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Original Research

Speciation Characteristics and Contamination Degree of Trace Elements in Coal Gangue Hill of a Mining Area in Huainan Coalfield, China

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Abstract

Coal gangue is one of the most accumulated solid wastes in China, its accumulation occupies a large amount of land resources and the potential environmental risks posed by coal gangue continue to rise. In this study, sequential extraction was employed to analyze the fractionation behavior of trace elements (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn), The contamination degree and potential ecological risk of trace elements were comprehensively evaluated by Geo-accumulation Index (I_{geo}), Potential ecological risk index and the Risk assessment code (RAC) method. The results of XRD shows that there are various minerals in coal gangue, with obvious diffraction peak characteristics, and the minerals with higher levels are quartz, kaolinite, dolomite and potassium feldspar. The trace elements are predominantly found in the residual state. The results of I_{geo} reveal that all trace elements are in a pollution-free state. The potential ecological risk level of Cd belongs to strong risk, while the level of the other elements is slight risk. The result of RAC indicates that the active forms of Mn may cause the greatest harm to the ecological environment, and which deserves further attention. The results can provide scientific basis for the stacking management and comprehensive utilization of coal gangue.

Keywords: speciation characteristics, coal gangue, trace elements, contamination degree

Introduction

Coal gangue is the solid waste discharged in the process of coal mining, washing and processing [1, 2]. The production of coal gangue accounts for about 10%-15% of the raw coal output [3], and it is one of the main sources of industrial solid waste in China [4, 5]. Accompanied by the huge consumption of coal resources, leading to the continuous generation of coal gangue. [6, 7]. Coal gangue is a mixture of a variety of rock and mineralogical components with low carbon content [4]. The discharge and open-air dumping of coal gangue occupy a large number of land resources, which also result in the release of environmentally sensitive trace elements and other toxic and harmful

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substances via weathering and leaching [8-10]. The trace elements will migrate to the surrounding soil or water environment with surface runoff [11], accumulated in the ecological environment and the organisms via the food chain, which may eventually accumulate in the human body and endanger human health [12, 13]. Coal gangue is the main source of heavy metal pollution in mining areas, which poses a serious threat to the ecological environment and human health [14].

In the process of weathering and pedogenesis, coal gangue will disintegrate gradually under the influence of weathering, rainfall, etc. [1], and the trace elements will be released into the environment via rainwater leaching [15]. Therefore, the higher the concentration of environmentally sensitive trace elements in coal gangue, the more serious the impact on the environment [10]. The total amount of trace elements in coal gangue may not provide enough information for evaluating its environmental effects [12]. Therefore, it is of great significance to conduct the chemical speciation of the trace elements and evaluate its mobility and bioavailability [16]. The occurrence state of trace elements determines their migration and transformation pathways in the environment and in the process of utilization [12], affecting the ease of release into the environment [17]. Previous studies have shown that the environmental behavior of trace elements in coal gangue is controlled not only by its concentration and occurrence state, but also by the mineral composition [18]. Therefore, conducting research on the mineral composition, total amount and occurrence state of trace elements in coal gangue is the basis for evaluating the environmental effects of coal gangue.

Huainan coalfield is an important coal area in China, which has made a great contribution to regional economic and social development [19]. However, as a result of the long-term high-load mining activities lead to dozens of gangue dumps have accumulated to different scales, which occupies a great quantity of the land resource and poses a huge challenge to the safe development of agricultural activities and products [20]. While the trace elements in coal gangue have a great impact on the environment, limited studies have been conducted on the distribution characteristics and environmental quality evaluation of the trace elements in the soil of mining area in Huainan coalfield [19, 21-24], but no further researches carry out ecological risk assessment of trace elements in coal gangue. It is necessary to conducted on the speciation distribution and ecological risk assessment of trace elements in Huainan coalfield in terms of the stacking management and comprehensive utilization of coal gangue.

In this study, representative coal gangue samples were collected in the Huainan coalfield, and were digested by the wet method. The concentrations of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn were determined by the ICP-OES method, and the occurrence of trace elements was determined by the sequential chemical extraction method. The main aims of this study are to: (1) Qualitative analysis of mineral composition characteristics of coal gangue and quantitative analysis concentration characteristics of trace elements; (2) Quantify the trace elements fraction in coal gangue, and determine the proportion of each fraction in different elements; (3) Assess the contamination degree by geo-accumulation index (I_{geo}), Potential ecological risk index method and the Risk assessment code (RAC), aiming to provide scientific suggestions for the reasonable disposal of coal gangue and the construction of ecological civilization in coalfield.

Materials and Methodology

Sample Collection

Representative coal gangue dumps were selected in the Panji mining area of Huainan Coalfield (Fig. 1), and sample collection was carried out according to the "Collection Method of Commercial Coal Samples" (GB 475-1996). Sampling points were arranged according to the shape of coal gangue piles, and samples were collected at the top, waist and bottom (0.5 m above the ground) of the coal gangue dumps. One mixed sample was collected from each gangue hill, and the sampling depth of each sample was 20 cm. Each mixed sample was composed of one sub-sample from the top, waist and bottom, and the sample was about 1 kg by the quartering method [25]. The samples were put into aluminum foil bags and taken back to the laboratory for air drying, grinding and sieving. All the samples were preserved in glass bottles.

Sample Handling and Testing

0.5g coal gangue powder was weighted and digested with HF-HNO_3-$HClO_4$ (10 ml: 5 ml: 5 ml) in an electric heating plate. Dilute nitric acid was used to achieve a constant volume before passing through the 0.45 μm microfiltration membrane. The concentration of Cd, Hg, Cr, Ni, Cu, Zn, Pb and other elements in the solution was determined by an inductively coupled plasma mass spectrometer (NexION 300X). The occurrence state of trace elements was analyzed by Tessier sequential chemical extraction method [26]. According to different extraction steps, the occurrence state can be divided into exchangeable state (F1), carbonate-associated state (F2), iron and manganese oxide-associated state (F3), organic-associated state (F4) and residue state (F5). Blank test, parallel test and standard addition recovery test were used for quality control. The relative deviation of the parallel test was less than ±10%, and the standard addition recovery was between 95% and 105%.

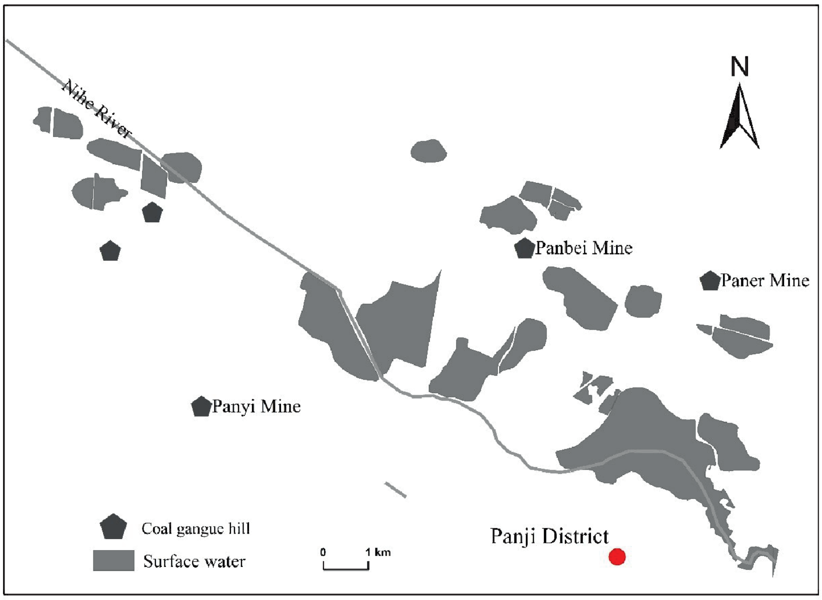

Fig. 1. Location and sampling sites of Panji mine.

Methods for Contamination Degree Assessment of Trace Elements in Coal Gangue

Geo-Accumulation Index Method

The geo-accumulation index (I_{geo}) method was widely used to analyse and evaluate the trace element pollution status comprehensively, which describe the spatial ecological accumulation and ecotoxicological reactions of trace elements in space by analyzing individual elements. It is calculated set by [27] as follows:

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

Where: C_i is the sum of unstable fraction of element *i* (You et al., 2021); B_i is the pre industrial geochemical background value of element *i*, and *k* is 1.5. In the present study, the Huainan soil background values of heavy metals were adopted as the B_i value, and the background value for Cd, Cr, Cu, Mn, Ni, Pb, V and Zn are 0.06, 64.93, 24.16, 416, 25.74, 30.47, 96.03 and 80.81 mg/kg, respectively [28]. Seven grades of I_{geo} were defined for the classification [16]: uncontaminated (I_{geo}≤0); uncontaminated to moderately contaminated (0<I_{geo}≤1); moderately contaminated (1<I_{geo}≤2); moderately contaminated to heavily contaminated (2<I_{geo}≤3); heavily contaminated (3<I_{geo}≤4); heavily to extremely contaminated (4<I_{geo}≤5); extremely contaminated (I_{geo}>5).

Hakanson Potential Ecological Risk Index Method

Ecological risk assessment is carried out by the worldwide well-known Hakanson [29] assessment. The interrelationship between the mass concentration of trace elements and various factors such as ecotoxicology and environmental pollution risk was applied to avoid analysing the effects of a single ecological factor on pollution evaluation from the aspect of regional content. As such, the extent of potential pollution of trace elements can be quantitatively graded, and the comprehensive potential ecological risk effect of multi-factor trace elements can be reflected.

The method is commonly used in potential ecological risk assessment of trace elements, and integrates the content and biological toxicity of trace elements and the sensitivity of the environment to the element. The calculation formula developed by Hakanson [29] as follows:

$$C_f^i = C_i / C_{i0} \quad (2)$$

$$E_r^i = T_r^i C_f^i \quad (3)$$

$$RI = \sum E_r^i \quad (4)$$

where C_f^i is the single pollution index of trace element *i* in the soil, C_i is the measured concentration of trace element *i* (mg/kg), and C_{i0} is the background value of trace element *i* in soil of Huainan city (as B_i in formula (1)), E_r^i is the potential ecological hazard index of trace element *i*, and T_r^i is the toxicity coefficient of element *i*, and the T_r^i of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn are 30, 2 , 5, 1, 5, 5, 2 and 1 [30], respectively. RI is the comprehensive potential ecological risk index, and the classification standard of E_r^i and RI are shown in Table 1.

Risk Assessment Code Method

The migration and bioavailability of trace elements highly depend on their active forms, and the impact

Table 1. Classification criteria of potential ecological risk.

E_r^i	RI	Risk level
E_r^i<30	RI<100	Slight
30≤E_r^i<60	100≤RI<200	Moderate
60≤E_r^i<120	200≤RI<400	Strong
120≤E_r^i<240	RI≥400	Very strong
E_r^i≥240		Extremely strong

of different occurrence states on the environmental effects varies dramatically.

The risk assessment code method (RAC) is an evaluation method based on the speciation of trace elements, which consider the environmental effects of trace elements by analysing the active forms in the environment [31]. In terms of the occurrence state of trace elements obtained by the Tessier five-step extraction method, the exchangeable state and carbonate-associated state were considered as the active form to evaluate, and the ratio of the active form to the total amount of trace elements was defined as RAC value. It is calculated as follows:

$$RAC = \frac{F_1+F_2}{C_t} * 100\% \tag{5}$$

where F_1 is the concentration of element in exchangeable fraction, F_2 is the concentration of element in carbonate fraction, C_t is total concentration of element in five fractions. The environment risk was classified on a scale of one to seven based on RAC value: (1) no risk (RAC<1%); (2) low risk (1%≤RAC<10%); (3) medium risk (11%≤RAC <30%); (4) high risk (31%≤RAC<50%); (5) very high risk (RAC≥75%).

Data Processing

Origin, SPSS 25, Excel and other software were used for mathematical statistical analysis of the experimental data.

Results and Discussion

Mineral Characteristics of Gangue

X-ray diffraction (XRD) analysis was conducted on the collected coal gangue samples, and the XRD results were shown in Fig. 2. According to XRD phase analysis, coal gangue contained various types of minerals, and the diffraction peak characteristics were obvious. The coal gangue samples contained minerals minerals with higher content, such as quartz, kaolinite, dolomite and potassium feldspar, etc., Plagioclase, siderite, quadrozeolite, pyrite, common pyroxene and iron dolomite were present in small amounts. In addition, there were also some non-crystals minerals. Previous studies have shown that the quartz content in weathered coal gangue is higher than that in unweathered top and intermediate gangue, and the clay content in unweathered coal gangue is higher than that in weathered coal gangue [18, 32].

Concentration Characteristics of Trace Elements

The statistical characteristics of trace element concentrations in coal gangue are shown in Table 2.

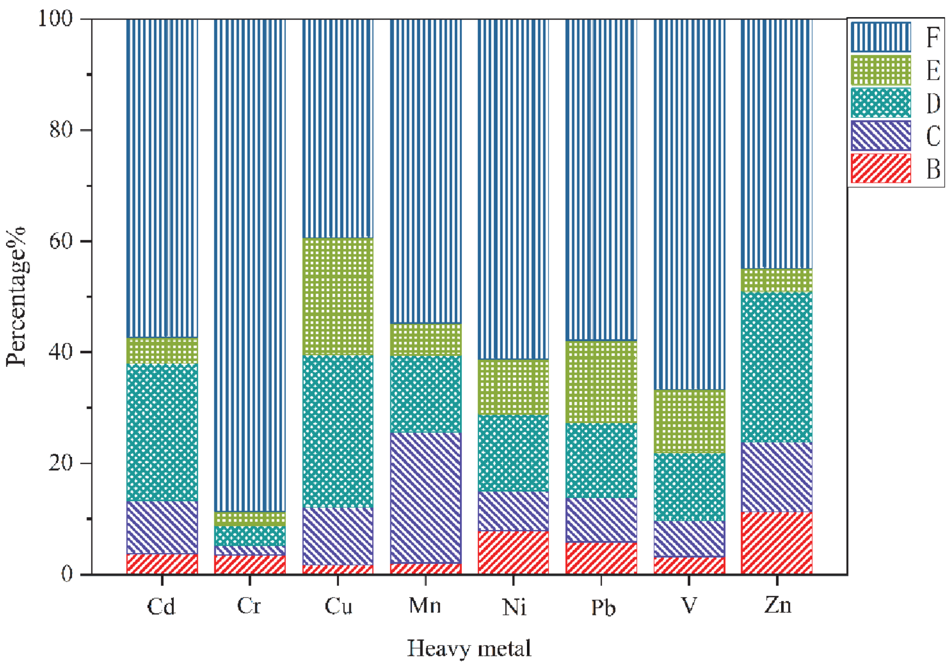

Fig. 2. Chemical speciation of trace elements in coal gangue from Huainan coalfield.

Table 2. Average content of trace elements in the coal gangue of the Huainan coalfield (mg/kg).

Item	Cd	Cr	Cu	Mn	Ni	Pb	V	Zn
Minimum	0.14	46.53	11.32	128.57	16.38	24.38	187.92	43.65
Maximum	0.18	51.39	13.64	234.17	19.13	29.57	228.54	59.82
Mean	0.16	48.46	12.45	173.95	17.58	26.21	205.11	52.31
Std. Deviation	0.02	2.09	0.96	43.99	1.34	2.45	17.58	6.65
Background value of soil in Huainan city	0.06	64.93	24.16	416.00	25.74	30.47	96.03	80.81

The concentrations of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn ranged from 0.14 to 0.18 mg/kg, 46.53 to 51.39 mg/kg, 11.32 to 13.64 mg/kg, 128.57 to 234.17 mg/kg, 16.38 to 19.13 mg/kg, 24.38 to 29.57 mg/kg, 187.92 to 228.54 mg/kg and 43.65 to 59.82 mg/kg, respectively, The descended order of average concentration is V (205.11 mg/kg)>Mn (173.95 mg/kg)>Zn (52.31 mg/kg)> Cr (48.46 mg/kg)>Pb (26.21 mg/kg)>Ni (17.58 mg/kg) >Cu (12.45 mg/kg)>Cd (0.16 mg/kg). Comparing the concentrations of trace elements in coal gangue with the background values of soil in Huainan City, the average concentrations of Cd and Mn are higher than the background value, and the average concentrations of the other six trace elements are lower than that in Huainan City.

Analysis the Speciation Characteristics of Trace Elements in Coal Gangue

The toxicity and migration efficacy of trace elements depends on both the total amount and the speciation. The contents of different specific chemical forms revealed the migration and transformation capability of trace elements, which also reflected the level of bioavailability and ecological risk of elements [33]. In general, the exchangeable state (F1) and carbonate-associated state (F2) are more bioavailable, while the iron and manganese oxide-associated state (F3) and the organic-associated state (F4) are potentially bioavailable. By contrast, the residue state (F5) is a stable state, which can exist stably for a long time without any bioavailability. As such, it is considered as a non-hazardous substance to the environment [16]. The average percentage of trace elements in different forms of coal gangue in the study area was shown in Fig. 2.

As shown in Fig. 2, the order of the mean content in different fractions of Cu was: residue (39.38%) >Fe-Mn oxide associated state (27.45%)>organic associated state (21.10%)>carbonate associated state (10.37%)>exchangeable state (1.71%). It has been reported that hat the percentage of residual content of Cu increases with the increase of coal gangue weathering degree [25]. The order of morphological content distribution of Cd was as follows: residue state (57.27%)>Fe-Mn oxide associated state (24.59%) >carbonate associated state (9.58%)>organic associated state (4.78%)>exchangeable state (3.78%). The iron manganese oxide binding state of Cd accounts for a considerable proportion. When environmental conditions change, it is easy to migrate and cause pollution to the ecological environment. Cd can readily migrate to other areas, and is easy to migrate to the external environment via weathering and leaching during the natural storage of coal gangue [25]. The mean contents of Cr in different fractions followed the order: residual state (88.63%) >Fe-Mn oxide associated state (3.57%)>exchangeable state (3.52%)>organic associated state (2.54%)>carbonate associated state (1.74%). Cr was mainly distributed in the residual state of coal gangue. It mainly existed in the crystal lattice of silicate or secondary minerals, and was relatively stable and had an obvious impact on the ecological system [34]. The order of Ni in different fractions was: residual state (61.25%)>Fe-Mn oxide-associated state (13.86%)>organic-associated state (9.78%)>exchangeable state (7.91%)>carbonate-associated state (7.21%). Cr and Ni mainly existed in residual form, and the percentage of each form was not affected by the weathering extent of coal gangue [25].

Mn was mainly distributed in the residual state, followed by the carbonate bound fraction (23.52%). Numerous studies demonstrated that Mn in gangue were mainly silicate bound fraction and carbonate bound fraction, and there was a certain amount of sulfide bound fraction [32, 35]. The percentage of residual state of Pb was 57.88%, followed by the organic bound fraction and the Fe-Mn oxide bound fraction (14.74% and 13.54%). Pb is reported to be associated with galena (PbS) in low-sulfur coal gangue existed in sulfide minerals, and also related to organic matter [35]. The percentage of V was also mainly distributed in the residual state (66.72%). [25] reported that the occurrence form of V was not affected by the weathering extent of coal gangue, and mainly existed in the lattice of silicate, primary and secondary minerals. Ribeiro et al. [36] studied the occurrence state of trace elements in the coal gangue of Douro coalfield in northwest Portugal and they found that V in coal gangue mainly existed in inorganic minerals, such as clay minerals. The specific chemical forms order of Zn was: residual (44.85%)>Fe-Mn oxide-associated state (27.17%)>carbonate-associated state (12.54%)>exchangeable state (11.29%)>organic-associated (4.16%). Yang Ya and Hongbing [25] reported that Zn existed mainly in residual form in coal gangue,

Table 3 The results of the trace element pollution degree in coal gangue

Item		Cd	Cr	Cu	Mn	Ni	Pb	V	Zn
I_{geo}	Min	-0.17	-3.96	-2.10	-2.61	-2.39	-1.84	-0.88	-1.91
	Max	-0.52	-4.58	-2.41	-3.39	-2.64	-2.20	-1.28	-2.30
	Ave	-0.42	-4.14	-2.26	-2.99	-2.50	-2.05	-1.08	-2.07
E_r^i	Min	70.00	1.43	2.34	0.31	3.18	4.00	3.91	0.54
	Max	90.00	1.58	2.82	0.56	3.72	4.85	4.76	0.74
	Ave	78.75	1.49	2.58	0.42	3.41	4.30	4.27	0.65

and the percentage increased with the increase in the weathering extent of coal gangue, while Zn in oxidizable form decreased with the increase in the weathering extent of coal gangue.

There were certain differences in the forms of different trace element in coal gangue, and the forms with the highest percentage in the samples were all in the residue state, indicating that a large proportion of trace elements existed in relatively stable forms. Yang Ya and Hongbing [25] found that the occurrence forms of most trace elements were controlled by the weathering extent of coal gangue, and the speciation characteristics of trace elements in coal gangue in different regions were inconsistent, which may be related to the compositions, physical and chemical properties and weathering extent of coal gangue.

Risk Assessment of Trace Elements in Soil

Evaluation Results of the Geo-Accumulation Index Method

The pollution levels of trace elements in coal gangue were shown in Table 3. The I_{geo} ranges for Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn are -0.52~-0.17, -4.58~-3.96, -2.41~-2.10, -3.39~-2.61, -2.64~-2.39, -2.20~-1.84, -1.28~-0.88, -2.30~-1.91, respectively. All the I_{geo} values of heavy metals were negative and existed as pollution-free degree. However, the I_{geo} values of each element were different. The order of I_{geo} average values is: Cd>V>Pb>Zn>Cu>Ni>Mn>Cr. The results of the Geo-accumulation index were related to the selected trace elements and background values. The content of trace elements in this study was the sum of the acid-soluble state, reducible state and oxidizable state, which was lower than the total concentration. The I_{geo} value was relatively low. The value of Cd was the greatest, suggesting that attention should be paid to the environmental risk induced by Cd.

Potential Risk Assessment of Trace Elements

The ecological risk index of trace elements in coal gangue was analysed based on the potential risk assessment method, and the results are shown in Table 3. The descended order of potential ecological hazard index was as follows: Cd (78.75)>Pb (4.30)>V (4.27)>Ni (3.41)>Cu (2.58)>Cr (1.49)>Zn (0.65)>Mn (0.42). The results demonstrated that Cd pose a strong ecological risk, the similar results were also reported by [18]. All values for the potential ecological risk index of Pb, V, Ni, Cu, Cr, Zn and Mn were less than 30, the risk level belong to slight risk (E_r^i<30). Cd is the main contributing factor that causes the comprehensive potential ecological hazard index (*RI*) of heavy metals to be with a strong pollution risk level, which is consistent with the evaluation by the geo-accumulation index method, indicating that under long-term accumulation conditions, Cd will pose a significant potential risk to the environment.

Mobility and Bioavailability Evaluation of Trace Elements in Coal Gangue

The migration and bioavailability of trace elements highly depend on their active forms, and the impact of different occurrence states on the environmental effects varies dramatically. Based on the RAC value of trace elements and the corresponding risk (Fig. 3), the extent of harm of trace elements in coal gangue to the environment was: Mn (25.61%)>Zn (23.82%)>Ni (15.12%)>Pb (13.86%)>Cd (13.36%)>Cu (12.08%)>V (9.72%)>Cr (5.26%), indicating medium risk (11%≤RAC <30%) of Mn, Zn, Ni, Pb, Cd and Cu, low risk (1%≤RAC

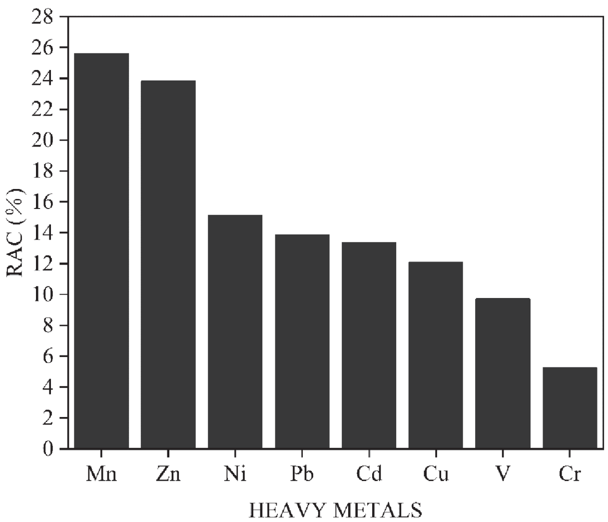

Fig. 3. Assessment of RAC of trace elements in coal gangue.

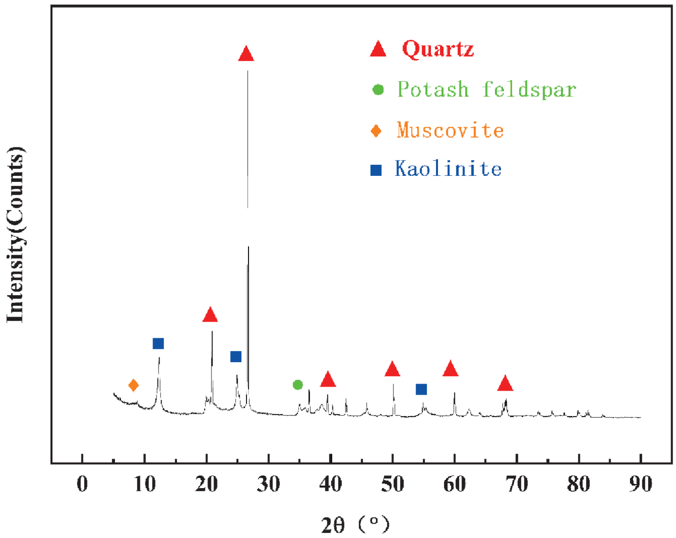

Fig. 4. X-ray diffraction pattern of coal gangue samples in the study area.

<10%) of V and Cr. The average RAC value of Mn was the highest (25.61), indicating that the natural weathering and precipitation leaching of Mn in active form may cause the greatest harm to the ecological environment. Attention should be paid to the possible pollution of soil and water in the surrounding areas of gangue dumps caused by Mn.

According to the results of XRD analysis in this paper, coal gangue in Huainan mining area is a deal raw material for brick making because of its high quartz content; and because of its similarity to the clay composition, it is also feasible to be used as a raw material for the production of cement. Coal gangue can be used to fill the coal mining subsidence, which can not only restore the land subsidence due to coal mining, but also reduce the accumulation of coal gangue.

In this study, only the types and fractionation behavior of trace elements in gangue were analyzed, kriging interpolation combined with ArcGIS software could be used to analyze the spatial distribution of heavy metals in the future;In the later stage, large-scale gangue samples can be collected, and the source of heavy metal elements in the Huainan mining area can be understood by isotope tracing method. And the soil, water body and sediment in the coal mining subsidence area can be combined as a water and soil system, and the above samples can be collected to analyze the pollution characteristics and levels of trace elements, so as to provide scientific guidance for the environmental pollution assessment and ecological civilization construction in the Huainan mining area.

Conclusion

In this study, the pollution characteristics, occurrence forms, and migration mechanisms of heavy metals in coal gangue was revealed, and the biological toxicity and environmental effects was evaluated. The result of XRD shows that coal gangue contains a variety of minerals, with obvious diffraction peak characteristics. The fractionation behavior of trace elements was found mainly in the residual-bound fraction. The values of Igeo showed that all trace elements were in a pollution-free state. The potential ecological risk level of Cd belongs to strong risk, while the other elements belong to slight risk.

The result of RAC indicates that the natural weathering and precipitation leaching of Mn in active form may cause the greatest harm to the ecological environment, and the possible environmental pollution caused by Mn around coal gangue hills should be paid attention to. The results have important practical significance for the prevention and control of heavy metal pollution in the soil around coal gangue hills, and provide a methodological basis for the evaluation of trace element pollution in mining waste.

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Author Contributions

Yixing Zhu: Writing - original draft, Writing - review & editing. Xing Chen: Supervision, Visualization, Methodology. Liugen Zheng: Supervision, Writing - review & editing. Yongchun Chen: Project administration, Data curation.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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