RESEARCH ARTICLE

Quantitative source identification and apportionment of heavy metals under two different land use types: comparison of two receptor models APCS-MLR and PMF

Min Zhang[1] · Xueping Wang[3] · Chang Liu[1] · Jiayu Lu[1] · Yuhong Qin[1] · Yunkan Mo[1] · Pengjun Xiao[1] · Ying Liu[1,2]

Abstract

At present, many researchers are increasingly aware of the importance of using models to identify heavy metal (HM) pollution sources. However, on the performance and application of different source identification models to HMs under different land use types had been studied little. In this study, comparison of absolute principal component scores-multiple linear regression (APCS-MLR) and positive matrix factorization (PMF) models and their application characteristics in identifying pollution sources were carried out by using 11 HMs in Zhongwei City farmland and Shizuishan industrial park, Ningxia. The results indicated that HM pollution in farmland mainly came from pesticides, fertilizers, and deposition of the Yellow River, while the pollution in industrial park mainly originated from atmospheric deposition and various industrial productions. The APCS-MLR model had the problem of less identification sources and the difficulty to explain the complex pollution, while the PMF model not only identified more pollution sources, but also distinguished heavy metal–related sources for two different land use types and different industrial production conditions. It is of great significance the formulation of agricultural-related pesticides' and chemical fertilizers' rational use and various industrial production–related raw materials put in and emission control strategies.

Keywords Source apportionment of HMs · Comparison study of APCS-MLR and PMF · Ningxia · Two different land use types

Introduction

With the urbanization and industrialization brought about by the rapid development of social economy (Li et al. 2018; Shi et al. 2017), the pollution of heavy metals (HMs) in soil had gradually attracted the attention of the global public. Its main sources were human activities such as agricultural fertilizers,

✉ Ying Liu
liuying4300@163.com

1   College of Life and Environmental Sciences, Minzu University of China, Beijing 100081, China

2   Beijing Engineering Research Center of Food Environment and Public Health, Minzu University of China, Beijing 100081, China

3   Guangxi Key Laboratory of Marine Disaster in the Beibu Gulf, Beibu Gulf University, Qinzhou 535011, China

industrial manufacturing, and vehicle exhaust (Chen et al. 2016; Huang et al. 2015). In the process of human transformation and utilization of land for production and construction, various land use types with different utilization directions and characteristics were formed, and the HM pollution was also affected under different land use types and divided into different types of pollution sources (Guan et al. 2019; El-Naggar et al. 2018; Zhou and Wang 2019; Khademi et al. 2018). Thus, the study under different land use types was very important to identify more comprehensively the types of HM pollution sources and their contribution rates for the prevention, regulation, and control of soil pollution in China. And we should provide basis for rational utilization of land resources, adjustment of land use structure, and determination of land use direction.

Absolute principal component scores-multiple linear regression (APCS-MLR) (Haji et al. 2017) and positive matrix factorization (PMF) (USEPA 2014) were two kinds of receptor models widely used in HM source analysis. Because of comprised different mathematical and physical constraints, two models had different advantages and shortcomings. APCS-MLR interpreted the variance of data by identifying

fewer independent factors; its statistics only considered the data value itself and ignored the uncertainty of data source process. PMF considers the "uncertainty" of data and decomposes the data matrix into factor contribution and factor distribution under non-negative constraints; it had the advantages of no need to measure the fingerprint spectrum of the source, non-negative factor, etc. However, it had a high requirement for the credibility of data. The elimination of some environmental outliers may cause the lack of analytical results of individual points. In the process of practical application, the calculation results of the two models for the same data may be quite different.

APCS-MLR and PMF were widely used in the source analysis of atmospheric particles and seldomly used in soil pollutants. One of the key steps for source analysis was to explain the source profiles and its distribution to the actual emission sources. Different from atmospheric particles, soil pollution was usually interfered by physical, chemical, and biological effects, and the clear source signatures may not exist. This further increased the difference between the recognition results of different source analytical models. Lv (2018) used robust geostatistics to compare the pros and cons of APCS-MLR and PMF models by source identification results and model fitting degree. The result showed that PMF, with its optimal non-negativity results, was adopted for source apportionment. Moriasi et al. (2007) believe that it is necessary to calibrate and verify the related model to simulated environmental protection.

At present, the use of analytical models for HM pollution sources in soil at home and abroad is still lack of comparative analysis of similarity and difference of model (Dong et al. 2019; Huang et al. 2010; Lv 2018). For the identification and assessment of HM pollution in soil, it is of great theoretical significance and application value to study APCS-MLR and PMF models by comparing the statistical parameters of different receptor models, identification results, and quantity of source profiles and source distribution results (Huang et al. 2015).

This study applied APCS-MLR and PMF models to two different types of soil areas, compared and evaluated the results, and focused on differences in identifying the source and distribution of HMs, in order to help people to enhance the understanding and use of two receptor models, explore the advantages and shortcomings under two different land use types, and master the method on source identification more comprehensively.

Materials and methods

Study area

Ningxia is located in the western part of China; the Yellow River flowed over 390 km through the Ningxia Plain with an irrigated area of 330,000 km^2. It is well known that since Qin Dynasty, the irrigation farmland water conservancy project formed by the Yellow River's self-flow has made the Ningxia Plain become one of the four major irrigation areas and one of the twelve commodity grain bases in the country. Meanwhile, the Ningxia Plain had formed an industrial system with regional characteristics on both sides of the Yellow River. The proportion of secondary industry was higher than the national average, and its industrial output value accounted for more than 96% of Ningxia's GDP. Therefore, the Ningxia Plain had formed a major agricultural model with irrigation by the Yellow River and an economic development model with a huge industrial park as mainstay.

Zhongwei City is located in the alluvial plain of the upper reaches of the Yellow River (Yuan et al. 2018). Under its unique irrigation mode, the soil types mainly belonged to the category of irrigation and silting soil (Farmland irrigated by the Yellow River 2011), which were formed by the irrigation of the Yellow River with a large amount of sediment and the interaction of the long-term irrigation and deposition and human farming and fertilization (Wang 2018; Zhang et al. 2012; Xiong 2001); the physical viscosity of the silting soil was mostly 20–60%; it belonged to loamy soil with more consistent soil structure and more pores. The clay minerals were mostly hydromica, and the silt was more; the chemical composition was similar, and the cation-exchange capacity was higher; it contained certain organic matter and nutrients, and the content was significantly higher than that of the parent material layer (Zhang et al. 2012; Xiong 2001). The suitability of silting soil was extensive; the crops of corn, wheat, rice, millet, beet, and so on and fruits, vegetables, and trees can be cultivated. In the sampling farmland of Zhongwei City, corn and wheat were planted in rotation. In recent years, because of the increasing shortage of water resources in the Yellow River and industrial and domestic wastewater, the water quality of the Yellow River irrigation area has been deteriorating (Zhang et al. 2018; Li et al. 2016; Ningxia Water Resources Bulletin 2016). In addition, HMs brought to soil by agricultural activities had increased in the past decades. And agricultural recession re-entered the Yellow River and led to the aggravation of HM pollution in the lower reaches of the Yellow River.

On the other hand, Shizuishan was a high As area in China, which were once a "coal city" and an old-brand heavy industry base. Although Shizuishan City was located along the Yellow River, it was the highland both sides of the Yellow River impact plain; the main soil type was sierozem; its characteristics were that the soil parent material was mainly quaternary proluvial impact material with coarse texture; there were more sand and less silt in physical composition (Wang 2018; Zhang et al. 2012; Xiong 2001). The main clay mineral was hydromica, followed by kaolinite and chlorite. The soil fertility was relatively low; in the study area, grass and small semi-shrubs were mainly grown (Zhang et al. 2012; Xiong

2001). The economy in this study area was relatively developed with the highest number of industrial enterprises and the lowest cultivated area in the province. Shizuishan industrial park was adjacent to the Yellow River in the east and Helan Mountains in the west, with rich mineral resources and convenient transportation (Wang 2018). There were 327 industrial enterprises in the development zone, of which 76 were above the scale. Under the huge industrial production mode, the pollution it faced should not be underestimated.

In this study, the farmland in the Yellow River irrigation area of Zhongwei City and Shizuishan industrial park were selected as the research objects.

Sampling and analysis

In Fig. 1, Site 1 was a typical Yellow River irrigation farmland (Farmland irrigated by the Yellow River 2011). The agricultural mode in this area was characterized by irrigation and drainage, and the drainage channel was also responsible for agricultural drainage, sewage discharge, and flood discharge (Ningxia Autonomous Region Environmental Protection Bureau 2012–2016). Thus, based on the trend of the main channel and drainage channel in the sampling area, the soil samples of the farmland beside the channels were collected. In order to provide more raw data for source analysis, sampling points were also set around the factory near the sampling area. Site 2 was located in a typical large industrial park in

Ningxia (Zhou 2008), covering an area of 60 km^2, with a planning area of 28 km^2. We collected soil samples in and around the industrial park. In particular, it is necessary to set up multiple sampling points near the densely distributed factories and the entrances and exits of transport vehicles. At the same time, suspicious pollution sources also needed to be recorded. About 1 kg of fresh soil samples was collected with stainless steel in self-sealed bags, and 48 samples were collected. Soil samples with 100-mesh sieves were digested by a microwave with HNO_3-HF-H_2O_2-HCl (6:2:2:2) mixed acid. The contents of 11 HMs were determined by inductively coupled plasma mass spectrometry (Agilent 7700 ICP-MS). Soil reference materials (GBW07410, GBW10020) provided by the Institute of Geophysics and Geochemistry, Chinese Academy of Geological Sciences, were used for quality control. The detection limits of 11 HMs detected by ICP-MS were 0.002–0.194 μg/L, respectively. The recoveries of all elements in soil were 84–109% (RSD of parallel detection by instrument were less than 5%, $n = 6$) (Supplementary data 1).

Data processing and statistical analysis

APCS-MLR model

The APCS-MLR model was proposed by Thurston and Spengler in 1985. Its basic principle is to take the absolute principal component factor score as the independent variable
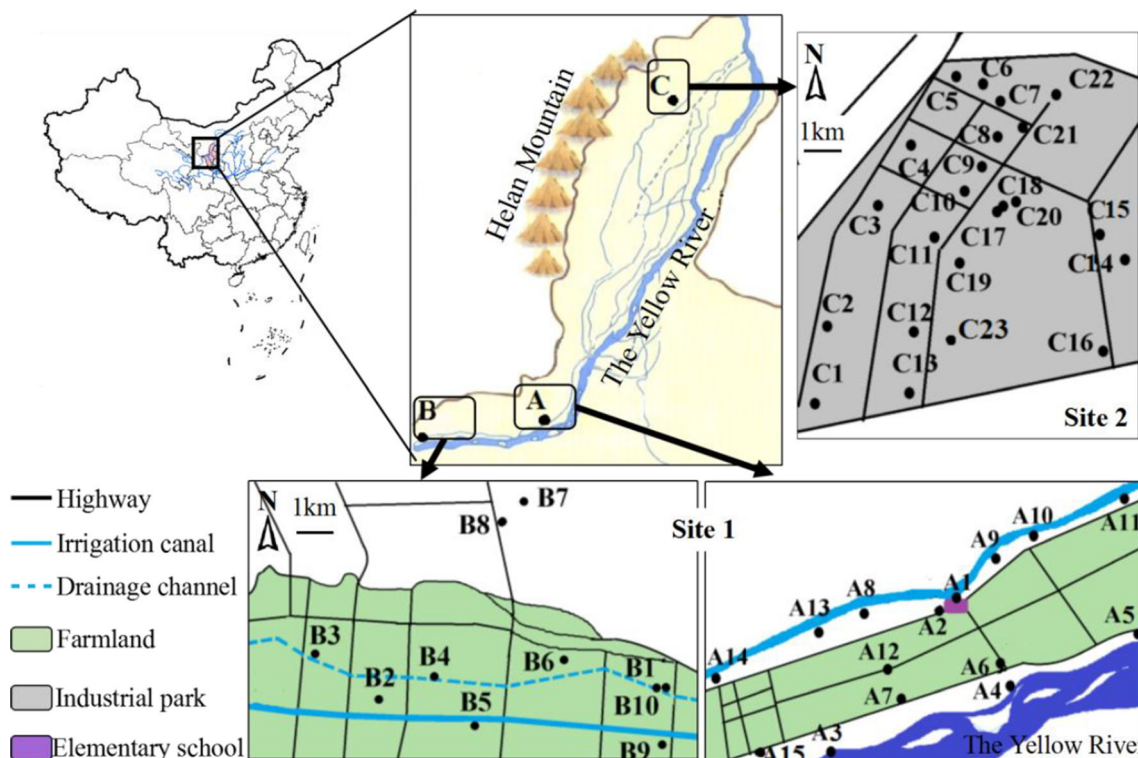

Fig. 1 Schematic map of sampling sites including the farmland in the Yellow River irrigation area of Zhongwei City (Site 1) and the Shizuishan industrial park (Site 2)

and the receptor content as the dependent variable for multiple linear regressions. The regression coefficient is used to calculate the contribution of the pollution source corresponding to each factor to the substance in the receptor.

In the calculation, the content data are standardized, and the 0 content artificial samples are introduced to calculate their factor scores. The absolute principal component factor score is obtained by subtracting the factor score of the artificial sample from the factor score of the original data. The linear regression operation is run and the contribution rate is calculated according to the following formula (Thurston and Spengler 1985):

$$Y = \sum_1^p m_i X_i + b \tag{1}$$

where Y refers to the HM content, p represents the number of extracted principal components, X_i is the score variable of factor i extracted as the principal component, m_i refers to the linear regression coefficient of factor i, and b is the constant of the regression model.

According to m_i, the average contribution rate (CS_i) of source i can be calculated as follows:

$$CS_i(\%) = \mathrm{mean}\sum P \times (m_i/\sum m_i) + m_i \partial P X_i \tag{2}$$

PMF model

PMF (USEPA 2014; Paatero and Hopke 2009; Paatero 1997) is a mathematical receptor model based on factor analysis, which has the advantages of no need to measure the fingerprint spectrum of the source, non-negative elements in the decomposition matrix, and can be optimized by using the standard deviation of data. The basic principles and equations of the PMF 5.0 model are described in the USEPA PMF 5.0 guidance manual (USEPA 2014). The PMF model decomposes the original matrix into two-factor matrices and a residual matrix, expressed as:

$$X\mathrm{ij} = \sum_{k=1}^p G\mathrm{i}kF\mathrm{j}k + E\mathrm{ij} \tag{3}$$

where X_{ij} is the sample concentration matrix, G_{ik} refers to the contribution of each factor to any given sample, F_{jk} represents the chemical composition matrix of p source, and E_{ij} is the residual matrix for each sample.

Factor contribution and profile are obtained from the PMF model, which minimizes objective function Q and is defined as follows:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij}/u_{ij})^2 \tag{4}$$

where Q is the sum of squares of the differences and e_{ij} is the PMF residual error for the ith sample and the jth specie, weighted by measurement uncertainty (u_{ij}). The PMF model

is run using concentration data and uncertainty data files that contain sampling and analysis errors.

Receptor model performance

In this study, two receptor models were compared and evaluated from the following four aspects in order to determine whether the model was applicable by calculating the concentration of HMs predicted by a model and comparing with the experimental results: (1) fitting degree (R^2) of detection concentration and prediction concentration in models, Nash-Sutcliffe efficiency (NSE) (Yang et al. 2013), and error (Moriasi et al. 2007); (2) fitting degree of HM concentration predicted values; (3) identification of the number and characteristics of sources; (4) contribution rate of different sources to different HMs.

Statistical analysis

The sources of HMs were identified by the APCS-MLR model (SPSS 22.0) and PMF model (USEPA PMF 5.0). All statistical charts were drawn in Origin Pro 2017 (Origin Lab, Northampton, MA).

Results and discussion

Overview of data

Table 1 was the basic data of HMs in soils including the farmland of the Yellow River irrigation in Zhongwei City (Site 1) and Shizuishan industrial park (Site 2).

According to the data of Site 1 in Table 1, the average contents of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, V, and Zn were 1.13–815.03 mg/kg, of which Mn was the highest and Cd was the lowest. Compared with the over-standard rate of HM pollution sites in Ningxia, the contents of As, Cd, Cr, Ni, and Pb exceeded the standard. Based on the background value of soil environment in China (Pb was based on the background value of soil in Ningxia), the average value of single-factor index (P_i) ranked as follows: Cd > As > Pb > Zn > Mn > Ni > Cr > Sn > Cu > Co > V. Among them, Cd and As were heavily polluted; Pb was moderately polluted; Cr, Cu, Mn, Ni, Sn, and Zn were lightly polluted; and Co and V were not polluted, respectively. The average contents of As, Cd, and Pb were about 3.2, 13.3, and 2.6 times of the background values of Ningxia, respectively, which indicated that the 3 heavy metals were significantly enriched in the farmland of the Yellow River irrigation, and which were mainly derived from man-made pollution. The coefficient of variation of Cd was the largest (CV = 1.63), followed by Pb, indicating that the spatial distributions of Cd and Pb were uneven, and the human disturbance was relatively large. Except for Cr and V,

Table 1 Descriptive statistics of soil HM contents in Site 1 and Site 2

Sites	HMs	Range/mg kg^{-1}	Mean/mg kg^{-1}	Skewness	Kurtosis	SD	CV	Background value/mg kg^{-1}	National standard/mg kg^{-1}
Site 1	As	20.27–107.10	37.05	2.27	6.81	19.07	0.52	11.6	11.2
	Cd	0.24–1.36	1.13	4.70	22.99	1.84	1.63	0.092	0.097
	Co	9.75–24.64	12.66	3.12	11.42	2.97	0.23	10.9	12.7
	Cr	63.54–131.03	83.21	0.99	− 0.14	19.48	0.23	61.3	61
	Cu	20.42–58.68	28.71	2.49	6.65	8.42	0.29	20.9	22.6
	Mn	517.32–1615.35	815.03	3.61	14.45	525.71	0.64	-	583
	Ni	28.35–130.72	36.97	4.78	23.51	19.80	0.54	29.2	26.9
	Pb	23.21–84.81	43.04	4.29	19.71	41.87	0.97	16.7	350
	Sn	1.94–3.72	3.36	1.09	6.73	0.57	0.17	-	2.6
	V	64.27–91.34	78.87	− 0.36	− 0.59	7.36	0.09	72.8	82.4
	Zn	73.60–318.75	148.30	3.03	10.80	104.19	0.70	63.6	74.2
Site 2	As	20.67–110.81	41.65	1.67	2.31	24.81	0.60	11.6	11.2
	Cd	0.33–6.06	1.77	1.62	2.82	1.40	0.79	0.092	0.097
	Co	8.59–128.46	26.84	2.68	8.21	27.43	1.02	10.9	12.7
	Cr	63.73–1250.33	227.31	2.43	5.93	296.84	1.31	61.3	61
	Cu	16.23–78.88	33.27	1.96	5.25	13.40	0.40	20.9	22.6
	Mn	498.86–45,380.13	6257.27	3.46	13.92	9488.21	1.52	-	583
	Ni	23.87–2926.62	388.19	2.65	7.48	700.63	1.80	29.2	26.9
	Pb	17.65–1906.39	186.52	4.40	20.34	385.03	2.06	16.7	350
	Sn	0.7–5.69	3.19	−0.36	−0.61	1.36	0.43	-	2.6
	V	59.97–120.99	74.04	2.15	6.88	13.11	0.18	72.8	82.4
	Zn	60.18–1016.06	338.19	1.18	0.69	277.17	0.82	63.6	74.2

the peak and skewness values of other HMs were larger, showing that these HMs were affected by human disturbance and external influence.

According to the data of Site 2 in Table 1, the average contents of 11 HMs in Shizuishan industrial park were 1.77–6257.27 mg/kg, and the ranks of Mn and Cd were the same as those in site 1 with the highest content of Mn and the lowest content of Cd. The over-standard rates of As, Cd, Cr, and Pb were 100%. Except for Cd and Sn, the contents of the other 9 HMs in industrial areas were significantly higher than those in farmland areas. The average P_i of HMs ranked as follows: Cd > Ni > Pb > Mn > Zn > Cr > As > Co > Cu > Sn > V. Except for V pollution-free, As, Cd, Cr, Mn, Ni, Pb, and Zn were all heavily polluted, Co was moderately polluted, and Cu and Sn were slightly polluted. The average contents of As, Cd, Cr, Mn, Ni, Pb, and Zn were about 3.6, 19.2, 3.7, 10.7, 13.3, 11.2, and 5.3 times of the background values of Ningxia, respectively. There were more exogenous inputs and more serious human pollution in this area. Except for Cu, Sn, and V, the variation coefficients of the other 8 heavy metals (CV > 0.6) were larger, and the spatial distributions of these metals were seriously uneven, which were greatly influenced by the factories near the sampling points.

Table 2 shows 5 sets of quality standards for HMs in soil at home and abroad, including agricultural land standard,

industrial land standard, and general standard, such as The Chinese National Standard (Ministry of Ecology and Environment of the People's Republic of China 2018a, b), American National Standard (USEPA 2018a, b), UK Soil Guideline Values (SGVs) (EA, DEFRA 2009), German National Standard (BBodSchG) (German Federal Ministry of the Environment 1999), and Canadian Environmental Quality Guidelines (SAIC 2002). As can be seen from Table 2, there were few standards available for Mn and Sn, and Germany's farmland standard and Canada's industrial standard limits were lower.

At Site 1, As content was 100% higher than the standards of four countries (China, the USA, the UK, and Germany). Comparing the content of Cd with the Chinese standard, Cd was partially over-standard. Co did not exceed the standards of China and Canada. Compared with the Canadian standard, the exceeding rate of Cr was close to 100%. The over-standard rate of Cu was 100% only compared with the German standard. When Ni was compared with the standards of Germany, Canada, and other three countries, the over-standard rate of Ni was 100%, partial over-standard, and no over-standard, respectively. Pb was partially over-standard in Chinese and Canadian standards. V did not exceed the 5 sets of quality standards. Zn partially exceeded the Chinese and Canadian standards.

Table 2 Quality standards for HMs in soil at home and abroad (mg/kg)

Project name	Land use types	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sn	V	Zn
Our study	Agriculture	20.27–107.10	0.24–1.36	9.75–24.64	63.54–131.03	20.42–58.68	517.32–1615.35	28.35–130.72	23.21–84.81	1.94–3.72	64.27–91.34	73.60–318.75
	Industrial park	20.67–110.81	0.33–6.06	8.59–128.46	63.73–1250.33	16.23–78.88	498.86–45,380.13	23.87–2926.62	17.65–1906.39	0.7–5.69	59.97–120.99	20.67–110.81
The Chinese National Standard (Ministry of Ecology and Environment of the People's Republic of China 2018a, b)	Agriculture	20	0.6	40	250	100	–	90	50	–	130	300
	Industrial	60	65	–	–	18000	–	900	800	–	–	–
American National Standard (USEPA 2018a, b)	Generic SSLs	0.4	78	–	390	–	–	1600	400	–	550	23000
	Industrial	2	900	–	3400	–	–	23000	–	–	7900	340000
UK Soil Guideline Values (SGVs) (EA, DEFRA 2009)	Agriculture	20	130	–	–	–	–	50	450	–	–	–
	Industrial	500	1400	–	5000	–	–	5000	150	–	–	–
German National Standard (BBodSchG) (German Federal Ministry of the Environment 1999)	Agriculture	0.4	–	–	–	1	–	1.5	–	–	–	2
	Industrial	140	60	–	1000	–	–	900	2000	–	–	–
Canadian Environmental Quality Guidelines (SAIC 2002)	Agriculture	–	1.4	40	64	63	–	50	70	5	130	200
	Industrial	12	22	300	87	91	–	50	600	–	130	360

"_" indicates no data available

In Site 2, compared with the American and Canadian standards, As exceeded 100%, but compared with the Chinese standard, As was partial over-standard. Cd did not exceed the 5 sets of quality standards. Cr was partial over-standard compared with the standards of Germany and Canada. For Cu, there was no over-standard. In addition to the British standard, Ni partially exceeded the standards compared with other four countries. Compared with the Chinese, British, and Canadian standards, the Pb partly exceeded the standards. V and Zn did not exceed 5 sets of quality standards for HMs in soil at home and abroad.

In conclusion, compared with foreign standards, As pollution in the farmland area was more serious. This result was consistent with that of the background value of soil environment in Ningxia. But Cd pollution in the farmland area was relatively light; the result was quite different from that of the background value of soil environment in Ningxia; this was because China's standard limit of farmland Cd was far lower than other countries. Similarly, the pollution of As was relatively serious; Cd, Cu, V, and Zn were not polluted in the industrial park, which were quite different from the background value of soil environment in Ningxia. These were due to the fact that the established HM standards in industrial areas of foreign countries were more relaxed than those in China, which led to the lower pollution level of HMs in industrial areas.

Comparison of APCS-MLR and PMF

Model reliability

The performances of APCS-MLR and PMF models applied in two different land use types are summarized in Table 3. Two models obtained more reasonable results in identifying pollution sources in the study areas, but the PMF model had higher fitting coefficients ($0.74 < R^2 < 1$) than APCS-MLR ($0.20 < R^2 < 0.94$), showing more reliable simulation results. The statistical results of error showed that the APCS-MLR model underestimated the model concentrations for most pollutants, especially Cd (errors in two sampling areas were $- 50\%$ and $- 80\%$, respectively), Mn ($- 16\%, - 182\%$), and Pb ($- 16\%, - 239\%$). The concentrations of pollutants fitted by the PMF model were mostly lower than the measured concentrations, and the errors were small ($- 33$ to $- 1\%$); among them, the error of Pb was the largest. Combining with the basic data of pollutants in Table 1, we can see that the coefficients of variation of Cd, Mn, and Pb were higher than those of other HMs, and their single-factor indexes were higher, and the external pollution caused by human disturbance was more complex. Thus, it can be seen that the fitting results of a receptor model were greatly influenced by the uniformity of the pollutant distribution. In addition, the NSE values of the PMF model (0.72–0.99, except for Ni) were closer to 1.0, and the fitting

results were more reliable, while the NSE values of the APCS-MLR model ($- 2.26$ to 0.97) were less reliable. However, the robust model of PMF can solve the influence of the measured value (outlier) of the fitting difference on the final optimal solution. The PMF model allowed the data points to be re-weighted between iterations in order to reduce the weight of the model fitting difference, resulting in lower fitting results than the actual concentration, and the model adopted non-negative constraints to avoid the occurrence of negative values. Thus, the fitting results were more reliable.

The results (Table 3) of the two models applied to two different land use types were as follows: the APCS-MLR model showed better fitting results for farmland with less pollution and more uniform distribution of pollutants, its error was close to 0, and NSE was close to 1.0. It underestimated the concentration of Ni in farmland, but overestimated the concentration of Ni in more polluted industrial areas and showed a higher fitting degree ($R^2 = 0.88$). Combining with the basic data of Ni in Table 1, we can see that the peak and skewness of Ni were higher and the coefficient of variation was lower in the farmland area, which indicated that the pollution degree of Ni in the farmland area was lighter, and the interference from external sources was less; thus, the APCS-MLR model was more suitable for Ni in the farmland area. But in the industrial park, because the non-normal distribution was more obvious, the APCS-MLR model was not suitable for use. On the other hand, the fitting results of the PMF model for HMs in the industrial park were more reliable. With larger coefficient of variation and more obvious non-normal distribution, the fitting results of both Cd in farmland and Ni in industrial soils were all better. In addition, with smaller coefficient of variation and more obvious normal distribution, the fitting result of Cr in the industrial area was also better. In conclusion, the fitting of the PMF model should be related to the degree of pollution, less affected by other pollution distributions, and the fitting results were not only more reliable than APCS-MLR but also more suitable for two different land use types.

Fitting of model prediction value

In farmland (Site 1), the results of source analysis of HMs were carried out using two receptor models and the predicted values of each sampling point were obtained (Fig. 2a, c). It was proved that PMF was more reliable in predicting the HM contents than the APCS-MLR model ($R^2 = 0.9965$). In industrial park (Site 2), the fitting results for HMs also showed that the PMF model was better ($R^2 = 0.9993$). Therefore, the PMF model can be applied to two different land use types. On the other hand, first, in comparing the fitting results of the same model in different sampling areas in Fig. 2a and d, we found that the fitting results of the APCS-MLR model in Site 1 ($R^2 = 0.408$) were better than those in Site 2 ($R^2 = 0.3377$), which

Table 3 Model evaluation statistics of APCS-MLR and PMF in Site 1 and Site 2

Sites	HMs	Experimental value (mg kg^{-1})	APCS-MLR				PMF			
			Modeled value (mg kg^{-1})	Error (%)	NSE	R^2	Modeled value (mg kg^{-1})	Error (%)	NSE	R^2
Site 1	As	37.05	32.14	−13	0.87	0.94	37.22	0	1	1
	Cd	1.13	0.48	−58	0.73	0.86	1.51	2	0.99	1
	Co	12.66	11.94	−6	0.65	0.72	12.50	−1	0.72	0.74
	Cr	83.21	77.82	−6	0.42	0.50	80.68	−3	0.79	0.80
	Cu	28.71	27.15	−5	0.55	0.59	28.84	0	1	1
	Mn	815.03	684.90	−16	0.19	0.25	817.48	0	1	1
	Ni	36.97	31.13	−16	0.11	0.20	34.57	−7	0.51	0.87
	Pb	43.04	27.36	−36	0.75	0.90	39.79	−8	0.93	0.97
	Sn	3.36	3.11	−7	0.97	0.88	3.37	0	1	1
	V	78.87	77.61	−2	0.77	0.81	79.32	1	1	1
	Zn	148.30	106.12	−28	0.72	0.89	137.72	−7	0.89	0.91
Site 2	As	41.65	29.76	−29	0.66	0.90	74.21	0	1	1
	Cd	1.77	0.36	−80	−0.41	0.66	98.30	−10	0.73	0.8
	Co	26.84	39.52	47	0.61	0.83	5500.34	−1	0.99	0.99
	Cr	227.31	455.77	101	0.31	0.88	16.00	−1	0.99	0.99
	Cu	33.27	17.07	−49	−0.88	0.65	57.57	0	1	1
	Mn	6257.27	−5139.80	−182	−1.04	0.47	31.44	−2	1	1
	Ni	388.19	892.98	130	0.34	0.88	282.47	2	1	1
	Pb	186.52	−259.55	−239	−1.02	0.38	40.78	−33	0.61	0.91
	Sn	3.19	2.05	−36	−0.22	0.52	1.42	0	1	1
	V	74.04	51.69	−30	−2.26	0.88	3.15	0	1	1
	Zn	338.19	91.22	−73	−0.09	0.74	111.28	−4	0.77	0.84

was consistent with the conclusion that "the APCS-MLR model had a better fitting effect on the soil with less human disturbance." However, in Fig. 2 c and f, the fitting results of the PMF model in two regions were close to 1, which showed again that the PMF model was less affected by the degree of soil pollution and human disturbance. Second, the fitting results of the PMF model in Site 1 ($R^2 = 0.9965$) were slightly lower than those in Site 2 ($R^2 = 0.9993$); it can be seen from Fig. 2 c that the fitting result of sampling point A14 was quite different from those of other points. It was predicted that this was the reason why the fitting results of the PMF model in Site 1 were poor.

In addition, according to the results of source identification and contribution rate distribution of two models in Figs. 3 and 4, the APCS-MLR model resolved four and three pollution sources, respectively, in farmland and industrial area, while PMF resolved five and six pollution sources. The PMF model identified additional sources at each site, which were not identified and quantified by APCS-MLR. The differences between these results were due to the different theoretical steps of source recognition between two receptor models. When the model was used to analyze the source data, the choice of

variables depended on the mathematical and physical conditions followed by the model itself. In a word, because the APCS-MLR model cannot separate covariant source and make appropriate error scaling for each data before eigenvalue analysis, thus, the APCS-MLR model cannot provide more robust source analysis, while the PMF model was a better choice for soil source analysis.

Source identification

Farmland of the Yellow River irrigation area in Zhongwei City (Site 1)

Contribution of the variables according to different factors (source) obtained by APCS-MLR (left) and PMF (right) receptor models in Site 1 can be seen from Fig. 3; the APCS-MLR model extracted four source factors, which accounted for 86% of the total variance. The PMF model divided the sources of HM pollution into five types and eliminated the abnormal value at the A10 sampling point. The source analysis methods of the two models were combined and the results were as follows:
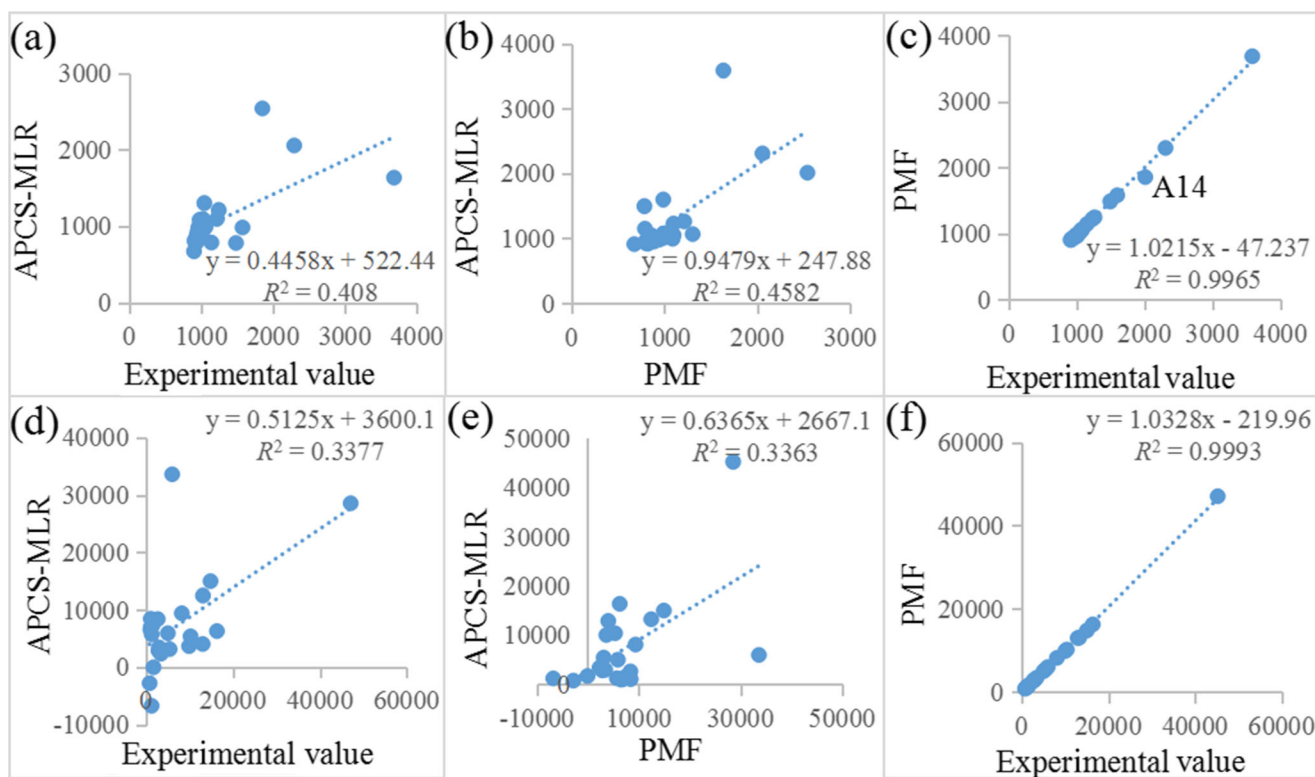
Fig. 2 Two receptor models were used to fit the predicted concentrations of 11 heavy metals in soils of two different land use types. Site 1: (a) APCS-MLR vs. experimental value, (b) APCS-MLR vs. PMF, (c) PMF vs. experimental value; Site 2: (d) APCS-MLR vs. experimental value, (e) APCS-MLR vs. PMF, (f) PMF vs. experimental value

Factor 1 had the highest relative concentration of As, followed by Cu, Sn, and V, and a small amount of Co, Cr, and Pb. Metal ions had the function of killing and inhibiting pathogen activity (Wang et al. 2009). The inorganic salts or complexes containing metal ions were the most widely used inorganic antimicrobial agents in the preparation of pesticides. Among them, As, Cu, and Pb were widely used (Xu et al. 2020). In addition, in the process of pesticide preparation, metal ions extracted from ores carried a large amount of Sn and V. The contribution of this factor at B1–B10 was significantly greater than that at A1–A15. This was due to the fact that a large number of main canals and drainage canals of the Yellow River were distributed at the B1–B10 farmland. Agricultural pollution carried by irrigation and agricultural drainage remained in the soil, resulting in the accumulation of HMs in the soil. Thus, factor 1 came from the unreasonable application of pesticides.

Factor 2 was associated with Co, Cr, Ni, Sn, and V. The coefficients of variation of Co, Sn, and V in the study area were small and the pollutions were light, mainly from the natural source of the parent material. Because Co, Cr, and Ni mainly came from weathered bedrock soil (Lv et al. 2015; Alloway 2013) and the artificial inputs of chemical fertilizers and manures to the two metals (Cr and Ni) were lower than the background contents in soil (Lu et al. 2017; Liu et al. 2016), it was generally believed that the three HMs

originated from the parent material of soil formation. Therefore, factor 2 can be identified as a natural source.

Factor 3 produced the dominant contributions of Cd, followed by Cr, Cu, Pb, and Zn. Agricultural pollution was the main cause of soil Cd pollution (Rodríguez Martín et al. 2013). Cd is an inherent component of phosphate rock, so phosphate fertilizer contained a lot of Cd (Nziguheba and Smolders 2008; Mortvedt 1996). According to Statistical Yearbook of Zhongwei City in 2017, the annual application amounts of nitrogen fertilizer, phosphorus fertilizer, potassium fertilizer, and compound fertilizer were 10.1, 2.3, 0.7, and 66,000 tons, respectively, and they contained Cr, Cu, Mn, Pb, and Zn (Wang and Ma 2004; Lu et al. 1992), while the average Cd contents in Chinese phosphate fertilizers and compound fertilizers were 0.6 and 0.18 mg/kg, respectively. Therefore, factor 3 caused agricultural pollution; Cd accumulated extensively; Cr, Cu, Mn, Pb, and Zn accumulated in small quantities; and factor 3 came from the unreasonable application of chemical fertilizers.

Factor 4 had higher relative concentrations for Cd, Cr, Cu, Pb, and Zn, followed by Co, Mn, Ni, Sn, and V, and the sum of factor 2 and factor 4 representing natural sources accounted for 0.7–1.2 times of soil background values in Ningxia (except for As 0.4 and Cd 3). The farmland soils in Zhongwei City were irrigated from the Yellow River and formed silted soil (Yuan et al. 2018; Dong et al. 2015); its main component was
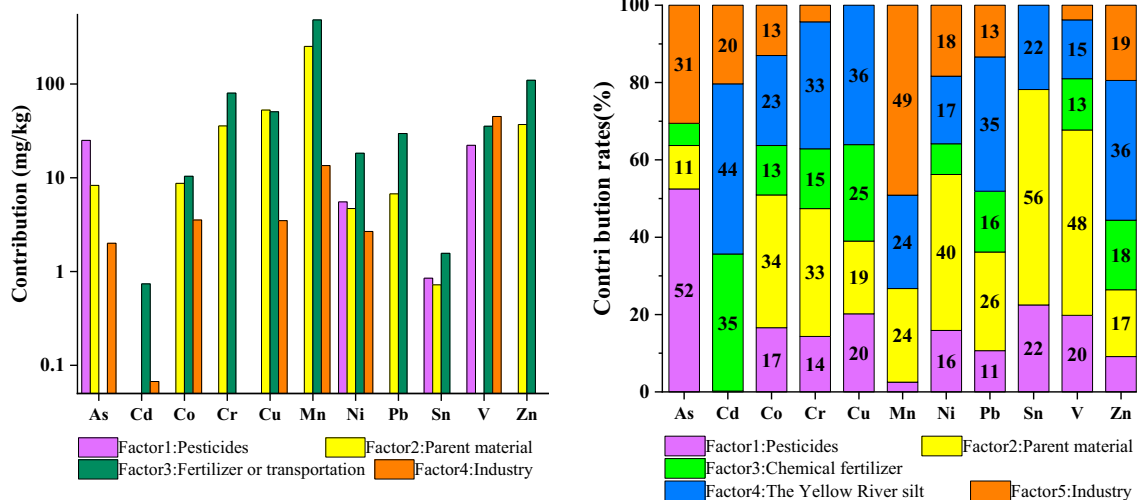
Fig. 3 Contribution of the variables according to different factors (source) obtained by APCS-MLR (left) and PMF (right) receptor models in Site 1

the deposition of the Yellow River, which belongs to clay minerals. Because clay mineral (Gu et al. 2018; Yariv and Cross 1979) was a kind of silicate with layered or chain structure and had a large specific surface area, it can adsorb metal ions in the environment through physical adsorption, chemical adsorption, and ion exchange, which resulted in a large amount of HMs in the deposited soil. At the same time, literature (Ma et al. 2016; Kong et al. 2014) found that there was a large amount of Cd pollution in the silt of Ningxia section in the upper reaches of the Yellow River, which was the main reason that the sum of contribution of factor 2 and factor 4 was much more than the background value of Ningxia soil. Factor 4 has the lowest contribution at A11 and B2 sampling points. With field investigation, we found that the two sampling points not only were located near a national highway but also were the source of drainage facilities of the main canal, which had constructed by man-made buildings. It was presumed that the original soil layer had been changed due to overburden and other reasons. Thus, factor 4 was the HM pollution carried

by the deposition of the Yellow River. The results were in agreement with those of other studies on the source apportionment of HMs in soil along the Yellow River (Zhang et al. 2018).

Factor 5 had higher relative concentration of Mn, followed by As and fewer Cd, Co, Ni, Pb, and Zn because there was a large manganese factory near the study area. The main waste residue of electrolytic manganese production was acid leaching residue, and other waste residues include anode mud, sulfide residue, chromium-containing residue, and domestic waste. The main pollutants of various waste residues were As, Cd, Pb, and Zn (Lv et al. 2019; Zhan et al. 2019). The main components of sulfide residue also contained nickel sulfide and cobalt sulfide (Wang et al. 2019b). In addition, contrary to the distribution of the contribution of sampling points in factor 1, the contribution of factor 5 in the B1–B10 sampling points was significantly less than that in A1–A15, which was consistent with the actual location of the medium manganese plant, which was closer to the A1–A15 sampling
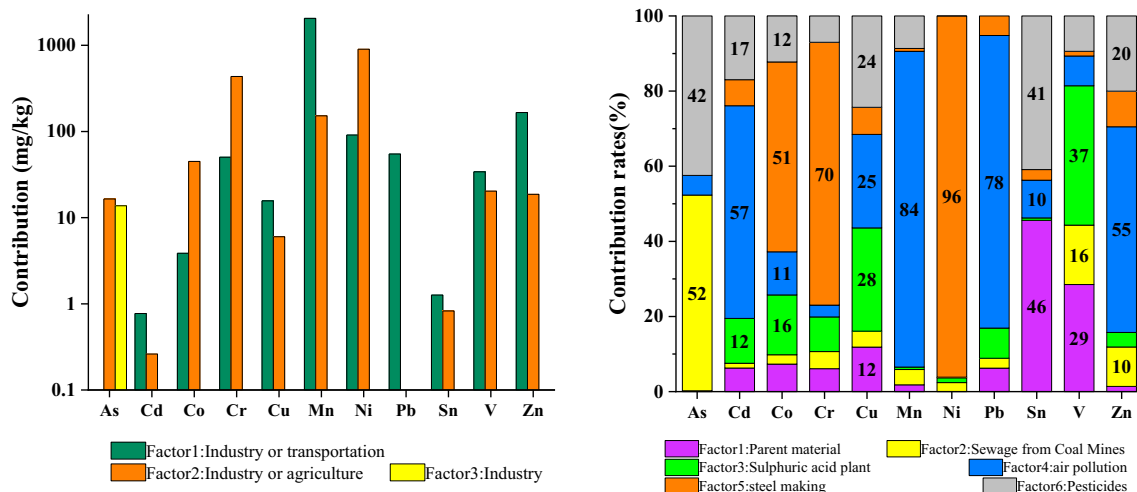

Fig. 4 Contribution of the variables according to different factors (source) obtained by APCS-MLR (left) and PMF (right) receptor models in Site 2

points. Thus, factor 5 came from industrial pollution caused by electrolytic manganese production.

Shizuishan industrial park (Site 2)

Contribution of the variables according to different factors (source) obtained by APCS-MLR (left) and PMF (right) receptor models in Site 2 are shown in Fig. 4. In Site 2, the APCS-MLR model extracted three source factors, which accounted for the majority of the total variance (83%), but the PMF model divided the sources of HM pollution into six categories, and all the data of sampling points entered the model and got high fitting parameters. Combining the source analysis results of the two models, the results were as follows:

Factor 1 was associated with Sn and V. Because the coefficient of variation of Sn and V and human disturbance were small, it was speculated that Sn and V came from the parent material of soil.

Factor 2 had the highest relative concentration of As. According to the relevant norms of Control plan of key endemic diseases in Ningxia (2004–2010) and National plan for prevention and control of endemic diseases during the 13th Five-Year Plan, drinking water-borne endemic arsenism had become one of the main endemic diseases in Ningxia (Jin et al. 2003; Xia and Liu 2004). This area was the groundwater spillover zone in front of Helan Mountains (Tian and Zhang 2010; Zhao et al. 2007) and a convergence zone of mountain floods, valleys, and streams. Meanwhile, the soil in this area was the clay of lacustrine muddy stratum and fine sand interbedded. It had strong adsorption capacity. It contacted with groundwater and absorbs arsenic, which increases the arsenic concentration in the stratum (Zhao and Luo 2017; Chen et al. 2014). The contribution of this factor fluctuated slightly and distributed evenly at all sampling points of Site 2. However, the contribution of C12 and C13 was the lowest. Near the two sampling points, a circular economy industrial park was built. The factory was the first national "resource-saving, environment-friendly" founding enterprise and had a "garden workshop," which made the contribution of factor 2 to the soil reached the lowest value. Thus, factor 2 came from high arsenic wastewater from coal mining.

Factor 3 produced the dominant contributions of Cu and V, and significant influences on Co and Cd. Because V was the catalyst for the process of SO_2 to SO_3 in sulfuric acid production by sulfur oxidation in industry (Wang et al. 2019a), chalcopyrite was the raw material for sulfuric acid production and contained HMs such as Co and Cd (Bortnikova et al. 2018; Rajabpour et al. 2017). In addition, chemical plants that can produce sulfuric acid were built near C18 and C19 sampling points. Thus, it was speculated that this factor came from the industrial production of sulfuric acid produced by chalcopyrite.

Factor 4 was the main source of Cd, Mn, Pb, and Zn, followed by Cu. Because Pb was the symbol element of traffic pollution and air dust pollution source, and 78% of Pb came from this factor, it was a possible reason that the pollution source of this factor was related to the polluted air particles (Xie et al. 2018; Miller 2011). The mixed pollutants of Cd, Pb, and Zn generally came from the dry and wet depositions of pollutants and the emission of automobile exhaust. Moreover, Cu was the main product of brake, tire, and body metal (Zhang et al. 2016; Chen et al. 2012). Pb, Cd, Cu, Mn, and Zn can be released from gasoline, engine, lubricating oil, and gold plating parts due to combustion or wear (Pfeifer et al. 2004; Falahi-Ardakani 1984). The study area was mostly northwest wind all the year round, so factor 4 reached the lowest value at the place far away from the well-developed industrial areas except for the C14 and C15 sampling points with upwind direction. Thus, factor 4 came from air pollution.

Factor 5 was the main source of Co, Cr, and Ni, which was different from factor 2 (Site 1) from the parent material; the factor 5 of industrial zone only included a large number of Co, Cr, and Ni, which was almost not related to other HMs. Therefore, this factor was not the source of parent material. Literature (Balaguru et al. 2019; Nagase et al. 2019; Shi et al. 2019) showed that Co, Cr, and Ni were the main pollutants in the manufacture of cast iron, wrought iron, and steel. Cr and Ni were mainly used in the manufacture of stainless steel and corrosion-resistant alloy (such as nickel base alloy Ni-Cr-Mo). Controlling Co content was an important step in the manufacturing process of steel and corrosion-resistant alloy. The contribution of this factor to the C5, C8, C18, and C19 sampling points reached the highest value. Combined with the industrial distribution near the sampling area, it can be seen that there were metallurgical, steel manufacturing or building materials manufacturing plants in above four sampling points of the industrial park. Therefore, this factor was the source of iron and steel industry.

Factor 6 had a high relative concentration of As and Sn, followed by Cu and Zn, and small amount of Cr and Co. The principle was consistent with the analysis result of factor 1 in Site 1, which came from the pollution phenomenon caused by the continuous accumulation of pesticides in the soil (Sun et al. 2019). Because of historical soil pollution and other reasons, agricultural pollution also existed in the soil of industrial park. So, this factor originated from agricultural pollution.

Source apportionment

For the source analysis of HMs in Ningxia farmland, from the comparison of contribution rate distribution of the two models in Fig. 3, it can be found that the estimated contribution rate of each potential pollution source was significantly different. The estimated results of the APCS-MLR model showed that the contribution rates of parent material, agricultural pollution

or traffic pollution, and industrial emission were about 30%, 64%, and 5%, respectively. The PMF model estimated that the related sources of parent material, pesticides, fertilizers, the Yellow River silt, and industrial emissions accounted for 28%, 17%, 14%, 26%, and 15%, respectively. It can be seen that (1) the results of the two models obtained the pollution sources of soil parent material, agriculture, and industry, which had certain guiding significance for the development of prevention and control measures. (2) Compared with APCS-MLR, the PMF model can more carefully distinguish the difference of HM sources under different land types. For example, in the mixed soil layer of the typical irrigation area of the Yellow River, factor 2 and factor 4 represented the original soil source and the sediment source of the Yellow River, respectively. (3) The PMF model was easier than the APCS-MLR model in identifying pollution sources represented by different source factors. As shown in Fig. 3, five factors of PMF fitting were identified, while the APCS-MLR model cannot determine whether factor 3 came from agriculture or traffic pollution. This was reason that all HMs of this factor were consistent with the assumption of two pollution sources, so the APCS-MLR model was impossible to get more accurate identification. (4) Because of the different operation principles of the two models, the source allocation results of the APCS-MLR model did not meet the physical meaning of the real conditions; specifically, its contributions contained a lot of negative values, such as the contributions of factor 1 to Cd, Co, Cr, Cu, Mn, Pb, and Zn in all sampling points that contained negative values, while the PMF model avoided this problem by limiting the matrix value of the factor to be non-negative.

For the source analysis of HMs in the industrial park, the estimated results of the APCS-MLR model were that the contribution rates of industrial pollution or traffic pollution, industrial pollution or agricultural-related sources were 61% and 39%, respectively. But, the PMF model estimated that the related sources of parent material, coal mining, sulfuric acid production, air pollution, steel manufacturing, and agricultural pollution accounted for 10%, 9%, 11%, 31%, 23%, and 16%, respectively. It can be seen that (1) the APCS-MLR model showed lower reliability in the distribution results of contribution: the third source factor accounted for less than 1%, and only included some As source, and the contribution rates to other HMs were negative; thus, the pollution source represented by factor 3 cannot be accurately identified. (2) Compared with the APCS-MLR model, the PMF model can more clearly identify pollution sources of different industrial production types. Because the area was an industrial park with many types of industries and complex pollution sources, and the degree of pollution was more inclined to point source pollution, such as steel plants near the C7 sampling point and chemical plants near C18 and C19. It was clear that PMF model can distinguish the components and different

proportions of major HM pollutants, but the APCS-MLR model will not be achieved. APCS-MLR is only for statistical analysis of experimental data, ignoring the process of data source and then expanding the uncertainty of its source apportionment results, which is the fundamental reason why PMF analysis results are better than APCS-MLR.

Combined with the above analysis, we found that the analysis results of the two models had certain guiding significance for the agricultural areas with light pollution degree and simple pollution source. But for industrial areas with complex pollution sources, the APCS-MLR model cannot distinguish different industrial sources. Therefore, the APCS-MLR model is recommended in the absence of reliable experimental error data, or in the light pollution area for source analysis. However, under the condition of sufficient data, PMF can provide more sufficient source analysis results for two different land use types.

Conclusions

In this study, the results of comparison of APCS-MLR and PMF models under two different land use types showed that for light pollution and simple pollution sources, both models could obtain good results. Under sufficient basic data (experimental error, etc.), PMF model was better. And the PMF model could more easily identify pollution sources and distinguish the HM-related sources than the APCS-MLR model. The results of source apportionment indicated that the PMF model was more consistent with the actual situation and provided research on the analysis of HM sources under two different land use types.

In conclusion, the results of quantitative source identification and apportionment showed that HM pollution existed in two land use types. Among them, HM pollution in Zhongwei City farmland mainly came from agricultural pollution (57%), including pesticides (17%), fertilizers (14%), and the Yellow River irrigation (26%). The unique mode by the Yellow River irrigation made the soil greatly affected by the water quality and sediment of the Yellow River. Thus, the improvement of the water quality and irrigation mode of the Yellow River not only affected the health of aquatic organisms, but also played an important role in the food safety of the people along the Yellow River. Meanwhile, optimized utilization rates of fertilizers and pesticides should be selected according to the needs of soil quality and crop demand in different areas. On the other hand, HM pollution in Shizuishan industrial park mainly came from various local industrial production (43%) and air pollution (31%). The identification of pollution sources will conducive to the targeted formulation of emission standards and the implementation of corresponding remediation. Through the division of pollution contributions, the construction of green ecological park will be gradually realized

from the industries with more serious pollution and greater harm.

References

Alloway BJ (2013) Heavy metals in soils. Springer, Dordrecht. https://doi.org/10.1007/978-94-007-4470-7

Balaguru S, Murali V, Chellapandi P, Gupta M (2019) Effect of dilution on micro hardness of Ni-Cr-B-Si alloy hardfaced on austenitic stainless steel plate for sodium-cooled fast reactor applications. Nucl Eng Technol 52:589–596. https://doi.org/10.1016/j.net.2019.08.011

Bortnikova SB, Yurkevich NV, Abrosimova NA, Devyatova AY, Edelev AV, Makas AL, Troshkov ML (2018) Assessment of emissions of trace elements and sulfur gases from sulfide tailings. J Geochem Explor 186:256–269. https://doi.org/10.1016/j.gexplo.2017.12.008

Chen XD, Lu XW, 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 98:73–78. https://doi.org/10.1016/j.catena.2012.06.007

Chen J, Liu GJ, Kang Y, Wu B, Sun RY, Zhou CCWD (2014) Coal utilization in China: environmental impacts and human health. Environ Geochem Health 36(4):735–753. https://doi.org/10.1007/s10653-013-9592-1

Chen HY, Teng YG, Chen RH, Li J, Wang JS (2016) Contamination characteristics and source apportionment of trace metals in soils around Miyun Reservoir. Environ Sci Pollut Res Int 23:15331–15342. https://doi.org/10.1007/s11356-016-6694-1

Dong LL, Yu DS, Zhang HD, Zhang ML, Jin WH, Liu Y, Shi XZ (2015) Long-term effect of sediment laden Yellow River irrigation water on soil organic carbon stocks in Ningxia, China. Soil Tillage Res 145:148–156. https://doi.org/10.1016/j.still.2014.09.009

Dong B, Zhang RZ, Gan YD, Cai LQ, Freidenreich A, Wang KP, Guo TW, Wang HB (2019) Multiple methods for the identification of heavy metal sources in cropland soils from a resource-based region. Sci Total Environ 651:3127–3138. https://doi.org/10.1016/j.scitotenv.2018.10.130

El-Naggar A, Shaheen SM, Ok YS, Rinklebe J (2018) Biochar affects the dissolved and colloidal concentrations of Cd, Cu, Ni, and Zn and their phytoavailability and potential mobility in a mining soil under dynamic redox-conditions. Sci Total Environ 624:1059–1071. https://doi.org/10.1016/j.scitotenv.2017.12.190

Falahi-Ardakani A (1984) Contamination of environment with heavy metals emitted from automotives. Ecotoxicol Environ Saf 8(2):152–161. https://doi.org/10.1016/0147-6513(84)90057-5

Farmland irrigated by the Yellow River (2011) Yellow River Conservancy Commission of the Ministry of Water Resources. http://www.yrcc.gov.cn/hhyl/yhgq/. Accessed 13 August 2011

German Federal Ministry of the Environment (1999) Nature Conservation and Nuclear Safety. Federal Soil Protection and Contaminated Sites Regulation (BBodSchG). The German. http://www.gesetze-im-internet.de/bbodschv/BJNR155400999.html#BJNR155400999BJNG000100305. Accessed 18 February 2020

Gu SQ, Kang XN, Wang L, Lichtfouse E, Wang CY (2018) Clay mineral adsorbents for heavy metal removal from wastewater: a review. Environ Chem Lett 17:629–654. https://doi.org/10.1007/s10311-018-0813-9

Guan QY, Zhao R, Pan NH, Wang FF, Yang YY, Luo HP (2019) Source apportionment of heavy metals in farmland soil of Wuwei, China: comparison of three receptor models. J Clean Prod 237:117792. https://doi.org/10.1016/j.jclepro.2019.117792

Haji GM, Melesse AM, Reddi L (2017) Water quality assessment and apportionment of pollution sources using APCS-MLR and PMF receptor modeling techniques in three major rivers of South Florida. Sci Total Environ 566–567:1552–1567. https://doi.org/10.1016/j.scitotenv.2016.06.046

Huang Y, Deng MH, Wu SF, Japenga J, Li TQ, Yang X, He ZL (2010) A modified receptor model for source apportionment of heavy metal pollution in soil. J Hazard Mater 354:161–169. https://doi.org/10.1016/j.jhazmat.2018.05.006

Huang Y, Li TQ, Wu CX, He ZL, Japenga J, Deng MH, Yang X (2015) An integrated approach to assess heavy metal source apportionment in peri-urban agricultural soils. J Hazard Mater 299:540–549. https://doi.org/10.1016/j.jhazmat.2015.07.041

Jin YL, Liang CK, He GL, Cao JX, Ma F, Wang HZ, Ying B, Ji RD (2003) Study on distribution of endemic arsenism in China. J Hyg Res 32(6):519–540. https://doi.org/10.3969/j.issn.1000-8020.2003.06.004

Khademi H, Gabarrón M, Abbaspour A, Martínez-Martínez S, Faz A, Acosta JA (2018) Environmental impact assessment of industrial activities on heavy metals distribution in street dust and soil. Chemosphere 217:695–705. https://doi.org/10.1016/j.chemosphere.2018.11.045

Kong XL, Cao J, Tang RY, Zhang SQ, Dong F (2014) Pollution of intensively managed greenhouse soils by nutrients and heavy metals in the Yellow River Irrigation Region. Northwest China. Environ Monit Assess 186(11):7719–7731. https://doi.org/10.1007/s10661-014-3962-8

Li M, Yang W, Sun T, Jin YW (2016) Potential ecological risk of heavy metal contamination in sediments and macrobenthos in coastal wetlands induced by freshwater releases: a case study in the Yellow River Delta, China. Mar Pollut Bull 103(1–2):227–239. https://doi.org/10.1016/j.marpolbul.2015.12.014

Li F, Cai Y, Zhang JD (2018) Spatial characteristics, health risk assessment and sustainable management of heavy metals and metalloids in soils from central China. Sustainability 10(2):91. https://doi.org/10.3390/su10010091

Liu Y, Ma ZW, Lv JS, Bi J (2016) Identifying sources and hazardous risks of heavy metals in topsoils of rapidly urbanizing East China. J Geogr Sci 26(6):735–749. https://doi.org/10.1007/s11442-016-1296-x

Lu RK, Shi ZY, Xiong LM (1992) Cadmium contents of rock phosphates and phosphate fertilizers of China and their effects on ecological environment. Acta Pedol Sin 29:150–157

Lu J, Li AC, Huang P (2017) Distribution, sources and contamination assessment of heavy metals in surface sediments of the South Yellow Sea and northern part of the East China Sea. Mar Pollut Bull 124:470–479. https://doi.org/10.1016/j.marpolbul.2017.07.007

Lv JS (2018) Multivariate receptor models and robust geostatistics to estimate source apportionment of heavy metals in soils. Environ Pollut 244:72–83. https://doi.org/10.1016/j.envpol.2018.09.147

Lv JS, Liu Y, Zhang ZL, Zhou RJ, Zhu YC (2015) Distinguishing anthropogenic and natural sources of trace elements in soils undergoing recent 10-year rapid urbanization: a case of Donggang, Eastern China. Environ Sci Pollut Res 22(14):10539–10550. https://doi.org/10.1007/s11356-015-4213-4

Lv Y, Li J, Ye HP, Du DY, Li JX, Sun P, Ma MY, Wen JX (2019) Bioleaching behaviors of silicon and metals in electrolytic

manganese residue using silicate bacteria. J Clean Prod 228:901–909. https://doi.org/10.1016/j.jclepro.2019.04.289.m

Ma XL, Zuo H, Tian MJ, Zhang LY, Meng J, Zhou XN, Min N, Chang XY, Liu Y (2016) Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. Chemosphere 144:264–272. https://doi.org/10.1016/j.chemosphere.2015.08.026

Miller BG (2011) The effect of coal usage on human health and the environment. Clean Coal Engineering Technology. Elsevier, pp 85–132. https://doi.org/10.1016/b978-1-85617-710-8.00004-2.

Ministry of Ecology and Environment of the People's Republic of China (2018a) State Administration for Market Regulation. Soil environmental quality—risk control standard for soil contamination of agricultural land GB 15618-2018. http://www.mee.gov.cn/gkml/sthjbgw/sthjbgg/201807/t20180703_445969.htm. Accessed 18 February 2020

Ministry of Ecology and Environment of the People's Republic of China (2018b) State Administration for Market Regulation. Soil environmental quality—risk control standard for soil contamination of development land GB 36600-2018. http://www.mee.gov.cn/ywgz/fgbz/bz/bzwb/trhj/201807/t20180703_446027.shtml. Accessed 18 February 2020

Moriasi DN, Arnold JG, Liew MWV, Bingner RL, Harmel RD, Veith TL (2007) Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. Trans ASABE 50(3):885–900. https://doi.org/10.13031/2013.23153

Mortvedt JJ (1996) Heavy metal contaminants in inorganic and organic fertilizers. Fertil Res 43:55–61. https://doi.org/10.1007/BF00747683

Nagase T, Kakeshita T, Matsumura K, Nakazawa K, Furuya S, Ozoe N, Yoshino K (2019) Development of Fe-Co-Cr-Mn-Ni-C high entropy cast iron (HE cast iron) available for casting in air atmosphere. Mater Des 184:108172. https://doi.org/10.1016/j.matdes.2019.108172

Ningxia Autonomous Region Environmental Protection Bureau (2012-2016) Ningxia Autonomous Region Environmental Bulletin http://www.nxep.gov.cn/hjjczxz/hjzl/hjzlxx/hjzkgb.htm. Accessed 18 February 2020

Ningxia water resources bulletin (2016) Ningxia water conservancy. http://slt.nx.gov.cn/pub/NXSLTGW05/SLZW_4294/ZFXXGK/GKML/GBXX/SZYGB/201608/t20160809_89346.html. Accessed 9 August 2016

Nziguheba G, Smolders E (2008) Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci Total Environ 390(1):53–57. https://doi.org/10.1016/j.scitotenv.2007.09.031

Paatero P (1997) Least squares formulation of robust non-negative factor analysis. Chemom Intell Lab Syst 37(1):23–35. https://doi.org/10.1016/S0169-7439(96)00044-5

Paatero P, Hopke PK (2009) Rotational tools for factor analytic models. J Chemom 23(2):91–100. https://doi.org/10.1002/cem.1197

Pfeifer GD, Roper JM, Dorman D, Lynam DR (2004) Health and environmental testing of manganese exhaust products from use of methylcyclopentadienyl manganese tricarbonyl in gasoline. Sci Total Environ 334–335:397–408. https://doi.org/10.1016/j.scitotenv.2004.04.043

Rajabpour S, Behzadi M, Jiang SY, Rasa I, Lehmann B, Ma Y (2017) Sulfide chemistry and sulfur isotope characteristics of the Cenozoic volcanic-hosted Kuh-Pang copper deposit, Saveh County, northwestern central Iran. Ore Geol Rev 86:563–583. https://doi.org/10.1016/j.oregeorev.2017.03.001

Rodríguez Martín JA, Ramos-Miras JJ, Boluda R, Gil C (2013) Spatial relations of heavy metals in arable and greenhouse soils of a Mediterranean environment region (Spain). Geoderma 200–201:180–188. https://doi.org/10.1016/j.geoderma.2013.02.014

SAIC (2002) Compilation and review of Canadian remediation guidelines, standards and regulations. Environmental Technologies Program, Ottawa

Shi YH, Huang JH, Zeng GM, Gu YL, Chen YN, Hu Y, Tang B, Zhou JX, Yang Y, Shi LX (2017) Exploiting extracellular polymeric substances (EPS) controlling strategies for performance enhancement of biological wastewater treatments: an overview. Chemosphere. 180:396–411. https://doi.org/10.1016/j.chemosphere.2017.04.042

Shi H, Jianu A, Weisenburger A, Tang CC, Heinzel A, Fetzer R, Lang FB, Stieglitz R, Müller G (2019) Corrosion resistance and microstructural stability of austenitic Fe-Cr-Al-Ni model alloys exposed to oxygen-containing molten lead. J Nucl Mater 524:177–190. https://doi.org/10.1016/j.jnucmat.2019.06.043

Sun L, Guo DK, Liu K, Meng H, Zheng YJ, Yuan FQ, Zhu GH (2019) Levels, sources, and spatial distribution of heavy metals in soils from a typical coal industrial city of Tangshan, China. Catena 175:101–109. https://doi.org/10.1016/j.catena.2018.12.014

Thurston GD, Spengler JD (1985) A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmos Environ 19(1):9–25. https://doi.org/10.1016/0004-6981(85)90132-5

Tian CY, Zhang FC (2010) Distribution and enrichment of As in groundwater in northern Yinbei Plain. Saf Environ Eng 17(2):22–25. https://doi.org/10.3969/j.issn.1671-1556.2010.02.006

USEPA (2014) U.S. Environmental protection agency. EPA positive matrix factorization (PMF) 5.0 fundamentals and user guide. Available at: https://www.epa.gov/sites/production/files/2015-02/documents/pmf_5.0_user_guide.pdf

USEPA (2018a) Soil screening guidance: technical background document (EPA/540/R-96/018). Appendix A: generic SSLs. Office of Solid Waste and Emergency Response. Washington. https://www.epa.gov/superfund/superfund-soil-screening-guidance. Accessed 18 February 2020

USEPA (2018b) Supplemental guidance for developing soil screening levels for superfund sites. Office of Solid Waste and Emergency Response, Washington https://www.epa.gov/superfund/superfund-soil-screening-guidance. Accessed 18 February 2020

Wang HN (2018) Landform of Ningxia. Ningxia Local History Editorial Review Committee, Ningxia

Wang QC, Ma ZW (2004) Heavy metals in chemical fertilizer and environmental risk. Rural Eco-Environ 20(2):62–64

Wang QY, Zhou DM, Cang L (2009) Microbial and enzyme properties of apple orchard soil as affected by long-term application of copper fungicide. Soil Biol Biochem 41:1504–1509. https://doi.org/10.1016/j.soilbio.2009.04.010

Wang X, Kang Y, Cui DY, Li J, Li D (2019a) Influence of lanthanum promoter on vanadium catalyst for sulfur dioxide oxidation. Catal Commun 118:39–45. https://doi.org/10.1016/j.catcom.2018.09.013

Wang YG, Gao SA, Liu XM, Tang BW, Mukiza E, Zhang N (2019b) Preparation of non-sintered permeable bricks using electrolytic manganese residue: Environmental and NH_3-N recovery benefits. J Hazard Mater 378:120768. https://doi.org/10.1016/j.jhazmat.2019.120768

Xia YJ, Liu J (2004) An overview on chronic arsenism via drinking water in PR China. Toxicology 198(1–3):25–29. https://doi.org/10.1016/j.tox.2004.01.016

Xie R, Wei DH, Han F, Lu Y, Fang JY, Liu Y, Wang JF (2018) The effect of traffic density on smog pollution: evidence from Chinese cities. Technol Forecast Soc Chang 144:421–427. https://doi.org/10.1016/j.techfore.2018.04.023

Xiong SG (2001) Basic soil science. China Agricultural University Press, Beijing

Xu CL, Shan YP, Bilal M, Xu B, Cao LD, Huang QL (2020) Copper ions chelated mesoporous silica nanoparticles via dopamine chemistry for controlled pesticide release regulated by coordination bonding. Chem Eng J 395:125093. https://doi.org/10.1016/j.cej.2020.125093

Yang B, Zhou LL, Xue ND, Li FS, Li YW, Vogt RD, Cong X, Yan YZ, Liu B (2013) Source apportionment of polycyclic aromatic hydrocarbons in soils of Huanghuai Plain, China: comparison of three receptor models. Sci Total Environ 443:31–39. https://doi.org/10.1016/j.scitotenv.2012.10.094

Yariv S, Cross H (1979) Colloid geochemistry of clay minerals. In: Geochemistry of colloid systems. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-67041-1-8.

Yuan XM, Tian FC, Wang XJ, Liu YS, Chen MT (2018) Small-scale sediment scouring and siltation laws in the evolution trends of fluvial facies in the Ningxia Plain Reaches of the Yellow River (NPRYR). Quat Int 476:14–25. https://doi.org/10.1016/j.quaint.2018.03.034

Zhan XY, Wang LA, Wang L, Wang X, Gong J, Yang L, Bai JS (2019) Enhanced geopolymeric co-disposal efficiency of heavy metals from MSWI fly ash and electrolytic manganese residue using complex alkaline and calcining pre-treatment. Waste Manag 98:135–143. https://doi.org/10.1016/j.wasman.2019.08.024

Zhang JY, Wang Q, Xia XZ (2012) Soil classes and distribution regularity of farmland in Ningxia agricultural reclamation area. Ningxia J Agric For Sci Technol 53(10):105–109. https://doi.org/10.3969/j.issn.1002-204X.2012.10.043

Zhang ZQ, Wang JJ, Ali A, DeLaune RD (2016) Heavy metals and metalloid contamination in Louisiana Lake Pontchartrain Estuary along I-10 Bridge. Transp Res D Transp Environ 44:66–77. https://doi.org/10.1016/j.trd.2016.02.014

Zhang PY, Qin CZ, Hong X, Kang GH, Qin MZ, Yang D, Pang B, Li YY, He JJ, Dick RP (2018) Risk assessment and source analysis of soil heavy metal pollution from lower reaches of Yellow River irrigation in China. Sci Total Environ 633:1136–1147. https://doi.org/10.1016/j.scitotenv.2018.03.228

Zhao C, Luo KL (2017) Sulfur, arsenic, fluorine and mercury emissions resulting from coal-washing byproducts: a critical component of China's emission inventory. Atmos Environ 152:270–278. https://doi.org/10.1016/j.atmosenv.2016.12.001

Zhao HG, Liu CY, Wang F, Wang JQ, Li Q, Yao YM (2007) Uplift and evolution of Helan Mountain. Sci China Ser D-Earth Sci 50(S2):217–226. https://doi.org/10.1007/s11430-007-6010-5

Zhou L (2008) A probe into the problem of city transformation of Shizuishan city from regional economy perspective. Journal of Ningxia Communist Party Institute 10(5):120–121. https://doi.org/10.3969/j.issn.1008-2921.2008.05.031

Zhou XY, Wang XR (2019) Impact of industrial activities on heavy metal contamination in soils in three major urban agglomerations of China. J Clean Prod. https://doi.org/10.1016/j.jclepro.2019.05.098

EA (The Environment Agency), DEFRA (Department of Environment, Food and Rural Affairs) (2009) A guide to using Soil Guideline Values (SGVs). London. https://www.gov.uk/government/publications/contaminated-soil-assessing-risks-on-human-health. Accessed 18 Feb 2020