Article

Heavy Metal Concentrations of Soil, Rock, and Coal Gangue in the Geological Profile of a Large Open-Pit Coal Mine in China

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Abstract: Risk assessment related to heavy metals in mining areas is crucial to ensuring the sustainable development of regional ecosystems and protecting human health. However, almost all research on the impact of mining activities on environmental quality entails field monitoring of surface soils or soil profiles. Here, to compare the variety of heavy metal concentrations in the geological profile, 39 samples (including soil, rock, and coal gangue) were collected and analyzed from hundreds of meters underground in the Pingshuo coal mine (Anjialing coal mine, Antaibao coal mine, and Donglutian coal mine), which is the largest open-pit coal mine in China. The mean heavy metal concentrations of Cd, Hg, As, Pb, Cr, Cu, Zn, and Ni in soils were 0.15 mg/kg, 0.02 mg/kg, 13.70 mg/kg, 27.12 mg/kg, 70.89 mg/kg, 26.10 mg/kg, 79.88 mg/kg, and 37.68 mg/kg, respectively; most of these metals were more concentrated in the soil samples than in the rock and coal gangue samples. A potential ecological risk assessment indicated that As, Pb, Cr, Cu, Zn, and Ni in all samples showed low risk, while the ecological risk degrees of Cd and Hg were higher and contributed most to the total risk index (*RI*). The highest E_{r^i} value (92.94) for Cd was found in rock samples, contributing to approximately 55.18% of the total *RI*. For Hg, four rock sampling sites had the highest E_{r^i} values (427.70, 270.78, 198.96, and 188.70), contributing approximately 68.36–88.07% of the total *RI*. Ranked after soil (0.15 mg/kg), limestone and shale showed high mean Cd concentrations (both 0.13 mg/kg). The highest mean concentration was found in coal gangue samples (0.1 mg/kg). Compared with the other types of samples, the mean concentrations of Cr, Cu, and Ni in soils, limestone, and mudstone were relatively higher. At different sites, heavy metal concentrations varied greatly at different depths, owing to diverse sample types and rock types. Correlations between heavy metals and soil nutrients indicated that N and P were closely correlated with heavy metals. Comparing the proportions of different heavy metals in various types of samples showed that heavy metals in soils were extremely similar to those in limestone, mudstone, and shale, implying that soils might indirectly inherit their features from their parent material.

Keywords: soil; rock; coal gangue; heavy metal; coal mine

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1. Introduction

Coal is one of the world's main energy sources, generating 40.4% of the world's electricity. It has therefore helped greatly with the development of society and the global economy. However, coal mining has a negative impact on the environment [1], especially in developing countries such as China [2]. With greater public awareness of the environment and human health, there has been an increasing interest in studying environmental problems arising from coal-mining areas.

Heavy metals are commonly found in the soil at various concentrations, owing to the pedogenetic process of weathering of the parent materials. Thus, parent materials are important for explaining changes in soil contamination [3,4]. Wu et al. [5] stated that soil parent materials dominant the concentrations of As and Cr in soils. Rock metal content is transferred to soils and greatly affects both the properties and trace metals of soils, determining their geochemical and mineralogical characteristics [6,7]. Unsurprisingly, parent rock metal content is transferred to soils, and this has the potential to alter metal concentration and mobility in soils. It is accepted that heavy metal concentrations in soils vary depending on the source material, mainly due to the presence of geochemically unique rocks [8]. Heavy-metal concentrations in soils are directly related to the type of rock that the soil originated from [9]. Rocks and soils are common solid wastes and are produced in large volumes during the process of open-pit coal mining. As they are usually used for backfilling pits and land reclamation, their environmental quality is vital for the regional environment. Currently, there is great interest in the use of natural rocks as soil amendments and nutrient sources because they are environmentally benign and widely available [10]. However, little attention has been paid to the elemental compositions of various fresh parent rocks in relation to cation imbalance and their potential for causing high concentrations of heavy metals in soils [10]. Toxic substances in coal gangue and rocks might migrate into recultivated soils, which might pollute soil [11–13] and threaten ecological environment and human health [14,15].

However, studies into changes in heavy-metal concentrations in the geological profile up to depths of hundreds of meters underground are still limited. Therefore, the objectives of this study were to: (1) compare differences in heavy-metal concentrations between soil, rock, and coal gangue and between different rock types at different depths; (2) assess the potential ecological risk of various types of samples; and (3) compare the proportions of different heavy metals after data normalization.

2. Materials and Methods

2.1. Study Area

Pingshuo coal mine, located in the northeastern Loess Plateau, is the largest open-pit coal mine in China. It covers an area of approximately 380 km². This region has a typical temperate arid to semi-arid continental monsoon climate. The mean annual temperature is 4.8–7.8 °C, and the mean annual precipitation is 428.2–449.0 mm. The soils in this zone are mainly chestnut soil and loessial soil, which are characterized by their low content of organic matter. Pingshuo coal mine consists of three mining areas: the Anjialing coal mine, Antaibao coal mine, and Donglutian coal mine. In this study, they were all chosen as specific study objectives; the sampling sites in these three coal mines are shown in Figure 1.

Figure 1. Study area and sampling sites of rock and soil in the mining pits.

2.2. Soil Sampling and Analysis

In August 2017, we collected 39 samples of soil, rock, and coal gangue in the mining pits of the Anjialing, Antaibao, and Donglutian coal mines, using either a rock pitch hammer or soil auger (Figure 2). The positions of all the sampling sites were acquired by a handheld global positioning system, recording the longitude, latitude, and altitude. After sampling, the samples were sealed in clean polyethylene bags and labeled. Samples were then ground and sieved through a 2-mm sieve and transported to a laboratory for further analysis. The analysis of soil fertility properties followed the standard methods described in Lu [16]. Briefly, soil pH was measured in soil slurry (1:2.5, soil: distilled water) with a pH meter. Soil organic matter (SOM) was determined by the potassium dichromate oxidation method. Total-N analysis followed the Kjeldahl digestion method. Total P was determined by the molybdate-blue colorimetric method. Total K was determined by the sodium-hydroxide melting-flame photometric method. Eight heavy metals (Cd, Hg, As, Pb, Cr, Cu, Ni, and Zn) were measured using inductively coupled plasma mass spectrometry (7900, Thermo Electron Corporation, Waltham, MA, USA, with the detection limit of 0.01 µg/g). The specific operation process followed that used in an previous study [17].

Figure 2. Potential ecological risk assessment of different samples. A shows the potential ecological risk coefficients of the referred heavy metals, and B shows the risk indexes of the samples.

2.3. Potential Ecological Risk Analysis

The potential ecological risk index (*RI*) proposed by Hakanson [18] is applied to determine the ecological risks of heavy metals in the environment. The method fully takes into account the potential effects of heavy metals on ecosystems and can be used to assess sediments and soil in large regional areas [19]. Here, the Hakanson potential ecological *RI* was calculated by the following equations:

$$P_i = C_d^i / C_r^i, P = \sum_{i=1}^m P_i \quad (1)$$

$$E_f^i = T_f^i P_i, RI = \sum_{i=1}^m E_f^i \quad (2)$$

where C_d^i is the measured heavy metal concentration; C_r^i is the background level. In this research, the background levels of heavy metals in Shanxi Province were adopted. T_f^i is the toxic response factor of the heavy metal I ; E_f^i is the individual potential ecological *RI* of the heavy metal I ; and *RI* is the potential ecological risk of the heavy metal. The toxic response factors were considered to be Cd = 30, Hg = 40, As = 10, Cu = Pb = Ni = 5, Cr = 2, and Zn = 1 [20,21]. Classification criteria of the potential ecological risk index is given in Table 1.

Table 1. Classification criteria of the potential ecological *RI*.

E_f^i	Risk Classification	<i>RI</i>	Risk Classification
<40	Low risk	<150	Low risk
40–80	Moderate risk	150–300	Moderate risk
80–160	Considerable risk	300–600	Considerable risk
160–320	High risk	≥600	High risk
≥320	Very high risk		

2.4. Statistical Analysis

Descriptive statistics of the analyzed soil data were determined using SPSS 19.0 software (IBM, Armonk, NY, USA). The Pearson correlation test was applied to test the possible relationships between heavy metals and soil chemical properties. The concentration spectra of heavy metals in various samples were then plotted after data normalization using the min–max scaling method.

3. Results and Discussion

3.1. Descriptive Statistics of Heavy Metals of Soil, Rock, and Coal Gangue

The heavy-metal concentrations of the soil, rock, and coal gangue samples are presented in Table 2. The mean heavy-metal concentrations of the soil samples showed a trend of Zn (79.88 mg/kg) > Cr (70.89 mg/kg) > Ni (37.68 mg/kg) > Pb (27.12 mg/kg) > Cu (26.10 mg/kg) > As (13.70 mg/kg) > Cd (0.15 mg/kg) > Hg (0.02 mg/kg). Compared with the background metal values of soil samples from Shanxi province (Shi et al., 1994), the mean heavy-metal concentrations of the soil samples in our study were relatively high, except in the case of Hg. The highest coefficient of variation (CV) in the soil samples was found for Hg (50%), followed by Cd (40%), indicating relatively more variation in these metal elements. This result agrees with a study conducted in India by Vinod et al. (2019). The rock samples showed a similar trend regarding their mean heavy-metal concentrations (except the rank of Pb > Ni). Compared with soils, lower concentrations were found in rocks for most metals (except Hg), which may be attributed to the fact that underground rocks receive less interference from mining activities than upper soils. A similar result was reported by Wang et al. (2004) [22], who showed that Cd, Pb, Cu, and Zn in soils obviously exceeded those in rocks in a Pb–Zn mine. However, the CVs in rocks were higher and covered a much wider range (39.99–104.52%). In particular, the CVs of Hg and As both exceeded 100%, demonstrating strong variation in heavy-metal concentrations in rocks. In rocks, all of the heavy metals except Zn recorded kurtosis values greater than zero, and all of the heavy metals except Zn and Ni recorded skewness values above one, suggesting right-handed skewness and leptokurtic kurtosis. Compared with the soil and rock samples, the coal gangue samples exhibited lower mean concentrations for most heavy metals and had a wider CV range (29.49–110.00%). This indicates the uneven distribution of heavy metals in coal gangue. Comparable heavy metal and CV values were also reported in nine coal mines in Shanxi Province [23].

Table 2. Descriptive statistics of heavy-metal concentrations in different types of samples.

Samples	Heavy Metals	Mean (mg/kg)	Min. (mg/kg)	Max. (mg/kg)	Std.	CV	Kurtosis	Skewness
Soils (N = 8)	Cd	0.15	0.11	0.30	0.06	40.00%	6.86	2.56
	Hg	0.02	0.01	0.04	0.01	50.00%	−1.02	0.84
	As	13.70	10.26	16.77	2.17	15.84%	−0.06	−0.69
	Pb	27.12	19.45	43.97	7.51	27.69%	4.34	1.82
	Cr	70.89	59.99	87.96	9.61	13.56%	0.08	1.06
	Cu	26.10	21.59	33.87	5.28	20.23%	−1.64	0.72
	Ni	37.68	28.13	46.47	6.54	17.36%	−1.23	0.01
	Zn	79.88	64.49	95.95	10.48	13.12%	−0.66	0.06
Rocks (N = 27)	Cd	0.10	0.01	0.32	0.07	70.00%	1.78	1.37
	Hg	0.05	0.01	0.25	0.05	100.00%	7.63	2.67
	As	3.10	0.85	18.15	3.24	104.52%	19.27	4.16
	Pb	22.10	8.05	54.85	9.63	43.57%	3.96	1.39
	Cr	33.46	10.04	89.44	17.77	53.11%	3.22	1.76
	Cu	9.41	2.73	28.72	7.48	79.49%	1.01	1.52
	Ni	15.66	5.61	40.15	9.13	58.30%	0.45	1.02
	Zn	73.96	11.10	124.50	29.58	39.99%	−0.39	−0.05

Table 2. Cont.

Coal gangues (N = 4)	Cd	0.10	0.04	0.16	0.06	60.00%	−5.18	0.13
	Hg	0.10	0.02	0.27	0.11	110.00%	1.84	1.48
	As	1.56	1.05	2.17	0.46	29.49%	1.72	0.64
	Pb	20.19	5.39	31.48	12.85	63.65%	−4.09	−0.33
	Cr	28.72	5.83	48.83	22.55	78.52%	−5.49	−0.08
	Cu	17.17	10.01	25.01	8.28	48.22%	−5.86	0.02
	Ni	10.59	2.99	17.81	8.04	75.92%	−5.84	−0.02
	Zn	44.54	15.03	69.79	26.64	59.81%	−4.44	−0.20

3.2. Potential Ecological Risk Assessment of Soil, Rock, and Coal Gangue Samples

The potential ecological index is used to assess the ecological risk of heavy metals in soils and sediments quantitatively [5]. However, there is little research on the potential ecological risk assessment of rocks and coal gangues in mines. Large amounts of heavy metals in heavy-metal-rich native rocks can enter soils during intense chemical weathering processes of rocks, posing great potential ecological risks to the surrounding ecosystem [24,25]. In this study, the potential ecological coefficients (E_r^i) of soils, rocks, and coal gangues, and the risk index of each sample, are illustrated in Figure 2. As shown, the RI for eight heavy metals in the soil sampling points ranged from 90.88 to 195.29 (Figure 2B). Specifically, low ecological risk ($RI < 150$) and moderate ecological risk ($150 < RI < 300$) accounted for 75% (six points) and 25% (two points), respectively. Compared with soils from a typical Chinese agricultural county [26], within which 60% of the sampling points presented moderate ecological risks, the soil samples in our study showed lower ecological risk. The rock samples showed greater variation in their RI values, with a range of 43.54–486.75. In total, 77.78% of the samples (21 points) were classified as having low ecological risk. Four and two rock samples were classified as having moderate and considerable ecological risk ($300 < RI < 600$), respectively. This result indicates that most of the rocks in this area pose a low ecological risk to the ecosystem. Of the four coal gangue samples, two had RI values below 150 (low ecological risk); one had a moderate ecological risk; and one had a considerable ecological risk. Ni et al. (2009) [27] also found significant enrichment of heavy metals from rocks to soils in the carbonate region of Beijing, China. With their higher clay content, which is responsible for the adsorption of heavy metals, soils tend to have a higher potential ecological risk than rocks and coal gangues.

The statistics of E_r^i for eight heavy metals are shown in Figure 2A. The E_r^i values of Cd and Hg were significantly high in all samples and contributed the most to the total RI. For Cd, four soil samples, seven rock samples, and two coal gangue samples had E_r^i values exceeding 40. Jiang et al. (2014) [28] also found Cd to be the key influencing factor for the potential ecological risk of soils around a coal gangue dump. The highest E_r^i value (92.94) for Cd was found in a rock sample; this represents approximately 55.18% of the contribution to the total RI. For Hg, four rock-sampling sites had high E_r^i values (427.70, 270.78, 198.96, and 188.70), classifying them into the high-risk level. These samples contributed approximately 68.36–88.07% to the total RI. Moderate-risk ($40 \leq E_r^i \leq 80$) sites and considerable-risk ($80 \leq E_r^i \leq 160$) sites of rock samples accounted for 37.04% (ten samples) and 7.41% of the total rock samples, respectively. High E_r^i values for Hg in soils and rocks can also be observed in Figure 2A, e.g., one rock sample had an E_r^i value of 463.30 and contributed 95.96% to the total RI; three soil samples were classified as having a moderate risk, with E_r^i values of 44.17, 57.22, and 62.09, respectively. The other six heavy metals this study examined showed low risk in all samples, with E_r^i values below 40. The high Hg and Cd ecological risks for both soils and rocks are in agreement with previous research on soils [29,30], sediments [31,32], and lakes [33–35].

3.3. Changes in Heavy-Metal Concentrations in Various Samples and at Different Depths

The rock samples in this study (27 sites) comprised six rock types: granite (N = 1), limestone (N = 3), mudstone (N = 2), sandstone (N = 9), diorite (N = 3), and shale (N = 9). To analyze the changes in heavy-metal concentrations in different types of rocks, soil, and coal gangues, the mean heavy-metal concentrations of different samples were compared, as shown in Figure 3. The highest concentration of Cd was found in soil samples, with a mean of 0.15 mg/kg. Limestone and shale also showed high Cd concentrations; both had a mean concentration of 0.13 mg/kg. Zhao et al. (2015) [36] reviewed soil contamination in China and also found that soils developed from limestone tended to accumulate much higher Cd concentrations than others. He et al. (2006) [37] compared heavy-metal concentrations between soils developed from various parent materials and concluded that Cd easily accumulated in soils derived from limestone and shale. Zhu et al. (2019) [38] found that fine mudstone (containing silt and clay) retains organic matter and Fe_2O_3 and therefore can incorporate heavy metals through complexation. However, in our study, mudstone was found to have a low Cd concentration (0.05 mg/kg). The difference mainly results from the different natures and exposure situations of mudstone. Hg exhibited different characteristics in its mean concentrations than Cd. The highest mean concentration (0.1 mg/kg) was found in coal gangue, whereas soil and diorite samples had low mean concentrations (0.02 mg/kg and 0.01 mg/kg, respectively). High Hg concentrations (0.3 mg/kg–6.3 mg/kg) in coal gangue were also found by Niu et al. (2017) [39]. Similar to Cd, elevated concentrations of As were also observed in soil (0.74 mg/kg) and limestone (0.42 mg/kg). This result is higher than the As concentrations measured in Ewekoro limestone from Southwestern Nigeria [40]. The other samples had lower or comparable As concentrations, ranging from 1.56 mg/kg to 2.83 mg/kg. Limestone was also found to be enriched with Pb (32.94 mg/kg). Comparable Pb concentrations (0.37 mg/kg–0.46 mg/kg) were found in granite, mudstone, shale, and soil. The distribution characteristics of the mean concentrations of Cr, Cu, and Ni in different samples were similar (Figure 3C,D). There were elevated concentrations in soils, limestone, and mudstone and lower concentrations in granite and diorite. Compared with other samples, including sediments and sandstones, lower concentrations of Cr and Ni were also found in the granite of Hunan province, China [41]. Shale had the highest Zn concentration (85.74 mg/kg) in all samples, whereas limestone, sandstone, and soil had similar Zn concentrations to shale.

The distribution of heavy metals may differ owing to discontinuous geological conditions [42]. To compare the differences in heavy-metal concentrations in the geological sections of the Anjialing, Antaibao, and Donglutian coal mines, heavy-metal concentrations at different depths are shown in Figure 4. Heavy-metal concentrations varied greatly at different sample sites with various depths, because of the diverse sample types and rock types. Similar results were also found in groundwater by Qiao et al. (2020) [43]. For Cd, higher concentrations were found at elevations of 1271 m (0.20 mg/kg), 1182 m (0.23 mg/kg), and 1204 m (0.32 mg/kg) in the three coal mines, with the sample types of limestone, shale, and soil, respectively. Hg concentrations varied between 0.01 mg/kg–0.04 mg/kg in the Antaibao coal mine, whereas they fluctuated in the Anjialing and Donglutian coal mines, with their highest concentrations of 0.27 mg/kg and 0.25 mg/kg at depths of 1268 m and 1236 m, respectively. The corresponding sample types were coal gangue and shale. Nine samples, at depths of 1428 m, 1382 m, and 1272 m in the Anjialing coal mine; 1287 m and 1282 m in the Antaibao coal mine; and at 1381 m, 1374 m, and 1321 m in the Donglutian coal mine, had particularly high As concentrations (Figure 4C). Of these nine samples, one was shale and eight were soils, indicating their As enrichment. Compared with samples in the Anjialing and Antaibao coal mines, samples in the Donglutian coal mine showed higher concentrations of Pb, with values of 54.9 mg/kg and 44.0 mg/kg at 1254 m (shale) and 1321 m (soil) depths, respectively. The high concentrations of Cr, Cu, Ni, and Zn in the three coal mines were comparable, and some of these samples with high concentrations had the same depths. For example, the concentrations of Cr, Cu, and Ni at depths of 1287 m, 1282 m, and 1153 m in the Antaibao coal mine were higher than those at other sampling

sites; Cr and Zn were present at a depth of 1378 m (sandstone) in the Anjialing coal mine at concentrations of 89.4 mg/kg and 119 mg/kg, respectively; these were the highest concentrations of these metals in all samples. These results indicate that the variations in the vertical distribution of heavy metals in the geological profiles of three coal mines were mostly attributed to the sample types collected.

Figure 3. Comparison of heavy-metal concentrations in different samples. (A–D) show the concentrations of different heavy metals in various kinds of samples.

Figure 4. Changes in heavy-metal concentrations at different depths. (A–H) show the concentration changes of Cd, Hg, As, Pb, Cr, Cu, Zn and Ni at different depths, respectively.

3.4. Correlation between Heavy Metals and Soil Nutrients

Heavy metals and nutrient parameters are crucial indexes of soils and rocks. Some studies have found positive correlations between soil nutrient properties, pH values, and heavy metals in soil [44,45]. In this study, we explored their correlations in soils, rocks, and gangues; the results of Pearson correlation analysis are shown in Table 3.

Table 3. Correlation coefficients between heavy metals and soil chemical parameters.

	Cd	Hg	As	Pb	Cr	Cu	Ni	Zn
Cd	1							
Hg	0.16	1						
As	0.38 *	−0.04	1					
Pb	0.30	0.00	0.09	1				
Cr	0.10	−0.33	0.58 **	0.41 *	1			
Cu	0.28	−0.25	0.63 **	0.58 **	0.75 **	1		
Ni	0.32	−0.18	0.82 **	0.38 *	0.74 **	0.87 **	1	
Zn	0.56 **	−0.01	−0.06	0.52 **	0.33	0.25	0.15	1
pH	0.22	−0.09	0.26	0.30	0.22	0.32	0.35 *	0.28
SOM	0.28	0.18	0.16	0.04	−0.08	0.09	0.23	−0.04
N	0.30	0.08	0.46 **	0.14	0.16	0.36 *	0.56 **	−0.07
P	0.26	−0.27	0.51 **	0.17	0.49 **	0.49 **	0.53 **	0.14
K	−0.08	−0.46 **	0.03	0.33	0.38 *	0.30	0.27	0.38 *

* indicates a significant correlation and $p < 0.05$. ** indicates a significant correlation and $p < 0.01$.

As, Pb, Cr, Cu, and Ni showed several correlations with each other. Specifically, As was significantly correlated with Cr, Cu, and Ni at $p < 0.01$. Pb showed significant correlation with Cu at $p < 0.01$ and with Cr and Ni at $p < 0.05$. Cr also showed significant correlations with Cu and Ni at $p < 0.01$, and Cu was significantly related to Ni at $p < 0.01$. Additionally, the pairs of Cd vs. Zn, Cd vs. As, and Zn vs. Pb were also found to be significantly correlated ($p < 0.01$ or $p < 0.05$), implying their common sources [46]. Hg was the only metal in this study that had no significant ($p < 0.05$) correlations with other heavy metals. Zhang et al. (2020) [42] also found that significant correlations ($p < 0.01$) existed among all five heavy metals (except Hg) in surface sediments of the Subei Shoal, China.

In the correlation analysis between heavy metals and chemical parameters, N and P were found to be closely correlated with heavy metals, e.g., significant and positive correlations were found to exist between N, P, As, Cu, and Ni at $p < 0.01$ or $p < 0.05$; P was significantly correlated with Cr at $p < 0.01$. Additionally, K and pH also exhibited significant correlations with heavy metals, with three pairs (K vs. Hg, K vs. Cr, and K vs. Zn) and one pair (pH vs. Ni) of significant correlations for K and pH, respectively. In contrast with previous studies [47], we found that SOM had no significant correlations with heavy metals in this study; this may be attributed to the coal gangue being enriched in soil organic C, which would influence the accurate determination of SOM.

3.5. Proportional Comparison of Different Heavy Metals in Various Types of Samples

To compare the proportion of heavy metals in different samples, the sum values of the eight heavy metals and individual heavy metals in various samples after data normalization were drawn and compared using the min–max scaling method (Figure 5).

Figure 5. Heavy-metal spectral diagrams in different samples. To make the data comparable, heavy-metal concentrations were normalized using the min–max scaling method.

As shown, the proportions of different heavy metals varied in different types of samples, which are characterized by the diagram height. Soil samples were found to have the highest sum of normalized value (4.62), with Ni, Cr, Cu, and As contributing most to the sum—their contributions were 17.28%, 16.85%, 16.25%, and 16.09%, respectively. Limestone ranked second when considering the sum value (3.84), followed by mudstone (2.86) > shale (2.56) > coal gangue (2.19) > sandstone (1.86) > granite (1.61) > diorite (1.21). The normalized values of most heavy metals in soil samples were also higher than in other samples. For example, the normalized values of Cd, As, Cr, Ni, and Zn were 0.46, 0.74, 0.78, 0.80, and 0.61, respectively. These values exceeded the corresponding values in other samples, implying the accumulation of heavy metals in soils [48]. Obviously, the accumulation of heavy metals in the soils of our study was not only related to rock and coal gangue, as they displayed diverse concentrations of heavy metals. Coal-related industrial activities and transport-vehicle emissions are possible anthropogenic sources [49]. However, the normalized values of Hg and Pb in soils were relatively low (0.045 and 0.44), especially for Hg, which only accounted for 12.5% of coal gangue (0.36) and 17.72% of shale (0.25), indicating these heavy metals in coal gangue and shale may transform into soils [12].

On the whole, the proportions of different heavy metals in soils were more similar in limestone, mudstone, and shale, implying soils might indirectly inherit their features from them through their parent material. As most heavy metals had lower concentrations in rock and gangue compared with soils, human activities such as agricultural production and industrial production, conducted before mining activities here, may also be contributing to the elevated heavy-metal concentrations in soils. Compared with soils, coal gangue and shale were more enriched with Hg, and limestone and granite were more enriched with Pb. During the practice of land reclamation, more attention should be paid to these types of rock.

4. Conclusions

This study investigated the concentrations, potential ecological risk, and variations with depth and sample type of heavy metals in a large open-pit coal mine in China. Compared with soils, lower mean concentrations were found in rocks and coal gangues for most metals (except Hg). Potential ecological risk assessment indicated that As, Pb, Cr, Cu, Zn, and Ni showed low risk in all samples, while the ecological risk degrees of Cd and Hg were higher than other heavy metals. In the rock samples, limestone and shale also showed high Cd concentrations. The mean concentrations of Cr, Cu, and Ni in different samples were similar, with elevated concentrations in soils, limestone, and mudstone, and lower concentrations in granite and diorite. As, Pb, Cr, Cu, and Ni had more correlation pairs with each other, and N and P were found to be closely correlated with heavy metals. The proportions of different heavy metals in soils were more similar in limestone, mudstone, and shale, implying that soils might indirectly inherit their features from them through their parent material.

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