Analyzing the possible sources of heavy metals in farmland soil around Weihe coal-fired plant based on multivariate statistical analysis

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Abstract. Contents of heavy metals Cu, Pb, Zn, As, Ni, Mn, V, Co and Cr in farmland soil around Weihe coal-fired plant were surveyed by applying X-ray fluorescence spectrometry to estimate the impact of coal-fired industrial activity on the surrounding soil environment. The possible sources of heavy metals analyzed in the soil were discriminated by utilizing multivariate statistical analysis methods, including principal component analysis, correlation analysis and cluster analysis, and the contribution of each source was apportioned applying principal component analysis subsequently multiple linear regression method. The results revealed that the content ranges of Cu, Pb, Zn, As, Ni, Mn, V, Co, and Cr were 18.1 to 45.9, 20.1 to 64.5, 38.7 to 69.7, 6.0 to 17.9, 23.9 to 39.1, 218.6 to 681.6, 64.5 to 104.2, 18.9 to 61.0, and 94.7 to 128.1 mg/kg with the average of 23.3, 28.3, 48.7, 9.4, 31.2, 564.7, 78.3, 29.1, and 110.7 mg/kg, respectively. Compared with the element background value of Shaanxi soil, the mean contents of Cu, Cr, Co, Pb, Ni and V were larger than their background values, while the mean contents of As, Zn and Mn were less than or close to their background values. Three main sources were discriminated for heavy metals investigated in the surrounding farmland soil of Weihe coal-fired plant. Zn, Cu, Pb, Ni and V derived from traffic and natural source. Co and Cr primarily derived from coal-fired plant discharge. Mn and As primarily came from natural source. The contributions of traffic and nature mixing source, natural source and coal-fired source to heavy metals in farmland soil around Weihe thermal power plant were 21.7%, 49.9% and 28.4%, respectively.

1. Introduction
Heavy metals, a kind of common and toxic pollutant, widely exist in environmental media, such as soil, water, sediment and atmospheric particulates [1-3]. Heavy metal contamination of soil is very serious in China owing to the rapid development, particularly in agricultural and industrial areas [4]. In terms of the latest Chinese national survey of soil pollution bulletin, the total over-limit ratio of pollutants in national soil is 16.1% and the over-limit ratio of investigation sites in farmland soil is 19.4%. Heavy metals were found the main pollutant of over-limit pollutants in Chinese arable soil. In China, there is about 10,000,000 tons’ loss of crop output every year due to farmland soil contaminated by heavy metal [5]. Heavy metals are indestructible, toxic, persistent, cumulative and abundant in environment [2]. Heavy metals accumulated in farmland soil could enter into human body by food chains and result in serious health risks to human beings [1]. Therefore, pollution degree, environmental hazard and source of heavy metal in farmland soil have drawn increasing attention.
The contents of heavy metals in soil including farmland/arable soil and urban soil were mainly impacted by soil parent material and human activities [1]. Excessive accumulating of heavy metals in surface soil primarily comes from man-made sources such as refining and mining of ores, metal processing and smelting, equipment manufacturing, chemical production, fertilizer, pesticides, wastewater irrigation, fossil fuel combustion, and vehicular exhaust, etc. [1, 4]. In China, coal accounts for 70% of the energy structure and is mainly used for power generation [3]. Heavy metals contained in coal release into the surrounding soil of coal-fired plant with the coal combustion for power generation. The effect of a coal-fired plant on its surrounding soil environment is related to the used coal quality, plant capacity, stack height, local meteorological conditions and the pollution control technology of the coal-fired plant. Owing to the diversity of the aforementioned factors in each coal-fired plant, it is essential to research the pollution characteristics and the possible sources of heavy metals in surrounding farmland soil of different coal-fired plant for crops safety and environmental protection.

Four objects of this research are: (1) to investigate the content characteristics of heavy metals in farmland soil around Weihe coal-fired plant; (2) to analyze the relationship among the investigated heavy metals; (3) to differentiate the possible sources of heavy metals investigated in the farmland soil around the plant; and (4) to quantify the contribution of every source. The results of this study would offer a scientific basis for environmental protection and pollution control of farmland soil around coal-fired plant.

2. Materials and methods

2.1. Sample and analytical methods
Soil samples were gathered from the farmland around Weihe coal-fired plant (WCFP) (108°54’21”E, 34°26’19”N), which is located in the northwest 20 km away from Xi’an downtown. The WCFP with a 210 m-high chimney and 1.2×10⁶ kWh annual energy production was built in 1991. The annual coal consumption of WCFP is approximately 145×10⁶ t and the consumed coal is mainly from WeiBei coal mines of Shaanxi province. WCFP has installed an electric precipitator system in 2015 to reduce particle emission. The prevailing wind direction in the investigation area is southwest in spring and summer, and is northeast in autumn and winter. In the study area, the zonal soil is cinnamon soil and the primary crops are vegetables and wheat. The west of WCFP is the airport expressway, the northeast is the approach track and the southeast is coal railway line.

Forty one soil sampling sites were distributed around WCFP at the distances of 100 m, 500 m and 1000 m. At each sampling site, about 1 kg surface soil (0-20 cm depth) sample was collected by using a stainless steel shove from the corners of a 4 m² (2 m × 2 m) sampling plot and packed in a polyethylene bag. All collected soil samples were air-dried naturally in the laboratory for two weeks, and then sifted through a 1 mm nylon mesh to eliminate small stones and other debris. About 100 g of every sieved soil sample (< 1 mm) was gotten by quartering method, and then milled to less than 0.075 mm for heavy metals measuring.

The contents of Cu, Pb, Zn, As, Ni, Mn, V, Co, and Cr in soil samples were determined by using X-ray fluorescence spectrometry (PW2403 apparatus, PANalytical) [3]. Standard reference materials (GSS-1, GSD-12) and 10% duplicate samples were applied for quality control in the experiment [6]. The measured values of all investigated heavy metals content in standard reference materials are in 95-103% the official values. The relative errors of all heavy metals measured in the duplicate samples are in 3-8%.

2.2. Statistical analysis methods
Content characteristics of heavy metals investigated in farmland soil around WCFP were described using maximum (Max), minimum (Min), arithmetic mean (AM), standard deviation (SD), and coefficient of variation (CV). Principal component analysis, correlation analysis and cluster analysis, widely used in literatures [6-9], were applied to judge the interrelationships of the heavy metals and to discriminate their potential sources in the investigated soil. Principal component analysis subsequently
multiple linear regression method was used to quantify the contribution of each source. Correlation analysis can determine the correlation relationship between two elements. Principal component analysis can reveal the relationships among the observed variables by reducing the number of correlated complex variables and extracting latent factors (principal components). Principal component analysis depends on an eigenvector decomposition of correlation matrix or covariance matrix. The initial data matrix is first decomposed into factor loading matrix, factor score matrix and residual matrix. Factor loading matrix is then rotated to attain the rotated component loading matrix and factor score is obtained by principal component analysis. In the study, principal component analysis was conducted by the method of varimax rotation with Kaiser Normalization of variables [10]. Cluster analysis can classify a group of observations into two or more incompatible clusters on basis of a combination of internal variable. It is often used to test the principal component analysis results [10]. Multiple linear regression analysis was performed after principal component analysis with the total heavy metals contents as the dependent variable and the factor scores of principal component analysis for heavy metal content as independent variables [9]. The detail method of principal component analysis subsequently multiple linear regression can be found in the literatures [9,11]. SPSS 19.0 software was used in the study to carry out all statistical analyses.

3. Results and discussion

3.1. Heavy metal contents in farmland soil

The descriptive statistics of Cu, Pb, Zn, As, Ni, Mn, V, Co and Cr contents in farmland soil around Weihe coal-fired plant (WCFP), and the element background values of Shaanxi soil [12], are displayed in table 1. The AMs of Cu, Pb, Zn, As, Ni, Mn, Cr, Co and V contents in the investigated soil samples were 23.3, 28.3, 48.7, 9.4, 31.2, 564.7, 110.7, 29.1 and 78.3 mg/kg, respectively. Compared to the element background value of Shaanxi soil, farmland soil around WCFP had elevated contents of Cu, Pb, Co, Cr, V and Ni. Their maximum contents were 45.9, 64.5, 61.0, 128.1, 104.2 and 39.1 mg/kg, which were 2.1, 3.0, 5.8, 2.1, 1.6 and 1.4-folds the element background values of Shaanxi soil, respectively. Coefficient of variation (CV) can reflect the disparity degree of observed variable. The CV values of Co, Pb and Cu content in the investigated soil samples are greater than other heavy metals, indicating that the varieties of these 3 heavy metals contents in the soil samples are bigger than other heavy metals.

| Table 1. The contents of heavy metals in surrounding farmland soil of WCFP and reference value (mg/kg). |
|-----------------|-----|-----|-----|-----|-----|-----|-----|
| Heavy metal     | Cu  | Pb  | Zn  | As  | Ni  | Mn  | Cr  |
| Min             | 18.1| 20.1| 38.7| 6.0 | 23.9| 218.6| 94.7| 18.9| 64.5|
| Max             | 45.9| 64.5| 69.7| 17.9| 39.1| 681.6| 128.1| 61.0| 104.2|
| AM              | 23.3| 28.3| 48.7| 9.4 | 31.2| 564.7| 110.7| 29.1| 78.3|
| SD              | 4.8 | 6.2 | 6.2 | 1.2 | 3.1 | 68.3 | 7.7  | 7.9 | 7.1 |
| CV(%)           | 20.4| 22.1| 12.7| 12.8| 10.0| 12.1 | 6.9 | 27.0| 9.1 |
| Reference value | 21.4| 21.4| 69.4| 11.1| 28.8| 557.0| 62.5 | 10.6| 66.9|

Compared with the contents of heavy metals in the surrounding soil of Baqiao coal-fired plant [3], another coal-fired plant situated in the northeast of Xi’an city, the contents of Zn, Cu and Pb in the surrounding soil of Baqiao coal-fired plant are remarkably higher, and the contents of Cr and Co in the surrounding soil of Baqiao coal-fired plant are lower, while the contents of other heavy metals in the surrounding soil of two power plants are proximity. The content diversities of heavy metals in the surrounding soil of two power plants maybe related with their sources. Baqiao power plant is closer to Xi’an city than WCFP. There are many roads around Baqiao power plant and where traffic congestion is frequent. Therefore, traffic emission plans a great influence on Zn, Cu and Pb contents in the surrounding soil of Baqiao power plant.
3.2. **Heavy metal sources in farmland soil**

**Table 2.** Rotated component matrix for heavy metal contents of farmland soil around WCFP.

| Element | Principal component 1 | Principal component 2 | Principal component 3 | Communality |
|---------|-----------------------|-----------------------|-----------------------|-------------|
| As      | 0.448                 | 0.711                 | 0.407                 | 0.872       |
| Co      | 0.111                 | -0.285                | 0.699                 | 0.807       |
| Cr      | -0.042                | 0.004                 | 0.935                 | 0.876       |
| Pb      | 0.738                 | -0.339                | -0.043                | 0.945       |
| Zn      | 0.823                 | -0.147                | 0.155                 | 0.725       |
| Cu      | 0.876                 | -0.364                | 0.041                 | 0.901       |
| Mn      | -0.076                | 0.894                 | -0.015                | 0.804       |
| Ni      | 0.779                 | 0.346                 | -0.185                | 0.761       |
| V       | 0.936                 | 0.043                 | 0.005                 | 0.878       |
| Eigenvalue | 3.556               | 2.660                 | 1.354                 |             |
| Variance contribution rate (%) | 39.508             | 29.557                | 15.041                |             |
| Cumulative variance contribution rate (%) | 39.508             | 69.065                | 84.106                |             |

**Figure 1.** Cluster dendrogram of heavy metals determined in the farmland soil around WCFP.

The principal component analysis results of Cu, Pb, Zn, As, Ni, Mn, V, Co and Cr contents in farmland soil around WCFP are shown in table 2. The results proved that three principal components were extracted, which account for 84.106% of the total variance. Principal component 1, explaining 39.508% of the total variance, mainly loads on V (0.936), Cu (0.876), Zn (0.823), Ni (0.779) and Pb (0.738), and moderately loads on As (0.448). Cu, Pb, Zn, V and Ni are remarkably positive correlation at P<0.01. Figure 1 shows that Zn, Cu, Pb, Ni and V are classified in one cluster. The results of principal component analysis, correlation analysis and cluster analysis disclose that Cu, Pb, Zn, V and Ni may have a similar source in the farmland soil. The contents of Zn in the investigated samples are less than its background value in Shaanxi soil except for in one sample approaches to the background value. The contents of Pb in the investigated soil samples are bigger than its background value in Shaanxi soil except for in one sample its content is close to the background value. The contents of Cu, Ni and V respectively in 78%, 75% and 54% soil samples approach to their corresponding background values in Shaanxi soil. The higher value sites of Zn, Cu, Pb, V and Ni content are same, which are situated near the airport expressway and the approach track. Many researches have proven that traffic source can discharge these
metals into surface environment [6,13,14]. Therefore, according to the content characteristics of these five metals in the investigated soil samples and the results of multivariate statistical analysis, we consider that Zn, Cu, Pb, V and Ni in farmland soil around WCFP maybe primarily came from nature and traffic mixing sources.

Principal component 2, mainly loaded by As and Mn, accounts for 29.557% of the total variance (table 2). As and Mn are classified together in cluster analysis (figure 1). They are remarkably positively correlation at P<0.001. These results demonstrate that As and Mn may have a similar source in farmland soil around WCFP. The contents of As and Mn in all investigated soil samples are less than or close to the background values in Shaanxi soil, which suggest that As and Mn in farmland soil around WCFP mainly derived from natural source.

Principal component 3 is loaded by Cr and Co, explaining 15.041% of the total variance (table 2). Cr and Co are remarkably positive correlation at P<0.01, and they belong to a cluster in cluster analysis (figure 1). The contents of Cr and Co in all investigated soil samples are respectively 1.5-2.0 times and 1.8-5.8 times their background values in local soil. These results show that Cr and Co contents in farmland soil around WCFP were impacted by local human activities. The coal used in WCFP came from Weibei coal fields and the contents of Co and Cr in Weibei coal are 5 to 39 mg/kg and 4 to 96 mg/kg, respectively [15]. Cr and Co in coal mainly exist in sulphate and clay minerals [16], which are incombustible components of coal. In the combustion process of coal, incombustible components come to fly ash and slag. In this investigation, the higher Co and Cr content samples distribute in the southwest of WCFP (downwind direction). Therefore, it is can be inferred that Co and Cr in farmland soil around WCFP mainly derived from coal-fired power generation discharge.

On the base of the sources identification of heavy metals in farmland soil around WCFP, the contribution of each source was apportioned using principal component analysis subsequently multiple linear regression method and the results indicated that the percentage contribution is 21.7% for traffic and nature mixing source, 49.9% for natural source and 28.4% for coal-fired source.

4. Conclusions
The contents of Co, Cr, Pb, V, Cu and Ni in farmland soil around Weihe coal-fired plant were greater than their background values in Shaanxi soil, while the contents of Zn, As and Mn in the farmland soil were less than or close to their background values in Shaanxi soil. Heavy metals investigated in farmland soil around Weihe coal-fired plant presented different variation characteristics. The variations of Pb, Cu and Co content are greater than other heavy metals in the farmland soil. Zn, Cu, Pb, Ni and V had the mixing source of traffic emission and nature. As and Mn originated from natural source. Cr and Co mainly originated from coal-fired plant discharge. The total amount of heavy metals investigated in the farmland soil around Weihe coal-fired plant mainly originated from natural source (contribution 49.9%). The percentage contribution was 28.4% for coal-fired power plant discharge and 21.7% for traffic and nature mixing source. This research indicates that the farmland soil around Weihe coal-fired plant was impacted by local traffic and coal-fired plant. Therefore, it is essential in the future that the continuous monitoring of heavy metal in the farmland soil and local crops.

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References
[1] Khalid S, Shahid M, Niazi N K, Murtaza B, Bibi I and Dumat C 2017 A comparison of technologies for remediation of heavy metal contaminated soils J. Geochem. Expl. 182 247-68
[2] Wang L, Yang D, Li Z T, Fu Y H, Liu X M, Brookes P C and Xu J M 2019 A comprehensive
mitigation strategy for heavy metal contamination of farmland around mining areas-screening of low accumulated cultivars, soil remediation and risk assessment *Environ. Pollut.* **245** 820-8

[3] Lu X W, Liu W, Zhao C F and Chen C C 2013 Environmental assessment of heavy metal and natural radioactivity in soil around a coal-fired power plant in China *J. Radioanal. Nucl. Chem.* **295** 1845-54

[4] Yang Q Q, Li Z Y, Lu X N, Duan Q N, Huang L and Bi J 2018 A review of soil heavy metal pollution from industrial and agricultural regions in China: Pollution and risk assessment *Sci. Total Environ.* **642** 690-700

[5] Wu G, Kang H B, Zhang X Y, Shao H B, Chu L Y and Ruan C J 2010 A critical review on the bio-removal of hazardous heavy metals from contaminated soils: Issues, progress, eco-environmental concerns and opportunities *J. Hazard. Mater.* **174** 1-8

[6] Chen X D, Lu X W and Yang G 2012 Sources identification of heavy metals in urban topsoil from inside the Xi’an Second Ringroad, NW China using multivariate statistical methods *Catena* **98** 73-8

[7] Wang P C, Li Z G, Liu J L, Bi X Y, Ning Y Q, Yang S C and Yang X J 2019 Apportionment of sources of heavy metals to agricultural soils using isotopes fingerprints and multivariate statistical analyses *Environ. Pollut.* **249** 208-16

[8] Strbova K, Ruzickova J and Raclavska H 2019 Application of multivariate statistical analysis using organic compounds: source identification at a local scale (Napajedla, Czechia) *J. Environ. Manage.* **238** 434-41

[9] Pan H Y, Lu X W and Lei K 2017 A comprehensive of heavy metals in urban road dust of Xi’an, China: Contamination, source apportionment and spatial distribution *Sci. Total Environ.* **609** 1361-9

[10] Lu X W, Wang L J, Li L Y and Lei K 2010 Multivariate statistical analysis of heavy metal in street dust of Baoji, NW China *J. Hazard. Mater.* **173** 744-9

[11] Nasir M F M, Samsudin M S, Mohamad I, Awaluddin M R A, Mansor M A, Juahir H and Ramli N 2011 River water quality modelling using combined principal component analysis (PCA) and multiple linear regressions (MLR): A case study at Klang River, Malaysia *World Appl. Sci. J.* **14** 73-82

[12] CNEMC (China National Environmental Monitoring Center) 1990 *The Background Values of Elements in Chinese Soils* (Beijing: Environmental Science Press of China) (In Chinese)

[13] Chen H, Lu X W, Li L Y, Gao T N and Chang Y Y 2014 Metal contamination in campus dust of Xi’an, China: A study based on multivariate statistics and spatial distribution *Sci. Total Environ.* **484** 27-35

[14] Han X F, Shi D Q and Lu X W 2018 Concentration and source of trace metals in street dust from an industrial city in semi-arid area of China *J. Environ. Sci. Manage.* **2** 90-9

[15] Lu X W, Luo K L, Wang L Z and Wang W Y 2003 The content of trace elements of coals in Weibei area, Shaanxi province *J. Jilin Univ. (Earth Sci. Edition).* **33** 178-82 (In Chinese)

[16] Yin L Q and Guan X Y 2005 The study of pollution of heavy metals from coal-fired power plant and its control *Elect. Power Tech. Environ. Prot.* **21** 31-4 (In Chinese)