

Original Research

Heavy Metals in the Surface Soil around a Coalmine: Pollution Assessment and Source Identification

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Abstract

Coal mining in northern Anhui Province of China has led to a series of environmental problems. In this study, a total of 68 surface soil samples around a representative coalmine (the Haizi coalmine) in the area have been collected and then analyzed for seven kinds of heavy metal concentrations (Cu, Fe, Zn, Co, Ni, Mn and Pb) for getting information about their pollution degrees and sources. The results indicate that the metal concentrations are Fe>Mn>Zn>Pb>Cu>Ni>Co, and all of them have coefficients of variation ranging between 0.13 and 0.75, and low p-values (<0.01) of normal distribution test except for Fe, Co and Ni, which suggests that their concentrations have been affected by multiple factors. The single pollution index and geo-accumulation index imply that zinc and lead are light pollution, and the Nemerow composite index and the potential ecological risk index suggest that the soils in this study are slightly polluted and with low potential ecological risk. The spatial distributions of the metal concentrations, along with the statistical analyses (including correlation, cluster and factor analyses) indicate that all of the metals can be classified to be two groups, the Fe-Co-Mn and Cu-Zn-Pb-Ni, which mean geogenic and anthropogenic sources, respectively, and their mean contributions for the heavy metal concentrations in the study area are 57.1% and 42.9%, respectively, as calculated by the Unmix model.

Keywords: heavy metals; pollution assessment; source identification; coalmine; surface soil

Introduction

Coal is the main energy consumed in China. However, the mining of coal has drastically adverse environmental impacts, including interference with

surface water, groundwater, air and land, and consequently leading to a series of environmental problems, e.g. coal mine accidents, land subsidence, damage to the water environment, mining waste disposal and air pollution [1-5]. Among these problems, heavy metal pollution has attracted more attention because of their toxicity for human health, and their mobility from the polluted soil/water/air to living beings. Therefore, a large number of studies related to heavy

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metal pollution in the coal mining areas of China have been carried out, with most of them focused on the pollution assessment of water and soil [6-8] and the remediation of the polluted system [9].

The coal field in northern Anhui Province is an important energy base in China. There are two main coal mining groups with more than 30 coal mines in the area, including the Wanbei Coal-Electricity Group and the Huaibei Mining Group, and the annual production of coal in the area is more than 100 million tons. Just because of the high production of coal, a series of environmental problems have been produced: e.g., surface subsidence [10], the pollution of soil, surface water and groundwater [11-13]. These environmental problems have a significant impact on the development of the region, because except for coal production, traditional agriculture is another dominant industry in the area, and northern Anhui Province of China is an important agricultural base of the nation.

As the basis of agriculture, soil and water have an irreplaceably important role. Their environmental quality is directly related to the quality of agricultural products and then affects the health of people. And therefore, environmental issues related to soil and water are important. In this study, a representative coalmine

(the Haizi coalmine) in the area has been chosen for the study of the heavy metal pollution of soils because it is surrounded by farmland, and getting the following information is the goal of the study: (1) heavy metal concentrations of the soils around the coalmine and their spatial distributions, (2) the extent of heavy metal pollution and the health risk and (3) the qualitative and quantitative source contributions responsible for the heavy metals.

Materials and Methods

Study Area

Haizi coalmine is located 40 km south of Huaibei City and 30 km west of Suzhou City in northern Anhui Province, China (Fig. 1). Latitude is 33°40'47"-33°43'50" and longitude is 116°34'31"-116°42'20", and total area of the mine is 33.7 km². The climate of the area is warm and belongs to semi-humid climate with an annual average temperature of 14.1°C. The average annual rainfall is 737 mm concentrated between July and August. The recoverable reserve of the coalmine is 65 million tons (in 2009) and the annual production

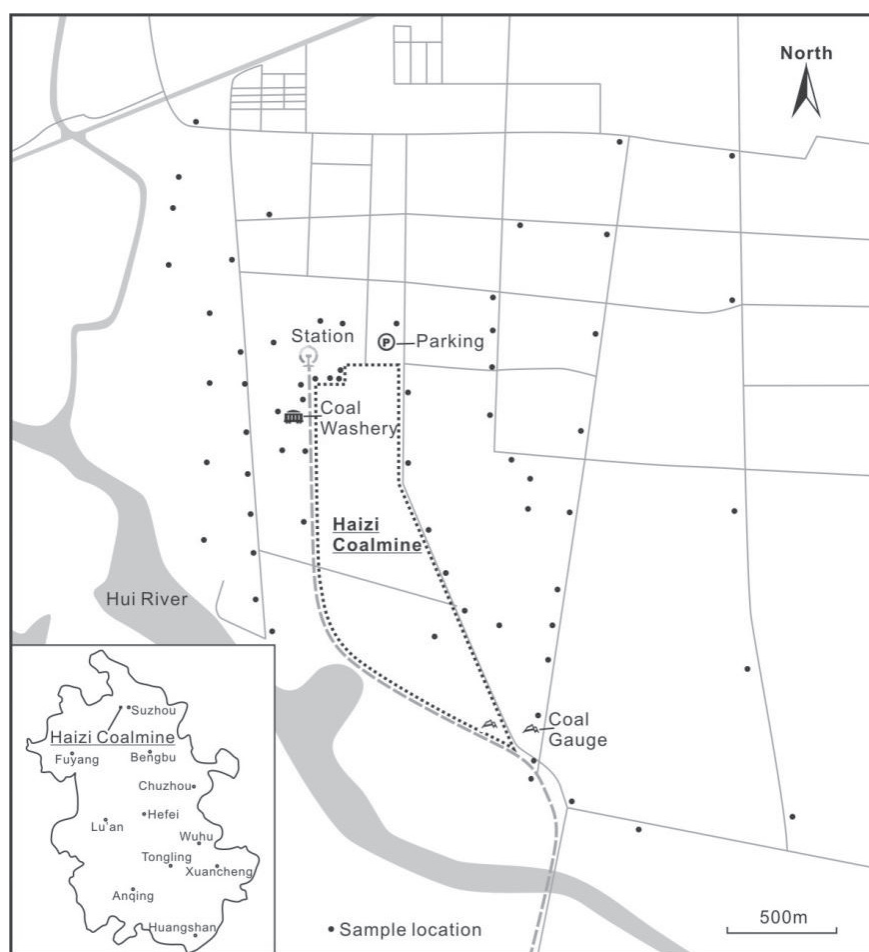


Fig. 1. Location of the study area and sample distributions.

Table 1. Descriptive statistics of heavy metal concentrations (mg/kg).

	Cu	Fe	Zn	Co	Ni	Mn	Pb
N of Cases	68	68	68	68	68	68	68
Minimum	3.39	15721	55.1	0.93	1.61	327	6.93
Maximum	72.2	36868	149	13.9	38.0	1086	59.6
Mean	15.5	29195	77.3	7.28	14.4	527	43.7
Standard Deviation	11.6	4121	14.8	2.67	6.18	113	5.69
Coefficient of Variation	0.75	0.14	0.19	0.37	0.43	0.22	0.13
p-value	<0.01	0.02	<0.01	>0.15	>0.15	<0.01	<0.01
Background [22]	22.6	29400	74.2	12.7	26.9	583	26.0
Mean Pi	0.69	0.99	1.04	0.57	0.54	0.90	1.68
Highest Pi	3.20	1.25	2.00	1.09	1.41	1.86	2.29
Igeo	-1.12	-0.60	-0.53	-1.39	-1.48	-0.73	0.16
Highest Igeo	1.09	-0.26	0.42	-0.46	-0.09	0.31	0.61

is near 1.5 million tons. Detailed information about the coalmine can be obtained from the Google satellite map with the latitude and longitude of the coalmine (not shown because of its clarity).

Sampling and Analysis

A total of 68 surface soil samples (less than 10 cm depth) around Haizi coalmine have been collected. All of the samples were collected from farmland randomly in April 2018, and detailed sample distributions are shown in Fig. 1. After collection, all of the samples were first air-dried in natural conditions, and the debris of animals and plants was removed by hands. Then the samples were powdered to 200 meshes (<0.075mm) after parching for 24 h at 80°C in a dryer. Samples were made into tablets using a 30 t condenser, and then analyzed by XRF (Innov-X Explorer 9000 SDD, USA) for measuring the concentrations of seven kinds of heavy metals (Cu, Fe, Zn, Co, Ni, Mn and Pb) in the Engineering and Technological Research Centre of Coal Exploration, Anhui Province, China. National standard sediment sample of China (GBW07307) was analyzed simultaneously for calibration (once per 10 samples), and the relative standard derivation is less than 10%.

Data Treatment

The data treatment processes are as follows:

- (1) All of the data were first processed for statistical analysis by Mystat 12 software, and the minimum, maximum, mean, standard deviation, coefficient of variation and the p-value of the normal distribution test were obtained.
- (2) The contour maps of the metal concentrations were plotted by the Surfer 11 software (with natural neighbor grid method), which has long been used for

environmental studies because of the visualization of the pollution [14], and the locations of the areas with high metal concentrations were compared with the actual field situation through the Google satellite map, including the area with coal accumulation, coal washery, coal gauge hill, the train station (for coal transportation) and the area with high density of traffic.

- (3) The methods applied for the pollution assessment of heavy metals (including the health risk assessment) include the single pollution index (P_i) [15], the geo-accumulation index (I_{geo}) [16], the Nemerow composite index (P_s) [17] and the potential ecological risk index (RI) [18] (detailed information about each method can be found in the following text).
- (4) Statistical analyses (including the correlation, cluster and factor analyses) [19] were applied for getting the qualitative information of the source of the seven kinds of metals, and then the Unmix model provided by the U.S. Environmental Protection Agency (EPA) [20] was applied for getting the quantitative information about the source of metals.

Results and Discussion

Heavy Metal Concentrations

The concentrations of the seven kinds of heavy metals are synthesized in Table 1. As can be seen, iron is the metal with the highest mean concentration (15721-36868 mg/kg, mean= 29195 mg/kg), and then followed by the Mn, Zn, Pb, Cu, Ni and Co, their mean concentrations are 527, 77.3, 43.7, 25.5, 24.4 and 7.28 mg/kg, respectively.

Coefficient of variation (CV = standard deviation/mean) is an index showing the extent of variability in

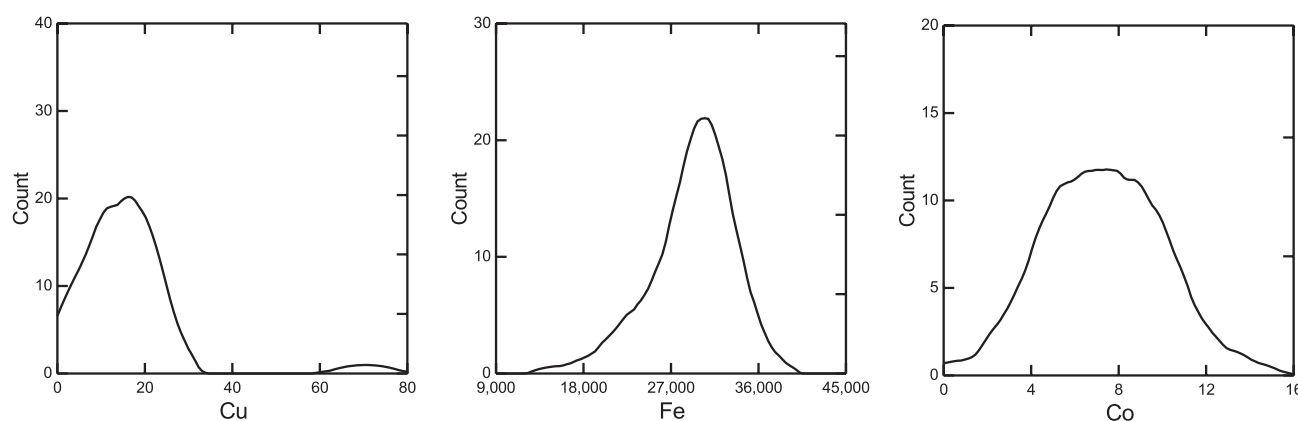


Fig. 2. Density plots of representative metals (Cu, Fe and Co).

relation to the mean of the population, which can be used for identifying the anthropogenic contribution degree for pollution in the environmental studies [21]. Previous studies [21] revealed $CV < 0.10$ and > 0.90 as mean low and high anthropogenic contributions, respectively. In this study, copper has the highest CV (0.75), which means that the concentrations of copper in the soil samples varied significantly from area to area, and it might be influenced by human activities. As to the other metals, they have lower CVs, ranging between 0.16 and 0.43, which indicate the moderate spatial inhomogeneity. Other information can also be achieved from the p-values of the normal distribution test. As can be seen from the table, Co and Ni have p-values higher than 0.15, and Fe has p-value = 0.02, whereas other metals have p-values lower than 0.01, implying that only Co and Ni can pass the normal distribution test, whereas others cannot pass (p-value > 0.05), which may also suggest that the metals except for cobalt and nickel might have been affected by mutli-factors [20]. Similar conclusions can also be identified from the density plots of the metals that copper has at least two peaks (Fig. 2).

Assessing Soil Pollution and Potential Ecological Risk

Previous studies revealed that the single pollution index ($P_i = C_m/C_s$, where C_m and C_s are the concentration of sample and background, respectively) is a good indicator for monitoring the degree of pollution, and 4 degrees had been subdivided: < 1 means light pollution, 1-3 means moderate pollution, and > 3 means considerable pollution [15]. The soil environmental background values of China [22] were chosen to be the C_s , and the results of calculated mean P_i values are listed in Table 1. The results indicate that the soils in this study are moderately polluted by Zn and Pb, because their P_i values are 1.04 and 1.68, respectively, whereas Cu, Fe, Co, Ni and Mn pollutions are considered to be light because their P_i values are < 1 . Additionally, although most of the average concentrations of the heavy metals with light pollution (Cu, Fe, Co, Ni and Mn) in this

study are lower than the soil environmental background values of China, there are differences between samples with different locations: it can be seen from the table that the maximum concentrations of Cu, Fe, Co, Ni and Mn (72.2, 36868, 13.9, 38.0 and 1086 mg/kg, respectively) are much higher than those of the background (22.6, 29400, 12.7, 26.9 and 583 mg/kg, respectively), and the highest P_i values for them are 3.20, 1.25, 1.09, 1.41 and 1.86, respectively, implying that the distribution of heavy metals in the study area is heterogeneous.

The geo-accumulation index (I_{geo}) enables the assessment of contamination degrees by comparing the current and pre-industrial concentrations, and it is calculated as $I_{geo} = \log_2 C_m / (1.5 \times C_s)$ [16]. The measurement of I_{geo} can be subdivided into 5 degrees: < 0 , unpolluted; 0-1, light pollution; 1-3, moderate pollution; 3-5, heavy pollution; and > 5 , serious pollution [16]. The calculated I_{geo} values are listed in Table 1 and imply “unpolluted” for all of the metals ($I_{geo} < 0$), except for lead with light pollution ($I_{geo} = 0.16$). However, it can also be identified from Table 1 that pollutions by heavy metals is different from sample to sample, with the highest I_{geo} values of the single sample for the Cu, Zn, Mn and Pb being 1.09, 0.42, 0.31 and 0.61, respectively, which indicates that the samples with the highest concentrations of these metals are moderately (Cu) and light-moderately (Zn, Mn and Pb) polluted, respectively.

Different from the P_i and the I_{geo} , the Nemerow composite index (P_s) method takes into account all the individual evaluation factors, and also highlights the importance of the most contaminated elements. The calculation of the P_s is $\text{SQRT}((P_m^2 + P_x^2)/2)$, where P_m is the average of single pollution index of all metals, and P_x is the maximum value of the single pollution index of all metals. The quality of soil environment is classified into 5 grades from the P_s : $P_s < 0.7$, safety domain; $0.7 \leq P_s < 1.0$, precaution domain; $1.0 \leq P_s < 2.0$, slightly polluted domain; $2.0 \leq P_s < 3.0$, moderately polluted domain; and $P_s \geq 3.0$, seriously polluted domain [17]. In this study, P_s was calculated to be 1.35, which means that the soils in this study can be classified as being slightly polluted.

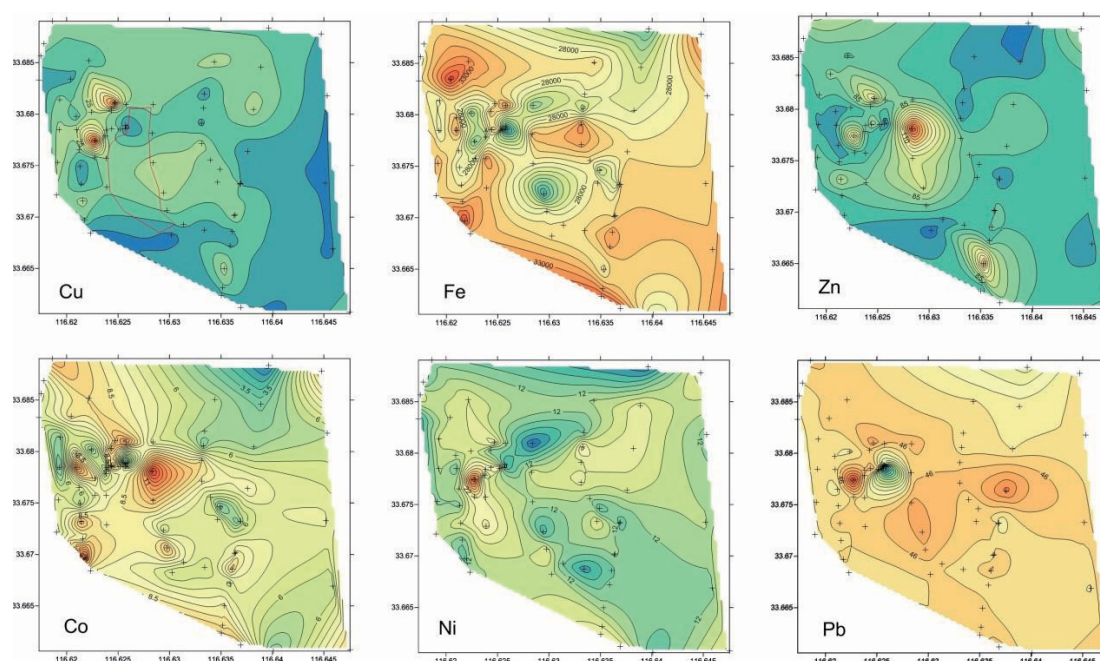


Fig. 3. Contour maps of the metals (unit in mg/kg); the red line in the Cu diagram shows the location of the coalmine.

The potential ecological risk index (RI) method proposed by Hakanson [18] has been applied to evaluate the heavy metal pollution in the soils, and also to associate ecological and environmental effects with their toxicology. Although the risk factor is originally used as a diagnostic tool for the purpose of controlling water pollution, it has been successfully used for assessing the quality of sediments and soils in terms of heavy metals pollution [1]. The calculation of the RI is $\sum_{i=1}^n E_r^i$, where E_r^i is potential ecological risk individual coefficient calculated by $T_r^i \times P_i$ and T_r^i is the toxicity response coefficient of metal toxicity proposed by Hakanson [18]. In this study, the T_r^i values are 1 for the Fe-Mn-Zn and 5 for the Cu-Co-Ni-Pb, respectively. In this study, the RI was calculated to be 20.3, which means low potential ecological risk ($RI < 90$) [18].

Spatial Distributions

As can be seen from the contour map of the metal concentrations in Fig. 3, two areas with high copper concentrations can be identified in the west-north of the study area. In comparison with the actual field situation (see Fig. 1, and it can be obtained from the Google satellite map with the latitude and longitude of the coalmine), it can be found that these two areas are near the train station (the north one for coal transportation) and coal washery (the south one), which indicates that the distribution of the Cu in the area is related to coal production. The areas with high concentrations of Zn, Ni, Pb and Mn (figure not shown) can also be identified near the coal washery, which suggests that coal production is responsible for these metals. Moreover, an area with high zinc concentrations can be found near the

center of the study area, along with the metal cobalt. In comparison with the field situation, the motor vehicle is considered to be responsible because this area is near the parking lot of the coalmine (see in Fig. 1, not for coal transportation). Moreover, another area with high zinc concentrations is located in the south of the study area, where there is a storage place for the coal gauge with high density of transportation. In conclusion, based on the spatial distributions of the metal concentrations, except for the geogenic factor, coal production (including coal transportation and washing) is responsible for the high concentrations of Cu, Zn, Ni, Pb and Mn, whereas transportation is responsible for the high concentrations of Zn and Co.

Statistical Analyses for Source Identification

A close inspection of correlation matrix is useful as it can point out associations between variables that can show the overall coherence of the data set, and thus indicate the participation of the individual chemical parameters in several influence factors [23]. The results of the correlation analysis are shown in Table 2. As can be seen from the table, close relationships have been identified between the following metals: Cu-Zn, Cu-Ni, Cu-Pb, Fe-Mn, Fe-Co, Fe-Pb, Zn-Co, Zn-Ni, Zn-Pb and Ni-Pb ($r > r_a = 0.31$, $\alpha = 0.01$). Such results suggest that these metal pairs might have similar sources or have been affected by similar factors: e.g., Cu, Zn, Ni and Pb can be affected by coal production, whereas Zn and Co are related to transportation.

Cluster analysis is comprised of a series of multivariate methods that are used to find true groups of data or stations. In clustering, the objects are grouped

Table 2. Results of correlation analysis.

	Cu	Fe	Zn	Co	Ni	Mn
Fe	-0.19					
Zn	0.49*	0.07				
Co	0.13	0.63*	0.50*			
Ni	0.46*	0.16	0.32*	0.27		
Mn	-0.11	0.70*	0.09	0.58*	0.08	
Pb	0.41*	0.36*	0.47*	0.36*	0.44*	0.23

*significant at $\alpha = 0.01$ level

such that similar objects fall into the same class. The method has long been used for environmental studies [24]. In this study, the hierarchical R-mode cluster analysis has been applied to the data, and the “Ward” linkage and the “Pearson” distance have been chosen for calculation, and the results are shown in Fig. 4 as a dendrogram. As can be seen from the figure, two main groups can be identified: Cu-Zn-Pb-Ni (Group 1) and Co-Fe-Mn (Group 2), which indicate that the metals in the similar group might have similar sources.

Factor analysis is a commonly used statistical method for classification, simplification of the data and finding the most important variables in the data set. During geochemical studies, factor analysis has long been used for tracing elemental sources [25]. In this study, based on the criterion of initial eigenvalue higher than one, two factors have been obtained based on the factor analysis (Mystat version 12.0) (Table 3). Moreover, according to previous studies [26], factor loadings can be classified as strong, medium and weak, with values of >0.75 , $0.75-0.50$ and $0.50-0.30$ respectively. As can be seen from the table, the first factor, which accounts for 34.3%

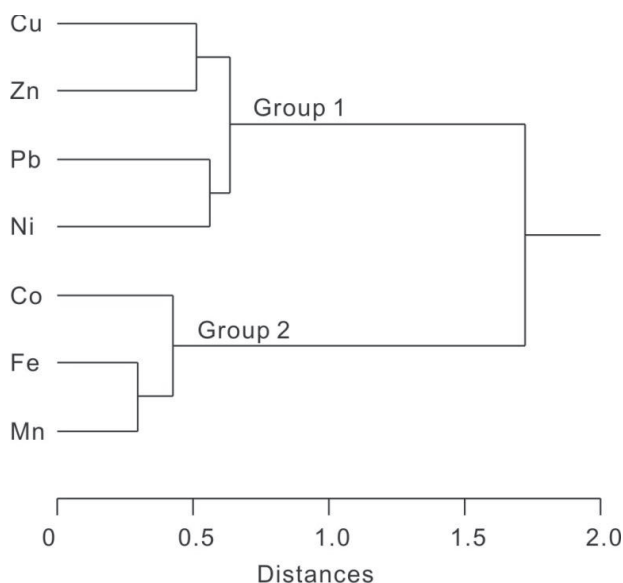


Fig. 4. Results of R-mode cluster analysis.

Table 3. Results of factor analysis.

Metals	Factor 1	Factor 2
Cu	-0.24	0.83
Fe	0.92	0.01
Zn	0.15	0.77
Co	0.77	0.39
Ni	0.11	0.70
Mn	0.87	-0.01
Pb	0.33	0.70
Eigen value	2.40	2.39
Variance Explained	34.3%	34.2%

of the total variance explanation, has strong positive loadings of Fe, Co and Mn, whereas the second factor with 34.2% of the total variance explanation has strong positive loadings of Cu and Zn, and medium positive loadings of Ni and Pb. Such results are similar to the results obtained by correlation and cluster analyses, and imply a similar origin for Fe-Co-Mn and Cu-Zn-Ni-Pb, respectively. In consideration with the spatial distributions of the metal concentrations, as well as the ideas obtained from them, the Fe-Co-Mn and Cu-Zn-Ni-Pb element associations can be explained to be geogenic and anthropogenic factors, respectively.

The Unmix model is a mathematical receptor model used for quantifying the sources of contaminants contributing to sediment, water and air samples. It is based on reducing the large number of variables in complex analytical data sets to combinations of species called source types and source contributions [20]. The source types are identified by comparing them to measured profiles, whereas the source contributions are used to determine how much each source contributed to a sample. Based on the calculation, two sources have been identified and the results are listed in Table 4 and shown in Fig. 5. These two sources have Min Rsq = 0.92 and Min Sig/Noise = 4.33, higher than the minimum requirement of the model (Min Rsq > 0.8

Table 4. Source profiles (mg/kg).

Metals	Source 1	Source 2	Contribution 1	Contribution 2
Cu	14.4	2.04	87.6%	12.4%
Fe	5420	23800	18.5%	81.5%
Zn	23.7	54.3	30.4%	69.6%
Co	1.56	5.98	20.7%	79.3%
Ni	5.99	9.00	40.0%	60.0%
Mn	93.2	437	17.6%	82.4%
Pb	11.9	31.9	27.2%	72.8%

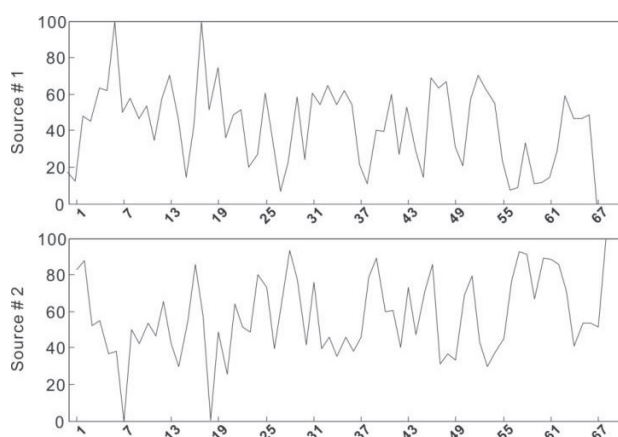


Fig. 5. Variations of source contributions.

and $\text{Min Sig/Noise} > 2$), suggesting that the modeling is efficient [27]. As can be seen from the table, the first source is characterized by high Cu content, whereas the second source is characterized by high contents of other metals. In combination with the above analyses, source 1 with high Cu content should be explained to be the anthropogenic (coal related) source, whereas source 2 should be explained to be the geogenic source. Moreover, the contribution of source 1 for the metal concentrations of all of the samples range from 0 to 100% (mean = 42.9%), whereas the source 2 contributions are 0 to 100% (mean = 57.1%), which indicate that the anthropogenic contribution in the study area is significant.

Conclusions

Based on the analyses of the concentrations of seven kinds of heavy metals in the surface soils around the Haizi coalmine, we reached the following conclusions:

- (1) The metal concentrations are $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Co}$, and all of them have medium coefficients of variation (0.13-0.75) and low p-values (< 0.01) of normal distribution test except for Fe, Co and Ni, implying that they have been affected by multi factors.
- (2) The single pollution and geo-accumulation indexes based on the mean concentrations of heavy metals imply that zinc and lead are light pollution, whereas the pollution of the single metal in the study area is heterogeneous. The Nemerow composite and the potential ecological risk indexes suggest that the soils in this study are slightly polluted and with low potential ecological risk.
- (3) Spatial distributions of the metal concentrations, in combination with the statistical analyses, indicate that the metals can be classified into two groups: geogenic (Fe-Co-Mn) and anthropogenic (Cu-Zn-Pb-Ni), and their mean contributions calculated by the Unmix model are 57.1% and 42.9%, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

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