

## Article

# Source Apportionment of Heavy Metal Pollution in Agricultural Soils around the Poyang Lake Region Using UNMIX Model

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**Abstract:** Rapid urbanization and industrialization have caused the continuous discharge of heavy metals into the soils of China's Poyang Lake region, where they pose a major threat to human health. Yet, the spatial characteristics of these heavy metals in farmland soils and their pollution sources in this region remain unclear. This study was conducted to document the pollution caused by heavy metals in the Poyang Lake region through sampling that consisted of the collection of 215 soil samples from agricultural fields. The UNMIX model provided identification of the sources causing heavy metal pollution and source contributions to soil pollution. ArcGIS was used to study the spatial distribution of the eleven heavy metals and to validate the apportionment of pollution sources provided by the UNMIX model. Soil concentrations of heavy metals were above the local background concentrations. The average content of eight heavy metals, including Cd, Mo, Zn, Cu, Sb, W, Pb, and Ni, was approximately 1–6 times greater than natural background levels (6.91, 2.0, 1.67, 1.53, 1.23, 1.38, 1.11, and 1.24, respectively), while the average content of V, Cr, and Co was lower than natural background levels. The average contents of Cr, Ni, Cu, Zn, Cd, and Pb were all lower than the screening levels for unacceptable risks in agricultural land soils. The percentage of Cd content exceeded the risk screening value in all sampling sites, up to 55%, indicating that agricultural soils may significantly be affected by cadmium contamination. Five pollution sources of heavy metals were identified: natural sources, copper mine tailings, agricultural activities, atmospheric depositions, and industrial activities. The contribution rates of the pollution sources were 7%, 13%, 20%, 29%, and 31%, respectively. The spatial pattern of heavy metals was closely aligned with the outputs of the UNMIX model. The foregoing supports the utility of the UNMIX model for the identification of pollution sources of heavy metals, apportionment study, and its implementation in agricultural soils in the Poyang Lake region.

**Keywords:** heavy metals; agricultural soil; UNMIX model; source apportionment



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## 1. Introduction

After severe events of atmospheric and water pollution in China, awareness of the importance of soil pollution and its consequence on public health is increasing [1]. Soil contamination due to the fact of rapid urbanization and industrialization has caused great concern around the world [2]. The emissions of heavy metals that end up in agricultural soils not only affect and change the ecological functions of the soil, but also endanger human health through accumulation in crops [3]. On 31 May 2016, China's State Council released an action plan for soil pollution prevention and remediation, aimed at ensuring over 90% of contaminated arable land can be utilized safely by 2020 and 95% by 2030 [4]. The prevention and treatment of heavy metal pollution in agricultural soil urgently requires an accurate analysis of its source distribution.

The levels of heavy metals in soil are affected by both natural processes and anthropogenic activities. The content of trace metals in soil depends primarily on the composition of geological parent material [5]. In developed and developing countries, various human activities, such as those derived from metallurgical industry, mining, coal combustion and atmospheric deposition, motor vehicle exhaust emissions, or due to the intensive use of pesticides and fertilizers have given rise to soil pollution associated with heavy metals and safety concerns in recent decades [6,7]. A wide variety of receptor models are currently available to identify and quantify the contributions from emission sources to the level of pollutants. Three of the most widespread receptor statistical tools are principal component analysis (PCA), positive matrix factorization (PMF), chemical mass balance method (CMB), and isotope labeling [8–12]. Alternatively, the UNMIX model, introduced more recently, is characterized by its simple calculation process and accurate results [12], although very few studies have applied it to the soil as a receptor medium of heavy metal pollution. On the other hand, there are still many instances where pollution of a receptor medium is a very complex process, and it is necessary for a more robust solution, for instance, by the combined application of different types of receptor models, constructed on the basis of their strengths, thus aiding in the comprehensive interpretation of the results [13].

The Poyang Lake Plain, located in Jiangxi Province, is a major site of grain production in China. Jiangxi Province has abundant mineral resources, and it is one of China's major locations for resources of non-ferrous metals, such as copper and tungsten, and rare earth mineral bases, accounting for one-tenth of the national non-ferrous metal industry. Although it is also one of the provinces with the highest pollution rates due to the emissions of heavy metals. The "three wastes" (i.e., solid, water, and gas) caused by the long-term activities of key mines and smelting have exerted great pressure on the surrounding agricultural soils that has led to the loss of nutrient components in agricultural soils and the degradation of soil biology and function [14,15]. The ecology of the Poyang Lake area has been seriously damaged and prevention measures are required. To act proactively, a detailed study is necessary to identify the polluting sources and determine their apportionment. Previous studies on heavy metals in agricultural soils mainly focused on a specific area, such as agricultural soil around the mining area [12], and the study's concern were only on Cu, Zn, Cd, and Pb, or at most eight heavy metals (i.e., Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As) [15]. Unfortunately, few studies have actually examined heavy metal pollution in the agricultural soils around Poyang Lake [16–18], especially around industrial and mining enterprise areas, irrigation areas, urban areas, and general farming areas. Heavy metal pollution in farmlands threatens the food security and sustainability of food crop production in the Poyang Lake region. The main purposes of this study were to (1) analyze the concentration and spatial distribution characteristics of heavy metals in agricultural soils in the area around Poyang Lake, (2) apply the UNMIX model to identify the pollution sources and quantify the contribution of each source, and (3) explore the applicability of the UNMIX model for determining the apportionment of sources and provide the scientific basis for the prevention and remediation of heavy metal pollution in agricultural soils in the area around Poyang Lake.

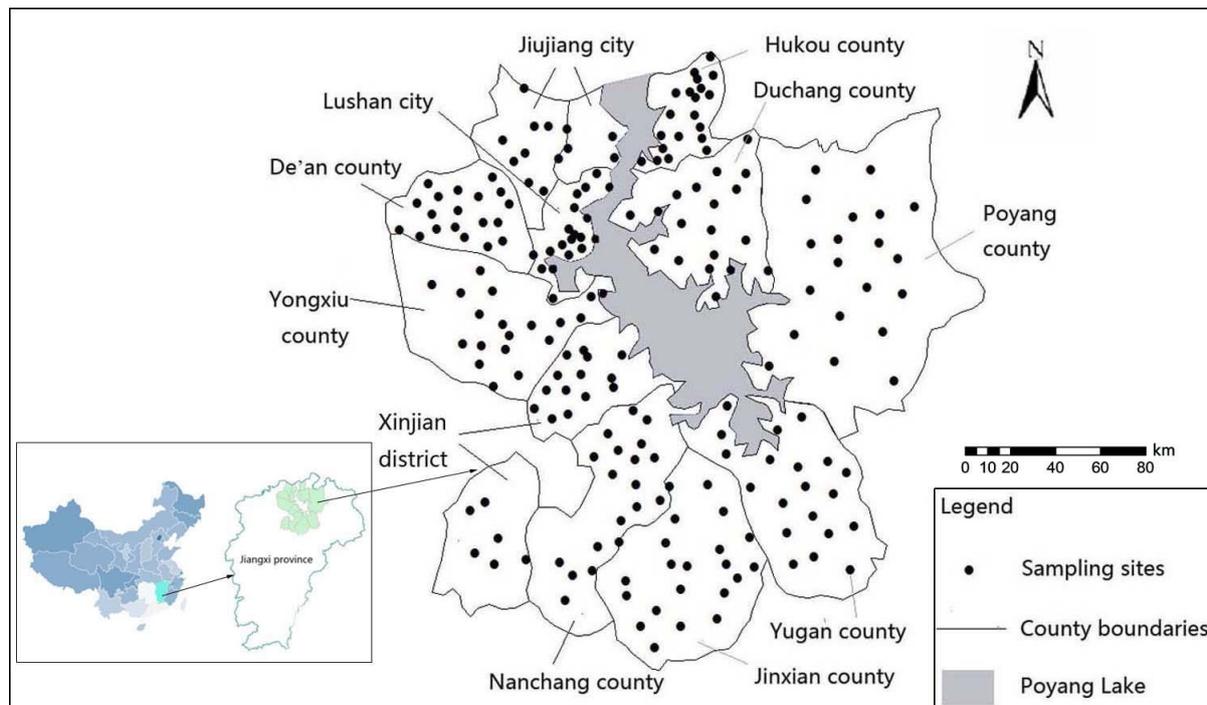
## 2. Materials and Methods

### 2.1. Study Area

Poyang Lake (115°49'–116°46' E, 28°24'–29°46' N) is the largest freshwater lake in China, radiating from north to south, located at the south bank of the Yangtze River in Jiangxi Province; it is also the second-largest lake nationwide. Poyang Lake, an important seasonal shallow lake in the Yangtze River basin, receives incoming waters of the five major river systems of Ganjiang, Fuhe, Xinjiang, Raohe, and Xiushui in Jiangxi Province and drains into the Yangtze River through a narrow outlet to the north. Parent materials of the study area are mainly quaternary red clay, river and lake deposits, weathered red sandstone, weathered argillaceous rock, weathered quartzite, and weathered acid crystalline rock. The

major soil types are anthrosols, ferralosols, and primosols, with small amounts of argosols and gleyosols.

The area around Poyang Lake was selected for the study, which mainly included the administrative areas such as Jiujiang, Hukou, De'an, Lushan, Duchang, Yongxiu, Poyang, Xinjian, Nanchang, Jinxian, and Yugan (Figure 1), with a total area of 21,117.58 km<sup>2</sup>, accounting for 12.7% of Jiangxi Province, where the crop planting area is 7178.55 km<sup>2</sup>, 12.9% of the province. Among them, Yugan County, which is a traditional agricultural county in Jiangxi Province, has the largest crop planting area (25.2%), while other counties have a crop planting area of less than 11%. Except for Jinxian County and Lushan City, other counties and areas around the Poyang Lake are rich in metal mineral resources and energy mines. The Poyang Lake District is also located in the Changjiu (Nanchang and Jiujiang) Industrial Corridor (including Jiujiang, Yongxiu, De'an, Nanchang, Nanchang County, and Xinjian District). The Changjiu Industrial Corridor has 24 industrial parks including the Jiujiang Development Zone, Nanchang High-Tech Zone, Xiaolan Economic Development Zone, and Changdong Industrial Park. The industrial base of each industrial park has its own characteristics. The main industries are metal smelting and rolling, coal, steel production, machinery manufacturing, electronics, chemical, and new materials.



**Figure 1.** Location of the study area and distribution of sampling sites.

## 2.2. Sample Collection and Concentration Determination

A total of 215 agricultural surface soil samples were collected from the study area (at a sampling depth of up to 20 cm, including farmland, vegetable fields, etc., and avoiding areas along the road and areas near waste disposal sites and other pollution sources). From 19 to 20 sampling points were arranged in each county (city, district), respectively. A multi-point mixing method was used for sampling, and a soil sample of approximately 1 kg was retained by the “quartile method”. The GPS coordinates of all sampling points were recorded, and their locations are shown in Figure 1. All samples were sealed in a Ziplock bag, labeled with their sampling location and sample number, and transported to the laboratory for further processing. The soil samples were placed in a dry and ventilated place to air dry, after removing plant debris, stones, and other debris, then grinded with an agate ball mill and passed through a 100-mesh sieve, and finally stored for later use.

To analyze the heavy metals in the agricultural soil, 0.1500 g of dry soil was weighed in 50 mL polytetrafluoroethylene tubes with an added mixture of concentrated HNO<sub>3</sub>–HF–HClO<sub>4</sub>(4:5:2) and then digested in a microwave oven [19]. The microwave digestion procedures are shown in Table 1. Once the digestion process was completed, samples were taken out and cooled to room temperature, the digestion tank was put on an electric heating plate at approximately 145 °C to drive the acid to near dryness. The digestion tank was cooled, 5 mL of 1% nitric acid was added, and the samples were put on the electric heating plate for approximately 10 min. The fraction of soluble residues was dissolved, and then the digestion tank removed and cooled to room temperature. Samples were diluted to 50 mL with ultrapure water, set aside to settle, the supernatant was filtered with a 0.45 µm filter membrane in a 50 mL volumetric flask to be tested. All samples were analyzed in the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. For the determination of the metal content (i.e., V, Cr, Co, Ni, Cu, Zn, Mo, Cd, Sb, W, and Pb), the ELEMENT XR high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Finnigan MAT, Germany) was used. During the analysis, one sample of each batch was randomly selected for three parallel experiments. At the same time, a blank experiment was performed, and quality control for the analysis of the soil composition's standard material (GBW07401) was used for the entire process of quality control to ensure the accuracy of the sample analysis. Except for the relative standard deviation of the measurement result for W of 5.39%, the relative standard deviations of the measurements of the other heavy metal elements were less than 5%, which meets the measurement requirements, and 11 heavy metal contents in all samples were detected.

**Table 1.** Microwave digestion heating process.

Heating Time	Digestion Temperature	Hold Time
7 min	Room temperature ~120 °C	3 min
5 min	120~160 °C	3 min
5 min	160~190 °C	25 min

### 2.3. Heavy Metal Pollution Assessment and Source Apportionment Methods

#### 2.3.1. Single-Factor Pollution Index Method

The single-factor pollution index method can be used to assess the soil pollution situation, and it is based on the following equation:  $P_i = C_m/C_s$ . Where  $P_i$  is the pollution index of heavy metal  $i$ ;  $C_m$  is the measured value of the element in the soils;  $C_s$  is the background value of the element in the soils. The pollution degree of  $P_i$  is divided into four categories:  $P_i < 1$ , refers to no pollution;  $1 \leq P_i < 3$ , light pollution;  $3 \leq P_i < 6$ , moderate pollution;  $P_i \geq 6$ , severe pollution. The "Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018)" was used to evaluate heavy metal pollution in agricultural soils around the Poyang Lake.

#### 2.3.2. UNMIX Model

Normally, the UNMIX model decomposes the matrix  $X$  (concentrations matrix) into a factor matrix  $G$  (or source contribution matrix), matrix  $F$  (source composition matrix), and a residue matrix  $E$ . Its rationales are based on the following equation:  $X = GF + E$ . Matrix  $F$  is defined as a matrix of chemical compositions of  $p$  sources relating to  $m$  chemical congeners, and  $G$  matrix describes the contribution of  $p$  sources (factors) to  $n$  sampling sites [20]. Compared with the traditional factor analysis model, the main feature of the UNMIX model is that it can obtain a non-negative source contribution rate, the result is more reasonable [21,22], and the calculation process is simpler.

The UNMIX model is a multivariate receptor model based on factor analysis that ensures that source component and source contributions obey non-negative constraints by geometric techniques of self-modeling curve resolution [23]. Each dimension in the multidimensional space represents a measured species, and then the principal component

analysis method is used to reduce the dimension of the data space to estimate the number of sources, the composition of source, and the source contribution. In  $n$  number of samples, the concentration of the  $j$  species in  $n$  number of analyzed species can be expressed by the following formula [24].

$$C_{ij} = \sum_{k=1}^m F_{jk}S_{jk} + E \quad (1)$$

where  $C_{ij}$  is the concentration of the  $j$ th species ( $j = 1, \dots, n$ ) in  $i$  number of samples ( $i = 1, \dots, n$ );  $F_{jk}$  is the mass fraction of the  $j$ th species in the source  $k$  ( $k = 1, \dots, m$ ), representing the composition of the source;  $S_{jk}$  is the total amount of source  $k$  in  $i$  number of samples, representing the source contribution rate;  $E$  is the standard deviation consisting of all the variability in  $C_{ij}$  not accounted for by the first  $n$  principal component, which is the difference between the model prediction and observed ambient data.

#### 2.4. Data Processing

Data processing and mapping of heavy metal concentrations were conducted using Excel 2010, and descriptive data, such as mean, minimum, maximum, standard deviation, and coefficient of variation, were calculated. Pearson correlation analysis was performed on heavy metal concentrations data using SPSS 17.0 software. The sampling sites of the study area and geostatistical spatial distribution was produced by ArcGIS 10.2 software, the ordinary kriging method was used for spatial interpolation, and the natural breaks classification method was used for determination of gradations of each metal concentration. The apportionment of heavy metal sources in agricultural soils was completed by USEPA UNMIX 6.0.

### 3. Results and Discussion

#### 3.1. Statistical Characteristics of Heavy Metals in Agricultural Soils

The statistical characteristics of 11 heavy metal and the respective contents detected in 215 samples of agricultural soils collected around the Poyang Lake area are shown in Table 2. All of the heavy metal content exhibited a skewed distribution, but after logarithmic conversion, they basically conformed to a normal distribution and, thus, they could be characterized by a geometric mean. According to Table 2, the average content of heavy metals increased in the following order: Cd < Mo < Sb < W < Co < Ni < Cu < Pb < Cr < V < Zn. In addition to V, Cr, and Co, the average content of eight heavy metals (i.e., Ni, Cu, Zn, Mo, Cd, Sb, W, and Pb) all exceeded the background values for soils in Jiangxi Province. In this study, the  $P_i$  values of V and Cr were 0.80 and 0.91, respectively, less than the background value. The  $P_i$  values of Co was 0.97, close to the background value. Otherwise, the average contents of the remaining eight heavy metals were all higher than the background values. The  $P_i$  values of Ni, Cu, Zn, Mo, Cd, Sb, W, and Pb were 1.24, 1.53, 1.67, 2.00, 6.91, 1.23, 1.38, and 1.11 times greater than natural background levels. The results indicate that V, Cr, and Co were pollution free; Ni, Cu, Zn, Mo, Sb, W, and Pb were considered as lightly polluting; while Cd was in the category of moderate pollution, close to the severe pollution level. The percentages of Mo and Cd exceeding the background value were relatively high, by 93% and 92%, respectively. According to Table 2, only the following elements, including Cr, Ni, Cu, Zn, Cd, and Pb, reached the corresponding screening value for the risk of soil pollution in agricultural land. From the average value, the contents of Cr, Ni, Cu, Zn, Cd, and Pb were all lower than the screening values for the risk of soil pollution of agricultural land in China. The maximum contents of Cr, Ni, Cu, Zn, and Pb were all lower than the pollution risk screening value for agricultural soils, and the percentage of Cd content in all sampling points exceeded the screening value by 55%, indicating that there may be risk of pollution caused by the emissions of Cd. The above analysis showed that the agricultural soil in the Poyang Lake area was polluted by heavy metals to varying degrees, although the Cd pollution was more serious.

**Table 2.** Descriptive statistical characteristics of different heavy metal concentrations in soil (mg·kg<sup>-1</sup>).

Element	Range	Average	SD	CV/%	Background Value <sup>1</sup> (Reference)	Over-Standard Rate/%	P <sub>i</sub>	Risk Screening Value <sup>2</sup>
V	55.82~111.24	76.72	11.89	15	95.8	6	0.80	-
Cr	14.11~100.30	41.56	18.62	45	45.8	33	0.91	300
Co	6.84~16.71	11.16	2.39	21	11.5	46	0.97	-
Ni	10.30~44.86	23.52	7.11	30	18.9	72	1.24	100
Cu	5.83~95.83	31.06	18.26	59	20.3	71	1.53	100
Zn	42.78~246.00	115.72	44.59	39	69.4	83	1.67	250
Mo	0.206~1.750	1.001	0.35	35	0.5	93	2.00	-
Cd	0.030~1.730	0.746	0.46	61	0.108	92	6.91	0.6
Sb	0.71~2.48	1.41	0.39	27	1.15	73	1.23	-
W	1.06~20.44	6.82	4.11	60	4.93	67	1.38	-
Pb	7.17~86.56	35.85	16.25	45	32.3	53	1.11	140

<sup>1</sup> The arithmetic mean value of the background value of each element of the layer A soil in Jiangxi Province. ("Chinese Soil Element Background Value", China Environmental Monitoring Station, 1990). <sup>2</sup> "Soil Environmental Quality Risk Control Standards for Soil Contamination of Agricultural Land" (GB 15618-2018, Screening Value of Agricultural Land Soil Pollution Risk, Paddy Field, pH 6.5~7.5).

### 3.2. Spatial Distribution Characteristics of Heavy Metals in Agricultural Soils

The coefficients of variation for Cd, W, and Cu all exceeded 50%, especially for Cd which had the highest coefficient of variation (CV = 61%), while other heavy metals had lower coefficients of variation, ranging between 15% and 45%. This indicates that the spatial variability of other heavy metals was relatively small. Figure 2 reveals spatial variation trends very similar for Cr, Zn, W, and Pb, and that the coefficients of variation of Cr and Pb were equal. Moreover, both the spatial distribution of W and the content of Zn had a decreasing trend from west to east. An enrichment in the content of Cr, Zn, W, and Pb was observed in Nanchang County, which is in the Changjiu Industrial Corridor. Nanchang County was not only a traditional agricultural county in Jiangxi, but also the second-largest commercial grain base in the province. It is also close to the industrially developed Nanchang urban area. There were several industrial parks, including three national and two provincial, mostly technological industries related to electronic, precision machinery manufacturing, or biomedicine. More recently, other industries have emerged, particularly the processing plants of copper and tungsten resources, which may also be the cause of why high levels of W appear in Nanchang County. It is a region with a great influence of human activity largely due to the industrial and urban development where metal contamination events have also taken place such as the enrichment of Cr, Zn, W, and Pb in agricultural soils around the lake area factor.

The spatial variations of V and Ni content were also similar, and both with high levels in Jinxian County. V had the smallest coefficient of variation. The content of V exceeded the background value in Jinxian County but not in the rest of the regions, indicating the entry of V into agricultural soils due to the fact of natural processes. High levels of Cd were found in counties of Duchang, Jinxian, and Yongxiu. In all the areas, except Poyang County, Cd content exceeded the background values. The coefficient of variation of Cd was the largest, showing a remarkable difference in the spatial distribution between different regions. The average Cd content of 5.06 times higher than the background value is indicative of the existence of pollution sources due to the fact of anthropogenic influence. Cu content was relatively high in Hukou County as a whole. Although Hukou County did not have metal mineral resources with mining value, it was a provincial key industrial park with a heavy chemical industry base and mainly based on iron and steel metallurgy, fine chemicals, electronics, or machinery. High levels of Mo were found in Duchang County, where the range exceeded the background value and it was even spread throughout the agricultural area. Despite Duchang County not being an industrially developed area, it borders Hukou County, a key industrial area where agricultural soil has also been affected by Mo, impacting on the surrounding environments. In the counties of Yongxiu and Duchang, high levels of Co were detected and there was also enrichment, although noticeably less, in other regions.

High levels of Sb were located in the counties of Poyang and Yugan, greater in the east than in the west. The Sb coefficient of variation was small, with an average content of 1.18 times higher than the background value, showing a distribution of Sb pollution relatively uniform in agricultural areas, probably associated with non-point pollution sources. It can be seen from Figure 2 that the background value rate of all heavy metals in Poyang County sampling sites was lower than that in other regions. This may be because Poyang County was in a lagging industrial development area and was not greatly affected by heavy metal pollution. However, the background value rate for all heavy metals in the Nanchang County, Jinxian County, and Xinjian District sampling points was ranked in the top three. The best explanation for this pattern is that the three counties are adjacent to the provincial capital city, so the “three wastes” discharged by various industrial bases and enterprises in the Nanchang urban area as well as the domestic sewage and pollutants from agricultural non-point sources in the towns around the county and district entered the soil of these three counties.

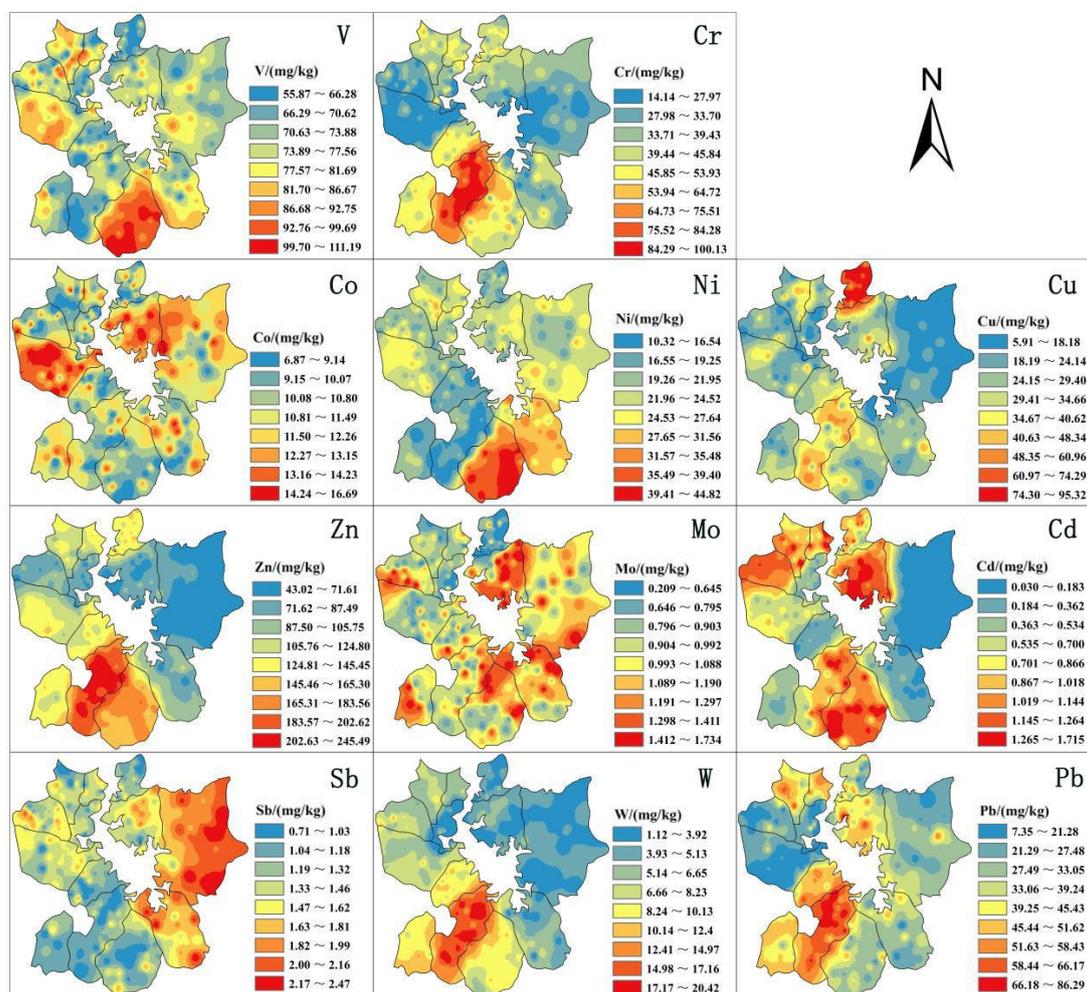


Figure 2. Spatial distribution of heavy metal content in agricultural soil around Poyang Lake.

### 3.3. UNMIX Model for Source Allocation of Heavy Metals in Agricultural Soils

Table 3 shows the Pearson correlation coefficients of 11 heavy metals. There were different degrees of correlation as follows: very strong correlations between Zn and W, W and Cr, Cr and Zn ( $p < 0.01$ ); significant correlations between Pb and Cr, Pb and Zn, Pb and W, Ni and V ( $p < 0.01$ ); low linear correlations between Zn and Cu, Zn and Cd, Cu and Cr, Cd and W, Pb and Cu, Pb and Cd, and Cu and Cd. There were very weak or

nonexistent relationships between Co, Mo, and Sb and other heavy metals. The pollution of agricultural soils was mainly due to the various anthropogenic sources entering the agricultural ecosystem through various paths. The results of the Pearson correlation coefficient was only a tool for the auxiliary receptor model to analyze the pollution source.

**Table 3.** Pearson correlation coefficient between different heavy metals.

	V	Cr	Co	Ni	Cu	Zn	Mo	Cd	Sb	W	Pb
V	1	−0.08	0.05	0.52 **	−0.18 **	0.14 *	0.13	0.20 **	−0.05	0.06	−0.16 *
Cr		1	−0.21 **	−0.17 *	0.31 **	0.68 **	−0.01	0.17 *	−0.28 **	0.68 **	0.60 **
Co			1	−0.05	−0.06	−0.16 *	−0.02	−0.05	0.11	−0.12	−0.17 *
Ni				1	−0.18 **	−0.03	0.18 **	0.11	0.10	−0.17 *	−0.20 **
Cu					1	0.40 **	−0.23 **	0.22 **	−0.28 **	0.12	0.26 **
Zn						1	−0.09	0.34 **	−0.48 **	0.71 **	0.48 **
Mo							1	0.10	0.17 *	0.13	0.09
Cd								1	−0.28 **	0.27 **	0.24 **
Sb									1	−0.31 **	−0.19 **
W										1	0.48 **
Pb											1

\* Correlation was significant at  $p < 0.05$  (two-tailed). \*\* Correlation was significant at  $p < 0.01$  (two-tailed).

All data for the 11 heavy metals in the standardized 215 sampling points were imported into EPA UNMIX 6.0 software for analysis. The Min Rsq of the five sources was 0.89 (the minimum of the decision coefficient  $r^2$  was 0.89, that is, the data variance of 89% explained by the model, which was greater than the minimum value 0.8 required by the system), Min Sig/Noise was 2.06 (the minimum signal-to-noise ratio was 2.06, which was greater than the minimum two required by the system); the results showed that the modeling was effective. Most of the residuals of all soil samples were between  $-3$  and  $3$ . The heavy metal concentration predicted by the UNMIX model was closely related to the determined concentration ( $r^2 = 0.997$ ), showing that heavy metals of soil were well apportioned by the UNMIX model. The total was the sum of the heavy metal concentrations at each sampling site. The UNMIX model analyzed the five main sources of heavy metals in agricultural soils around the lake area. The contribution rates of the five sources were 7%, 13%, 20%, 29%, and 31%, respectively. The source composition spectrum is shown in Table 4.

**Table 4.** Source components of heavy metals in soils from the UNMIX model.

Species	Source 1	Source 2	Source 3	Source 4	Source 5
V	−0.008	−0.007	−0.008	0.113	0.287
Cr	−0.073	0.042	0.189	0.097	0.063
Co	0.394	0.029	0.017	0.051	−0.054
Ni	−0.140	0.041	−0.052	0.241	0.292
Cu	−0.038	0.253	0.042	−0.005	0.028
Zn	0.005	0.068	0.176	−0.029	0.138
Mo	0.000	−0.017	0.054	0.314	0.162
Cd	0.214	0.091	0.087	−0.169	0.200
Sb	−0.090	0.029	−0.047	0.461	0.046
W	0.070	−0.045	0.203	0.000	0.069
Pb	−0.033	0.063	0.154	0.131	0.047
Total	0.299	0.548	0.816	1.210	1.280
Source contributions	7%	13%	20%	29%	31%

Source 1 had a high positive load value of Co and Cd in the source component spectrum. Yalcin et al. [25], in a case study carried out in Sultan Marsh, Turkey, found that high concentrations of Co and Cd came from Pb–Zn and Fe ores. Other studies described the presence of Co associated with natural processes [26]. The coefficient of variation of Co was only greater than V ( $CV = 21\%$ ) in agricultural soils around the lake area. This indicates that the distribution of Co content in the soil was relatively uniform, and 92%

of the soil samples had a Co content lower than the background value, which laterally reflected that the soil samples were non-contaminated, and the Co found in the agricultural soils around the lake, mostly came from source 1. From the analysis of source 1, it can be seen that this source was mainly affected by natural sources and, therefore, classified as such.

Source 2 was mainly loaded on Cu, which was also much higher than the other four sources. Copper was generally considered an important source of copper mining and refining [16]. Upstream of the Le'an River, one of the rivers entering into Poyang Lake, there are several copper deposits including the Dexing Copper Mine and the Zhushahong/Fujiawu Copper–Molybdenum Mine, among which the Dexing Copper Mine is the largest open-pit copper mine in Asia [27]. Every day, approximately  $1 \times 10^5$  t flotation tailings are deposited in its 4# tailings pond (with an area of  $14.3 \text{ km}^2$ ), and approximately  $1.3 \times 10^4$  t of acid mine drainage is poured into the 4# tailings pond [28]. The wastewater, tailings, and waste slag discharged from the mining enterprises, including mining, beneficiation, and smelting production activities can lead to Cu pollution in the regional environment [29], and the surrounding areas of Poyang Lake are dotted with many copper industries such as the Guixi and Yongping copper mines and metallurgy. Therefore, source 2 may originate from the discharge of wastewater and waste residue from copper mine tailing ponds, and copper mine tailings could be the source of the pollution.

The contents of W, Cr, Zn, and Pb were significantly higher in source 3 than that of the other four sources. The Pearson correlation results showed that there was a significant positive correlation between these four heavy metals, especially between W and Zn ( $p < 0.01$ ,  $r = 0.71$ ) and with a very similar spatial distribution pattern. In China, fertilizers containing inorganic compounds and minerals are usually the main sources of Zn and Pb in agricultural applications. Some phosphate fertilizers contain Cr up to 30–3000 mg/kg [30]. Moreover, the amount of fertilization per hectare in China is much higher than the world's average level at approximately 55 million tons of fertilizer on farmland every year [31]. According to statistics, it was estimated that a total of 1565 t of Pb and 7847 t of Zn were applied annually as fertilizer products to agricultural land in China [32]. Long-term use of excessive amounts of fertilizers became an important agricultural non-point source pollution; Zn was mainly used for certain sterilization processes of food and as an economic active ingredient for crops. Zn was still a widely used element of many approved pesticides in China [32]. In addition, animal manure was also generally considered to be another major source of Zn in the topsoil [33]. Source 3 was considered to be largely caused by agricultural activities.

Sb, Mo, Ni, and Pb had higher positive loads in source 4, with load values of 0.461, 0.314, 0.241, and 0.131, respectively. The Pearson correlation between Sb, Mo, Ni, and Pb indicated that there was a very weak positive correlation or no correlation between the three metals ( $p < 0.01$ ). According to the survey, Mo mainly originated from the Zhushahong/Fujiawu copper–molybdenum mine in the southeast of the Poyang Lake area. Manta et al. [34] studied the green areas of Palermo (Sicily, Italy) and the surface soil of the park and showed that Sb originated from human activity. Other studies have shown that mining activities and the release of coal consumption were important sources of Ni and Pb emissions. The high content of Pb was related to industrial activity, with the combustion of coal and atmospheric deposition [35,36]. In addition to the mineral resources mentioned above in the study area, Fengcheng and Pingxiang in the lower reaches of the Ganjiang River Basin and Yongshan Coal Mine in the middle and lower reaches of the Le'an River were the main coal mines in Jiangxi Province. Industrial mining activities and coal combustion release gaseous pollutants containing Sb, Mo, Ni, and Pb, which are mainly accumulated in the surrounding soils through atmospheric deposition and precipitation, causing enrichment of the contents of Sb, Mo, Ni, and Pb in agricultural soils, exceeding the natural background levels. Therefore, source 4 was related to atmospheric deposition pollution.

Source 5 was mainly composed of Ni, V, Cd, Mo, and Zn. Industrial activities of metal ore mining and smelting operations were considered to be one of the most important sources of metal pollution [37]. In this study, the coefficient of variation of V was the smallest (CV = 15%), the distribution in the soil was relatively uniform, and in 96% of soil samples, it was lower than its background value. The high coefficient of variation might reflect stronger human influence. Cd had the largest CV (61.35%), indicating the influence of human sources; in approximately 92.56% of samples, the Cd content was higher than the background value, so it was attributed to an artificial activity. In China, many scientific studies showed that Ni came from mining and other industries, including smelting ore, steel production, and metal processing, over many years of activity [8,38]. The metallurgical industry is considered to be one of the main sources of Cd [39]. Cd was a common impurity in Zn and Pb ores, generated mostly during the production of Zn. The smelting production was mainly to recover Zn and Pb, and Cd, which cannot be recycled [40], was released into the environment. In light of the survey, there was a Yinshan lead–zinc mine in Dexing City, southeast of Poyang Lake District, which was usually accompanied by a high Cd content. The development and utilization of mineral resources and the metal smelting process will generate a large amount of “three wastes” and discharge them into the environment. It can be seen from Figure 2 that the areas where the contents of Cd and Mo in agricultural soil exceeded their background values were basically throughout the entire range. Therefore, source 5 can be considered as a source of industrial activity pollution.

The UNMIX model was used to analyze the source of heavy metals in agricultural soils around the lake. The results showed that the main sources of heavy metals in agricultural soils around the lake were industrial activity pollution sources, accounting for 31% of all pollution sources, followed by atmospheric deposition, with a contribution rate of 29%. This was followed by agricultural activities (20%) and copper mine tailings pollution sources (13%). The contribution rate from natural sources was the smallest at 7%. Therefore, human activities had a great influence on heavy metals in agricultural soils around the lake area, which cannot be ignored. In view of this, small-scale mining enterprises should be properly conditioned and restrict releases. The “three wastes” released from industrial and mining enterprises should be strictly controlled, and appropriate measures should be taken to prevent atmospheric subsidence, and tailings should be repaired and treated as required to vigorously strengthen the management of heavy metal pollution around the lake area. It is needed to intensify efforts to optimize the industrial structure. In agriculture, farmers are encouraged to use organic fertilizers to develop ecological recycling agriculture.

#### 4. Conclusions

Except for V, Cr, and Co, the average content of Ni, Cu, Zn, Mo, Cd, Sb, W, and Pb in agricultural soils around the lake area exceeded the background value of Jiangxi Province. Cr, Ni, Cu, Zn, Cd, and the average content of Pb were lower than the screening value of agricultural land soil pollution risk in China. The percentage of Cd content in all sampling points exceeded the screening value of agricultural land soil pollution risk; at 55%, this indicates a pollution risk by Cd.

The background value rates of all heavy metals in sampling sites in Poyang County was lower than that in other regions, while the background value rate of all heavy metals in sampling sites in Nanchang County, Jinxian County, and Xinjian District ranks in the top three. This may be caused by emissions of the “three wastes” from enterprises in the industrial bases in Nanchang urban areas, as well as the domestic sewage and pollutants from the agricultural non-point sources in the towns surrounding the county.

The UNMIX model analyzed five pollution sources of heavy metals in agricultural soils around the lake area. The major pollution inputs in source 1 were Co and Cd, classified as a natural source with a contribution rate of 7%. In source 2, it was Cu, mostly due to the fact of copper mine tailings and with a contribution rate of 13%. In source 3, the main pollutants were W, Cr, Zn, and Pb, associated with agricultural activities, with a

contribution rate of 20%. In source 4, the pollution related to Sb, Mo, Ni, and Pb was attributed to atmospheric deposition phenomena with a contribution rate of 29%. The main pollutants of source 5 were Ni, V, Cd, Mo, and Zn, mostly derived from industrial activities with a contribution rate of 31%. The correlation coefficient of the measured and predicted values of the total species of the UNMIX model reached 0.998, indicating that the results of the source apportionment of the model for heavy metals in agricultural soils around the lake area were more accurate and reasonable.

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