	-0.232	-0.403	0.447	0.732	-0.038	-0.094	0.968	-0.063
Cd	-0.587	0.660	0.147	0.090	-0.132	0.883	0.078	-0.071
Pb	0.827	0.128	0.229	-0.290	0.693	-0.332	-0.390	-0.309
Eigenvalue	2.132	1.544	1.138	1.041	1.868	1.691	1.179	1.118
Variance contribution rate/%	30.461	22.062	16.263	14.874	26.687	24.160	16.849	15.965
Total variance contribution rate/%	30.461	52.525	68.787	83.662	26.687	50.848	67.696	83.662

considered to be controlled by human factors. As the sampling site is located in the farmland area near gangue hill and power plant, as well as along the main road of the mining area, there are frequent passing vehicles and serious automobile exhaust emissions. While Cu and Pb are the marking elements of automobile exhaust [42], Zn mainly comes from the wear of tires and brake pads [43]. Therefore, PC1 can be interpreted as automobile exhaust emission and transportation dust.

The contribution rate of principle component 2 (PC2) accounted for 24.160% of the total contribution rate. In this study area, the accumulation degree and ecological hazard of Cd were the most serious. The reason was that the long-term stacked coal gangue hill was leached by rainwater, and the heavy metal Cd migrated into the surrounding soil with the flow of water, forming accumulation. The source of Ni in

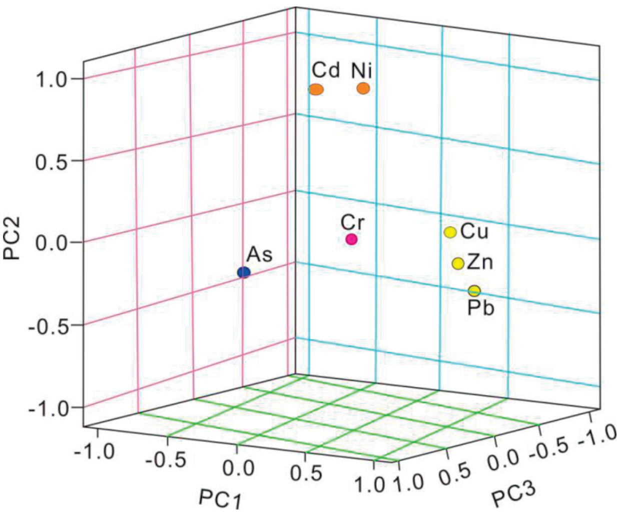

Fig. 8. Three dimensional scatter diagram of soil heavy metal factor loading.

soil was mainly the result of geological effects, which is closely related to the formation processes of soil, rock and rock weathering [44]. However, the variation coefficient of Ni in the study area was relatively large, which indicated that it was also influenced by human factors. Ni is widely used in the production of industrial machinery and precision electronic instruments, metallurgy, electroplating and other fields, and Ni oxides and hydroxides can also be used in rechargeable batteries [44]. There is an electronics factory 2500 m south of the study area, due to the prevailing southeast wind in the area in the summer, it will accumulated heavy metals Ni in the soil of the study area. Therefore, PC2 can be resolved into geological effects (ie natural resources) and coal gangue leaching, followed by industrial pollutant emissions.

Principle component 3 (PC3) explained 16.849% of the contribution rate of total variance, and the load of As was large, which was consistent with the above correlation analysis results. Because the sampling site is located in the farmland area, a large amount of fertilizer is needed for planting crops, and the harmful heavy metal elements (such as As, Cd, Pb, etc.) in the fertilizer may be stored in the soil in the form of fertilizer, resulting in a large accumulation of As [45]. Thus, PC3 represents agricultural activity.

The contribution rate of principle component 4 (PC4) to the total variance was 15.965%, and the heavy metal with large load was Cr, which was consistent with the correlation analysis results. Cr can enter the surrounding soil through sewage discharge, atmospheric settlement and other means during the operation of coal-fired power plants, causing certain accumulation. Therefore, PC4 can be interpreted as coal combustion.

Generally speaking, there are three main ways of soil pollution, one is natural sources, the other is man-made sources, and the third is the combination of natural and man-made sources. Man-made sources mainly include traffic pollution, industrial activities, agricultural activities, fossil fuel combustion, mining activities and so on. Yazhu Wang [46] et al. analyzed the sources of heavy metals in the soil of Jiangsu Province, showing that Cr, Cu, Zn, and As were affected by both natural and anthropogenic sources, while Cd and Pb were mainly affected by the latter. Gaoqi Jin [47] et al. studied the heavy metals in the cultivated soils in Shaoxing City, Zhejiang Province, and found that the Pb mainly came from mining activities, Ni and Zn were mainly affected by its parent material, Cu and Zn were mainly affected by agricultural activities, and Cd mainly came from chemical fertilizers. Kuangjia Li [48] et al. analyzed the source of heavy metals in the soil around a coal mine in Henan Province and concluded that Cd, Pb, Cu and Zn came from gangue heap. Jun Liu [49] et al. by studying the soil heavy metals in upland farmland around the coal mine in grassland area, found that Zn mainly came from transportation, Ni mainly came from agricultural production, and Cd, Hg came from natural mother materials and human activities.

According to previous studies, Cu, Zn and Pb were mainly derived from transportation, Cd and Cr pollution was mainly caused by agricultural activities, Ni and As were mainly related to parent materials. In this study, the sources of Cu, Zn and Pb were basically consistent with previous studies, while the sources of Cd, Cr, Ni and As were slightly different from previous studies. The main reason is that Luning coal mine has a long mining history and strong environmental cumulative effect. In addition, there are not only mining activities in this research area, but also power plants and electronic enterprises, etc. Industrial and mining activities and the surrounding environment are complex, so the judgment of soil pollution sources has multiple solutions.

Conclusions

The conclusions drawn from this research suggested that except for Ni and Zn, the average contents of the other 5 heavy metals (Cr, Pb, Cu, As and Cd) in the soil of the study area all exceeded the background values of surface soil in Anhui Province. However, the average contents of the 7 heavy metals were all less than the soil pollution risk screening values of Chinese soil environmental quality and the standard guide maximum allowable limits of Europe, indicating a low risk of soil ecological environment. The single factor pollution index results showed that the pollution index of Cd was the largest, followed by As, and 14 sampling points of Cd reached the alert limit. Nemero composite pollution index values ranged from 0.43 to 0.70, and only 1 sampling point reached the alert limit. According to the potential ecological hazard index of a single heavy metal, Cd had the largest ecological hazard index, with 95% of the samples in moderate hazard and 5% in strong hazard. The potential ecological hazard index values of several heavy metals were 81.81~121.41, all of which were low ecological hazard. The characteristics of the heavy metal profile in the soil indicated that the heavy metal contents in the soil in this study area did not gradually decrease with increasing depth. The contents of 5 heavy metals (Cr, Ni, Cu, Zn, As) in the range of 0~30 cm had obvious fluctuations, indicating that these 5 heavy metal elements had obvious migration in the range of 0~30 cm. The difficulty of vertical migration of soil heavy metals in the study area was ranked from easy to difficult: Cr>Ni&Cu>As>Zn>Cd&Pb. The reasons for this difference were related to the contents of organic matter and lime in the soil, the types and quantities of clay minerals, the adsorption abilities of heavy metals to these negative charged surfaces, the adsorption capabilities of plant roots to heavy metals, and the evaporation of water in the soil. Pearson correlation analysis showed that there were strong correlations between heavy metals Cd and Ni, Cd and Pb, Zn, Cu and Pb in the study area, reflecting the two main pollution source characteristics of coal gangue hills and power plants. The principle component analysis results showed that Cu, Zn and Pb were related to automobile exhaust emissions and transportation dust, Cd and Ni were mainly caused by natural geological processes, leaching of coal gangue hill and the discharge of industrial pollutants, As was mainly caused by agricultural activities, and Cr was closely related to coal combustion.

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Conflict of Interest

The authors declare no conflict of interest.

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