

# Factorial Kriging analysis and sources of heavy metals in soils of different land-use types in the Yangtze River Delta of Eastern China

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**Abstract** The objectives of this study are to analyse the pollution status and spatial correlation of soil heavy metals and identify natural and anthropogenic sources of these heavy metals at different spatial scales. Two hundred and twenty-four soil samples (0–20 cm) were collected and analysed for eight heavy metals (Cd, Hg, As, Cu, Pb, Cr, Zn and Ni) in soils of different land-use types in the Yangtze River Delta of Eastern China. The multivariate methods and factorial Kriging analysis were used to achieve the research objectives. The results indicated that the human and natural effects of different land-use types on the contents of soil heavy metals were different. The Cd, Hg, Cu, Pb and Zn in soils of industrial area were affected by human activities, and the pollution level of these heavy metals in this area was moderate. The Pb in soils of traffic area was affected by human activities, and eight heavy metals in soils of residential area and farmland area were affected by natural factor. The ecological risk status of eight heavy metals in soils of the whole study area was light. The heavy metals in soils showed three spatial scales (nugget effect, short range and long range). At the nugget effect and short range scales, the Cd, Hg, Cu, Pb and Zn in

soils were affected by human and natural factors. At three spatial scales, the As, Cr and Ni in soils were affected by soil parent materials.

**Keywords** Soil pollution · Heavy metal · Factorial Kriging analysis · Land-use type · Ecological risk

## Introduction

The concentrations of heavy metals in soils are contributed by soil weathering and external anthropogenic inputs, for example, improper industrial emissions, atmospheric deposition, living garbage discharge, and the application of fertilizer etc. (Hu and Cheng, 2013; Boquete et al., 2014).

The contents and sources of heavy metals in soils were different for the different land-use types; these heavy metals would directly/indirectly affect human health. The soils of urban area (e.g. residential area, traffic area) were polluted by heavy metals (e.g. Hg, Cu and Pb), the high contents of heavy metals in urban soils have posed adverse influences to human health because of the possible transfer of metals to human body through suspended dust and water resources or by direct contact (Gržtić, 2008; Lai et al., 2010; Wei and Yang, 2010; Li et al., 2013; Schröder et al., 2013; Szolnoki et al., 2013; Luo et al., 2015). Due to industrial emissions, the soils of industrial area or agricultural area were seriously affected by heavy metals, which also seriously affected the human health (Cui et al., 2004; Zheng et al., 2007; Wang et al., 2010; Olumuyiwa et al., 2014). Meanwhile, because of the use of chemical fertilizer and pesticides, the soils of the agricultural/farmland including the vegetable fields were influenced by the heavy metals (e.g. As, Cu and Pb). Heavy metals in agricultural soils could be enriched in plants and then transported into the body through the food chain, which would become a major threat to human

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health (Gutiérrez-Ginés et al., 2012; Reimann et al., 2012; Niu et al., 2013; Chang et al., 2014; Chai et al., 2015).

The multivariate analysis and geostatistics were applied to analyse the effects of natural and anthropogenic activities on the contents of heavy metals in soils (Facchinelli et al. 2001; Harley et al., 2009; Lu et al., 2012). It mainly includes principal component analysis (PCA), correlation analysis, factor analysis (FA), cluster analysis (CA) and so on. Multivariate analysis has been used in lots of research fields, such as population statistics, agricultural statistics, ground research, pollutant analysis, including the pollution assessment, and source identification of heavy metals in soils (Wold et al., 1987; Webster and Oliver, 2001; Davis et al., 2009; Shan et al., 2013). For example, the research showed that the heavy metals (e.g., Cd, Pb and Zn) in soils were easily polluted by anthropogenic activities (Korre, 1999; Sun et al., 2013; Zhang et al., 2016). Soil parent materials are the temporal-spatio continuous variant, which have a high degree of spatial heterogeneity. Natural and anthropogenic factors can cause the spatial and temporal changes of soil heavy metals; therefore, the relation among heavy metals in soils exists the complex correlation and variability. Compared with multivariate analysis, spatial analysis has the advantages for analysing the pollution sources of soil heavy metals (Shine et al., 1995; Webster and Oliver, 2001; Rodriguez Martin et al., 2013). Factorial Kriging analysis (FKA) is a way of the geostatistics, and the spatial analysis method is used to decompose the spatial variability structures of the soil heavy metals into spatial components with different scales (Goovaerts, 1992; Bocchia et al., 2000; Imrie et al., 2008). According to the research, the spatial varieties of soil heavy metal concentrations had the certain correlation with the land-use types (Fang et al., 2005; Lee et al., 2006). Principal component analysis combined with FKA of the geostatistics can identify influential factors of specific spatial variability in different scales, which has obvious advantages in the analysis of pollution sources (Ha et al., 2014).

In this study, the objectives were (1) to analyse the relation among the concentrations of heavy metals in soils of different land-use types by using the statistical correlation and spatial correlation and (2) to assess the pollution status of heavy metals in soils of the whole area and to identify their potential pollution sources. The result can help decision-makers formulate pollution-control policies and effective soil remediation and management strategies, reducing the risk of heavy metals to crops and human health.

## Materials and methods

### Study area

Gaoyou, which is located in the middle part of the Jiangsu Province of Eastern China, is about 65 km away from the

Yangtze River. It covers a total terrestrial area of 1156 km<sup>2</sup>. Gaoyou has been area-dominated by agriculture so far, which has thousands of years of wheat and paddy rice planting history; at present, the main crops grown in this region include wheat and rice. In 2013, the region was named the ecological county of national level, so the potential ecological risk was strictly controlled. According to land-use type, the study area was divided into four types: industrial area, residential area, traffic area and farmland area.

### Sampling and experimental analysis

The soil sample collection was used by a relatively even sampling distribution (within an area of 4–5 km<sup>2</sup> for each sampling site), a total of 224 soil samples from 0 to 20 cm depth were collected across the whole study area (Fig. 1). Each soil sample from the sampling sites consisted of three or five sub-samples, and each sample was obtained with a wooden shovel and packed into a polyethylene. The locations of sampling sites were recorded by using GPS, including land-use type.

The soil samples were dried at about 90 °C, sieved through a 2.0-mm nylon sieve to remove sand, gravel and plant debris, and then stored in glass bottles at 20 °C. Samples of dried soils were finely powdered and sieved to pass a 0.15-mm (100-mesh) nylon sieve. The samples were digested by the mixed liquid including HNO<sub>3</sub> and HF. After evaporating the digestion liquids to dryness, the residuals were redissolved with HNO<sub>3</sub> and triple-distilled water. The total concentrations of Cd in soils were quantified using graphite atomic absorption spectrometer. The total concentrations of Cu, Pb, Cr, Zn and Ni in soils were quantified using inductively coupled plasma mass spectrometry (Elan DRC-e), and the total concentrations of Hg and As in soils were determined by using an atomic fluorospectro-photometer (AFS-2200a). The quality control and assurance was verified using the Chinese standardized reference materials: GSS-1, GSS-3, GSS-5 and GSS-8.

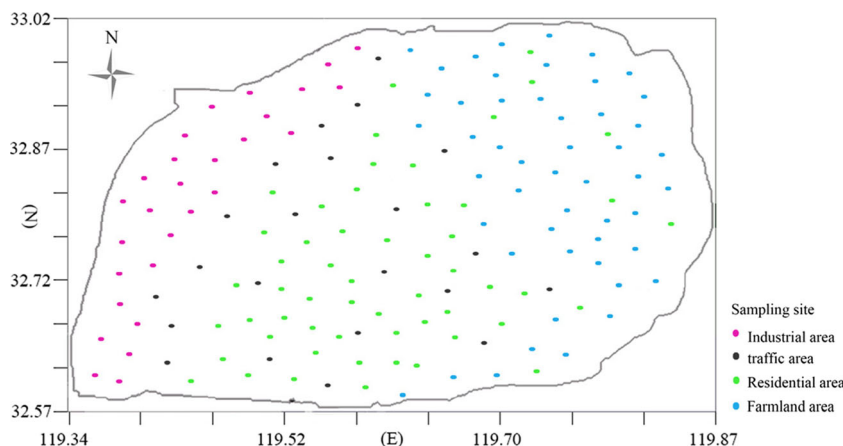
### Evaluation methods

The overall pollution status of soil heavy metals is assessed by Nemerow pollution index (PI<sub>N</sub>). Nemerow pollution index takes the mean and maximum of single pollution level of all evaluation factors into consideration, so the evaluated areas can be reflected more scientific and comprehensive in environment quality conditions. The equation is

$$PI_N = \sqrt{\frac{PI_{iave}^2 + PI_{imax}^2}{2}}, \quad (1)$$

where PI<sub>iave</sub> and PI<sub>imax</sub> are the mean and maximum of the pollution indices for heavy metal *i*, respectively. The soils polluted by heavy metals are classified into five levels based

**Fig. 1** Distribution map of soil sampling sites in this study area



on the corresponding  $PI_N$  values:  $PI_N < 0.7$ , clean;  $0.7 \leq PI_N < 1$ , relatively clean;  $1 \leq PI_N < 2$ , light pollution;  $2 \leq PI_N < 3$ , moderate pollution;  $PI_N \geq 3$ , significant pollution (Zhou et al., 2016).

The index of geo-accumulation ( $I_{geo}$ ) is used to assess the pollution level of soil heavy metals. This index not only considers anthropogenic factor and environmental geochemistry background value, but also considers the influence of natural factor on the background value. The index of geo-accumulation is calculated as

$$I_{geo} = \log_2 \left( \frac{C_i}{1.5B_i} \right), \tag{2}$$

where  $C_i$  is the concentration of the heavy metal  $i$  of the soil sample,  $B_i$  is the natural background value of the heavy metal  $i$ . The soil status polluted by heavy metals is classified into seven levels based on the corresponding  $I_{geo}$  values:  $I_{geo} < 0$ , clean;  $0 \leq I_{geo} < 1$ , clean-light pollution;  $1 \leq I_{geo} < 2$ , moderate pollution;  $2 \leq I_{geo} < 3$ , moderate-significant pollution;  $3 \leq I_{geo} < 4$ , significant pollution;  $4 \leq I_{geo} < 5$ , significant-extreme pollution;  $I_{geo} \geq 5$ , extreme pollution (Zhou et al., 2016).

The potential pollution risk of soil heavy metals is evaluated using the ecological risk index (RI) introduced by Hakanson (1980). The RI is calculated as the sum of the values of single ecological risk index of heavy metals:

$$RI = \sum E_i = \sum T_i f_i = \sum T_i \frac{C_i}{B_i}, \tag{3}$$

where  $E_i$  is the value of the single ecological risk index for heavy metal  $i$ ,  $T_i$  is the toxic-response factor for heavy metal  $i$ . The  $T_i$  values for Hg, Cd, As, Ni, Cu, Pb, Cr and Zn are 40, 30, 10, 5, 5, 5, 2 and 1, respectively. The  $f_i$  is the ratio of the heavy metal pollution factor calculated between the measured concentration  $C_i$  and the background values  $B_i$ . The potential ecological risk of heavy metals in soils is classified into four levels based on the values of  $E_i$  and RI:  $E_i < 40$  or  $RI < 150$

clean-light pollution;  $40 \leq E_i < 80$  or  $150 \leq RI < 300$ , moderate pollution;  $80 \leq E_i < 160$  or  $300 \leq RI < 600$ , significant pollution;  $160 \leq E_i < 320$  or  $RI > 600$ , extreme pollution (Zhou et al., 2016).

The enrichment factor (EF) is also used to assess the pollution level of soil heavy metals. The results help us judge the contributions of anthropogenic sources to the concentrations of soil heavy metals. The EF value of single heavy metal in soils is calculated as

$$EF_i = \frac{C_i/C_r}{B_i/B_r}, \tag{4}$$

where  $EF_i$  is the enrichment factor for the heavy metal  $i$ ,  $C_i$  is the concentration of the heavy metal in the soil sample,  $C_r$  is the concentration of the reference metal used for normalization in the soil sample, while  $B_i$  is the background concentration of the heavy metal  $i$ .  $B_r$  is the background concentration of the reference metal. In this study, Al is chosen as reference metal, its background value is  $39.26 \text{ mg kg}^{-1}$ . The pollution status of soil heavy metals is classified into five levels based on the corresponding  $EF_i$  values:  $EF < 2$ , clean - light pollution;  $2 \leq EF < 5$ , moderate pollution;  $5 \leq EF < 20$ , significant pollution;  $20 \leq EF < 40$ , strong pollution;  $EF \geq 40$ , extreme pollution (Zhou et al., 2016).

### Data analysis

The concentrations of soil heavy metals were treated and analysed by using Origin software, including principal component analysis (PCA), cluster analysis (CA), Pearson correlation analysis. The influence of human activities on soil heavy metals accumulation was evaluated by the index of geo-accumulation and enrichment factor. Factorial Kriging analysis (FKA) was used to analyse the spatial correlation of the concentrations of heavy metals in soils at different scales. FKA and spatial

distribution maps of the concentrations of soil heavy metals were made by Matlab, GS+ and Arcgis software.

## Results and discussion

### Concentrations of heavy metals in soils

The descriptive statistics of the concentrations of soil heavy metals in different land-use types are summarized in Table 1. In the whole area, the means of the concentrations of heavy metals in soils did not exceed their standard values. However, in the industrial area, the means of Cd, Cu and Zn contents exceeded their standard values. The concentrations of Cd, Hg, Cu, Pb and Zn in soils exceeded their standard values by 27, 13, 27, 2 and 32 sampling sites, respectively. In the traffic area, these soil heavy metals also exceeded their standard values, but the numbers of soil sampling sites exceeding the standard values were less than the industrial area, which indicated that the concentrations of heavy metals in the industrial area were influenced by human activities, and heavy metals concentrations of sampling sites of the traffic area were influenced by human activities. Especially near the industrial area,

the concentrations of heavy metals in soils were higher. For the Cu and Zn in soils of the residential area, only the concentrations of one sampling site exceeded their standard values, other heavy metals in soils of the residential area and farmland area did not exceed their standard values, these sampling sites were unpolluted, suggesting that soil parent materials might contribute more to heavy metal concentrations at these sampling sites than chemical fertilizer inputs. Except the contents of As, Cr and Ni in soils of the whole area did not exceed their standard values, other heavy metals in soils of the different area existed the phenomenon of exceeding their standard values.

### Pollution assessment of soil heavy metals

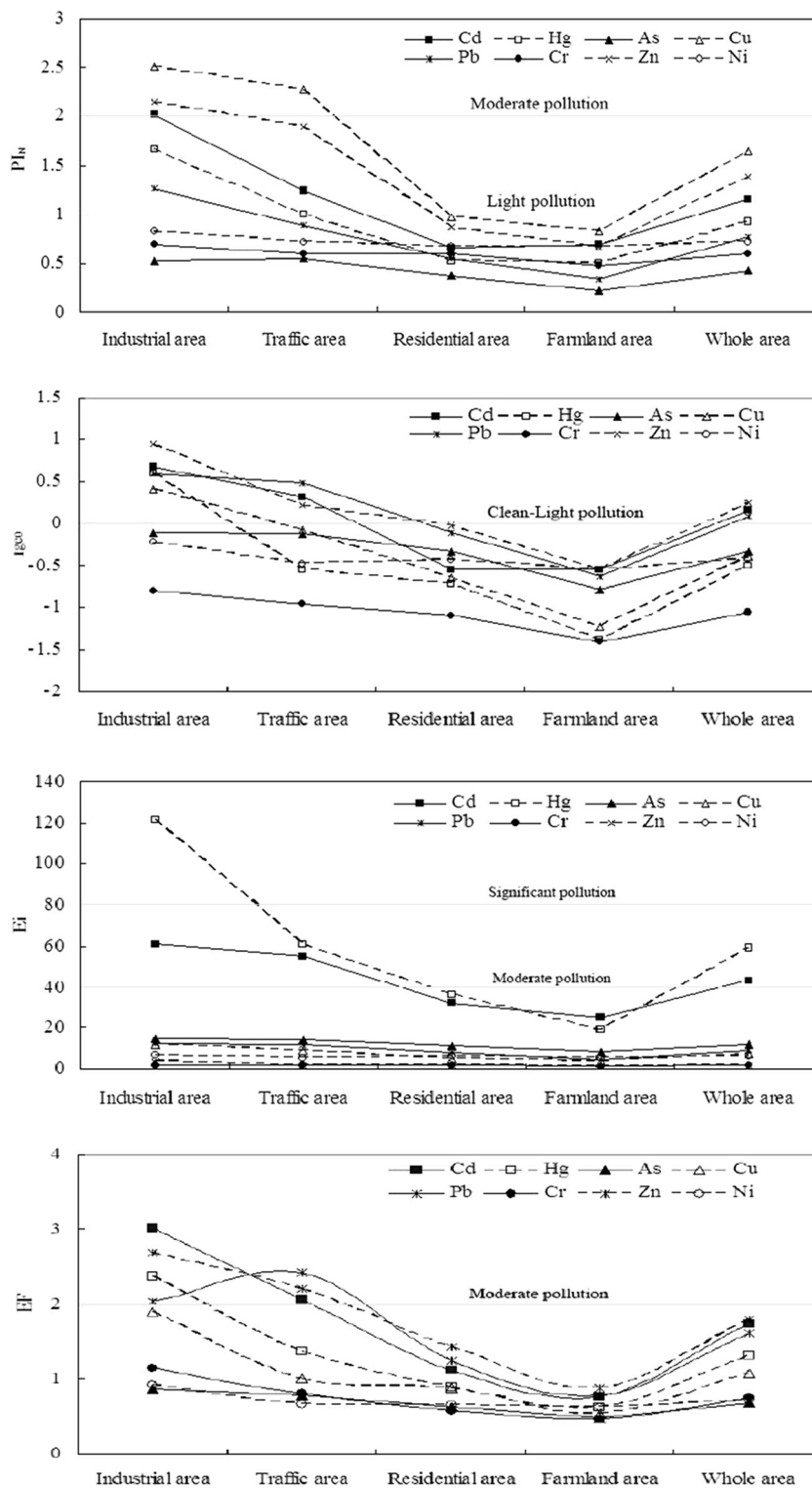
According to Fig. 2, the  $PI_N$  values of Cd, Cu and Zn in soils of the whole area were between one and two, which indicated the soil was light pollution by these heavy metals. But, the  $PI_N$  values of Cd, Cu and Zn in soils of the industrial area and Cu in soils of the traffic area were greater than two, which indicated that soil sampling sites were moderately polluted. The  $PI_N$  values of other heavy metals indicated that the soils in this area were clean or relatively clean. Overall, the  $PI_N$  values

**Table 1** Descriptive statistics of soil heavy metals concentrations (mg kg<sup>-1</sup> dry weight)

		Cd	Hg	As	Cu	Pb	Cr	Zn	Ni
IA ( <i>n</i> = 57)	Mean ± SD	0.33 ± 0.16	0.19 ± 0.16	9.08 ± 4.85	65.67 ± 41.96	96.62 ± 73.11	57.41 ± 25.92	246.19 ± 125.49	20.83 ± 6.87
	Min	0.11	0.01	3.67	18.38	31.24	26.25	75.91	9.60
	Max	0.82	0.68	27.84	164.85	434.80	135.58	554.80	37.91
	CV (%)	48.76	84.69	53.43	63.89	75.67	45.15	50.97	32.98
	NES	27	13	0	27	2	0	32	0
TA ( <i>n</i> = 36)	Mean ± SD	0.24 ± 0.08	0.09 ± 0.10	8.79 ± 5.03	48.25 ± 37.45	90.43 ± 64.00	50.82 ± 21.24	152.83 ± 110.33	17.09 ± 4.77
	Min	0.09	0.01	3.89	16.10	33.51	26.12	63.76	9.79
	Max	0.47	0.41	30.13	152.82	301.54	115.14	512.96	37.28
	CV (%)	34.12	104.05	57.21	77.62	70.77	41.79	72.19	27.90
	NES	7	3	0	13	2	0	7	0
RA ( <i>n</i> = 53)	Mean ± SD	0.14 ± 0.05	0.07 ± 0.06	7.64 ± 3.89	26.95 ± 8.44	55.97 ± 30.77	45.63 ± 17.41	114.67 ± 34.21	17.75 ± 4.99
	Min	0.05	0.01	3.30	15.46	27.01	18.08	53.37	6.98
	Max	0.24	0.21	20.09	57.52	185.59	118.21	214.69	33.50
	CV (%)	35.83	76.57	50.88	31.31	54.97	38.16	29.84	28.16
	NES	0	0	0	1	0	0	1	0
FA ( <i>n</i> = 78)	Mean ± SD	0.15 ± 0.06	0.04 ± 0.03	4.59 ± 1.63	19.10 ± 9.45	37.20 ± 16.67	37.77 ± 17.04	81.21 ± 32.56	16.66 ± 5.61
	Min	0.03	0.01	2.34	8.30	19.68	16.20	34.39	5.51
	Max	0.25	0.21	10.99	59.66	113.84	92.76	172.53	34.03
	CV (%)	38.58	65.52	35.40	49.49	44.80	45.11	40.09	33.70
	NES	0	0	0	0	0	0	0	0
WA	Mean ± SD	0.22 ± 0.11	0.10 ± 0.11	7.53 ± 4.13	39.99 ± 32.80	70.06 ± 54.32	47.91 ± 21.70	148.73 ± 103.77	18.08 ± 5.91
	BV	0.13	0.06	5.80	27.00	35.90	61.00	74.00	15.40
	SV (pH < 6.5)	0.3	0.3	40	50	250	150	200	40

SD standard deviation, CV coefficients of variation, BV background values, SV standard values (CMEP, 1995), IA industrial area, RA residential area, TA traffic area, FA farmland area, WA whole area, NES number of sampling sites with concentration exceeded the standard value

**Fig. 2** The values and pollution levels of  $PI_N$ ,  $I_{geo}$ ,  $E_i$  and  $EF$  of heavy metals in soils of different area



showed that the pollution level of soil heavy metals in the whole study area decreased in the order of  $Cu > Zn > Cd > Hg > Pb > Ni > Cr > As$ .

The  $I_{geo}$  values of Cd, Hg, Cu, Pb and Zn in soils of the industrial area were between zero and one, their pollution levels

were light, which showed that soil sampling sites were possibly influenced by natural and anthropogenic factors. However, the average  $I_{geo}$  values of Hg and Cu in the whole area were less than zero, their pollution levels were clean, which showed that the concentrations of Hg and Cu in soils of the industrial area

were mainly affected by human activities. The pollution level of  $I_{geo}$  of soil heavy metals in this study area decreased in the order of  $Cd \sim Pb \sim Zn > Hg \sim As \sim Cu \sim Cr \sim Ni$ .

The pollution levels of single ecological risk index for eight heavy metals in soils of different areas were different (Fig. 2). The single ecological risk index of Hg in soils of the industrial area was greatest, with a mean of 121.76, which indicated that the Hg in soils was in the significant ecological pollution status. The Cd in soils existed moderate pollution with a mean of 61.27. In the traffic area, the Cd and Hg in soils also existed the moderate pollution. However, in residential area and farmland area, eight heavy metals existed much lower ecological risk levels, because the average values of their indices were less than forty. Although sampling sites in the industrial area and traffic area were polluted by Cu, Pb and Zn, their ecological risk pollution levels were light, because their  $T_i$  values were little. Be similar to the distribution of the  $I_{geo}$ , the single ecological risk index of soil heavy metals in this whole area decreased in the order of  $Cd > Hg > Cu \sim Pb \sim Ni \sim Zn \sim As > Cr$ . The order of single ecological risk index of heavy metals in soils of the industrial area was similar to that of the whole area. Lastly, the RI (multi ecological) of heavy metals in soils was used to assess the ecological risk status of this study area, it was calculated with the sum of average values of the single ecological risk factor, the RI of the whole area was 140.66, indicating the ecological risk status of the heavy metals in soils of this whole area was light.

### Enrichment level of soil heavy metals

Figure 2 presents the average EF values of soil heavy metals at the different land-use types. The average EF values of these heavy metals ranged from 0.46 to 3.01, which indicated that the soil pollution levels were from clean to moderate. The average EF values of Cd and Zn in soils were significantly higher than those of other heavy metals in the whole area. The average EF values of Cd, Hg, Pb and Zn in soils of the industrial area were greater than two, suggesting that soil sampling sites of this area were moderately polluted, and their concentrations were affected by anthropogenic sources. However, in the traffic area, the average EF value of Pb in soils was greatest, which indicated that it was obviously influenced by human activities (e.g. vehicle exhaust) compared with other heavy metals. The average EF values of eight heavy metals in soils of the residential area and farmland area were less than two, which indicated that these soil sampling sites were relatively clean. The average EF value of As was close to that of Ni in the whole area, which were both less than one, suggesting that they were impacted by natural factor. Because in recent years, the green agriculture was implemented in this region, although the soils of farmland area were possibly affected by chemical fertilizer and pesticides, these factors had little effect on the concentration of heavy metals in soils. In the

whole area, the enrichment level of soil heavy metals decreased in the order of  $Zn > Cd > Pb > Hg > Cu > Cr > Ni > As$ .

### Ecological risk pollution level of heavy metals

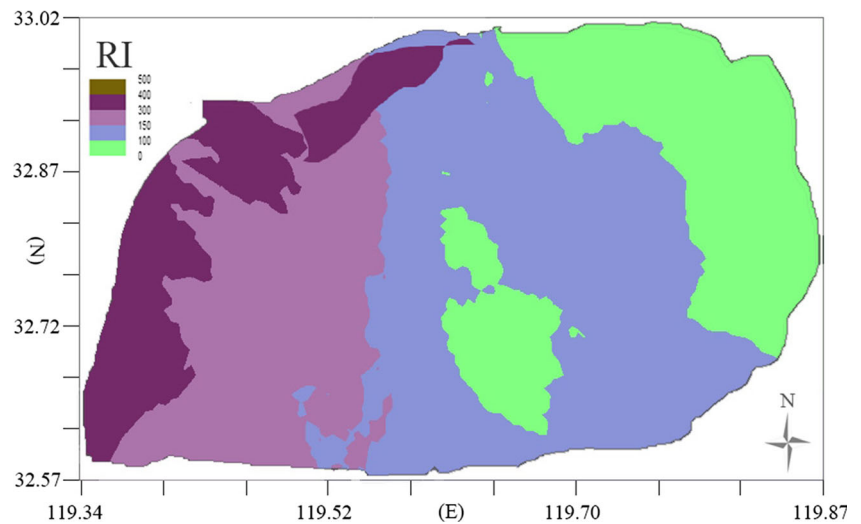
Figure 3 shows the spatial distribution map of the potential ecological risk index of heavy metals pollution in the whole area. As expected, the potential ecological pollution level of heavy metals in soils of the industrial area was higher than that of other areas. Therefore, care must be taken to prevent and reduce soil pollution by heavy metals in the course of economic development. The potential ecological pollution level of heavy metals in soils of the farmland area was lowest, suggesting the contents of heavy metals in soils of this area were safe for crops and agricultural product. In addition, for the farmland soils near the industrial area, soil heavy metal pollution by human activities should be prevented. By turning the soils of this area into other land-use types (e.g. park land), which can reduce the pollution risk of the agricultural soils caused by human activities.

### Spatial analysis of soil heavy metals

The spatial variation parameters of the contents of soil heavy metals are listed in Table 3. The variation is considered as strong spatial correlation when the ratio ( $C_o/(C_o + C)$ ) is  $< 25\%$ , as moderate spatial correlation when the ratio is between 25 and 75 %, and as weak spatial correlation when the ratio is  $> 75\%$  (You 2014). The ratios ( $C_o/(C_o + C)$ ) of eight heavy metals in soils were from 17.25 to 42.16 %. Except As, Cr and Ni, the ratios ( $C_o/(C_o + C)$ ) of other heavy metals were less than 25 %, other heavy metals had strong spatial correlation, which indicated these heavy metals were influenced by human activities, such as industrial emissions, automobile exhaust, atmospheric deposition with heavy metals. The long range of As and Cr was larger than those of other heavy metals, which showed that their content change was relatively small and the correlation was significant, they were greatly impacted by natural factor (soil parent materials). According to Table 2, the distributions of eight heavy metals were best fit with spherical model. The fitting spherical structure model had two scales, including short range (3.787–6.998 km) and long range (8.644–14.059 km). The short range represents the partial variation, and the long range represents the regional variation.

In this study, factorial Kriging analysis (FKA) is used to explore the spatial relations between heavy metals and to identify the potential sources of the variations regarding heavy metal concentrations at different spatial scales. A nested variogram model encompassing three basic variogram functions with different scales is used to fit the linear model of co-regionalization (LMC) to obtain the co-regionalization matrix. Table 3 shows the general correlation and spatial correlation

**Fig. 3** Spatial distribution of RI of heavy metals in soils of this study area



(nugget effect, short range and long range) between the heavy metals in soils. The general correlation can show the obvious correlation (positive/negative) among heavy metals. However, it exists certain insufficiency, the correlation values are averaged with the obvious variation of different spatial scales, and the result can not reflect the spatial variation. The spatial correlation among heavy metals can be differentiated according to the different spatial scales. At the nugget effect scale, significant correlations among the heavy metals indicated that the source of heavy metals was regarded as the single pollution source at a small range. At the spatial relation of short and long range, the heavy metals existed significant or highly significant correlation, which indicated that they were influenced by human activities. If the feature of negative correlation is more obvious than other features at the long-range scale, which indicates that these heavy metals exist multiple pollution sources at this scale (Zhong et al., 2007).

The correlations of Cd, Hg, Cu, Pb and Zn in soils were larger at the nugget effect scale than those at the short/long range scale, which showed that in a small range (e.g. industrial area) the concentrations of these heavy metals were impacted by human activities. However, the correlations among these heavy metals were relatively small at the short range and long

range scales, which indicated that the concentrations of these heavy metals were contributed by natural and anthropogenic activities. The Hg and Pb concentrations were small correlation with the other heavy metals at the long range scale, which showed that in partial area the influences of point sources on Hg and Pb in soils were stronger than large scale factor (e.g. soil parent materials). At the nugget effect, short range and long range scales, the strong and positive correlations among As, Cr and Ni in soils indicated that the concentrations of these heavy metals were impacted by the same factor. According to Table 1, the concentrations of these three heavy metals did not exceed their standard values, which suggested the concentrations of these soil heavy metals were affected by soil parent materials.

Principal component analysis was used to make the results of Pearson correlation matrix more easily interpretable. Figure 4 is the loading maps of soil heavy metals. Two factors were extracted from all factors for further analysis in the whole area. Factor 1 showed that eight heavy metals were positive correlation. Factor 2 showed that As, Pb, Cr and Ni were positive correlation and Cd, Hg, Zn and Cu were negative correlation. Cluster analysis (CA) was also used to get clearly the relation among soil heavy metals. In the CA, the

**Table 2** Fitting results of experimental variogram and cross-variogram of heavy metals in soils

Metal	Model	$C_0$	$C_0 + C$	$C_0 / (C_0 + C)$ (%)	Range1 (km)	Range2 (km)
Cd	Spherical	0.189	0.886	21.32	4.131	10.938
Hg	Spherical	0.329	1.416	23.23	4.936	9.314
As	Spherical	0.105	0.249	42.16	6.998	14.059
Cu	Spherical	0.066	0.383	17.25	4.346	9.108
Pb	Spherical	0.037	0.171	21.70	4.131	9.873
Cr	Spherical	0.098	0.241	40.63	6.886	13.971
Zn	Spherical	0.084	0.431	19.47	3.787	8.644
Ni	Spherical	0.081	0.258	31.45	5.571	11.297

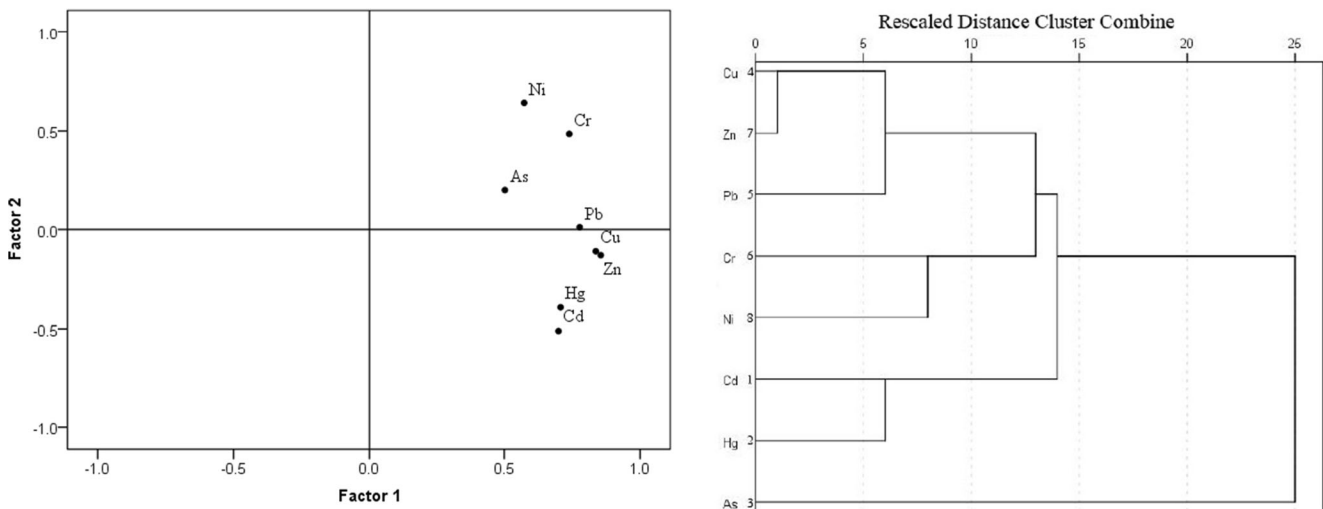
**Table 3** Correlation coefficient of heavy metals concentrations in soils at different scales

	Cd	Hg	As	Cu	Pb	Cr	Zn	Ni
General correlation								
Cd	1.000							
Hg	0.139*	1.000						
As	0.098	0.038	1.000					
Cu	0.475**	0.467**	-0.247**	1.000				
Pb	0.438**	-0.415**	-0.161*	0.684**	1.000			
Cr	0.377**	-0.329**	-0.182*	0.629**	0.677**	1.000		
Zn	0.659**	0.535**	0.054	0.720**	0.638**	0.571**	1.000	
Ni	-0.162*	0.074	0.240**	0.060	-0.167*	0.066	0.185*	1.000
Nugget effect								
Cd	1.000							
Hg	0.039	1.000						
As	0.098	0.038	1.000					
Cu	0.375**	0.067	-0.247**	1.000				
Pb	0.038	-0.215*	-0.161*	0.684**	1.000			
Cr	0.277**	-0.329**	-0.182*	0.029	0.177*	1.000		
Zn	0.059	0.105	0.054	0.020	0.038	0.171*	1.000	
Ni	-0.162*	0.074	0.240**	0.060	-0.167*	0.066	0.185*	1.000
Short range (4.5 km)								
Cd	1.000							
Hg	0.267**	1.000						
As	0.073	0.054	1.000					
Cu	0.159*	0.421**	0.077	1.000				
Pb	0.396**	0.334**	-0.101	0.656**	1.000			
Cr	0.122	-0.189*	0.112	0.182*	0.087	1.000		
Zn	0.618**	0.428**	0.067	0.714**	0.428**	0.434**	1.000	
Ni	0.099	0.051	0.272**	0.120	-0.208*	0.188*	0.212*	1.000
Long range (12 km)								
Cd	1.000							
Hg	0.788**	1.000						
As	0.031	0.249**	1.000					
Cu	0.531**	0.510**	0.046	1.000				
Pb	0.456**	0.373**	0.010	0.495**	1.000			
Cr	0.113	0.234*	0.272*	0.074	0.223*	1.000		
Zn	0.348**	0.533**	0.075	0.829**	0.683**	0.408**	1.000	
Ni	0.194*	0.287*	0.296**	0.050	0.009	0.014	0.129*	1.000

\* $p < 0.05$ ; \*\* $p < 0.01$

raw data was standardized to a mean of zero and a standard variation of one, and then classified using the nearest

neighbour element with the Pearson correlation as the similar measurement. Figure 4 shows that Cu and Zn were



**Fig. 4** Maps of PCA loading and single-linkage cluster analysis of soil heavy metals in the study area



significantly correlated with each other and formed a cluster, which were associated with Cd and Hg at later stages. Another relation was also observed between Cr and Ni, which were associated with As at later stages.

**Sources of soil heavy metals at different scales**

Spatial principal component of different scales can be obtained according to the LMC matrices of different scales, and the result can better explain the spatial feature of heavy metals in soils. Two spatial principal component factors were extracted from all factors. The loading maps of spatial principal component were obtained by two principal components of the co-regionalization matrix at each spatial scale (Fig. 5). The map was more intuitive to understand the spatial correlation among heavy metals. At the nugget effect scale, the first group included Cd, Cu and Zn. The concentrations of these heavy metals in soils were higher than standard values, which were affected by human activities. The second group included As, Cr and Ni; the contents of these heavy metals in soils were lower than standard values, which came from natural source. Hg and Pb made up the third group, the concentrations of these heavy metals in soils were contributed by natural and anthropogenic factors. Because the nugget effect exists, the systematic error (e.g. sample collection and determination etc.), structural analysis cannot reveal a smaller change; therefore, at the nugget scale the principal component pollution sources cannot be accurately analysed.

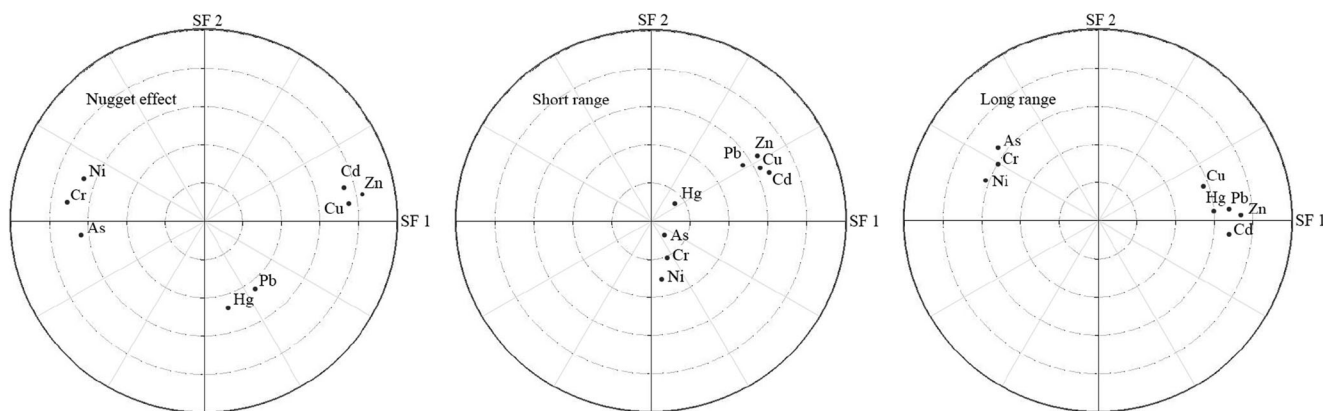
At the short-range scale, the concentrations of Cd, Cu, Pb and Zn in soils had the higher positive loading in the spatial factor 1, Table 3 also indicates that Cd, Cu, Pb and Zn existed significant positive correlation, respectively. The results indicated that the contents of these four heavy metals were affected by potential point pollution sources, such as electroplating wastewater emission. According to Table 1, the concentrations of these heavy metals in the industrial area were higher than those in other areas, but in the traffic area the concentrations of Pb in soils were highest, because Pb was regarded as the

identification element of vehicle pollution sources. The spatial factor 2 included Hg, As, Cr and Ni, the spatial variation of these heavy metals was similar. The concentrations of As, Cr and Ni in the whole area did not exceed their standard values, they were impacted by soil parent materials. However, the Hg concentrations of some sampling sites (e.g. industrial area/traffic area) exceeded its standard value, which were polluted by anthropogenic sources. The research indicated that a little of Hg was discharged into the environment through anthropogenic activities, such as combustion of fossil fuels, improper disposal of some electrical switches and relays (Santschi et al., 1999). The result showed that in the short-range scale the influence of land-use types was especially obvious.

At the long-range scale, Cd, Hg, Cu, Pb and Zn existed stronger correlation. The spatial variability of these heavy metals was affected by natural and anthropogenic factors. At this scale, the effect of soil parent materials on As, Cr and Ni in soils was more significant. But at the short-range scale, Hg in soils existed certain correlation with As, Cr and Ni in soils. At three spatial scales, As, Cr and Ni in soils showed the strong correlation. The concentrations of these three heavy metals in soils of the whole area were affected by soil parent materials, which indicated that the contents of these heavy metals in soils were safe for crops and human health.

**Conclusions**

In this study, in order to assess the pollution level and analyse the correlation of eight heavy metals in soils, 224 samples were collected from different land-use types, including industrial area, traffic area, residential area, and farmland area. The results of  $PI_N$ ,  $I_{geo}$  and  $Ei/RI$  indicated that the pollution level and potential ecological risk status of heavy metals in soils decreased in the order of industrial area > traffic area > residential area > farmland area. The enrichment level of soil heavy metals in the whole area decreased in the order of  $Zn > Cd > Pb > Hg > Cu > Cr > Ni > As$ . The ecological risk



**Fig. 5** PCA loading Maps of soil heavy metals at three spatial scales

status of heavy metals in soils of the whole area was light. The Cd, Hg, Cu, Pb and Zn in soils of industrial area were affected by human activities. Meanwhile, the contents of Pb in soils of the traffic area were also affected by human activities. Eight heavy metals in the residential area and farmland area were affected by natural factor. The heavy metals in soils of the whole area existed three spatial scales (nugget effect, short range and long range). At the different spatial scales, the sources of heavy metals were different. The Cd, Hg, Cu, Pb and Zn in soils at the nugget effect and short-range scales were affected by natural and human activities. At three different spatial scales, the As, Cr and Ni in soils were affected by soil parent materials.

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