Source Apportionment and Model Applicability of Heavy Metal Pollution in Farmland Soil Based on Three Receptor Models

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Source apportionment and model applicability of heavy metal pollution in farmland soil based on three receptor models

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Abstract: The identification of the source of heavy metal pollution and its quantification are the prerequisite of soil pollution control. The APCS-MLR, UNMIX and PMF models were employed to apportion pollution sources of Cu, Zn, Pb, Cd, Cr and Ni of the farmland soil in vicinity of an abandoned iron and steel plant. The sources, contribution rates and applicability of the models were evaluated. The potential ecological risk index revealed greatest ecological risk from Cd. The results of source apportionment illustrated that APCS-MLR and UNMIX models can verify each other for accurate allocation of pollution sources. The industrial sources were the main sources of pollution (32.41% ~ 38.42%), followed by agricultural sources (29.35% ~ 31.65%), traffic emission sources (21.03% ~ 21.51%), and natural sources of pollution were accounted for smallest proportion (11.2% ~ 14.42%). The PMF model was easily affected by outliers, its fitting degree was not ideal, and it was unable to get more accurate results of source analysis. The combination of multiple models can effectively improve accuracy of pollution source analysis of soil heavy metals. These results can provide a scientific basis for further remediation of heavy metal pollution in farmland soil.

Keywords: Heavy metals; Source apportionment; APCS-MLR; UNMIX; PMF.

1. Introduction

Soil is an important material basis for agricultural production and human survival(Drobnik et al., 2018). In recent decades, with gradual increase in population and rapid development of industry and agriculture, the problem of heavy metal pollution in farmland soil in China has become a crucial problem (Chen et al., 2008; Yang et al., 2017). Heavy metals in farmland soil are highly related to safety of agricultural products, which has attracted worldwide public attention (Chabukdhara and Nema, 2013; Shi et al., 2017). Heavy metals can not only threaten soil quality and ecological

environment, but can accumulate in human body with transmission of food chain(Zhao et al., 2012; Guan et al., 2018). The measures should be taken to control and remediate heavy metal pollution in farmland soil, which is essential to ensure quality of soil environment and safety of agricultural products. Furthermore, assessment of the current status and sources of soil heavy metal pollution is a prerequisite for effective prevention of pollution.

Heavy metals in soil mainly originated from soil parent materials and human activities. Heavy metals contained in parent materials are enriched in the soil by weathering and leaching(Huang et al., 2015). Human activities mainly include high-intensity industrial and mining activities, agricultural activities and transportation, which contribute heavy metals to farmland soil through atmospheric deposition, sewage irrigation, fertilizer input and solid waste (Lu et al., 2014; Shi et al., 2018; Sun et al., 2019). Existing methods of source apportionment of heavy metals can be roughly divided in two categories, one is qualitative source identification, the other is quantitative source apportionment(Huang et al., 2018). The former mainly uses multivariate statistical analysis (principal component analysis, cluster analysis, correlation analysis, etc.) and geostatistical analysis to identify major pollution sources(Slavković et al., 2004; Luo et al., 2011; Yuan et al., 2015). The latter uses physical and chemical characteristics of pollutants in receptor to identify pollution source and to quantify its contribution rate(Huang et al., 2018).Among receptor models, absolute principal component scores-multivariate linear regression(APCS-MLR), UNMIX and positive matrix factorization (PMF) were widely used in source apportionment of heavy metals in soils(Lang et al., 2015; Bilal et al., 2019; Jin et al., 2019). APCS-MLR combines factor analysis and multiple linear regression to quantify pollution sources, with simple operation and fast calculation speed (Liu et al., 2019). The UNMIX model automatically removes unreasonable data through the system built in the

model, and does not need to set the number and uncertainty of pollution sources, which reduces the impact of human factors(Ogundele et al., 2016). The PMF model limits the factor scores and factor loads to be non-negative during solution process, which can handle missing and inaccurate data (Lu et al., 2018). The receptor models are widely used to perform source apportionment of atmosphere, water, sediment and soil(Fei et al., 2016; Ogundele et al., 2016; Sun et al., 2016; Chen et al., 2019).

The research on source apportionment of heavy metals has mainly focused on analysis of potential pollution sources and their contributions in contaminated sites, but applicability of receptor models is rarely considered. Since soil is not a homogeneous body, it has a high degree of spatial heterogeneity(Zhang, 2006). The types, quantity and pollution status of pollution sources are different in different regions. The analytical results of receptor model are affected by factors such as sample data value errors and modeling errors, using a single receptor model which cannot obtain information of pollution source accurately, and its conclusion is controversial. Therefore, this study has employed several commonly used source analysis methods to analyze sources of heavy metals and to assess potential risks of heavy metals in farmland soils. The variation between validation models was compared and its causes were analyzed to accomplish more reliable results of source apportionment and to set a perfect foundation for prevention and control of heavy metal pollution in farmland soil.

The objectives of this study are: (1) to investigate the soil heavy metal pollution in the study area; (2) to analyze the sources and contributions of heavy metals in the study area by using APCS-MLR, UNMIX and PMF models, and compare the applicability of the models; (3) to evaluate the potential impact of heavy metal pollution in the study area in terms of ecological risk.

2. Materials and methods

2.1Study area

The study area is located in the southeast of China, a town of Lishui City, Zhejiang Province. The study area covers an area of 2.12km^2, ranging from 119°42′44.7″~119°42′5.5″E and 27°46′50.6″~27°47′54.3″N. The study area belongs to subtropical monsoon climate zone, with annual average temperature and precipitation of 17.8 ℃ and 1568.4mm respectively. The northeast wind prevails in the study area. The farmland in the study area is in vicinity of the township residential area. The waste steel plant is located in the south of the study area, and bamboo processing plant is in the east (Fig. 1). The farmland is terraced field, and the river flows from south to north. The water for farmland irrigation mainly comes from rainfall and river water pumping irrigation. The main crop in the study area is single cropping rice.

2.2. Sample collection and preparation

According to grid density of 50 m×50m, 101 surface soil samples (0-20 cm) were collected. Each soil sample was composed of 5 subsamples, one in the center and four in the surrounding area. The samples were put into PVC bags and coordinates of sampling points were recorded. The four soil profile samples were collected. The sampling point map is shown in Figure 1.The soil samples were air dried with natural conditions and visible intrusion of plants from samples were removed. The air dried soil samples were passed through a 2mm aperture sieve. The grounded samples were passed through a 100 mesh sieve, and stored in sample bags. The soil pH was measured by pH meter with soil water ratio of 1:2.5. Soil organic matter (SOM) was determined by heating mixture of potassium dichromate and concentrated sulfuric acid at 180℃, and then titrated with ferrous sulfate solution. The content of heavy metals was determined by HF (7ml) - HNO_3 (5ml) - $HClO_3$ (1ml) mixed solution. After decocting, the samples were filtered with constant volume and stored for

testing. The contents of copper (Cu), zinc (Zn), lead (Pb), chromium (Cr) and nickel (Ni) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Leeman prodigy 7 USA). The cadmium (Cd) was analyzed by graphite furnace atomic absorption spectrometry (GFAAS, PerkinElmer AA800, USA). The accuracy of measurement was verified with Chinese Standard Reference Material (GSS-5). The recovery of each element was in the range of 90%-110%. The detection limits of Cr, Pb, Cu, Zn, Ni, and Cd were 0.004, 0.003, 0.002, 0.002, 0.004 and 0.002mg/kg, respectively. All data are the average of three replicates.

2.3Source apportionment models

2.3.1 Absolute principal component scores-multivariate linear regression (APCS-MLR)

The APCS-MLR was proposed by Thurston and Spengler in 1985. According to results of principal component analysis, the factor score was transformed to normalized factor score, and multiple linear regression was performed on receptor content. The contribution rate of pollution source corresponding to each factor of the substance in the receptor was calculated with regression coefficient as follows:

$$Z_{ij} = \frac{C_{ij} - \overline{C_i}}{\sigma_i} \tag{3.1}$$

$$(Z_0)_i = \frac{0 - \overline{C_i}}{\sigma_i} = -\frac{\overline{C_i}}{\sigma_i} \tag{3.2}$$

$$APCS_p = (Z_0)_i - Z_{ij} \tag{3.3}$$

$$C_i = b_{0i} + \sum_{p=1}^{n} (APCS_p \times b_{pi}) \tag{3.4}$$

Where C_{ij} is the content of heavy metal *i* at the *j*th sampling point; $\overline{C_i}$ is the mean content; σ_i is the standard deviation; Z_{ij} is normalization matrix of element content; $(Z_0)_i$ is the factor score of "zero" pollution point, where all element contents are equal to 0. The principal component analysis was conducted for Z_{ij} and $(Z_0)_i$,*p* is the number of factors obtained in principal component

analysis. The $APCS_p$ is absolute principal component scores;b_{0i} is a constant term obtained by multiple linear regression for metal element *i*; $b_{pi}$is the linear regression coefficient of element *i* on factor *p*. The contribution of each source was calculated by b_{pi} and $APCS_p$.

2.3.2 UNMIX model

The UNMIX model is a receptor model developed by the U.S. Environmental Protection Agency. Based on the contribution of different pollution sources to receptor (soil), it is a linear combination of different source components(Henry, 2003). The equation is listed below:

$$C_{ij} = \sum_{k=1}^{m} F_{jk} S_{jk} + E \tag{3.5}$$

Where, the C_{ij} is the content of heavy metal *i* in the *j*th sampling point, F_{jk} is the percentage of element *j* in the *k* source, S_{ik} is the contribution of *k* source in sample *i*, and *E* is the standard deviation of analysis. The source component spectrum parsed by model needs to meet minimum system requirements that can be interpreted by the model (Min Rsq>0.8, Min Sig/Noise>2).

UNMIX model was standardized before importing data to the model. The data were dimensionless and value range of observation value was between 0-1. The standard formula of dispersion was as follows (Zhang et al., 2019):

$$X_k = \frac{X_i - X_{i\ min}}{X_{i\ max} - X_{i\ min}} \tag{3.6}$$

Where X_k is the value after deviation standardization, X_i is the initial analysis value of the sample, $X_{i\ \mathrm{min}}$ is minimum analysis value, $X_{i\ \mathrm{max}}$ is maximum analysis value.

2.3.3Positive matrix factorization (PMF)

PMF model is a multivariate factor analysis tool, which decomposes the receptor concentration data matrix into factor contribution matrix and factor distribution matrix under non negative constraint(Jiang et al., 2020). The goal of PMF is to analyze pollution sources and source

contributions based on synthetic data sets(Lv, 2019). The calculation method is as follows:

$$X_{ij} = \sum_{k=1}^{p} G_{ik} F_{kj} + E_{ij} \tag{3.7}$$

Where: X_{ij} is concentration matrix of the jth heavy metal in the ith sample; G_{ik} is the contribution of the kth source to sample i;F_{kj} is the value of the kth source to concentration of heavy metal j, and p is the number of factors; E_{ij} is the residual.

The PMF model is defined and iterated on the basis of weighted least square method. The factor contribution and distribution were obtained by minimizing the objective function Q of the PMF model(Xue et al., 2014). The calculation method is as follows:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{E_{ij}}{U_{ij}} \right)^2 \tag{3.8}$$

Where U_{ij} is uncertainty of element j in sample i.

The PMF model was run with concentration data and uncertainty data. The uncertainty data includes sampling and analysis errors(Tan et al., 2016). In this study, the contents of Cu, Zn, Pb, Cd, Cr, Ni in the soil were all higher than detection limit *MDL*. The calculation method of uncertainty *Unc* was as follows:

$$U_{nc} = \sqrt{\left(\theta \times C_{ij}\right)^2 + (MDL)^2} \tag{3.9}$$

Where: C_{ij} is concentration of heavy metal i in the jth sample; *MDL* is the detection limit of the sample; θ is the relative standard deviation; signal to noise ratio (S/N) can be calculated by PMF, S/N> 2 can be considered as good data quality, and the sample with 0.2 <S/N <2 can be considered as poor data quality, unable to provide sufficient concentration change(Sharma et al., 2016).

2.4Potential ecological risk index

Potential ecological risk index (*RI*) combines ecological and environmental effects of heavy

metals with toxicology (Wu et al., 2018). The calculation formula for *RI* is as follows:

$$E_r^i = T_r^i \times (\frac{C_i}{S_i}) \tag{3.10}$$

$$RI = \sum_i^n T_r^i \times (\frac{C_i}{S_i}) \tag{3.11}$$

where T_r^i is the biological toxicity of different elements *i*, which was determined as Zn = 1 < Cr=2 < Cu =Ni =Pb = 5 < Cd = 30. The C_i is measured value of heavy metal *i* (mg·kg^{-1}), S_i is the reference value of heavy metal *i* in soil (background value in Zhejiang Province). E_r^i represent potential ecological risk factors.*RI* is the comprehensive potential ecological risk index of heavy metals. E_r^i< 40, *RI* < 150, indicates low potential ecological risk; 40 ≤E_r^i< 80, 150 <*RI*< 300 indicate moderate potential ecological risk; 80 ≤ E_r^i< 160,300 ≤*RI*< 600 shows considerable potential ecological risk; 160 ≤ E_r^i< 320, 600 ≤ RI < 1200 exhibit high potential ecological risk; E_r^i ≥ 320, *RI* ≥ 1200 reveal very high potential ecological risk.

2.5. Data processing and statistical analysis

The soil sampling points in the study area was located with ArcGIS 10.2; The descriptive analysis, correlation analysis and APCS-MLR model calculation was conducted with SPSS 22.0. The analysis chart was drawn with Oringin8.5. The source apportionment of heavy metals was determined with PMF model (EPA PMF 5.0) and UNMIX model (EPA UNMIX 6.0).

3.Results and discussion

3.1Descriptive statistical analysis of heavy metals in soil

Table 1. reveals descriptive statistical analysis of heavy metal (Cu, Zn, Pb, Cd, Cr, Ni) and physical and chemical properties of farmland soil in the study area. The pH of soil acidic and ranged from 3.94 to 5.37. The mean contents of Cu, Zn, Pb, Cd, Cr and Ni were 30.26,271.50,151.41,0.37,67.81and 29.07mg·kg^{-1}, respectively. The average contents of heavy

183 metals in the study area were 1.72, 3.85, 6.39, 5.33, 1.28 and 1.18 times of their background values
184 respectively compared with background values of Zhejiang Province(Wang et al., 2007). The over
185 standard rates of Cu, Zn, Pb, Cd, Cr and Ni in soil were 3.96%, 86.14%, 97.03%, 70.30%, 0%,
186 0.99%, respectively compared with screening values of agricultural soil environmental risks in
187 China (GB 15618-2018). The coefficient of variation (CV) reflect variability and dispersion of
188 heavy metal elements in soil. The strong variability indicates that spatial distribution of heavy metals
189 was seriously affected by external factors (McGrath et al., 2003; Gallardo and Paramá, 2007). The
190 CVs of heavy metals can be classified as follows: CV ≤ 15% means weak variation, 15% < CV <36%
191 means moderate variation, CV ≥36% means high variation. The CV of Pb, Cd, Ni in the study area
192 were 38.5%, 40.17%, 39.03%, which indicate high variation. The elements of other heavy metals
193 showed moderate variation, which showed that external factors had a significant impact on
194 accumulation of heavy metals in soil.

195 *3.2Heavy metal content in soil profile*

196 Four profiles were collected in the study area. Fig2. demonstrates depth distribution of soil pH,
197 organic matter (OM) and heavy metals in soil profiles. The pH value of surface (0-20 cm) soil was
198 lowest compared with highest of bottom (60-80cm) soil. Excessive use of nitrogen fertilizer has led
199 to serious acidification of agricultural soil in China. The nitrogen fertilizer has been identified as the
200 main driving force of acidification in farmland soil by affecting process of nitrogen transformation
201 (Hao et al., 2020). The content of SOM in topsoil was highest and decreased with increase of depth,
202 which was mainly attributed to application of fertilizer in farmland soil and popularization of straw
203 returning technology(PAN et al., 2004; Xiao-Lin et al., 2021). The contents of Cu, Zn, Pb, Cd and
204 Ni in surface soil were significantly higher than deep soil (40-60 cm) and bottom soil (60-80 cm)

soil, which indicated that these heavy metals were greatly affected by input of external activities. The content of Cr in the bottom (60-80 cm) soil was significantly higher than surface soil (0-20 cm), which indicated that Cr was mainly affected by soil parent material. The contents of SOM and Cu in P3 were significantly higher than other three sections which illustrated that the area was greatly affected by agricultural activities. However, the Zn and Pb contents in P1 were significantly higher than other three sections, which has confirmed the sources of potential heavy metal pollution in this area.

3.3 Results of three models

The source distribution of heavy metals in the study area was analyzed with APCS-MLR, UNMIX and PMF models. The APCS-MLR has extracted four factors, which accounted for 88.58% of the data variance. The explained variances were 25.13%, 25.0%, 20.91% and 17.6% respectively. The PMF model has set the number of factors 4 ~ 7 and the number of runs was 20. The optimal number of factors was finally determined to be 4 after comprehensive trial calculation of Q value. The UNMIX model resolves 4 factors, among which Min Rsq=0.95, Min Sig/Noise=2.03, which meets minimum value required by the system (Min Rsq>0.8, Min Sig/Noise>2).

Fig. 3(a, b, c) exhibits composition of factors was analyzed by APCS-MLR, PMF and UNMIX models. The factor components of APCS-MLR and UNMIX model were similar. In factor 1, Cu and Ni had higher loads. Factor 2 was Cd and Zn, factor 3 was Pb, and factor 4 was Cr. In addition, the fitted parameters with three models were described in Table 2. The minimum value of $r^2$was Cu (0.79) in APCS-MLR, and r^2 of the other heavy metal elements was greater than 0.8 both in APCS-MLR and UNMIX, which reveals ideal fitness of the two models. In PMF model, the factor composition was quite different from APCS-MLR and UNMIX. The Factor 1 was dominated by Cu,

227 Zn, Pb, Cd, Ni, factor 2 was Cu, Zn, Pb, Cr, Ni, factor 3 was Cd, and factor 4 was Cr., The r^2 between
228 predicted and observed values of Cu, Cd and Ni in PMF was close to 1 according to components
229 fitting results (Table 2). The r^2 of Zn, Pb and Cr were 0.402, 0.119 and 0.403 respectively however,
230 fitness of results was not ideal. The studies revealed that PMF model was abnormally sensitive to
231 outliers, and can not acquire reasonable results without elimination of outliers.

232 The 13 sampling points were deleted according to unified residual value of each point until Q_{robust}
233 and Q_{ture} were in proximity to unreliable results of source analysis using complete data in PMF. Four
234 factors were obtained in PMF, the factor composition was presented in Figure 3 (d)., The proportion
235 of factor 1 in each heavy metal element increases compared with complete data, while proportion
236 of factor 3 decreases after excluding abnormal values. The fitness of the model has improved, r^2
237 values of Zn, Pb, and Cr and its observed r^2 values were 0.448, 0.213, and 0.61, respectively.
238 However, no more reliable fitting results were obtained, which was consistent with results of Xue
239 et al(Xue et al., 2014).

240 *3.4Source apportionment of heavy metals in soil*

241 The composition of pollution sources of APCS-MLR and UNMIX models were similar. In the
242 composition spectrum of factor 1 (Fig.3), the load of Cu and Ni was higher than other elements. The
243 Zn, Pb, Cd and Cr were distributed in a small amount. The studies reported that human activities
244 could significantly change spatial characteristics of Ni in soil, and diffusion of Ni in environment
245 was mainly affected by atmospheric deposition and sewage irrigation(Li et al., 2009; Huang et al.,
246 2019). In industrial enterprises, iron and steel plant was a significant source of heavy metal pollution.
247 In the past few decades, due to lack of environmental protection technology to address the dust and
248 waste produced in the iron and steel smelting process, the Cu content in the surrounding soil was 5

times higher than background value(Orescanin et al., 2004). The study of heavy metal content in soil near a steel plant in Serbia showed that concentrations of Cd, Cu, Ni, Pb and Zn were higher than reported in European soils and higher than world average(Dragović et al., 2014). The abandoned iron and steel plant was located in the north of the study area, in the upper reaches of the river, and the terrain was higher than farmland. Dust and sewage generated in the process of steel smelting and processing were accumulated in soil with atmospheric sedimentation, rain erosion and farmland irrigation. Therefore, factor 1 represented industrial pollution source.

In factor 2, the calculation results of APCS-MLR and UNMIX models suggested that Cd and Zn were marker elements (Fig. 3a, b). Pearson correlation analysis results of heavy metal content and physical and chemical properties in soil are reported in table 3.SOM has significant correlation with Cd and Zn at $P<0.05$, and its correlation coefficients were 0.487 and 0.437, respectively. As discussed in the previous sections, Cd usually exists in phosphate rock, and as chemical fertilizers, especially phosphate fertilizers, were brought to farmland soil(Lu et al., 2012). The Zn was widely used in livestock feed as additives, which was excreted out of the body with feces(Yang et al., 2016). Long term application of chemical fertilizer, organic fertilizer and animal manure in agricultural activities will enhance concentration of Zn and Cd in soil. (Bigalke et al., 2017; Zhuang et al., 2020). According to field survey, the farmers bred livestock and poultry directly in the farmland after harvest, which transferred heavy metals to soil from manure of livestock. In addition, this was an important reason why the content of SOM in this study was significantly higher than average level of Zhejiang Province. Accordingly, factor 2 could be identified as agricultural source.

Factor 3 represent transportation which is major cause of pollution due to Pb, Cu and Zn. Due to combustion of fuels and use of engine catalysts, Pb was main indicator of traffic emissions(Xiao et

al., 2019; Wang et al., 2020). Although the production, sale and use of leaded gasoline have been banned since 2000, the accumulation of Pb in soil has not been eliminated (Chen et al., 2016).The Cu is usually used in metal parts of automobiles. The Zn in surface soils is related to wearing of tires and corrosion of galvanized parts(Smichowski et al., 2008; Cai et al., 2019). In this study area, a large number of farmland is distributed along the road. The major cause of Pb, Cu and Zn pollution of farmland soil was due to road dust. Furthermore, in profile 1(Fig.2), the Pb content in topsoil was significantly higher than other three sections of soil. The heavy metal (Pb) in the soil was enriched by intensive transportation. In factor 4, the ratios of Cr determined by APCS-MLR and UNMIX models accounted for 79.75% and 93.37% of the total, respectively. The concentration of Cr in the study area was significantly lower than background value. According to the soil profile analysis (Fig. 2), Cr in the soil originated from parent material, which had been verified in previous studies (Franco-Uría et al., 2009; Cai et al., 2012). Therefore, factor 4 represents natural sources.

In the PMF-1 model, the main elements in factor 1 were Cr and Cu, but Zn, Pb and Ni have large loads; in PMF-2, the proportion of heavy metal elements in factor 1 was significantly increased, which indicated that due to calculation of PMF, the natural source accounts for large proportion, so factor 1 is the natural source. In factor 2 of PMF-1, Cu and Ni account for large proportion, representing industrial pollution sources; PMF-2 subdivides industrial pollution sources in factor 2 and factor 3. Factor 2 represents atmospheric deposition pollution source, and factor 3 represents irrigation water pollution source. Previous studies on heavy metal input flux of farmland soil reported that input percentage of Cr from atmospheric deposition was highest, followed by irrigation. The percentage of Ni entering farmland through irrigation was highest(Chen et al., 2018). In PMF-1, the main elements in factor 3 was Cd, Cu, Zn and Pb, in which Cd, Cu, Zn were significantly

correlated with SOM content, and Pb was main indicator of traffic emission., The factor 3 was mixed pollution source of organic fertilizer input and traffic emission. The main element of factor 4 was Cd, mainly from chemical fertilizer. In PMF-2, the main elements in factor 4 were Cd and Zn, which were the comprehensive sources of organic fertilizer and chemical fertilizer.

3.5Source contribution analysis

, The contribution of each pollution source as calculated by three models of APCS-MLR, PMF and UNMIX is demonstrated in Fig.4. The proportions of industrial sources, agricultural sources, traffic emission sources, and natural sources in the APCS-MLR model are 32.41%, 31.65%, 21.51% and 14.42% respectively. The proportions of the above four sources are 38.42%. 29.35%, 21.03%, 11.2% in UNMIX model. The contributions of natural sources, industrial sources, mixed sources of organic fertilizer and traffic emissions, and chemical fertilizer sources are 41.88%, 27.7%, 20.35% and 10.06% respectively in PMF-1. The contribution rates of natural sources, atmospheric deposition, irrigation and fertilizer sources are 48.84%, 22.47%, 13.78% and 14.91% respectively in PMF-2.

According to contribution rate of three models, the results of APCS-MLR and UNMIX model are consistent. The composition and contribution of pollution sources are highly similar, which indicates that results of source apportionment are reliable. The natural sources account for largest proportion in PMF model. Except Cr, other elements in factor 1 have high load. The correlation analysis indicates that Cr is significantly correlated with Cu ($P < 0.05$), and correlated with Ni ($P < 0.1$). Which indicated that Cr, Cu and Ni have common sources. The Zn and Pb in factor 1 are from other pollution sources. It was observed that the fitting effect of Zn and Pb is the worst in the PMF model analysis process (table 2), which may be due to wide sources of Zn and Pb in the study area and its

high content in the soil. Several areas were interfered by a variety of pollution sources with high intensity and long pollution time, due to which PMF model was unable to accurately identify their pollution sources. The proportion of natural sources in PMF model increased significantly after elimination of outliers, which indicated that PMF model is very sensitive to outliers. The contribution of corresponding pollution sources will be underestimated after exclusion of outliers. The PMF model will minimize Q value of the objective function if outliers are retained. The model itself will give priority to fitting of outliers., As a result, the factor contribution tends to outliers, and accurate source analysis data can not be obtained. Therefore, influence of outliers on analytical results of PMF model should be carefully considered in the selection of receptor model.

3.6Evaluation of potential ecological risk index

The potential ecological risk index has evaluated pollution of heavy metals in the soil of study area (table 4). The results showed that average risk index of heavy metals in the soil of the study area was Cd (160.01) > Pb (31.94) > Ni (10.69) > Cu (8.60) > Zn (3.85) > Cr (2.56). The mean value of Cd indicated a strong ecological risk degree, and Cd showed a very strong risk degree in a few sampling points. The comprehensive potential ecological risk index ranged from 92.37 to 489.68, with an average value of 217.65. There was a large difference in the risk level, and overall risk level was medium. The contribution of Cd to comprehensive potential ecological risk was 73.52%, which was the main source of potential ecological risk of heavy metals in the study area.

4. Conclusion

The pollution of heavy metals Pb, Zn and Cd in farmland soil is more serious due to rapid development of industry and agriculture. The Cu, Zn, Pb, Cd and Ni were enriched in topsoil, while Cr was mainly affected by soil parent material. The potential ecological risk index revealed that Cd

was the main element causing risk of heavy metal pollution in the region. The sources of heavy metals in soil were analyzed with APCS-MLR, UNMIX and PMF models. The industrial sources, agricultural sources, traffic emission sources and natural sources accounted for 32.41% (38.42%), 31.65% (29.35%), 21.51% (21.03%) and 14.42% (11.2%) respectively. These two models can better explain the source and contribution of heavy metal pollution in soil, and are more appropriate for this kind of study. However, the PMF model can be easily affected by outliers, and the fitting effect of Zn and Pb is not ideal, which leads to its high proportion in natural sources, which reduces credibility of source apportionment results. The APCS-MLR and UNMIX models are more appropriate for this study. According to potential ecological risk index, Cd has greatest ecological risk. Therefore, in the process of soil pollution control, priority should be given to control the harm of Cd to local ecological environment. The receptor model should be carefully selected in the process of soil heavy metal source apportionment. The comprehensive application of multiple models can facilitate improvement in reliability of source apportionment results.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors confirm that the data and materials supporting the findings of this study are available within the article.

Author contribution

Under the supervision of Liu Dan, Hong Liu and Shiyan Liao performed sample preparation and data analysis, wrote the first draft. Gul Rukh reviewed and edited the writing. Dongtao Wu, Xiangdong Wu and Zhenhua Chen managed the project. Linlin Xiao and Bin Zhong carried out sample preparation and experimental operation. All authors read and contributed to the manuscript.

Animal research

No animals were used in this experiment.

Consent to Participate and Consent to Publish

Informed consent was obtained from all individual participants included in the study.

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Figures

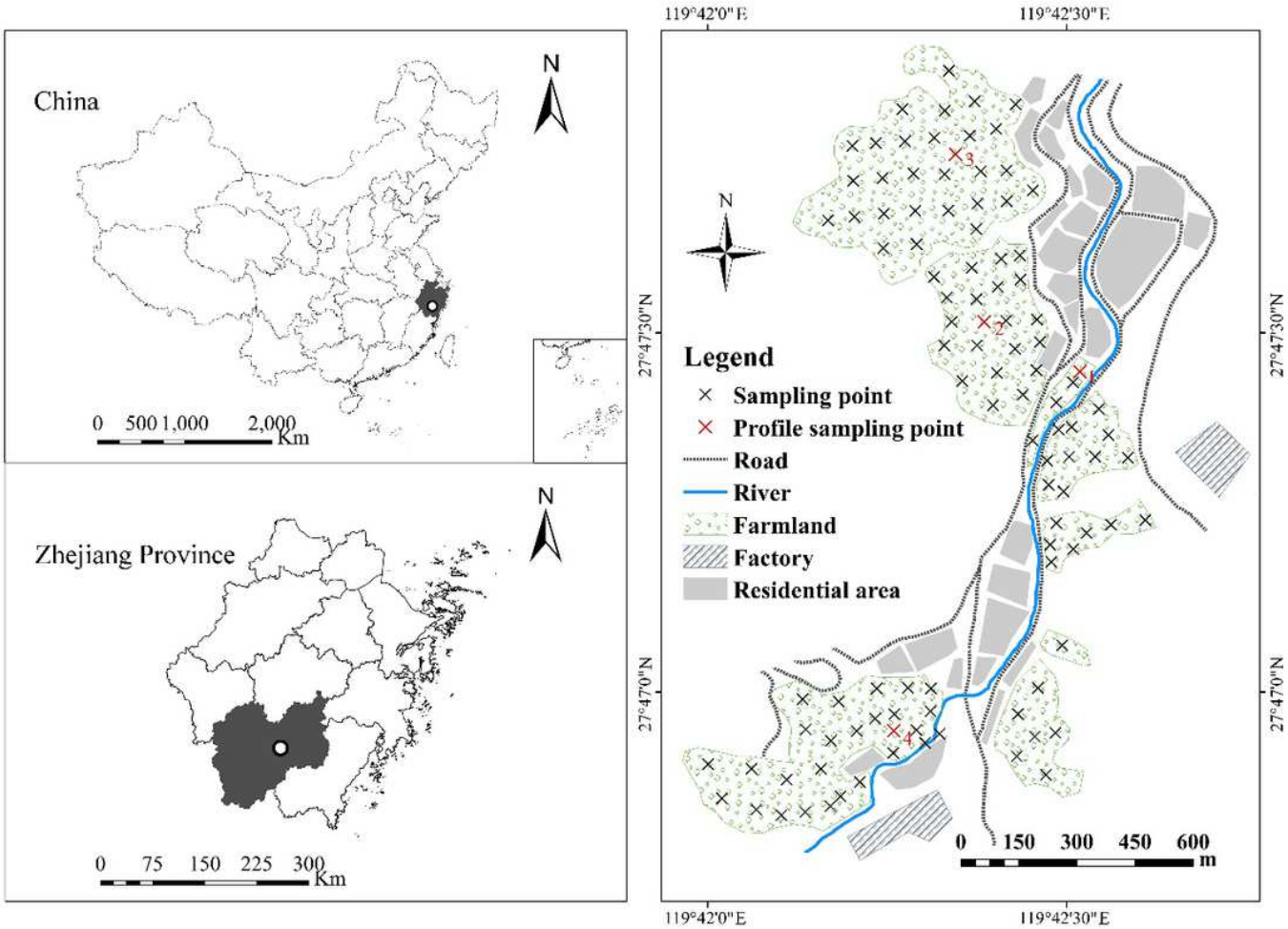

Figure 1

Distribution of sampling sites in the study area.

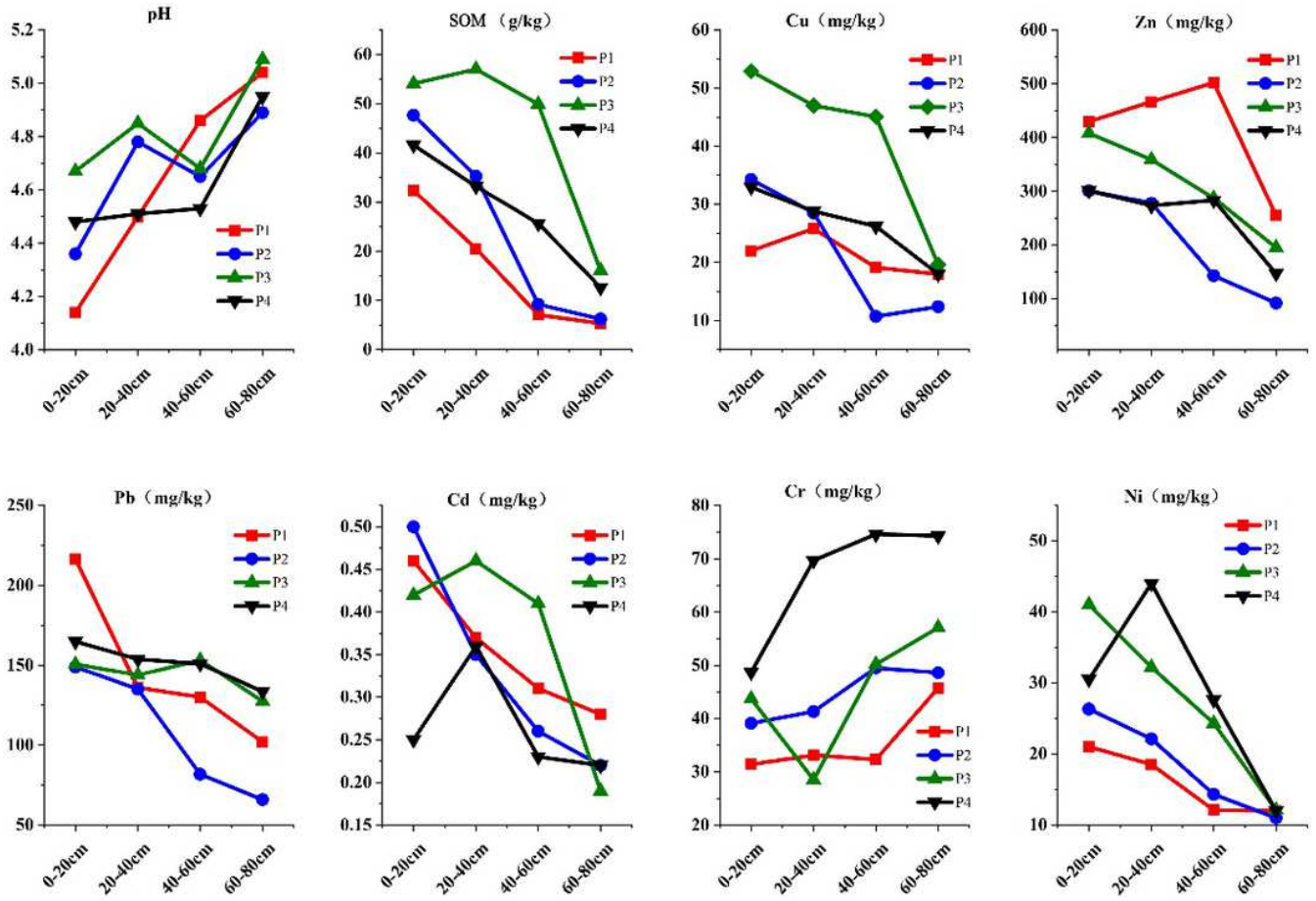

Figure 2

Distribution of heavy metals, pH and organic matter in soil profile

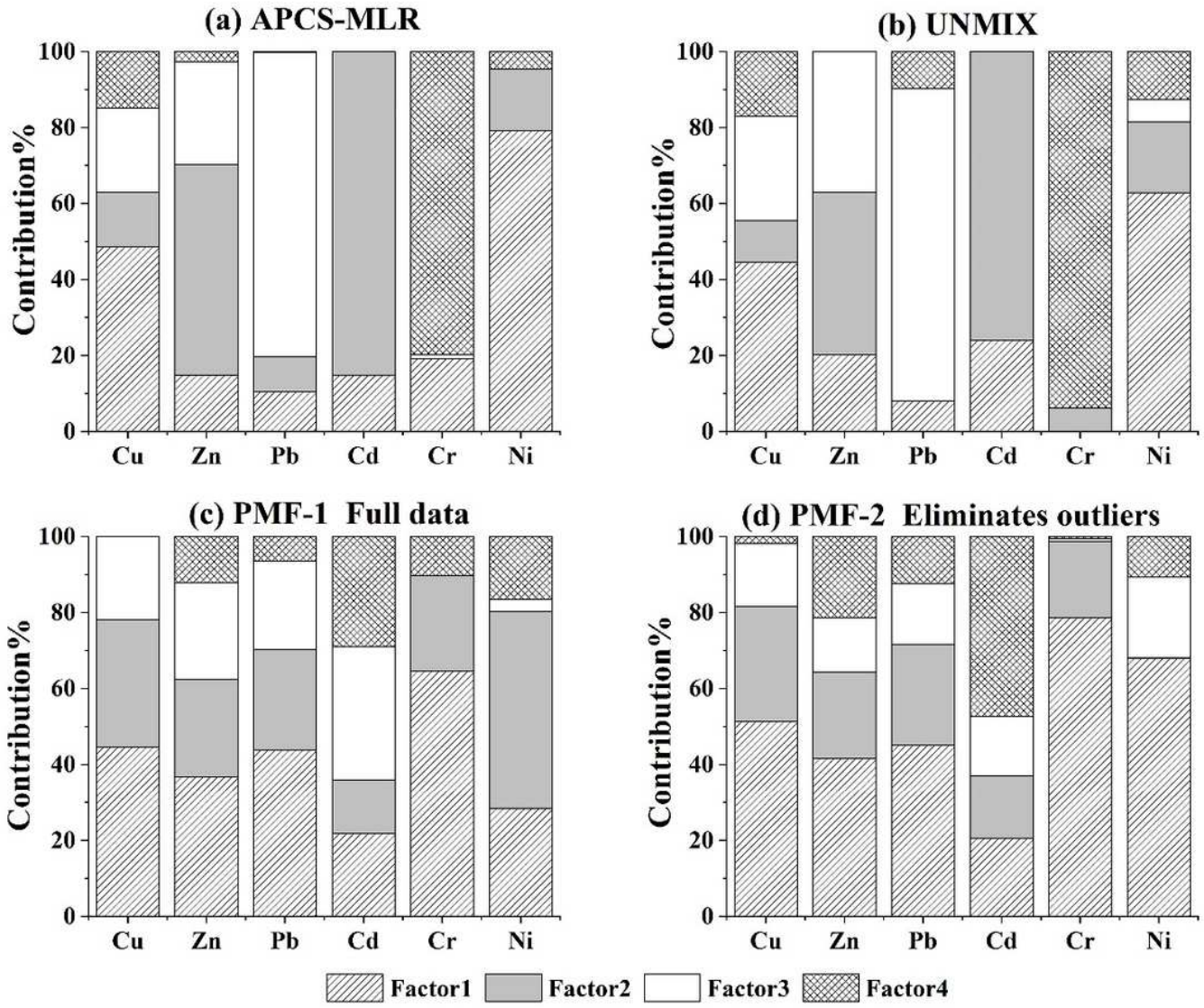

Figure 3

Source factor analysis of soil heavy metals in the study area

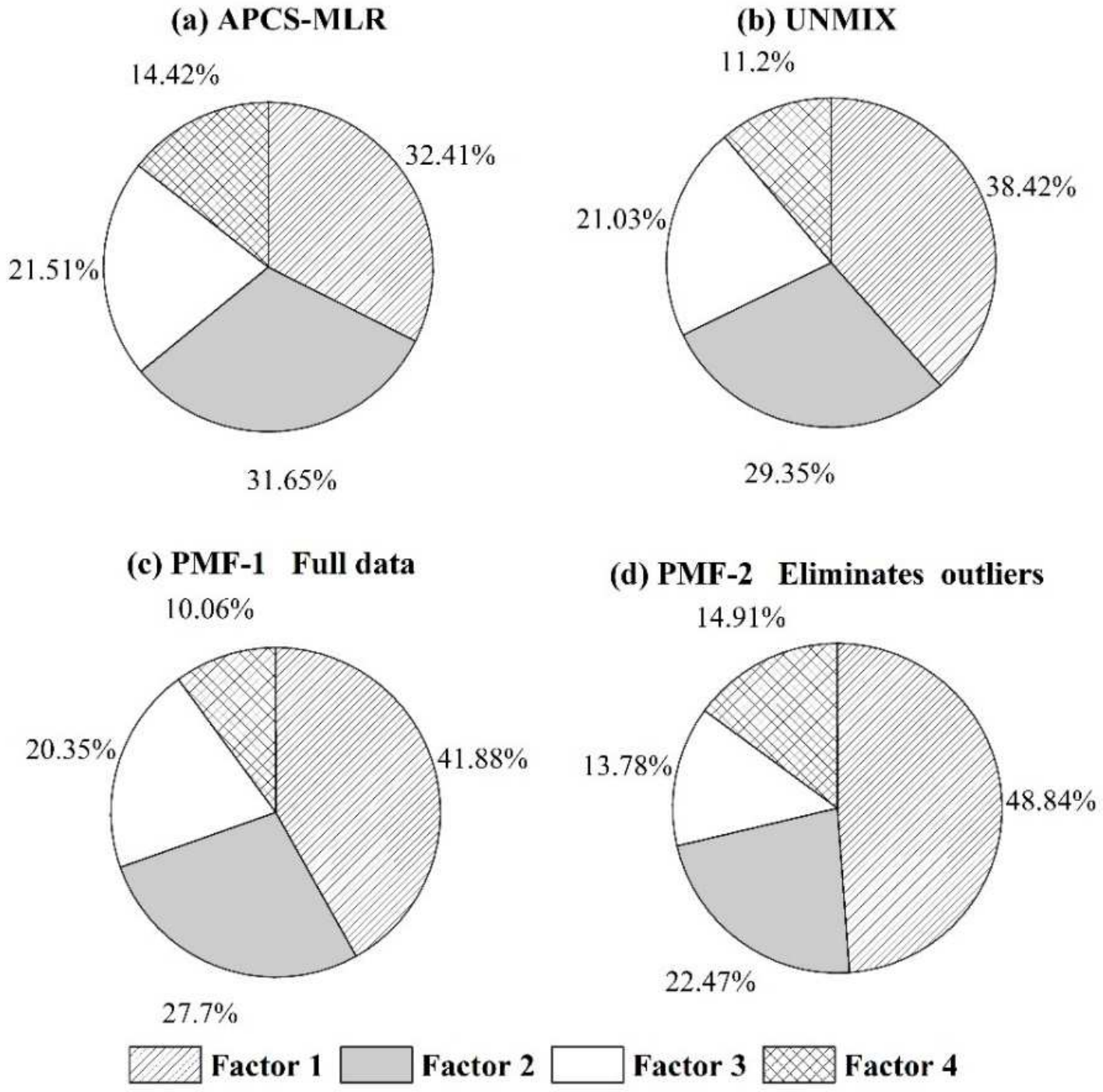

Figure 4

Factor contribution analysis of APCS-MLR, UNMIX and PMF models