Geochemical characteristics and source analysis of soil heavy metals in Luling coal mine, northern Anhui Province

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Abstract. In order to understand the characteristics of soil heavy metal pollution in Luling Coalmine Area, we collected 26 soil samples, and using X-ray fluorescence to determine the concentrations of heavy metal elements. The method of factor analysis and cluster analysis are applied to identify the sources of heavy metal pollution. Results show that: (1) the average contents of heavy metal elements in soil is: Co<Pb<Cu<Ti<Zn<Cr<V<Mn, coefficient of variation shows the coal mining activities have a certain degree of pollution of Zn, Cu, Co. (2) Co and (Mn, Cu), Ti and (Cr, V) are significantly correlation, V and (Mn, Cr), Cu and Mn have a certain correlation, low correlation between Pb, Zn and other elements; (3) the results of factor analysis showed that heavy metal elements can be extracted into three factors, FC1 is controlled by Mn-Pb-Cu-Co, FC2 controlled by Ti-Cr-V, while the FC3 is controlled by Zn, combined with the practical, consider three factors representing coal mining factors, natural factors, traffic factors; cluster analysis also has consistent conclusion with the factor analysis.

1. Introduction
Huainan-Huaibei Coal Mines is an important coal production base in China. The development and utilization of coal resources provide a strong guarantee for the local and national economic development, but it also brings a series of environmental problems, especially the problem of heavy metal pollution around the mining area. Heavy metal elements will cause serious harm to soil properties and vegetation, and to a great extent, inhibit agricultural production activities. More importantly, heavy metal elements will enter the human body through food chain, groundwater, ground dust and other channels and accumulate continuously, which seriously threatens the lives and health of local residents[1-2]. At present, the study of heavy metals in the soils of the northern Anhui mining area is mainly focused on pollution assessment[3-4]. However, there are few studies has been done on the sources of heavy metal pollution in this area. In this paper, the soil around Luling Coal Mine in Suzhou City was systematically sampled and tested, the geochemical characteristics of heavy metals were analyzed, and the main controlling factors were discussed by statistical analysis, so as to provide a reference for the comprehensive treatment of environmental problems in this mining area.

2. Survey of the Study Area
Suzhou City is located in the north of Anhui Province. The coal resources are abundant and the coal quality is excellent. There are two large coal companies, namely Wanbei Coal & Electricity Group and Huaibei Mining Group. Luling Coal Mine is located about 20 kilometers southeast of Suzhou City.
The coordinate of the main well is E117°06′30″, N33°35′59″, which was put into operation in 1969. The original designed production capacity was 1.5 million tons. In recent years, after reconstruction and expansion, the annual output of raw coal remained at around 2 million tons. The mine has convenient transportation, and there are two provincial roads (figure 1). In the north, there is Suzhou-Si County Provincial highway (S303), and in the south, there is Suzhou-Bengbu Provincial Road (S101), and the mining road is connected to it. Except for the subsidence area formed by mining, the mine area is farmland and village, and the terrain is flat. The overall trend is high in the northwest and low in the southeast, with an elevation of +22 to +25m. The main crops in this area are mainly corn, wheat and soybean.

![Figure 1. Location of the study area](image)

3. Materials and Methods

3.1 Sample collection and testing
Taking Luling mining area as the center, in the surrounding NE, SE, NW, and SW directions, we use a self-made sampler to collect 0-15 cm soil samples at a distance of 50 m. Each sample is 1~2 kg, placed in a polyethylene plastic sealed bag and numbered, a total of 26 samples were collected. The soil samples collected in the field were placed in a laboratory under ventilated conditions. After natural air drying, the roots of the plants were removed and kept in an oven (80°C) for 24h. Subsequently, it was ground to below 200 mesh with an agate crucible, and 4 g of powder was accurately weighed for each sample, and subjected to tableting treatment using a 30 t tablet press, and then tested by XRF. The test analysis work was completed at the Anhui Coal Mine Exploration Engineering Technology Research Center. The instrument was Explorer 9000SDD. After each test of 3 samples, the instrument was calibrated with the standard sample. The specific test procedure is described in the literature[5].

3.2 Methods
Multivariate statistical analysis is the theory and method of using mathematical statistics to study multivariate problems[6]. It includes regression analysis, discriminant analysis, cluster analysis, principal component analysis, factor analysis, correspondence analysis and so on. It has been widely applied in education, medicine, economics, environmental science and other disciplines. Many scholars at home and abroad use this method to identify the pollution sources of soil or sediment[1,7-9]. This paper mainly uses two methods: factor analysis and cluster analysis, and statistical analysis process involved in this paper is completed by SPSS software.
4. Results and Analysis

4.1 Content characteristics of heavy metals

Statistical analysis of test data is shown in Table 1. From the table, we can see that the content of heavy metal elements changes in a certain range, and the order from few to more is Co<Pb<Cu<Zn<Ti<V<Cr<Mn. The average value of Cu was 20.6 mg/kg, slightly higher than the background value of soil environment in Anhui Province; the average value of Zn was 62.0 mg/kg, which was consistent with the background value of soil environment in Anhui Province (AB) [10]; the average values of Cr and Ti were 62.5 mg/kg and 39.19 mg/kg, slightly higher than the national background value (NB) [10], while the average values of Co, Pb, V and Mn were lower than the background value. By contrast, it can be found that the background value of the area is basically the same as that of Anhui and the whole country.

|        | V   | Cr  | Mn  | Cu  | Zn  | Pb  | Co  | Ti  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|
| Minimum value | 64.0 | 39.0 | 262.0 | 14.0 | 36.00 | 16.0 | 3.0 | 32.8 |
| Maximum value | 92.0 | 76.0 | 613.0 | 29.0 | 137.0 | 27.0 | 8.0 | 42.5 |
| Mean    | 80.2 | 62.5 | 430  | 20.6 | 62.0  | 19.9 | 5.7 | 39.1 |
| Standard deviation | 7.1 | 8.0 | 88.6 | 4.7 | 20.9  | 2.4 | 1.3 | 234 |
| Skewness | -   | -   | 0.10 | 0.57 | 1.89  | 1.47 | 0.2 | -   |
| Kurtosis | -   | 1.71 | -0.47 | -    | 5.69  | 3.18 | -   | 0.91 |
| Coefficient of | 0.09 | 0.13 | 0.21 | 0.23 | 0.34  | 0.12 | 0.2 | 0.06 |
| AB      | 98.2 | 66.5 | 530  | 20.4 | 62.0  | 26.6 | 16.0| 47  |
| NB      | 82.4 | 61  | 583  | 22.6 | 74.2  | 26   | 12.0| 38  |

Generally speaking, in the same geological background, if the region is in natural conditions, the difference of heavy metal content in the soil is not too great, but mining, waste heap, agricultural production and other human activities, will cause changes in element content. Therefore, the average value is not enough to represent the intrinsic information of each sample, can only explain the overall situation of the mining area soil relative to the background value. The coefficient of variation can eliminate the influence of average value and measure the discrete degree of heavy metal content. And if the coefficient of variation is large, indicating that it is relatively influenced by mining activities [11]. The variation coefficients of heavy metals are Ti<V<Pb<Cr<Mn<Co=Cu<Zn, so the pollution of Zn, Cu and Co by coal mining activities in this area is more serious, but the influence of Ti and V is less. At the same time, the deviation and kurtosis of Zn have reached 1.89 and 5.69, and the deviation and kurtosis of Pb are 1.47 and 3.18. It can be considered that the probability distribution of the data is slightly right deviation, and the contents of heavy metal elements Zn and Pb deviate from the normal population, which reflects that coal mining or human activities have a certain impact on the soil quality in this area.

Yuan Xin-tian etc., used the single factor pollution index method and the ground accumulation index method to evaluate the heavy element pollution status of the soil in four mining areas of Suzhou City, and drew the conclusion that Cr was heavy pollution and slight pollution respectively, but the result of this paper was not polluted or slightly polluted [12]. Fan Jin-shuan pointed out that the content of Cr in the soil of coal gangue land in each mining area was very significant difference, and the content of Cr in the soil of any two coal gangue land was also significantly different [13]. Therefore, this inconsistent conclusion may be caused by the composition of gangue minerals, sampling location, sampling time and the different absorption of heavy metals by different vegetation in the mining area.
4.2 Correlation analysis of heavy metal elements

The correlation coefficients of heavy metal elements in soil samples were listed in Table 2. As can be seen from Table 2, there is a difference in the correlation of each heavy metal element. There is a significant correlation between Co and Mn, Cu, Ti and Cr, V (P<0.01), and the correlation coefficients are 0.622, 0.617, 0.561, 0.508, respectively. There is a certain correlation between V and Mn, Cr, Cu and Mn (P<0.05), the correlation coefficients were 0.480, 0.449, and 0.477, respectively. The correlation between elements can indicate whether the source is consistent. Usually, the elements with strong correlation are considered to be the same source, while the weaker correlations are considered come from different sources, such as the correlation between Pb and Zn. The sources of Pb and Zn in this area are inconsistent with other sources and may be affected by coal mining or human activities.

| V    | Cr    | Mn    | Cu    | Zn    | Pb    | Co    |
|------|-------|-------|-------|-------|-------|-------|
| V    | 1     |       |       |       |       |       |
| Cr   | 0.449*|       |       |       |       |       |
| Mn   | 0.480*| 0.185 |       |       |       |       |
| Cu   | 0.174 | 0.150 | 0.477*|       |       |       |
| Zn   | 0.055 | 0.112 | 0.219 | 0.388 | 1     |       |
| Pb   | 0.211 | 0.221 | 0.381 | 0.312 | 0.027 | 1     |
| Co   | 0.353 | 0.338 | 0.622**| 0.617**| 0.201 | 0.212 | 1     |
| Ti   | 0.508**| 0.561**| 0.170 | 0.081 | 0.142 | 0.103 | 0.267 | 1     |

Note: ** and * mean correlations are significant at the 0.01 and 0.05 level, respectively.

4.3 Factor Analysis

The content of heavy metals is not only determined by regional geological environment, but also affected by industrial and agricultural activities. According to the above analysis, heavy metals in this area are polluted to some extent. In order to identify the sources of pollution, factor analysis was carried out on heavy metal elements. According to the eigenvalues and cumulative contribution rate, three factors were extracted (Table 3). The explanations of variance were 27.64%, 25.66%, 16.67%, and the explanations of cumulative variance were 69.97%. In order to accurately understand the information represented by each factor, the factor is rotated by the method of maximum variance.

From Table 3, FC1 is controlled by the combination of Mn, Pb, Cu and Co elements, with loads of 0.804, 0.710, 0.669 and 0.676, and FC2 is controlled by the combination of Ti, Cr and V elements, with loads of 0.872, 0.808, 0.717 in turn. FC3 is mainly controlled by Zn and the load is 0.877.

| Table 2. Correlation coefficients between heavy metals |
|------------------------------------------------------|
| V | Cr | Mn | Cu | Zn | Pb | Co | Ti |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| V  | 1   |     |     |     |     |     |     |
| Cr | 0.449*|     |     |     |     |     |     |
| Mn | 0.480*| 0.185 |     |     |     |     |     |
| Cu | 0.174 | 0.150 | 0.477*|     |     |     |     |
| Zn | 0.055 | 0.112 | 0.219 | 0.388 | 1 |     |     |
| Pb | 0.211 | 0.221 | 0.381 | 0.312 | 0.027 | 1 |     |
| Co | 0.353 | 0.338 | 0.622**| 0.617**| 0.201 | 0.212 | 1 |
| Ti | 0.508**| 0.561**| 0.170 | 0.081 | 0.142 | 0.103 | 0.267 | 1 |

Table 3. Total variance explained and component matrices for heavy metal contents

| Components | Extraction Sums of Squared Loadings | Rotation squared sums loading |
|------------|------------------------------------|-----------------------------|
| Total      | % of Variance | Cumulative % | Total      | % of Variance | Cumulative % |
| PC1        | 3.106 | 38.82 | 38.82 | 2.211 | 27.64 | 27.64 |
| PC2        | 1.469 | 18.36 | 57.18 | 2.053 | 25.66 | 53.30 |
| PC3        | 1.023 | 12.79 | 69.97 | 1.333 | 16.67 | 69.97 |

| Component matrix Rotated component matrix |
|------------------------------------------|
| V | Cr | Mn | Cu | Zn | Pb | Co | Ti |
| V | 0.677 | 0.422 | -0.136 | 0.369 | 0.717 | -0.069 |
| Cr | 0.601 | 0.547 | 0.109 | 0.130 | 0.808 | 0.059 |
| Mn | 0.756 | -0.290 | -0.240 | 0.804 | 0.192 | 0.172 |
| Cu | 0.659 | -0.553 | 0.118 | 0.669 | -0.017 | 0.553 |
| Zn | 0.368 | -0.335 | 0.728 | 0.044 | 0.074 | 0.877 |
| Pb | 0.476 | -0.147 | -0.578 | 0.710 | 0.082 | -0.266 |
Wiechua D\textsuperscript{14} pointed out that a large part of the increase in Mn content in the environment was caused by industrial pollution and smelter emissions; Kongweihu i\textsuperscript{15} pointed out that Pb, Cu, Co, Zn, Cd, Sn and other elements in the coal combustion process have escaped, which will pollute the surrounding environment. Combined with field investigation, there are no other large-scale industrial pollution sources around the mining area. Accordingly, FC1 can be expressed as the influence of coal mining activities. Generally, Cu and Zn exhibit similar geochemical behavior in natural soils\textsuperscript{16}, but here Zn is separately extracted as FC3, so Zn in soils is more or less affected by human factors, which is also confirmed by the lower correlation coefficient between Cu and Zn ($r = 0.388$). Zn can be used as a marker element of traffic pollution. Zn is widely used as a detergent. Friction between tires and the ground can produce particulate matter containing higher Zn. It is the main source of increasing Zn content in urban surface soil. The use frequency of coal transport vehicles in mining areas is very high, so FC3 can be regarded as traffic pollution. Source. At the same time, inconsistent geochemical behaviors of Cu and Zn also show the characteristics of elements in the coal mine area. For FC2, Ti, Cr and V can be considered as natural sources, mainly from parent materials, because the three elements in the combination are lower than the provincial soil background value and the coefficient of variation is low, human production activities have not caused pollution to it.

As mentioned earlier, clustering analysis divides data into several categories according to distance, so as to minimize the "difference" of the data within the category and maximize the "difference" between the categories. This method can verify the conclusion of factor analysis\textsuperscript{18}. Through cluster analysis(figure 2), eight heavy metal elements in the mining area were classified into three categories: Mn, Co, Cu, Pb were clustered into one group; V, Cr, Ti were clustered into the second group; and the third category was Zn, which was consistent with the results of factor analysis, indicating that the factor analysis method had a certain identification effect on heavy metal pollution sources in the soil in this area.

![Figure 2. Clustering analysis of heavy elements in soil](image)

5. Conclusion

Through the systematic sampling and analysis, following conclusions can be drawn:

1. The content of heavy metals in soil varies within a certain range, and the order of change from small to large is Co<Pb<Cu<Ti<Zn<Cr<V<Mn. The coefficient of variation shows that coal mining activities in this area pollute Zn, Cu and Co to a certain extent, but have little influence on Ti and V.

2. Co and Mn, Cu, Ti and Cr, V have significant correlation, whereas, V and Mn, Cr, Cu and Mn have certain correlation. The correlation between elements can indicate whether their sources are
consistent or not, and the elements with strong correlation can be regarded as the same source. The correlation between Pb, Zn and other elements in this area is low, suggesting that the sources of Pb, Zn and other elements in this area are inconsistent, and may be affected by coal mining or human activities.

(3) Factor analysis and cluster analysis were used to extract three factors: FC1 was controlled by the element combination of Mn-Pb-Cu-Co, FC2 was controlled by the element combination of Ti-Cr-V, and FC3 was controlled by Zn, representing coal mining factor, natural factor and traffic factor respectively.

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