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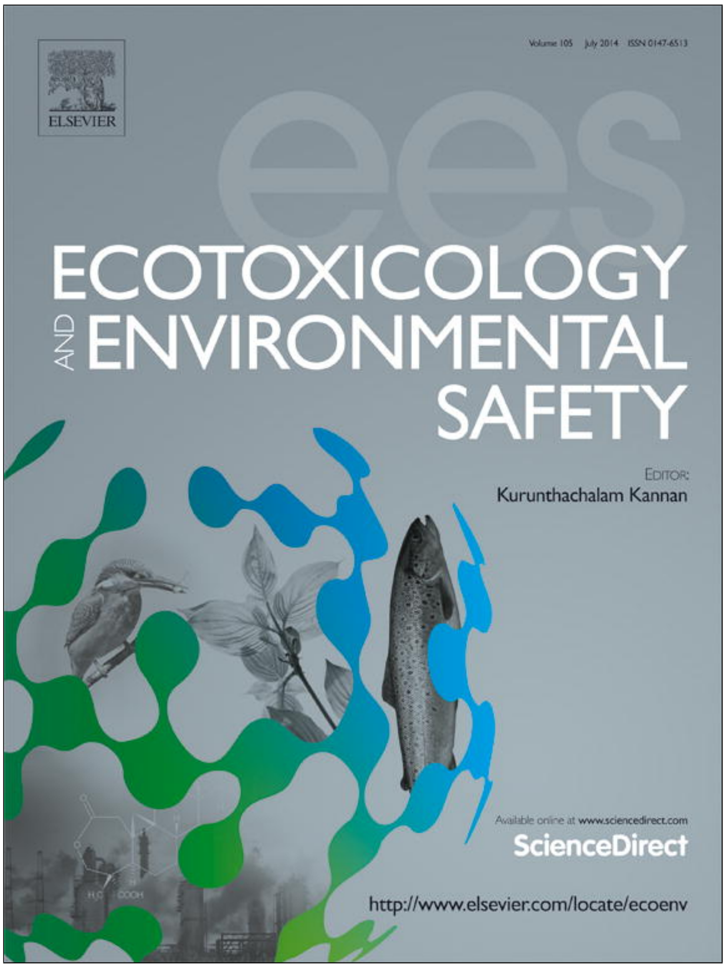

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Identification of heavy metal sources in the reclaimed farmland soils of the pearl river estuary in China using a multivariate geostatistical approach

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ABSTRACT

Heavy metals in the reclaimed farmland soils of the Pearl River Estuary in China have attracted much attention because of the health risk posed to local residents. The identification of heavy metal sources in these soils is necessary to reduce their health risk. Reclaimed farmland soil samples were collected from 144 sites in the Pearl River Estuary and the contents of heavy metals (Cd, Pb, Cr, Ni, Cu, and Zn) were determined. All these heavy metals showed concentrations substantially higher than their background values, indicating possible anthropogenic pollution. The results of a multivariate geostatistical method demonstrate that grouped Cd, Cr, and Cu were mainly controlled by chemical fertilizers. Grouped Pb and Zn were the most severely impacted by atmospheric deposition from Guangzhou and Foshan, and Ni was primarily impacted by electroplating factories' wastewater discharge.

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1. Introduction

Soil contamination with heavy metals has elicited significant attention because of its potential threat to food safety and detrimental effects on the ecosystem. Heavy metals may originate from natural or anthropogenic sources. Natural concentrations of heavy metals in soils depend primarily on composition of geological parent materials.

Anthropogenic activities such as urban-industrial expansion, fossil fuel combustion and agricultural practices also influence heavy metal contents in soils (Alloway, 1995). Heavy metals in reclaimed soils have increased mainly due to the excessive use of fertilizers and pesticides, wastewater irrigation, sewage sludge application and elevated atmospheric deposition (Sridhara Chary et al., 2008; Lu et al., 2012; Hu and Cheng, 2013).

The spatial variation of heavy metals in soils is correlated with their natural and anthropogenic sources (Facchinelli et al., 2001; Lofts et al., 2007; Rodríguez Martín et al., 2013). The sources of heavy metals in soils can be identified through spatial variability analysis. Multivariate analysis is a powerful method for extracting the majority of meaningful information from datasets without losing useful information. The principal component analysis (PCA) is used to classify the interrelationship between heavy metals (Rodríguez Martín et al., 2006; Gu et al., 2012; Li and Feng, 2012). However, PCA ignores the spatial correlations among sampling points, which may lead to loss of important information (Zhang and Selinus, 1998; Rodríguez Martín et al., 2006; Luo et al., 2007). Geostatistical approaches are useful techniques for quantifying spatial features of soil parameters and assessing spatial interpolation (Einax and Soldt, 1999; Dormann et al., 2007; Haining et al., 2010). However, geostatistical analysis cannot reduce the dimensionality of a complex data set and come up with one or more new variables or factors, each of which represents a cluster of interrelated variables within the original data set (Zhang and Selinus, 1998; Einax and Soldt, 1999; Acosta et al., 2010). Therefore, a multivariate and geostatistical method is an effective way for distinguishing pollution characteristics of heavy metals in soils and identifying their sources. This combined method has been successfully applied in some soils of the Zagreb Region in Northwest Croatia (Sollitto et al., 2010), Duero River Basin in Spain

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(Nanos and Rodríguez Martín, 2012), and Guanting Reservoir in China (Luo et al., 2007).

The reclamation of tidal flats is an important approach to replenish arable land in coastal countries. However, many tidal flats are severely contaminated with heavy metals, resulting in heavy metal pollution in reclaimed farmland soils (Li et al., 2007, 2012). The Pearl River Estuary (PRE) is a representative region of a fragile coastal ecosystem where excessive human-activities, especially large-scale reclamation, have caused extensive wetland loss since the 1960s (Li et al., 2007; Bai et al., 2011). Rapid economic growth and urban development in this region has led to the reclamation of as much as 6.0×10^4 ha of coastal wetlands between 1981 and 2004 (Cui, 2004; Li et al., 2007). As the development of electronic and industries related to metals has dramatically increased in this area, the annual industrial wastewater and sewage water discharges rose to 200 million tons and 40 million tons, respectively (Bai et al., 2011). Among these wastewater discharges, as much as 8813 t of human-introduced heavy metal inputs came from direct fluvial transport by the Pearl River (SOAC, 2012). The use of agrochemicals caused 40% of cropland to be contaminated by heavy metals and 10% of the land exceeded the national standards for Cd, Cu and Ni (Bai et al., 2011). Previous research only focused on the regional investigation and spatial distribution of heavy metals in the soils of the PRE (Wong et al., 2002; Ip et al., 2007; Li et al., 2007, 2012; Bai et al., 2011). However, the spatial characteristics and sources of heavy metal in the reclaimed farmland soils of the PRE call for further study.

Therefore, an intensive survey was performed in the present study to profile the heavy metal concentrations in the reclaimed farmland soils in PRE. A total of 144 soil samples were collected and analyzed for Cd, Pb, Cr, Ni, Cu and Zn. Multivariate and geostatistical analyses were combined to investigate the current state of soil heavy metal contamination in this region and to identify the spatial patterns and the possible sources of heavy metals. Such research will provide a scientific basis for effective target policies to protect the reclaimed farmland soils from long-term accumulation of heavy metals.

2. Materials and methods

2.1. Sample collection and chemical analysis

The study region is located mainly at the estuary delta between the riverways of Hengmen and Jiaomen, southwest of the PRE (Fig. 1). This region covers an area of 1.86×10^4 ha (Global Mapper 11, Global Mapper LLC, US), most of which was reclaimed into farmland from 1978 to 2003. In August 2008, a total of 144 topsoil samples (0–10 cm depth) were collected in the PRE region (Fig. 1). The sampling design was based on the distribution of local agricultural land use. For each sample, five sub-samples were obtained from different cells with a grid of approximately 5 m^2 to form a composite sample to enhance the representativeness of the sample at each sampling site. Immediately after collection, the samples were placed in self-sealing polyethylene bags, transferred to the laboratory, air-dried at room temperature to constant weight, sieved through a 2 mm nylon sieve to remove coarse debris, ground gently with agate pestle and mortar, sieved with 63 μm-mesh sieve for homogenization, and stored in self-sealing polyethylene bags until analyses. For analysis of the concentrations of soil Cd, Pb, Cr, Ni, Cu and Zn, soil samples were digested by $HCl–HNO_3–HF–HClO_4$ mixture in Teflon tubes. Quality assurance and quality control were evaluated using duplicates, Reagent blanks and Chinese National Standard Materials (GBW07403) with each batch of samples (1 blank and 1 standard for every 10 samples). The recoveries of samples spiked with standards were between 87% and 118%. The concentrations of heavy metals were determined by atomic absorption spectrophotometry (AAS, Hitachi Z2000).

2.2. Multivariate geostatistical analysis

Prior to the above multivariate geostatistical analysis, a Q–Q plot of each variable was applied to evaluate the normality of the dataset. According to Q–Q plot, the concentrations of Cr and Ni and those of Box-Cox transformed Cd, Pb, Cu, and Ln-transformed Zn all exhibited normal distribution. Then the non-transformed and transformed variables were standardized for Pearson correlation coefficients (r), principal component analysis (PCA) and geostatistics. Geostatistics is mainly used in soil science to assess, predict, and map the soil attributes in an unsampled area based on an experimental semivariogram. The experimental semivariogram was determined by Cambardella et al. (1994) using the following equation:

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

where $Z(x_i)$ is the measured value for soil heavy metal at location x_i, $r(h)$ is the variogram for a lag distance h between observations $Z(x_i)$ and $Z(x_i+h)$, and $N(h)$ is the number of data pairs separated by h.

Pearson correlation coefficients and PCA were performed using IBM SPSS Statistics 19. Experimental semivariogram models were constructed using the software package GS^+9.0 (Gamma Design Software), and kriging and mapping were performed using the geostatistical analyst extension of ArcGIS 10.0.

3. Results and discussion

3.1. Descriptive statistics of heavy metal pollution

Table 1 shows the basic descriptive statistics for heavy metal concentrations in the surface soils of the PRE region and summarizes the number of samples in different classes of soil quality according to the Environmental Quality Standard for Soils in China (GB 15618-1995). The soil heavy metal concentrations in the reclaimed farmland of the PRE were significantly higher than their corresponding background values in Guangdong Province soils based on the one-sample t test ($p < 0.01$), strongly indicating suggestive of anthropogenic enrichment.

According to the soil quality standards in China (GB 15618-1995), the concentrations of Cd, Pb, Cr, Ni, Cu, and Zn exceeded the class II standards in 139 samples (96.5%) of Cd, 132 samples (91.7%) of Pb, 115 samples (79.9%) of Cr, 79 samples (54.9%) of Ni, 138 samples (95.8%) of Cu, and 128 samples (88.9%) of Zn. Only 15 samples had Ni concentrations and 1 sample had Cu concentration exceeding the class II standards. Meanwhile, Cd pollution appeared to be the most widespread with 139 samples (96.5%) concentrations above the class II standard and even though 44 samples showed Cd concentrations higher than the class III standard, suggesting that the heavy metal pollutions in the reclaimed farmland soils have resulted in serious ecological risk for the current reclamation.

3.2. Correlation coefficients among heavy metal contents

The Pearson's correlation coefficients among the heavy metal contents are listed in Table S1. Inter-element relationships provided interesting information on the source and pathways of the heavy metals. A significantly positive correlation was found between the elemental pairs Pb–Ni and Pb–Zn at $p < 0.05$ and $p < 0.01$, respectively. Positive correlations were detected between Cr and Cu, Cr and Zn, Ni and Cu, and Cu and Zn at $p < 0.01$ level. The significant correlated coefficients between metals could result from potential same sources of pollution (Li and Feng, 2012).

3.3. PCA

PCA is an effective method to reduce the high dimensionality of variable space so as to better understand the relationships among trace elements (Gu et al., 2012). In our study, we used PCA (VARIMAX rotation mode) to identify three principal components (F) for all stations based on eigenvalues (eigenvalue > 1), representing 73.85% of the total variance of the dataset. The VARIMAX rotation of the matrix can eliminate ambiguities.

The loadings of heavy metals on the factors for different datasets are listed in Table 2. Based on the component matrix, for the first component (F1, 30.70% of the total variance), Cd has strong negative loading, and Cr and Cu have strong positive

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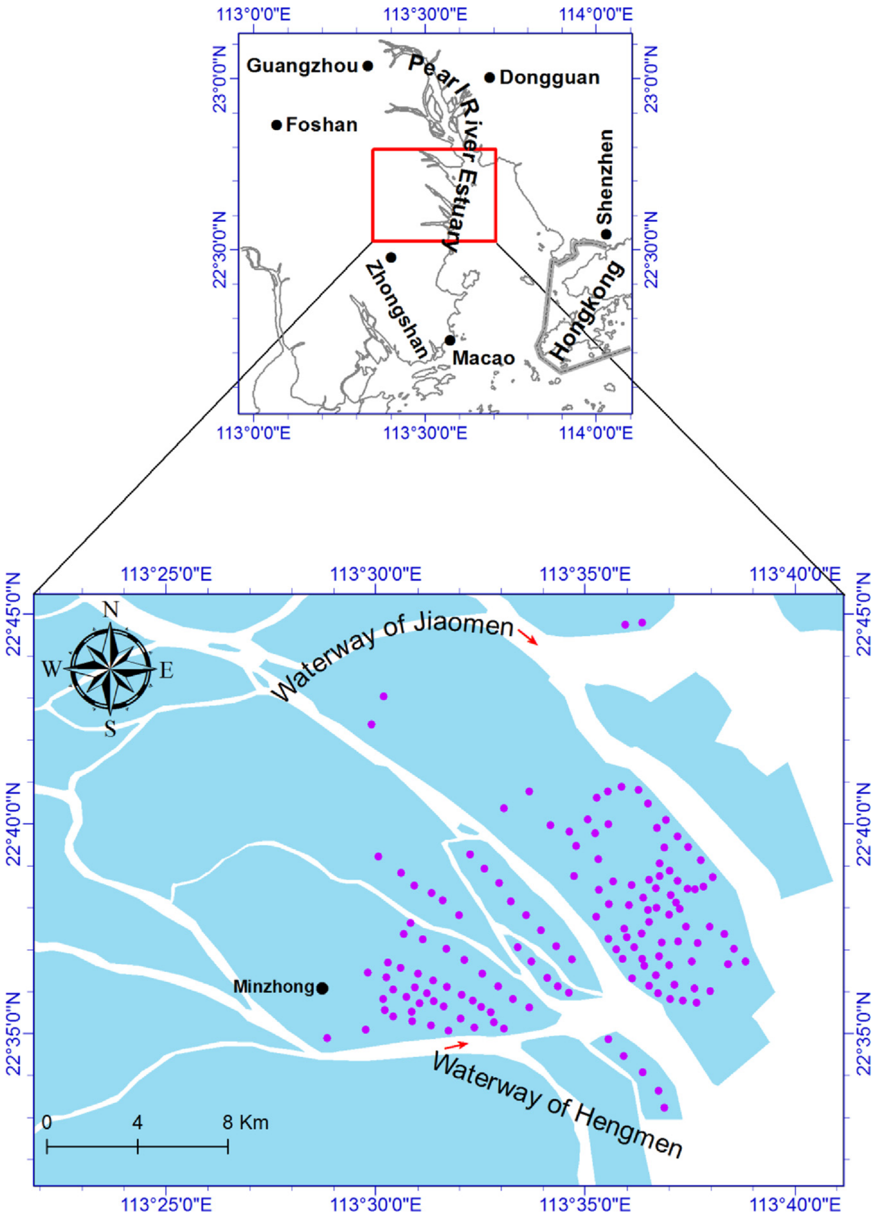

Fig. 1. Map of the sampling sites in the Pearl River Estuary region.

Table 1
Basic statistics of soil heavy metal concentrations (mg/kg dry wt.) in the study region ($n = 144$) and their classification.

Metal	Mean, SD	Median	Range	CV%	BV[a]	No. of samples in each class of soil quality[b]			
						I	II	III	Exceeding III
Cd	$0.9^{**} \pm 0.6$	0.8	0.05–3.78	62.3	0.056	5	5	90	44
Pb	$48.6^{**} \pm 12.8$	45.7	14.3–103.2	26.3	36.0	12	132	0	0
Cr	$106.7^{**} \pm 20.5$	110.0	46.0–148.9	19.2	50.5	29	115	0	0
Ni	$41.0^{**} \pm 6.4$	40.4	24.6–64.5	15.7	18.2	65	64	15	0
Cu	$55.8^{**} \pm 13.3$	57.9	23.4–169.6	23.8	17.0	6	137	1	0
Zn	$194.9^{**} \pm 110.3$	149.9	32.3–586.7	56.6	47.3	11	101	27	5

Note:

** $p < 0.01$ significant level.

[a] Background value of soils in Guangdong Province (CEMS, 1990).

[b] According to the soil quality standards in China (GB15618-1995), class I is defined as unpolluted, classes II and III are slightly and moderately polluted, respectively whereas exceeding the threshold of class III shows heavy pollution.

loadings. For the second component (F2, 24.66% of the total variance), Pb and Zn have strong positive loadings. Ni is the only metal with strong, positive loading in the third component (F3, 18.49% of the total variance). The factor loadings show the grouping of metals in the first three factors. Several studies have proved that the association of elements with factors can be

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indicated by anthropogenic or a lithogenic origin (Romic and Romic, 2003; Davis et al., 2009; Gu et al., 2012; Rodríguez Martín et al., 2013). Some fertilizers and pesticides are well known to contain various levels of heavy metals, such as Cd and Cu (Rodríguez Martín et al., 2006; Luo et al., 2012). Ni, which is corrosion resistant, is commonly used in alloys and in the manufacture of coins, magnets, and common household utensils (Gu et al., 2012). In soils of PRE, previous studies showed Cu originated from Cu-based agrochemicals related to specific agronomic practices while Pb and Zn were mainly from atmospheric deposition with considerable traffic transportation or factories discharging solid particles and toxic fumes in atmosphere (Wong et al., 2003; Ip et al., 2007; Bai et al., 2011). Thus, F1, F2 and F3 could be defined as three different types of human sources.

However, the correlation coefficients and PCA offer little information about the scale-dependent relationships among heavy metals. Geostatistical analysis has the advantage of providing insights into the scale-dependent relationships of regionalized variables (Rossi et al., 1992; Luo et al., 2007). Therefore, a semivariogram analysis was conducted to further substantiate the results of PCA.

Table 2
Loadings of heavy metals on VARIMAX-rotated factors of different datasets.

Heavy metals	F1	F2	F3
Cd	−0.68	0.33	0.05
Pb	−0.12	0.78	0.29
Cr	0.89	0.16	0.02
Ni	0.10	0.02	0.94
Cu	0.71	0.32	0.27
Zn	0.26	0.79	−0.24
Eigen value	1.84	1.48	1.11
Percentage of total variance (%)	30.70	24.66	18.49
Cumulative percentage variance (%)	30.70	55.36	73.85

Table 3
Best-fitted semivariogram models of soil heavy metals and their parameters.

Factor	Model	Nugget (C_0)	Sill (C_0+C)	Nugget/sill ($C_0/(C_0+C)$)	Range (km)	R^2	RSS
F1	Spherical	0.49	1.62	0.70	21.38	0.93	0.06
F2	Exponential	0.49	0.98	0.51	3.36	0.30	0.21
F3	Exponential	0.02	0.92	0.92	2.22	0.97	0.03

$C_0/(C_0+C)$, proportion of spatial structure; R^2, regression coefficient; RSS, residual sums of squares.

3.4. Geostatistical spatial structure analysis

The attributes of the semivariograms for F1, F2, and F3 data are summarized in Table 3. The semivariograms demonstrate that F1 and F3 completely fit the spherical model (R^2=0.93) and the exponential model (R^2=0.97), respectively, and F2 fits the exponential model (R^2=0.30).

The ratio of nugget/sill ($C_0/(C_0+C)$) can be regarded as a criterion to classify the spatial dependence of the soil properties. Ratios less than 0.25, between 0.25 and 0.75, and greater than 0.75 can be used to describe the proportion of spatial structures that show strong, moderate, and weak spatial autocorrelation, respectively (Cambardella et al., 1994). To some extent, this criterion reflects the predominant factors that impact the spatial variability of soil heavy metals between intrinsic factors (i.e., natural factor such as soil parent materials) and extrinsic factors (i.e., human factor such as agricultural practices) (Wu et al., 2009). Generally, weak spatial autocorrelation can be attributed to extrinsic factors, moderate spatial autocorrelation can be due to both intrinsic and extrinsic aspects, and strong spatial autocorrelation can be ascribed to intrinsic factors (Cambardella et al., 1994; Rodríguez Martín et al., 2006).

This study shows that the spatial variability of heavy metal soils may be affected by both intrinsic and extrinsic aspects. The theoretical model (Fig. 2) was plotted for each factor obtained. The nugget effect, representing the undetectable experimental error and field variation within the minimum sampling space, is large relative to the sill (C_0+C). This result represents the total

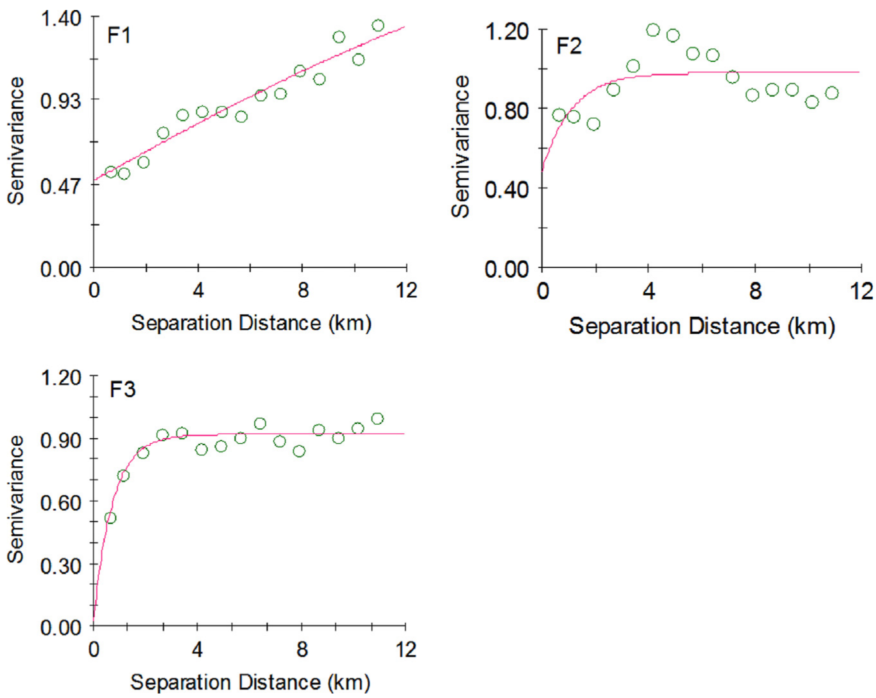

Fig. 2. Experimental semivariograms of F1, F2, and F3 with the fitted models.

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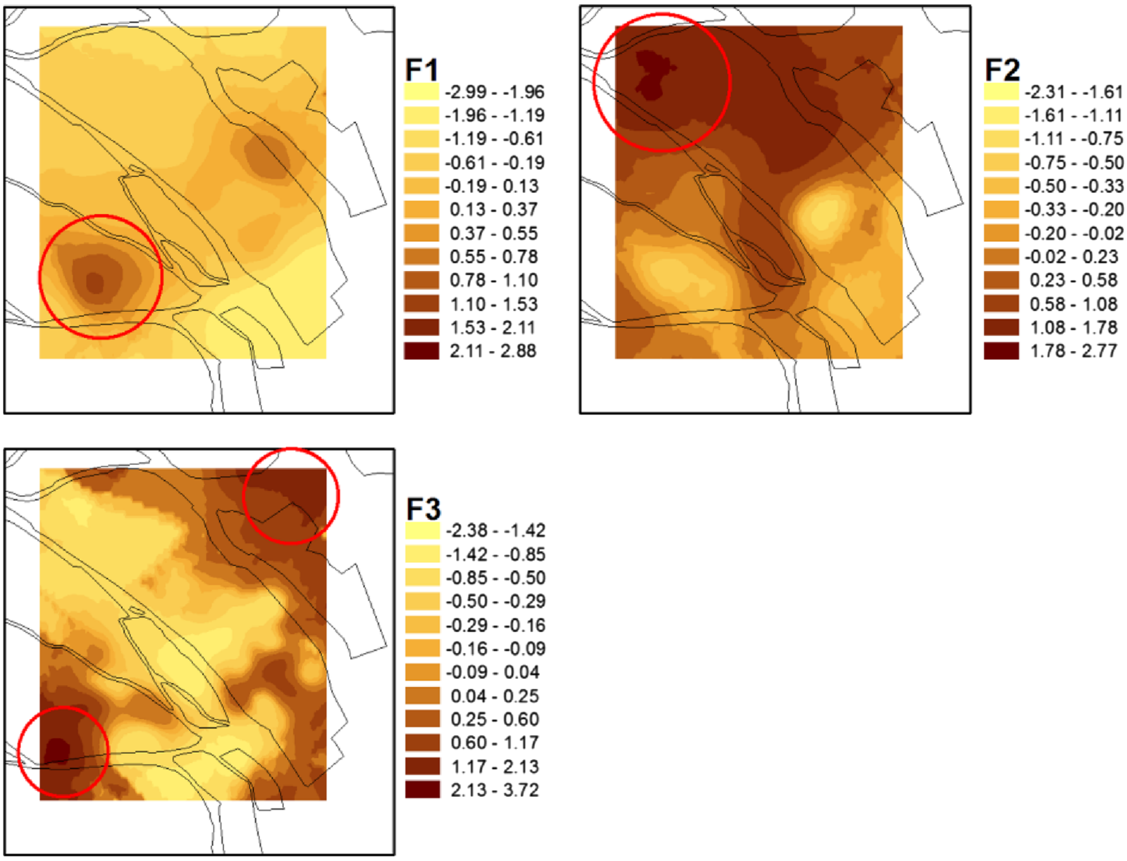

Fig. 3. Contour maps showing the scores of the principal components F1, F2, and F3. Red circles represent the "hotspots".

spatial variation (Gallardo, 2003; Shahbazi et al., 2013). The sill (C_0+C) value represents the total spatial variation, and the range is regarded as the distance beyond which observations are not spatially dependent (Sun et al., 2003). The spatial structures of variables are controlled by geological effects, which are relatively long range, and human activities, which are relatively short range (Webster et al., 1994). Comparing the range of the three factors, F1 distinctly has a longer substantial range than F2 and F3 (Table 3), suggesting that F1 has better spatial autocorrelation and less variation caused by human activities. F2 almost cannot be represented by the best-fit model, indicating that F2 is the most severely impacted by anthropogenic influence. F3 is mainly controlled by random human influence, consistent with the earlier discussion on multivariate statistics. Combining the earlier model analysis and the heavy metal source hypothesis suggests that Pb and Zn are dominated the worst by extrinsic factors, Ni is mainly controlled by extrinsic factors, and Cd, Cr, and Cu are mainly controlled by a combination of intrinsic and extrinsic factors.

3.5. *Spatial distribution of factor scores*

The hotspots of heavy metals and human impacts of the three factors were determined on a spatial scale. Kriging interpolation was conducted to visualize the contour maps using the factor scores (Fig. 3). The spatial distribution of F1 (Cd, Cr, and Cu) reveals a major hotspot. This hotspot occurred in the southwest near the Minzhong town (Figs. 1 and 3), where rice farming (about 1.5×10^4 ha of rice cultivation) led to intensive utilization of fertilizers in 2002. Chemical fertilizers, in particular, phosphate fertilizers contain high levels of Cd because of its presence in phosphate rocks (Li and Feng, 2012; Mar and Okazaki, 2012). This suggests that rice farming may contribute to the contamination of Cd, Cr, and Cu.

The kriging contour map of F2 (Pb and Zn) illustrates the distribution of Pb and Zn (Fig. 3) with a decreasing trend from northwest to southeast. Pb and Zn can be transported long distance by air; their most important sources are fuel combustion and coal combustion (Bruland et al., 1991; Weckwerth, 2001; Lee et al., 2007). Previous studies reveal that soil heavy metals in the Pearl River Delta are mainly polluted by atmospheric deposition (Wong et al., 2002, 2003; Lee et al., 2007). The hotspot was detected in the northwestern area, which is near Foshan and Guangzhou. According to Wong et al. (2003), the atmospheric Pb and Zn deposition reduced more than half from Guangzhou/Foshan city centers to a station located within our study area. Accordingly, the Pb and Zn pollution sources are likely impacted by atmospheric deposition, such as industrial and vehicular emissions.

The spatial distribution of F3 (Ni) was observed, and it was characterized by a relatively high spatial variability. The northeastern and southwestern hotspots occurred right at the places where two electroplating factories discharge wastewater into the Jiaomen and Hengmen riverways (Figs. 1 and 3). Therefore, the source of F3 was mainly influenced by wastewater from electroplating factories.

4. Conclusions

Multivariate statistical and geostatistical analyses were performed on six heavy metals. Three principal components were identified that represent the variability of heavy metals in reclaimed farmland soils. The first principal component F1 (Cd,

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Cr, and Cu), and the second principal component F2 (Pb and Zn) and the third principal component F3 (Ni) were controlled by extrinsic factors. F1 was controlled by chemical fertilizers. F2 was impacted by atmospheric deposition from Guangzhou and Foshan. F3 was mainly influenced by wastewater from electroplating factories. These results are significant for controlling soil heavy metal pollution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2014.04.003.

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