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Pollution Evaluation of a Phosphorus-Rich Area of Zhongxiang City

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ABSTRACT

An extensive survey was carried out to understand the spatial distribution and possible sources of soil heavy metals in a phosphorus-rich area. A total of 615 topsoil samples were gathered, utilizing a regular sampling grid of 1×1 km squares, and the contents of arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) were analysed to investigate the spatial distribution of these heavy metals, identify their sources, and assess levels of pollution. The results showed that the enrichment factor (EF) of the studied metals decreased in the order Cd > As > Pb > Co > Ni > Cr = Cu > Zn, and the mean contents of Cd, As and Pb were significantly higher than the background values. According to potential ecological risk (RI), 11.2% of the study areas had considerable potential ecological risk and the other areas had low to moderate potential ecological risk. The results of multivariate and geostatistical analyses indicated that Co, Cr, Ni and V, and to a lesser extent Cu and Zn, mostly originated from natural sources; while As and Pb, and to a lesser extent Cd, Cu and Zn, mainly originated from phosphorus-related industrial activities. The results also showed that Cd was affected by water with Cd pollution from the Hanjiang River. These results are useful for establishing policies for protecting local soil quality.

INTRODUCTION

Soil is not only a medium for plants to grow, or a sink for disposal of undesirable materials, but also acts as an important environmental component closely associated with the atmosphere, groundwater, and plant life (Cai et al. 2015, Chen et al. 2008). Soil pollution has become an important environmental issue. Among kinds of soil pollution, heavy metal contamination is an important issue due to its characteristics of non-biodegradability and persistence (Cai et al. 2015, Shan et al. 2013, Wang et al. 2014). Excessive accumulation of heavy metals in soils may pose serious health risks to humans and may have adverse impacts on the ecosystem (Chen et al. 2011).

The contents of heavy metals in soils are usually affected by many factors such as parent material and human activities (Shi et al. 2006, Zhang et al. 2009). In recent decades, the natural input of heavy metals to soils due to pedogenesis has been exceeded by human input, even on a regional scale (Chen et al. 2008, Shi et al. 2006). Under the joint influences of natural and human inputs, the sources of heavy metals may be complicated and difficult to interpret. Meanwhile, because the soil itself has spatial heterogeneity, and the pollution sources vary geographically due to differing local environments and development conditions, the contents of heavy metals change conspicuously over space (Luo et al. 2007b). Relying solely on multivariate statistical analysis or geostatistics, it is difficult both to identify heavy metal sources and to characterize their spatial variability and possible hotspots. Fortunately, a combination of these two methods provide an appropriate solution and has been proved to be feasible in previous studies (Chen et al. 2008, Wu & Zhang 2010).

With the rapid economic development of the last several decades, soil pollution by heavy metals in China has become a serious problem (Chen et al. 2011). Many pollution surveys about soil heavy metals have been carried out in China (Yuan et al. 2014, Zhang et al. 2009, Zhong et al. 2012), but few studies have been performed in areas with rich phosphate rock resources, where the sources of soil heavy metals may be different from other areas. A phosphorus-rich area was selected as the study area. Local environmental problems, especially soil heavy metal pollution, are becoming increasingly serious. The primary objectives of the study were (1) understand the contents of soil heavy metals; (2) identify their possible sources; (3) identify the contamination degree of soil heavy metals.

MATERIALS AND METHODS

Study area: The study area is in the central region of Hubei Province, China (Fig. 1). The study area lies within 112°7'-112°31' E and 31°11'-31°33' N, and the total area is about 777 km^2. It belongs to the northern subtropical zone of the monsoonal climate, with four distinct seasons. The Hanjiang River flows alongside the southeastern part of the study area, and is the major water resource for nearby regions for agricultural, domestic and industrial uses (Fig. 1). The study area is an important agricultural region of Zhongxiang City, and the main agricultural products are rice, corn and rape.

The study area has a great quantity of phosphate rock resources and has a long history of mining of these resources. The biggest industrial park in the study area, Jingxiang Phosphorus Industrial Park, lies 2 km west of the seat of the Huji town government.

Soil sampling and chemical analysis: A total of 615 topsoil samples (0-20 cm depth) were collected from the study area in 2014. The sample sites were based on a regular grid of 1×1 km, and each grid square had at least one sample site (Fig. 1). Each soil sample was a mixture of 5 sub-samples, and each sampling point was recorded by a GPS device. The soil samples were air-dried at room temperature, and stones and other debris were removed. Portions of soil samples were ground in an agate grinder to pass through a 0.149 mm sieve, and stored in plastic bags prior to analysis.

A small portion of each sample (2-5 g) was digested with HNO_3-HCl-$HClO_4$ and the total contents of cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Another small portion of each sample (about 0.5 g) was digested by aqua regia (1:1 HCl:HNO_3) and the total content of arsenic (As) was measured by atomic fluorescence spectrometry (AFS). The analytical precision for replicate samples was within ±10% and the measurement errors between determined and certified values ranged from 92% to 108%.

Contamination degree and ecological risk: There are many

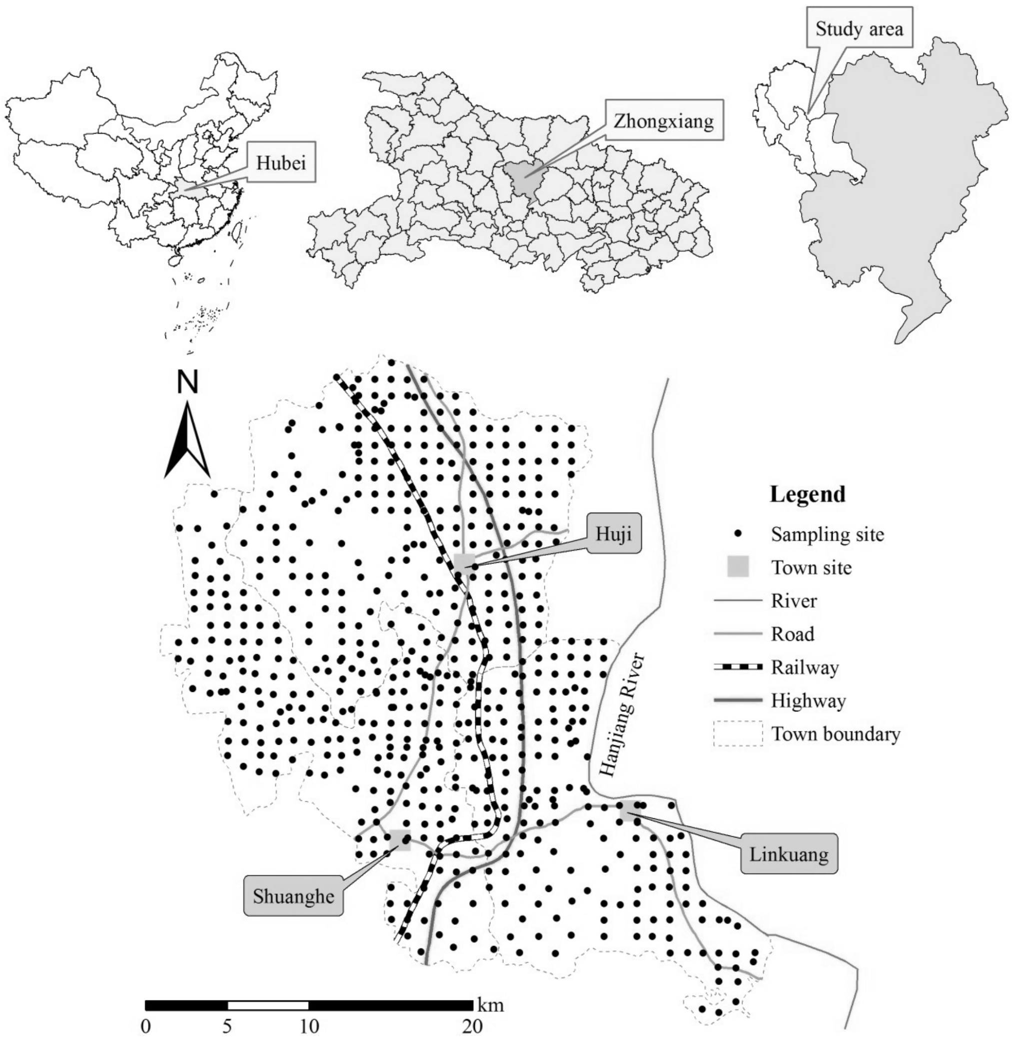

Fig. 1: The location of the study area and distribution of the sampling sites.

kinds of evaluation methods for quantifying the pollution level and potential eco-risks of heavy metals (Mirzaei et al. 2014). In this study, the enrichment factor (EF) was used to determine the degree of enrichment of individual metals in soils, and is calculated by the following formula (Wu et al. 2015):

$$\mathrm{EF} = \left(C_x/C_{ref}\right)_{sample} / (C_x/C_{ref})_{background} \quad ...(1)$$

Where, EF is the enrichment factor of the heavy metal *x*, C_x is the content of element *x* in the soil, C_{ref} is the content of a reference element, and (C_x/C_{ref}) is the ratio of the content of heavy metal *x* to the content of the reference element, either in the sample or background. When calculating the EF values, V was selected as the reference element because it usually originates from the parent materials, and showed weak correlation with the metals affected by anthropogenic factors (Wu et al. 2015). The heavy metal background content in the soils of Hubei Province was selected as the background value. Considering the conventional grading standards and the characteristics of EF (Wu et al. 2015, Yuan et al. 2012), pollution levels of metals are classified as low (EF <1.5), middle (1.5 ≤ EF <3), or high (EF ≥3).

RI, which considers the potential toxic-response factors of heavy metals, was first developed by Hakanson (1980), and has been used by many researchers to evaluate heavy metal ecological risk (Islam et al. 2015, Li et al. 2013, Mirzaei et al. 2014). RI can be calculated as follows:

$$\mathrm{RI} = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i = \sum_{i=1}^{n} T_r^i \times C_o^i/C_n^i \quad ...(2)$$

Where, RI is the sum of the all risk indices for elements in the soil, E_r^i is the monomial potential risk index, and T_r^i is the metal toxic-response factor. The toxic-response factors for As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn are 10, 30, 5, 2, 5, 5, 5, 2 and 1, respectively (Yuan et al. 2014). C^i_f is the metal pollution factor, C^i_o is the heavy metal content in the soil, and C^i_n is a reference value for metals. The value is defined as low risk (E^i_r<40), moderate risk (40 ≤ E^i_r< 80), considerable risk (80 ≤ E^i_r<160), high risk (160 ≤ E^i_r< 320), and very high risk (E^i_r ≥ 320) (Hakanson 1980). The following thresholds are classified for the RI value: RI<65, low ecological risk; 65 ≤ RI <130, moderate ecological risk; 130 ≤ RI < 260, considerable ecological risk; RI ≥260, high ecological risk (Hakanson 1980, Luo et al. 2007a).

Geostatistical analysis and multivariate analysis: In multivariate statistics and linear geostatistics, the variables under study will preferably be normally distributed (Simasuwannarong et al. 2011). Data transformation was carried out on all heavy metal contents. Among the many transformation methods available, logarithmic transformation is frequently used (Simasuwannarong et al. 2011, Webster & Oliver 2001). However, some studies have found that environmental variables do not always follow the log normal distribution (McGrath et al. 2004). In this study, a power transformation, the Box-Cox transformation, was employed to normalize the variables. More detailed information related to the Box-Cox transformation can be found in other references, such as Box & Cox (1964).

Geostatistics is based on the theory of a regionalized variable (Matheron 1963), which has spatial coordinates and exhibits spatial autocorrelation such that samples close together in space are more alike than those that are further apart (McGrath et al. 2004). Geostatistics employs a semivariogram to measure the spatial variability of a regionalized variable and provides input parameters for spatial interpolation by kriging (Chen et al. 2008, McGrath et al. 2004). In our study, a semivariogram was employed to analyse discrete soil samples. The equation is expressed as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i + h) - Z(x_i)]^2 \quad ...(3)$$

Where, *N (h)* is the number of observed pairs of sample sites separated by the lag distance, and $Z(x_i)$ is the value of the variable *Z* at the site. After analysing the semivariogram, the best fit model and the corresponding parameters for kriging interpolation can be obtained. Ordinary kriging was selected to generate the spatial distribution maps of transformed heavy metal contents, using the nearest 16 sampling sites and a maximum searching distance equal to the range distance of the regionalized variable. More detailed information on geostatistics can be found in other references, such as Webster & Oliver (2001). The geostatistical analysis was performed using GS+® (version 9.0), and based on the best fit semivariogram models, the spatial distribution maps were generated with ArcGIS® (version 9.3).

In this study, multivariate statistical methods (including correlation analysis, PCA and CA) were used to assist the interpretation of the environmental data set, and distinguish anthropogenic sources from natural sources (Mamat et al. 2014, Wu & Zhang 2010). For the correlation analysis, Spearman's nonparametric correlation coefficient was employed because in some cases the heavy metal contents were not normally distributed. PCA was used to extract the most important information from the original data with a minimum loss of useful information (Gu et al. 2012). To facilitate the interpretation of results, varimax rotation was used to clarify the loading of heavy metals (Chen et al. 2008). CA was used to classify environmental variables into groups and to assist PCA results (Wu & Zhang 2010). The results of the hierarchical clustering procedure were visualized with a dendrogram. Multivariate analysis was performed with SPSS ® (version 19.0).

RESULTS AND DISCUSSION

Descriptive statistics: A descriptive summary of the metal contents of the soils is given in Table 1. The concentration ranges of As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn were 5.5-48.7, 0.059-0.577, 7.9-32.9, 50.6-119.0, 16.0-64.7, 19.1-70.4, 17.8-53.8, 61.6-164.7 and 40.0-142.3 mg.kg^{-1}, respectively. The mean contents of the metals studied in the soils followed a descending order as follows: V> Cr > Zn >Ni >Cu >Pb > Co>As >Cd. The coefficient of variation (CV) of the heavy metal concentrations varied from 14.0% to 48.5%. The CV values of the metal concentrations follow the order: Cd> As> Pb> Zn> Co > Ni> Cu> V> Cr. Cd had the highest CV value (48.5%), indicating Cd may have the highest possibility of being affected by extrinsic factors such as human activities (Chen et al. 2008). Cr had the lowest CV value at 14.0%, implying that Cr had quite a homogeneous distribution (Cai et al. 2015).

The mean contents of Co, Cr, Cu, Ni, V and Zn were close to the background values, whereas the mean contents of As, Cd and Pb were significantly higher than the background values (Liu & Ma 2012). The average contents of As, Cd, Cr, Cu, Ni, Pb and Zn all fall within the guidelines based on the Environmental Quality Standard for Soils in China (SEPAC 1995). However, 4.5% and 14.0% of samples for As and Cd, respectively, exceeded their corresponding guideline values, indicating that As and Cd might have pollution issues. 4.9% of samples had Ni concentrations above the guideline value, but this might be because Ni had a high background value (Table 1).

Geostatistical analysis: Prior to multivariate analysis and geostatistical analysis, the normality of the nine metal contents were tested. The parameters of skewness, kurtosis, and the significance level of the Kolmogorov-Smirnov test for normality (K-S p) for raw, log-transformed and Box-Cox transformed data are presented in Table 2. In this study, it can be observed that only Co, Cr and Pb passed the Kolmogorov-Smirnov normality test (K-S p> 0.05) before data transformation, and some metals, such as As and Cu, were skewed, with skewness significantly higher than 0, meaning that these metals have several extremely high values (Zhang et al. 2009). Their kurtoses were also sharp, caused by the fact that the majority of samples were clustered at relatively low values (Zhang et al. 2009). Log-transformation and Box-Cox transformation were employed to normalize the raw data. As Table 2 shows, compared with log-transformation, the Box-Cox transformation generally resulted in smaller skewness values, pushing them toward “0”. Although As, Cu, Ni and V did not pass the normality test after the Box-Cox transformation, low skewness values meant their transformed distributions were very close to the normal distribution.

Spatial structure analysis: Soil heavy metals are regionalized variables as they are distributed in geographical space. They have spatial structure, with spatial auto correlation (Chen et al. 2011). In our study, geostatistics was employed to analyze the spatial structure and visualize the interpolation results. The semivariograms and the best fit models for the nine metals are shown in Fig. 2. The attributes (including nugget variance, sill variance, Nugget/Sill ratio, range value and coefficients of determination) of the semivariogram for each metal are summarized in Table 3.

Table 1: Summary statistics for soil heavy metal contents (mg.kg^{-1}).

Elements	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
Mean	15.17	0.198	17.00	85.75	30.39	38.31	30.10	107.65	76.46
Maximum	48.7	0.577	32.9	119.0	64.7	70.4	53.8	164.7	142.3
Minimum	5.5	0.059	7.9	50.6	16.0	19.1	17.8	61.6	43.0
SD	5.08	0.10	3.48	11.97	5.67	7.43	9.30	16.73	16.74
CV(%)	33.5	48.5	20.5	14.0	18.7	19.4	30.9	15.5	21.9
Skewness	2.52	1.40	0.26	-0.18	1.30	-0.01	0.92	0.60	0.94
Kurtosis	10.71	1.92	1.42	0.27	4.93	0.77	3.71	1.18	1.16
Background value[a]	10.5	0.114	14.6	79.0	28.2	34.7	25.7	104.2	77.5
Guideline value[b]	25	0.3	-	300	100	50	300	-	250
Samples exceeding guideline value (%)	4.5	14.0	-	0.0	0.0	4.9	0.0	-	0.0

[a]Heavy metal background value in soils of Hubei Province (Liu & Ma 2012).
[b]Environmental Quality Standard for Soils in China (Grade II), i.e. the maximum allowable content of heavy metals in farmland soils, including arable land (vegetable, tea and fruit) and grazing land, formulated by the State Environmental Protection Administration of China (SEPAC 1995).

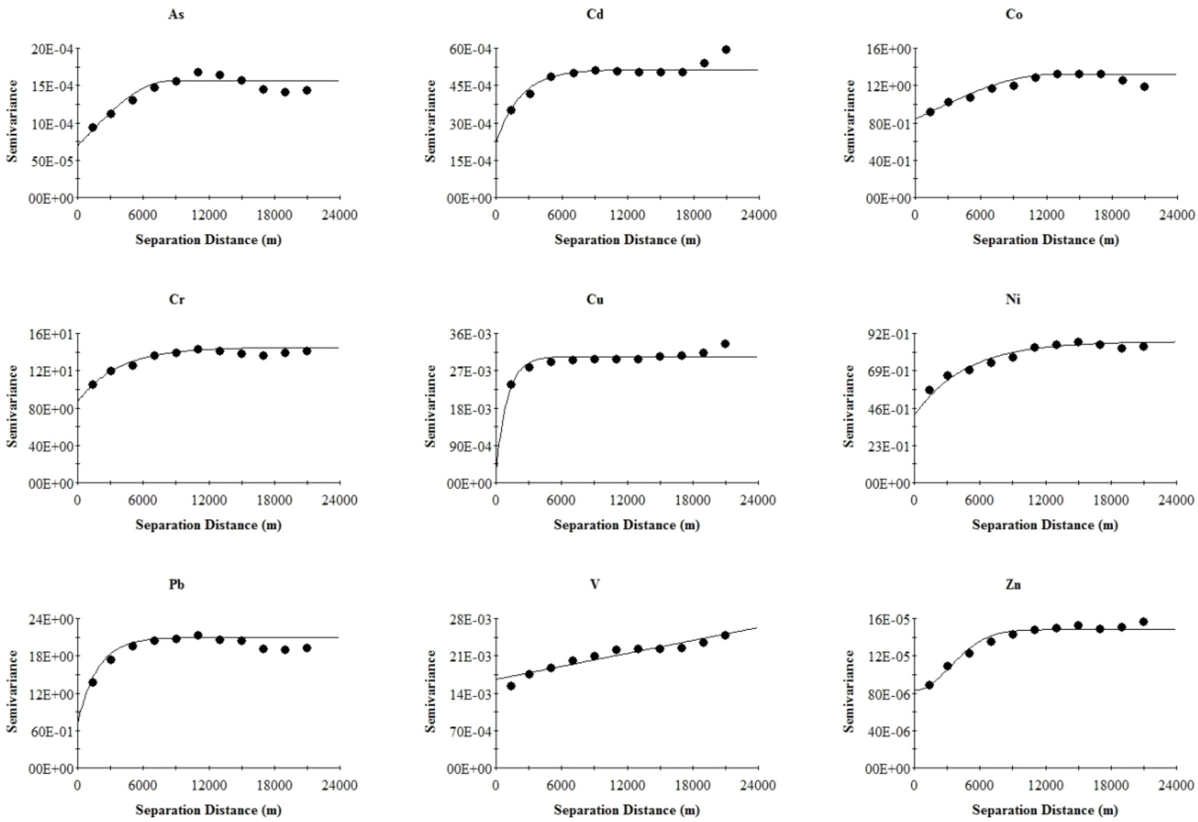

Fig. 2: Experimental semivariograms of heavy metals with best fit models.

The semivariograms show that As and Co were fitted for a spherical model; V was fitted for a liner model; Cd, Cr, Cu, Ni and Pb were fitted for an exponential model; and Zn was fitted for a Gaussian model.

In geostatistics, the Nugget/Sill ratio can be assumed to be a criterion to classify the spatial dependence of soil properties, such as heavy metal concentrations. If the ratio is less than 0.25, the variable shows strong spatial dependence. If the ratio is between 0.25 and 0.75, the variable shows moderate spatial dependence. If the ratio is greater than 0.75, the variable has weak spatial dependence (Cambardella et al. 1994). It has been indicated that strong spatial dependence can be ascribed to intrinsic factors (soil formation factors, e.g. soil parent materials, soil types and topography) and weak spatial dependence can be attributed to extrinsic factors (human contamination) (Cambardella et al. 1994). The Nugget/Sill ratio of Cu, lower than 0.25, indicated that Cu had a strong spatial dependency, and the spatial dependence of Cu may be attributed to natural factors. The Nugget/Sill ratios of the other eight metals, between 0.25 and 0.75, indicated that they have moderate spatial dependence.

The range value is considered as a measure of extension where spatial autocorrelation exists (Wu & Zhang 2010). The spatial structures of Cu had short ranges (3,120 m) and those of As, Cd, Pb and Zn had moderate ranges (5,467-8,370 m), whereas the variation of Co, Cr, Ni and V was dominated by long range spatial correlation (11,105-20,942 m). The shortest range of spatial correlation, presented by Cu, was 3,120 m, confirming the rationale of the sampling design, which used a 1×1 km grid for the precise environmental investigation of the nine heavy metals in our study. The sample grid length could thus be increased for the metals with longer ranges such as Ni and V. The short-range spatial correlation of Cu indicated anthropogenic factors influencing Cu. However, the low Nugget/Sill ratio (0.084), and the mean content close to the background value, suggested that natural factors are also affecting Cu distribution. Therefore, it is reasonable to conclude that Cu is controlled by both anthropogenic factors and natural factors. Of the nine heavy metals, V had longest effective range, meaning that V had better spatial structure and less variability due to extrinsic factors. According to the descriptive statistics, the mean content of V was close to the background

Table 2: Skewness, kurtosis and significance level of the Kolmogorov-Smirnov test (K-S *p*) of the raw, log-transformed and Box-Cox transformed data sets of heavy metal concentrations.

Data set	Parameter	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
Raw data	Skewness	2.52	1.40	0.26	-0.18	1.30	-0.01	0.92	0.60	0.94
	Kurtosis	10.71	1.92	1.42	0.27	4.93	0.77	3.71	1.18	1.16
	K-S *p*	0.00	0.00	0.10	0.14	0.00	0.00	0.05	0.01	0.00
Log	Skewness	0.47	0.25			0.19	-0.76		-0.07	0.26
	Kurtosis	2.53	-0.13			1.88	0.94		1.07	0.30
	K-S *p*	0.00	0.11			0.00	0.00		0.02	0.02
Box-Cox	Skewness	0.11	-0.09			0.19	-0.16		-0.07	0.10
	Kurtosis	2.12	-0.14			1.88	0.67		1.07	0.36
	K-S *p*	0.00	0.38			0.00	0.02		0.02	0.08
λ		-0.32	-0.13			0.00	0.80		0.00	-0.50

Table 3: Best fit semivariogram models of heavy metals and their parameters.

Element	Model	C_0	$C+C_0$	$C_0/(C+C_0)$	Range (m)	R^2
As	Spherical	6.9E-4	1.6E-3	0.445	8370	0.859
Cd	Exponential	2.2E-3	5.1E-3	0.429	6710	0.817
Co	Spherical	8.4E+0	1.3E+1	0.635	12646	0.911
Cr	Exponential	8.7E+1	1.5E+2	0.599	11105	0.949
Cu	Exponential	2.6E-3	3.0E-2	0.084	3120	0.706
Ni	Exponential	4.8E+0	8.7E+0	0.546	14130	0.952
Pb	Exponential	7.1E+0	2.1E+1	0.342	5467	0.872
V	Linear	1.7E-2	2.5E-2	0.662	20942	0.907
Zn	Gaussian	8.3E-5	1.5E-4	0.561	8046	0.954

C_0: nugget variance, C: structural variance, $C+C_0$: sill variance, R^2: coefficient of determination.

level, indicating that natural sources play an important role in controlling V content.

Spatial distribution: In order to understand the spatial distribution of the heavy metals, Ordinary Kriging interpolation was employed to generate the filled contour maps (Fig. 3). Co, Cr, Ni and V showed similar spatial trends, with high contents in the southern, southeastern and northwestern parts of the study area, and low contents in other regions. When considering the whole spatial distribution pattern, Cu and Zn were similar to Co, Cr, Ni and V. However, unlike Co, Cr, Ni and V, Cu and Zn had a hotspot, situated in the northern part of the study area where the contents of Cd, Pb and As were also clearly higher than in surrounding areas. As had another hotspot in the northwestern part of the study area. According to spatial distribution maps, Cd had higher contents in the soils adjacent to the Hanjiang River, and as the distance to Hanjiang River increased, the Cd contents decreased sharply, indicating the influence of the river.

Pollution and eco-risk assessment: EFs of the metals are presented in Table 4. The mean EFs of Co, Cr, Cu, Ni and Zn were approximately 1.13, 1.05, 1.05, 1.06 and 0.96, respectively. About 96.7%, 99.8%, 99.0%, 99.3%, 98.9% of sample of Co, Cr, Cu, Ni and Zn, respectively, were classified as being at a low pollution level, indicating that these metals did not pose obvious pollution problems. The EF of Pb ranged from 0.64 to 2.24, suggesting that there may be Pb pollution in soils. About 25.7% and 51.4% of samples of As and Cd, respectively, were at a middle or high pollution level, indicating the occurrence of As and Cd contamination in soils. According to previous studies, As and Cd contributes significantly to pollution, and a high pollution level of As and Cd may be attributed to the addition of such metals from anthropogenic sources (Cai et al. 2015, Mirzaei et al. 2014).

The potential ecological risks of metals are displayed in Table 4, and the potential ecological risk map is depicted in Fig. 4. The RI values for all the metals were ranked in the following order: Cd > As >Pb >Co >Ni >Cu >Cr >V >Zn. The E^i_r values for Co, Cr, Cu, Ni, Pb, V and Zn in all soil samples were under 40, indicating that these heavy metals posed a low potential risk. Conversely, the E^i_r values for As and Cd had a broader range. For Cd, 62.9% of the samples had a moderate or considerable ecological risk. The RI values of samples were computed to evaluate pollution from multiple heavy metals. The RI values for 88.8% of the study areas were less than 130, meaning that most areas had low or moderate ecological risk from heavy metals. The RI values varied from 130 to 260 for 11.2% of the study areas, indicat-

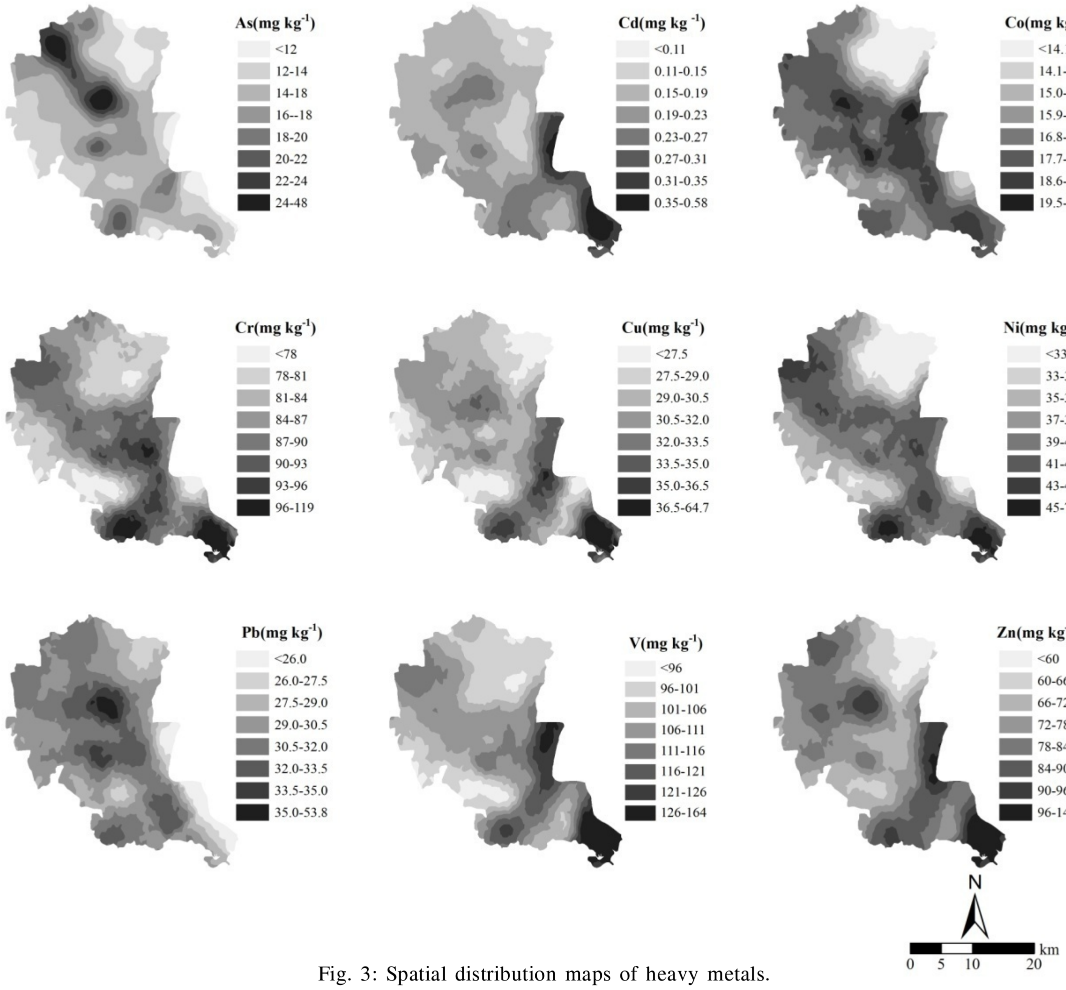

Fig. 3: Spatial distribution maps of heavy metals.

ing that some areas had considerable potential ecological risk. Fig. 4 shows that the highest RI values were situated in the areas adjacent to the Hanjiang river. It is apparent that the content of Cd was the decisive factor in evaluating the potential ecological risk in the soils of the study area (Table 4 and Fig. 3).

Correlation analysis: In order to obtain important information on heavy metal sources and pathways, Spearman's nonparametric correlation coefficients between the nine metals are presented in Table 5. Strong correlations were found between Co, Cr, Ni and V, implying that these metals may have similar sources. This can be confirmed by the fact that they have similar spatial trends. Cu and Zn showed moderate correlation with Co, Cr, Ni and V, consistent with having similar whole spatial distributions to these elements. It is reasonable to conclude that the distribution maps can provide a spatial refinement for reconfirming the correlation analysis. Arsenic (As) showed a significant positive correlation with Pb, indicating that they may share common sources. Cd was relatively poorly correlated with other metals, indicating that the sources of Cd were considerably different from those of other metals. These results indicate that there are several different sources influencing soil heavy metal contents in the study area.

Principal components analysis: In order to reduce the high dimensionality of the variable space, and better understand the relationships between the eight heavy metals, PCA was used to the Box-Cox transformed data. The results of the PCA are shown in Table 6. Two principal components (PC) with eigen values greater than 1 were extracted, which explained about 72% of the total variance. The first principal component (PC1) explained 37.88% of the total variance and was dominated by Co, Cr, Cu, Ni, V and Zn. The second principal component (PC2), dominated by As, Cd, Cu, Pb and Zn, explained 33.73% of the total variance.

Cluster analysis: The heavy metal contents of the soils were standardized, and Pearson coefficients for similarities among variables were calculated. Then hierarchical clustering was

Table 4: Statistical results for the enrichment factor (EF) and the potential ecological risk (RI) of heavy metals.

Element	EF			Percentage of samples (%)		
	Min	Max	Mean	Low	Middle	High
As	0.58	5.10	1.41	74.3	23.7	2.0
Cd	0.41	6.16	1.70	48.6	46.3	5.1
Co	0.51	2.05	1.13	96.7	3.3	0.0
Cr	0.78	1.88	1.05	99.8	0.2	0.0
Cu	0.62	2.32	1.05	99.0	1.0	0.0
Ni	0.61	2.21	1.06	99.3	0.7	0.0
Pb	0.64	2.24	1.19	87.8	12.2	0.0
Zn	0.60	2.40	0.96	98.9	1.1	0.0

Potential ecological risk of all the nine heavy metals			
Heavy metal	Potential ecological index range (E^i_r)	Mean(E^i_r)	SD
As	5-46	14	4.84
Cd	16-152	52	25.36
Co	3-11	6	1.19
Cr	1-3	2	0.30
Cu	3-11	5	1.01
Ni	3-10	6	1.07
Pb	3-10	6	1.81
V	1-3	2	0.32
Zn	1-2	1	0.22
RI	51-222	94	27.84

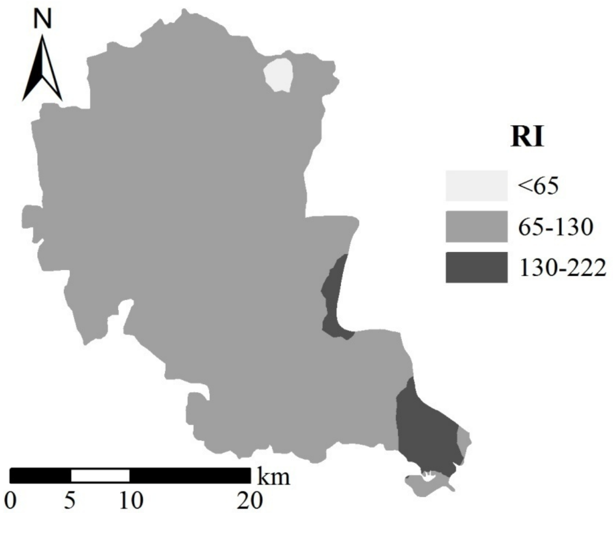

Fig. 4: The potential ecological risk map for heavy metals.

carried out on the standardized data using between-groups linkage (Fig. 5). It can be observed that the dendrogram for the nine heavy metals has four distinct clusters: (1) Co-Cr-Ni- V, (2) Cu-Zn, (3) As-Pb, (4) Cd.

Source identification: Co, Cr, Ni and V, and to a lesser degree Cu and Zn, could be considered to be largely derived from natural sources. V is usually originated from parent material, and according to the geostatistical analysis V had better spatial structure, and less variability due to extrinsic factors such as human contamination (Wu et al. 2015). Co, Cr, Ni and V are generally controlled by the geological background, which indicates that their concentrations in the soils might be largely influenced by natural sources (Mamat et al. 2014, Šajn et al. 2011). Besides, their mean contents were close to the background values and their CVs were low. Therefore, the high contents of Co, Cr, Ni, Cu, and Zn in southern, southeastern and northwestern parts of the study area may be attributed to input from natural sources.

Heavy metals such as As, Cd, Pb, and to a lesser degree Cu and Zn, were related to anthropogenic sources. As, Cd and Pb had higher CVs, which clearly demonstrates the influence of anthropogenic sources. In addition, according to the geostatistical analysis, the variation of As, Cd, Pb, Cu and Zn was dominated by short-range spatial correlation, which indicates that these metals were affected by extrinsic factors, such as human contamination. As Fig. 3 shows, As, Cd, Pb, Cu and Zn had a hotspot in the northern part of the study area where the Jingxiang Phosphorous Industrial Park is situated, and their contents were obviously higher here compared to the surrounding areas. Thus, the hotspot of As, Cd, Pb, Cu and Zn in the northern part of the study area is most likely ascribed to phosphorus-related industrial activities. Sulphuric acid is routinely used in the phosphorus industry, and during sulphuric acid production, wastewater and residues that contain many kinds of heavy metals, such

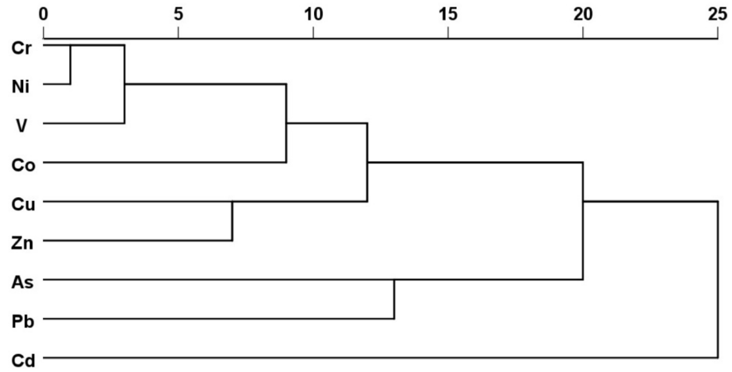

Fig. 5: Dendrogram of the cluster analysis of heavy metals, using the between-groups linkage method.

Table 5: The nonparametric correlation coefficients between contents of the nine heavy metals.

	As	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
As	1								
Cd	-0.105a	1							
Co	0.578a	-0.056	1						
Cr	0.533a	-0.114a	0.673a	1					
Cu	0.418a	0.256a	0.512a	0.681a	1				
Ni	0.565a	0.004	0.759a	0.894a	0.713a	1			
Pb	0.634a	-0.037	0.497a	0.343a	0.357a	0.322a	1		
V	0.420a	0.073	0.648a	0.862a	0.691a	0.819a	0.197a	1	
Zn	0.316a	0.436a	0.423a	0.455a	0.755a	0.594a	0.210a	0.590a	1

[a]Significant at the 0.01 probability level (two-tailed)

Table 6: Total variance explained and component matrix for heavy metal contents.

Component	Initial eigenvalues			Rotation sums of squared loading		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	4.837	53.75	53.75	3.409	37.88	37.88
2	1.608	17.86	71.61	3.036	33.73	71.61
3	0.987	10.97				
4	0.509	5.65				
5	0.421	4.68				
6	0.258	2.87				
7	0.192	2.13				
8	0.139	1.55				
9	0.049	0.54				

Element	Component matrix		Rotated component matrix	
	PC1	PC2	PC1	PC2
As	0.834	0.232	0.468	0.728
Cd	0.341	0.799	-0.277	0.823
Co	0.741	-0.338	0.778	0.240
Cr	0.878	-0.176	0.773	0.452
Cu	0.914	-0.126	0.766	0.514
Ni	0.552	-0.402	0.680	0.067
Pb	0.761	0.499	0.237	0.879
V	0.485	-0.555	0.731	-0.092
Zn	0.867	0.191	0.520	0.719

As, Cd, Pb, Cu and Zn, are released into soils. In addition, a great deal of phospho-gypsum is sometime stacked in the vicinity of the phosphate rock mining enterprises, and also affects local soil quality. These findings should be taken into account in decision making regarding changes to the phosphorus chemical industry. Old arsenic enterprises were situated in another hotspot in the northwestern part of the study area. Although these arsenic enterprises were closed, and local government has prioritized the improvement of the soil quality in recent years, complete elimination of As pollution in this area still requires a long period of time.

For Cd, as the distance to the Hanjiang River increases, its content decreases sharply. These findings agree with the spatial trends that had been discovered for the distribution of Cd in paddy soils around Dongting Lake, central-south China (Zhong et al. 2012). The water quality of the Hanjiang River is substantially effected by wastewater discharge from cities along the river (Lei et al. 2015). It was found that the sediments of the middle and lower Hanjiang River were seriously polluted by Cd, and the enrichment factor of Cd was up to 300 (Gao et al. 2011), indicating that there was Cd pollution in the water of the middle and lower Hanjiang River. Unavoidably, irrigation with water from the Hanjiang River may induce Cd pollution of the soil.

To summarize, Co, Cr, Ni and V, and to a lesser extent Cu and Zn, mostly originate from natural sources, while As and Pb, and to a lesser extent Cd, Cu and Zn, mainly originate from phosphorous-related industrial activities; and Cd in the soils adjacent to the Hanjiang River originates in polluted water from that river.

CONCLUSIONS

The mean contents of Co, Cr, Cu, Ni, V and Zn were close to the background values in the soils, whereas As, Cd and Pb were significantly higher than local background values. Of the nine heavy metals, Cd had the highest CV value, reaching 48.5%. EF value of the metals studied decreased in the order Cd > As > Pb > Co > Ni > Cr = Cu > Zn. According to the EF values, Co, Cr, Cu, Ni and Zn are not causing obvious pollution, but As, Cd and Pb were in the middle or high pollution range. It was found that Cd was the decisive element for evaluating the degree of potential ecological risk in this study area. The results of multivariate and geostatistical analyses were similar to the EF results, which indicated that Co, Cr, Ni and V, and to a lesser degree Cu and Zn, mostly originated from natural sources, while As and Pb, and to a lesser degree Cd, Cu and Zn, mainly originated from phosphorus-related industrial activities.

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