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Potentially hazardous metals contamination in soil-rice system and it's spatial variation in Shengzhou City, China

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ABSTRACT

There is an increasing concern for potentially hazardous metals pollution, which can threaten crops production and human health. A total of 94 pairs of soil and rice samples were collected from Shengzhou City, southern China. The results showed that the mean concentrations of Cd, Cu, Ni, Pb, Zn in soils were 0.20, 28.64, 27.03, 38.51 and 98.74 mg kg^{-1}, respectively. Compared with the guideline values, the potentially hazardous metals were enriched to different degrees in paddy soils of the study areas and some were contaminated with these metals. However, the potentially hazardous metals in rice remained at a safe level. The total concentrations of Cd, Cu, Ni, Pb, Zn in soils had moderate variability coefficients of 45%, 47%, 82%, 18%, 32%, respectively. Kriging interpolation procedure and the Local Moran's I index detected the locations of pollution hotspots of these five potentially hazardous metals. The concentrations of Cd, Cu, Ni, Zn in soils had a very similar spatial pattern, with contamination hotspots located together in the middle part of the study area, which is probably due to industrialization and other anthropogenic activities. The accumulation and availability of potentially hazardous metals in soil and rice is influenced by both metal concentrations in soil, and soil-plant physico-chemical properties that influence their uptake by rice. Therefore, we conclude that necessary environmental measures should be taken to control soil pollution in order to limit possible potentially hazardous metals contamination of the food chain in Shengzhou City.

1. Introduction

Food security is one of the most important public health issues worldwide. Soil pollution is one of the main factors leading to the problem of food security (Chen et al., 2010; Chen et al., 2011; Zhang et al., 2015). Potentially hazardous metals contamination in soil is especially dangerous due to its toxicity, non-biodegradability and persistence (Yan et al., 2013). Nowadays, with the rapid development of industry and increasing application of fertilizer, persistent accumulation of potentially hazardous metals in agricultural fields is of great concern to the public (Rogan et al., 2009; Römkens et al., 2009), especially in the southern part of China with its rapid industrial and economic growth.

Rice is the most important agricultural crop in China. The quality of rice directly influences human health. Paddy soil (it's related to land use but not to any strict definition of soil in the pedology in this paper) have received serious potentially hazardous metals pollution in China (Ding and Li, 2012). It was reported (Cheng et al., 2005) that the cultivated land area in China polluted by Cd, Cr, Pb and other metals is nearly 200,000 km^2. A total of 13,300 ha cultivated land was contaminated with Cd, leading to a decrease of >1000 t crop yield each year, causing total economic losses of $20 billion per year at least. The crop grown plays an important role in the accumulation of potentially hazardous metals. Some plants accumulate a large amount of potentially hazardous metals, causing pollution of grains and affect the safety of the crops (Wu and Chen, 2013). Long-term consumption of contaminated crops would pose a potentially high health risk. Therefore, both the qualities of soil and rice can be closely related to local public health. So, it is of great importance to protect agricultural soils and ensure sustainable food security.

Potentially hazardous metals bioavailability and accumulation in paddy soils has been studied extensively (Wang et al., 2003; Zeng et al., 2005), and most of the research is based on pot experiments. Field crop conditions are more complex and results are often different from pot experiment result (Wang et al., 2001; Xie et al., 2005). Little information is available on potentially hazardous metals accumulation in paddy fields at regional scales, and the spatial correlation between

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potentially hazardous metals in soils and rice has seldom been investigated.

Geostatistical methods have been successfully applied to investigate the spatial variability of environment variables (Zhang, 2006; Zhao et al., 2010; Wu et al., 2014). Semivariogram, one of the geostatistical methods, is considered a useful method to explore the spatial variation of Cd, Cu, Ni, Pb and Zn. The main objectives of this study were (1) to investigate the concentrations of potentially hazardous metals in soil and rice grain, (2) to determine the spatial correlations and distribution of potentially hazardous metals in soil and rice grain, and (3) to identify the main soil properties influencing potentially hazardous metal concentrations in rice grain.

2. Material and methods

2.1. Study area and sampling site description

This study was carried out in Shengzhou City, southern China. Shengzhou covers an area of 1789 km^2 (120°7′ to 120°28′ E, 29°20′ to 29°50′ N) with a population of 0.73 million. Shengzhou is surrounded by mountains, its elevation decreases from northwest to southeast. It has a subtropical marine monsoon climate with mean annual temperature of 16.4 °C and an average annual rainfall of 1446.8 mm. Paddy field cultivation is the major land use in the study area. Rice is the dominant agricultural crop. Shengzhou is famous as “the home of Chinese kitchen utensils”.

In the harvest season of October 2013, 94 pairs of rice and their corresponding soil samples were collected in Shengzhou. For each sample, five sub-samples of soil and rice grain were collected within a radius of 10 m surrounding each sampling location, and then mixed to provide an individual composite sample. At least 1 kg soil (at 0–15 cm in depth) and 0.5 kg rice were collected for each sample. The longitudes and latitudes of the sampling points were recorded by GPS receiver. The distribution of sample points in the study area is shown in Fig. 1.

2.2. Laboratory analyses

Soil samples were air-dried in the laboratory and sieved to pass a 2 mm nylon mesh (Lu, 1999). A portion of the soils was ground in an agate mortar to pass through 100 meshes. Rice grain samples were oven-dried at 105 °C for 1 h, and then at 70 °C to constant weight. All rice grains were hulled and ground to pass through 100 meshes. All samples were stored in closed polythene bags for analysis.

Soil properties were determined according to the methods of the Agricultural Chemistry Committee of China (1983). Soil pH and electrical conductivity (EC) were analyzed with a soil/water ratio of 1:2.5 and 1:5, respectively, in an aqueous suspension. Soil organic carbon was measured by the potassium dichromate oxidation method. Particle size distribution of the soils was determined by using the hydrometer method.

Total potentially hazardous metal concentrations were determined in soils by digestion with the mixture of HF, HNO_3 and $HClO_4$, and in rice by digestion with HNO_3 and H_2O_2. The total concentration of Cd in soil and concentrations of Cd, Cu, Ni and Pb in rice were determined using graphite furnace atomic absorption spectroscopy (GFAAS, PerkinElmer AA800, USA). The concentrations of Cu, Ni, Pb and Zn in the soil samples and Zn in the rice were determined by flame-atomic absorption spectroscopy (FAAS, PerkinElmer AA800, USA). In this study, the concentrations of Pb in the extracted solution of rice were below the limit of detection (0.05 mg L^{-1}). Therefore, the concentration of Pb in rice was not detected.

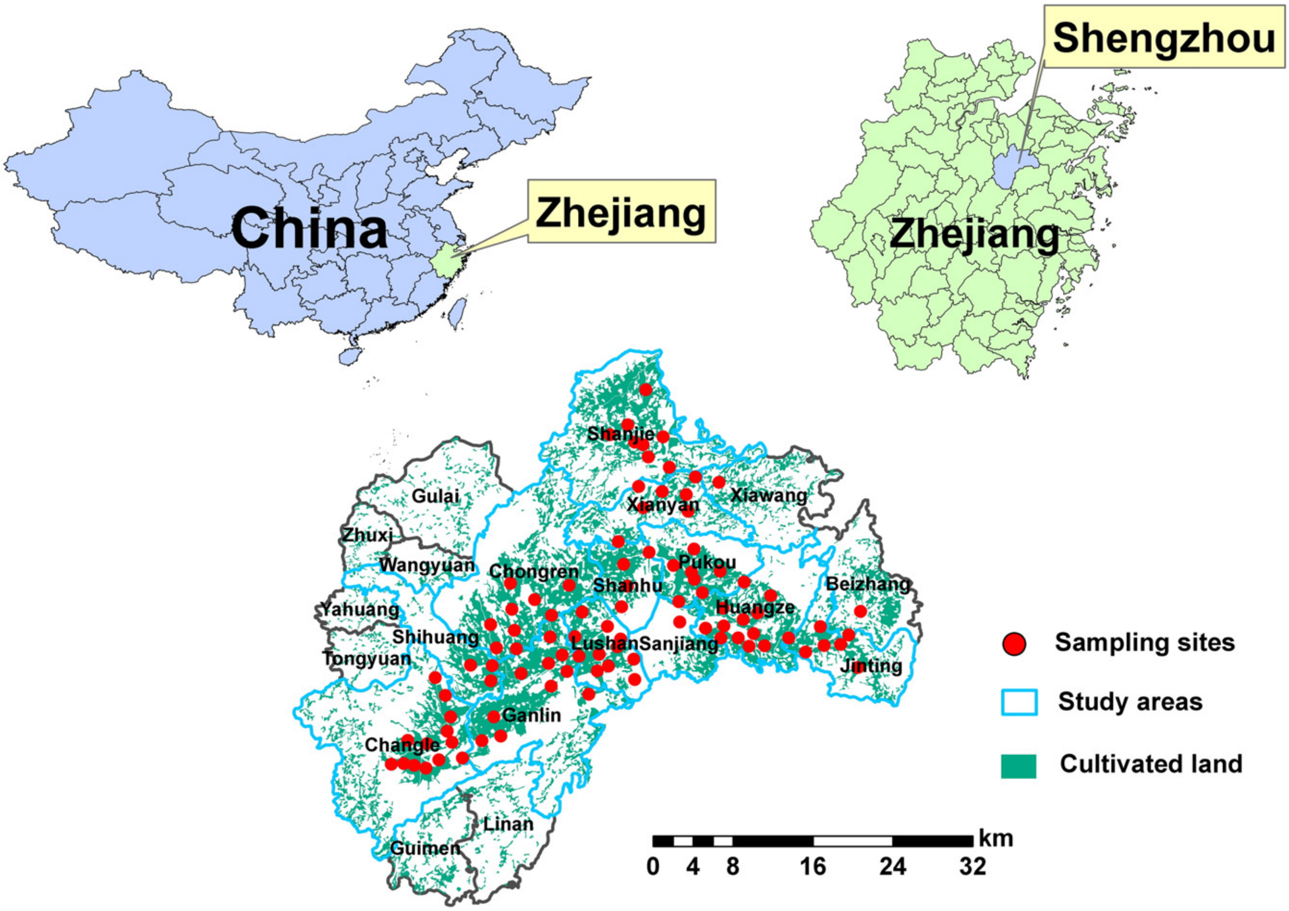

Fig. 1. Location of the study site and samples.

2.3. Evaluation method for soil pollution and standard

To evaluate heavy metal pollution in soils, single factor pollution index (SFPI) was first applied. It was calculated using the following formula:

$$P_i = C_i / S_i \tag{1}$$

where P_i is pollution index of pollutant i (potentially hazardous metals: Cd, Cu, Ni, Pb, Zn), C_i is the measured value of i, S_i is the guideline value of i. When $P_i \leq 1$, it stands for no heavy metal pollution, when $P_i > 1$, it represents heavy metal pollution in the studied area.

While SFPI quantifies the individual heavy metal pollution in soils, the Nemerow multi-factor pollution index (China Green Food Development Center, 1994) measures the overall heavy metal pollution. Nemerow multi-factor pollution can be expressed as:

$$I = \left[\left({P_i}^2{}_{max} + {P_i}^2{}_{ave}\right)/2\right]^{1/2} \tag{2}$$

where I is Nemerow multi-factor pollution index at location i, P_{imax} and P_{iave} represent the maximum and average values of SFPI, respectively. Based on Nemerow multi-factor pollution index, the environmental quality is divided into five levels, including Clean level ($I \leq 0.7$), Precaution level ($0.7 < I < 1.0$), Light pollution level ($1.0 < I \leq 2.0$), Moderate level ($2.0 < I \leq 3.0$), Heavy pollution level ($I > 3.0$).

2.4. Spatial autocorrelation analyses

Spatial autocorrelation refers to the correlation of the same variable in different space position, to measure the cluster degree of spatial unit property value (Huang et al., 2014; Li et al., 2014; Zhao et al., 2014). Moran's I is a commonly used indicator of spatial auto-association. Global Moran's I is used to study the overall spatial autocorrelation, while the Local Indicators of Spatial Association (LISA) measures the degree of spatial autocorrelation in each specific location by using local Moran's I. The latter is also useful to identify local spatial cluster patterns and spatial outliers. Local Moran's I index can be expressed as:

$$I_i = \frac{z_i - \bar{z}}{\sigma^2} \sum_{j=1, j \neq i}^{n} \left[W_{ij}(z_j - \bar{z})\right] \tag{3}$$

where $\bar{z}$ is the mean value of z with the sample number of n; z_i is the value of the variable at location i; z_j is the value at other locations (where $j \neq i$); σ^2 is the variance of z; and W_{ij} is a distance weighting between z_i and z_j, which can be defined as the inverse of the distance. The weight W_{ij} can also be determined by a distance band: the same weight is given to samples within a distance band, while the weight of zero is given to those outside the distance band (Zhang et al., 2008).

Table 2
The evaluated results of single factor pollution index for potentially hazardous metals in soils of Shengzhou.

	Background value of soils in Zhejiang as critical value				Second grade standardized value as critical value			
Metals	Mean	Min	Max	Ratio(%)	Mean	Min	Max	Ratio(%)
Cd	1.53	0.54	6.23	86.17	0.66	0.23	2.68	8.51
Cu	0.94	0.38	2.85	28.72	0.57	0.23	1.74	4.26
Ni	0.74	0.15	3.12	18.09	0.68	0.13	2.85	17.02
Pb	1.26	0.77	2.05	90.43	0.15	0.09	0.25	0
Zn	0.92	0.33	2.39	31.91	0.49	0.18	1.29	1.06

The results of local Moran's I index can be standardized, so its significance level can be tested. When using local Moran's I index to analyze in Geoda software the results were affected by the definition of weight function, data transformation and existence of extreme values (Zhang et al., 2008). Its values are from −1 to 1.When $I > 0$ indicates positive spatial autocorrelation, while $I < 0$ suggests negative spatial autocorrelation. When there is positive local spatial autocorrelation, LISA has two kinds of spatial clusters: high-high cluster (high values in a high value neighborhood) and low-low clusters (low values in a low value neighborhood). Meanwhile, a high negative local Moran's I value implies a potential spatial outlier, which may be high-low (a high value in a low value neighborhood) or low-high (a low value in a high value neighborhood) outlier (Lalor and Zhang, 2001; Fu et al., 2016).

2.5. Geostatistical analysis

Geostatistics is based on the theory of regionalized variables, which is used to estimate and map soil properties in previously unsampled areas (Chen et al., 2009). A semi-variogram is used to quantify the spatial variability of a regionalized variable and derives important input parameters for Kriging spatial interpolation (Wang, 1999; Chen et al., 2008; Chen et al., 2009; Zhao et al., 2010; Huang et al., 2014). It can be expressed as:

$$\mathrm{r(h)} = \frac{1}{2\mathrm{N(h)}} \sum_{i=1}^{\mathrm{N(h)}} \left[\mathrm{Z(x_i + h) - Z(x_i)}\right]^2 \tag{4}$$

where $\mathrm{Z(x_i)}$ is the value of the variable Z at location of $\mathrm{x_i}$, h is the lag, and N(h)is the number of data pairs separated by h. Several standard models are available to fit the experimental semivariograms including spherical, exponential, Gaussian, and linear models (Wang, 1999).

Table 1
Descriptive statistics for soil physico-chemical properties, potentially hazardous metals in soils and rice (mg kg^{-1}).

Metals	Mean	SD	Min	Max	Kurtosis	Skewness	C.V. (%)	Background value[a]	Standard value[b]
Cd_{soil}	0.20	0.09	0.07	0.80	19.80	3.68	45	0.129	0.3
Cu_{soil}	28.64	13.36	11.70	87.01	5.02	1.95	47	30.54	100
Ni_{soil}	27.03	22.04	5.30	113.98	3.68	1.97	82	36.48	50
Pb_{soil}	38.51	6.96	23.31	62.44	1.26	0.71	18	30.46	300
Zn_{soil}	98.74	32.06	36.01	257.34	5.70	1.73	32	107.79	250
Cd_{rice}	0.09	0.10	0.01	0.64	10.70	2.73	111	–	0.2
Cu_{rice}	2.98	1.08	0.94	5.34	−0.69	0.14	36	–	10
Ni_{rice}	0.35	0.278	0.07	1.87	13.58	3.07	79	–	10
Zn_{rice}	22.41	3.54	14.11	34.92	1.03	0.54	16	–	50
pH	5.52	0.63	4.72	7.88	2.60	1.57	11	–	–
SOM	3.94	0.96	1.85	6.44	0.09	0.46	24	–	–
EC	172	114	49	547	1.26	1.37	66	–	–
Sand	15.24	12.3	0.81	71.70	4.33	1.82	81	–	–
Silt	49.33	13.6	9.85	83.90	0.94	1.42	28	–	–
Clay	20.90	4.64	5.43	52.35	1.36	0.95	22	–	–

SOM, soil organic matter (%); EC, electrical conductivity (μS cm^{-1}); Sand, Silt, Clay: %; C.V.% was SD in percent to the mean.

[a] The background value of potentially hazardous metals for agricultural soil in the Zhejiang Province (Environmental Monitoring Administration of China, 1990).

[b] Environmental Quality Standards for Soils (EQSS) in China (2005).

Table 3
The overall evaluated results of soil potentially hazardous metal pollution in Shengzhou (%).

Standard	Clean $I < 0.7$	Precaution level $0.7 < I < 1$	Light pollution $1 < I < 2$	Moderate pollution $2 < I < 3$	Heavy pollution $I > 3$
Background value	1	13	76	10	1
Second grade standardized value	71	13	14	2	0

For spatial data, the semivariogram generally rises with the increase of distance between neighboring samples that are correlated and then stabilizes at the sill, indicating the distance (a) beyond which samples are considered to be spatially independent. Variance that exists at a scale shorter than the field sampling is found at zero lag distance and is known as the nugget effect (C_0). The nugget effect reflects the uncertainty caused by sampling errors or short-scale variability.

The fitted model provides information about the spatial structure and the input parameters for kriging. Therefore, kriging guarantees a minimum variance unbiased prediction as well as an estimate of the prediction variance (Fu et al., 2010). In this study, Ordinary Kriging is used to map the spatial distribution of heavy metals (Goovaerts, 1999; Liu et al., 2008).

Otherwise, in this study, disjunctive kriging was applied (Liu et al., 2006). The disjunctive kriging is the principal technical tool to estimate the probability that the true values at the target points exceed some threshold. It is based on the assumption that the data are a realization of a process with a second order stationary bivariate distribution. The assumption of second order stationary means that the covariance function exists and that the variogram is therefore bounded. It is assumed that the concentration of a heavy metal is a realization of a random variable $Z(x)$, where x denotes the spatial coordinates in two dimensions. If a threshold concentration Z_c is defined, marking the limit of what is acceptable, then the scale is dissected into two classes which is less and more than Z_c, respectively. The value 0 and 1 can be assigned to two classes. A new binary variable, or indicator, is denoted by $\Omega[Z(x) \geq Z_c]$. At the sampling points the values of Z are known, and so the values 0 and 1 can be assigned with certainty. Elsewhere, one can at best estimate $\Omega[Z(x) \geq Z_c]$. In fact, it is necessary to do this in such a way that the estimate at any place x_0 approximates the conditional probability, given the data, that $Z(x)$ equals or exceeds Z_c (Liu et al., 2006; Zhao et al., 2015).

2.6. Data analysis with computer software

The raw data with outliers were transformed to normal distribution, which was necessary for the studied variables. All the results were stored in Microsoft Excel® spreadsheets. The descriptive parameters were calculated using Microsoft Excel® and SPSS® for Windows (version 15.0). Local Indicators of Spatial Association values were measured in the GeoDa software (version 0.95i, Spatial Analysis Laboratory, 2007). All maps were produced using GIS software ArcMap® (version 9.2).

3. Results and discussion

3.1. Heavy metal concentrations in the soil-rice system

The descriptive statistics for potentially hazardous metal concentrations in soils and rice are listed in Table 1. Compared to the background values of Zhejiang Province (Environmental Monitoring Administration of China, 1990), the average concentrations of Cd and Pb in soils exceeded the background value, while the average concentrations of Cu, Ni, Zn in soils didn't. The average concentrations of Cd, Ni, and Cu in soils of this study was lower than that in the E-waste dismantling area of Wenling, southern part of Zhejiang (Zhao et al., 2010; Fu et al., 2013) and waste water irrigation area in Jilin province, Northeast part of China (Wang, 2014), while higher than that of the traditional agricultural area in the Northern part of Zhejiang Province (Zhao et al., 2016).

The coefficient of variation (C.V.) is used to describe the degree of variation of studied variables. According to Zhang et al.'s (2007), the variable is considered to have a weak variability if the C.V. value is <10%, a moderate variability if the value is between 10% and 90%, an extensive variability if the value is >90%. Therefore, all the heavy metals had a moderate variability. Soil Cd had a large C.V. value and relatively high average, indicating that Cd was obviously enriched in some parts of the study area.

The average concentrations of Cd, Cu, Ni, Zn in rice did not exceed the food safety standards of China. Both Cd and Ni in rice had highly positive kurtosis and skewness values. Meanwhile, they had relatively high C.V. values (Table 1). The concentrations of Cd in rice had an extensive variability and the other potentially hazardous metals tested had moderate variability. Some of the samples were higher than the guideline value for food safety (Table 1), indicating Cd accumulation in rice in the study area.

Table 4
The non-parametric correlations between potentially hazardous metals in soils and soil properties.

	pH	SOM	EC	Sand	Clay	Silt	Cd_{soil}	Cu_{soil}	Ni_{soil}	Pb_{soil}	Zn_{soil}	EI_{Cd}	EI_{Cu}	EI_{Ni}	EI_{Zn}
pH															
SOM	−0.21*														
EC	–	0.28**													
Sand	0.28**	–	–												
Clay	–	−0.30**	−0.27**	−0.77**											
Silt	−0.41**	–	–	−0.68**	0.65**										
Cd_{soil}	0.33**	–	0.62**	–	–	–									
Cu_{soil}	0.36**	–	0.40**	–	–	–	0.64**								
Ni_{soil}	0.29**	–	–	−0.23*	0.29**	0.33**	–	0.68**							
Pb_{soil}	–	0.33**	0.29**	–	–	–	0.36**	–	–						
Zn_{soil}	0.32**	–	0.53**	–	–	–	0.68**	0.78**	0.45**	0.35**					
EI_{Cd}	−0.23*	–	−0.24*	–	–	–	–	−0.25*	–	–	–				
EI_{Cu}	–	−0.24*	−0.40**	–	–	–	−0.37**	−0.60**	−0.44**	−0.22*	−0.49**	0.61**			
EI_{Ni}	–	–	−0.36**	–	–	–	−0.34**	−0.47**	−0.44**	–	−0.44**	0.53**	0.82**		
EI_{Zn}	−0.34**	–	−0.32**	–	–	–	−0.46**	−0.53**	−0.40**	−0.30**	−0.76**	–	0.54**	0.54**	

SOM, soil organic matter; EC, electrical conductivity.
** Correlation is significant at the 0.01 level.
* Correlation is significant at the 0.05 level.

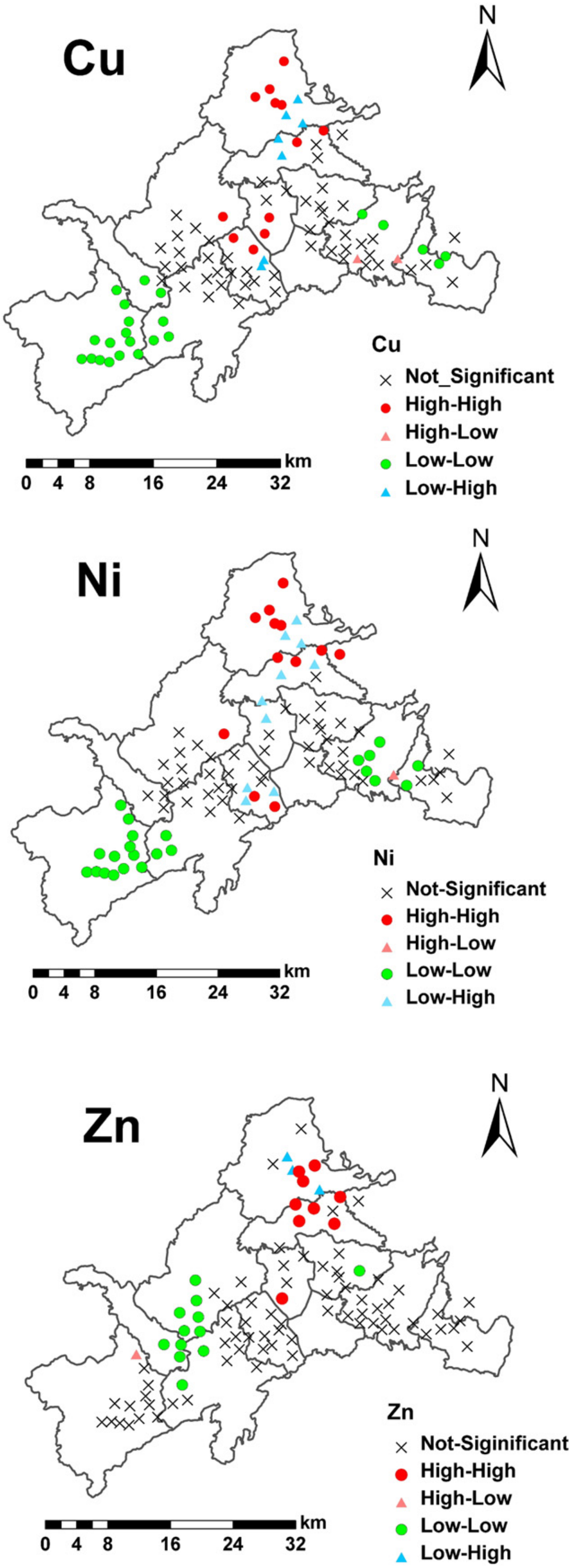

Fig. 2. LISA maps for Cu, Ni and Zn in soil.

3.2. The accumulation and pollution of heavy metals in paddy fields

The background values of potentially hazardous metals from agricultural soils in Zhejiang Province (Environmental Monitoring Administration of China, 1990) and Environmental Quality Standards for Soils (EQSS) in China (2005) (Table 1) were used as guideline values for the assessment of potentially hazardous metal accumulation and pollution, respectively.

Compared with the potentially hazardous metal background values in Zhejiang Province, the average SFPI values of Cd, Pb in soils were higher than unity (Table 2). The accumulation ratio followed the order of Pb > Cd > Zn > Cu > Ni. For total concentrations of Pb in soils, about 90.43% of the soil samples exceeded the background value, indicating obvious Pb accumulation in paddy soils of the study area. Compared with second grade standardized value of EQSS in China, the average SFPI values were lower than unity, indicating that the overall soil quality in the study area was safe for agricultural production. But attention should be paid to the particular locations where the concentrations of potentially hazardous metals such as Cd and Ni, exceeded the guideline values (Table 2).

The Nemerow multi-factor pollution index results (Table 3) showed that 76% of the soil samples belonged to light pollution level based on background values, indicating the widespread accumulation of metals in study area. While 71% and 13% of soil samples belonged to clean and precaution levels, respectively, based on second grade standardized value of EQSS, indicating the potentially hazardous metal pollution in Shengzhou.

3.3. Correlation analysis

In order to understand the relationship of potentially hazardous metals in soil-rice system, the enrichment index (EI) was determined in this study, which was defined as the metal concentration in rice divided by that in soils (Zhao et al., 2010). Enrichment index was used to represent the capacity of the rice to uptake the metal from soils and to translocate the metal from roots to the rice grain. Table 4 showed the non-parametric correlations between physico-chemical properties and metals in soil. The pH is an important physic-chemical property of soil, and is considered to be the main factor influencing plant uptake of soil metals (Reddy and Patrick, 1977; Jung and Thornton, 1997; Basta et al., 2005). Concentrations of Cd, Cu, Ni, Zn in soil had significantly positive correlation with pH (Table 4), and the EI of Cd had negative correlation with pH, while that of Zn had significantly negative correlation. Concentrations of Pb in soils were significantly positive correlated with soil organic matter (SOM), and the EI of Cu had negative correlation with SOM. Concentrations of Cd, Cu, Pb, Zn in soils had significantly positive correlation with electrical conductivity (EC), while Ni had no significant correlation with EC. The EIs of Cd, Cu, Pb, Zn were also negative correlated with EC. Potentially hazardous metals in soils and their enrichment indexes had correlation with soil physical and chemical properties, indicating that potentially hazardous metals absorption and enrichment of crops were not only influenced by the total concentration of potentially hazardous metals in soil, but also influenced by the soil physical and chemical properties. Previous studies (Kirkham, 2006; Tang, 2007) also showed that soil pH and organic matter had a significant influence on crop absorption of potentially hazardous metals.

3.4. Spatial-cluster and spatial-outlier analyses

The results of LISA analysis for total concentrations of Cu, Ni, Zn in soils are presented in Fig. 2. In general, the higher the value of Moran's I, the stronger a spatial autocorrelation exists (Huo et al., 2012). Significantly positively spatial autocorrelations, revealed by local Moran's I value, were found for concentrations of Cu (Moran's $I = 0.25$), Ni (Moran's $I = 0.27$), Zn (Moran's $I = 0.31$) in soils ($P < 0.01$), showing the existence of clear spatial patterns in their spatial distributions (Fu

Table 5
The theoretical semivariogram models and corresponding parameters for potentially hazardous metals in soil and rice in Shengzhou.

Metals	Distribution type	Models	(Nugget) C_0	(Sill) $C_0 + C$	(Nugget/Sill %) $C_0/(C_0 + C)$	(Range) *a* (km)	R^2
Cd_{soil}	Log-normal	Exponential	0.017	0.119	13.9	4.74	0.915
Cu_{soil}	Log-normal	Exponential	0.044	0.152	28.6	10.29	0.940
Ni_{soil}	Log-normal	Exponential	0.013	0.425	3.0	12.45	0.971
Pb_{soil}	Normal	Exponential	3.30	43.88	7.5	3.30	0.903
Zn_{soil}	Normal	Exponential	427.0	864.3	49.4	6.69	0.855
Cd_{rice}	Log-normal	Exponential	0.0468	0.998	46.9	5.79	0.867
Cu_{rice}	Normal	Exponential	0.472	1.228	38.4	4.62	0.943
Ni_{rice}	Log-normal	Spherical	0.027	0.376	7.2	2.74	0.940
Zn_{rice}	Normal	Exponential	2.38	12.85	18.5	2.37	0.868

et al., 2011). The spatial cluster maps of total concentrations of Cd (Moran's $I = 0.07$) and Pb (Moran's $I = 0.16$) in soils were not shown due to weak spatial autocorrelation ($P > 0.05$).

For total concentrations of Cu, Ni and Zn in soils, clear spatial clusters were observed, including a high-high cluster at the north and middle part of the study area, and a low-low cluster at southwest and southeast parts of the county. The high-high clusters of total concentrations of Cu, Ni and Zn in soils were strongly related to industrial activities (Fig. 2). The industries including electric production, small electrical and mechanical parts production, are well developed in the north part of Shengzhou. These industries are one of the main sources for the accumulation of metals in local soils (Zhao et al., 2010). The low-low spatial cluster for total concentrations of Cu, Ni and Zn in soils, in the south part of the study area, is because it is far away from industry and has remained under traditional agricultural management. The high-low outliers were in or near the low-low cluster areas, as these samples had much higher concentrations of Cu, Ni, Zn than those in the neighborhood. In these areas, there were no significant industrial or mining activities based on our survey. The high metals concentrations in soils were probably related to traffic pollution (Zhang, 2006). On the other hand, the low-high clusters were mainly distributed near to the high-high spatial cluster area.

3.5. Spatial structure and spatial distribution

The semivariance models and their key parameters are given in Table 5. The semivariograms of total concentrations of Cd, Cu, Ni, Pb, Zn in soils were well fitted to the exponential model. The Cd, Cu and Ni concentrations in rice closely fitted an exponential model while concentration of Zn in rice was best fitted using a spherical model.

The Nugget/Sill ratio can be used to express the extent of spatial autocorrelations of environmental variables. The ratio value of <25% indicates strong spatial autocorrelation, 25–75% is considered the moderate spatial autocorrelation, and >75% implies the weak spatial autocorrelation (Cambardella et al., 1994). Range is one of the important parameters and indicators of spatial variability, reflecting the scope of spatial correlation in a certain scale. The concentrations of Cd, Ni and Pb in soil had strong spatial autocorrelations (Table 5), indicating that variability was controlled more by intrinsic factors such as soil parent material. But the concentrations of Cd, Pb in soils had a short range (4.74 and 3.30 km, respectively), showing that they were affected by human activities such as agricultural fertilizers, and industrial activities. The range of Ni is 12.45 km, indicating that Ni was affected by the structural factors such as soil parent material. The concentrations of Cu, Zn in soils were moderately spatially dependent, this was attributed to both intrinsic factors and extrinsic factors. The concentrations of Cd and Cu in rice had longer ranges compared to the Ni and Zn. The range of concentrations of Cu, Ni, Zn in rice was shorter than that in soil, indicating that metals in rice may be influenced by intrinsic and environmental factors, which weakened the spatial correlation.

The kriging estimates can be mapped, to reveal the overall trend of the data (Burgos et al., 2006). As shown in Fig. 3, the concentrations of Cd, Cu, Ni, and Zn in soils had similar spatial distribution patterns, with low concentrations located in the southeast and southwest parts

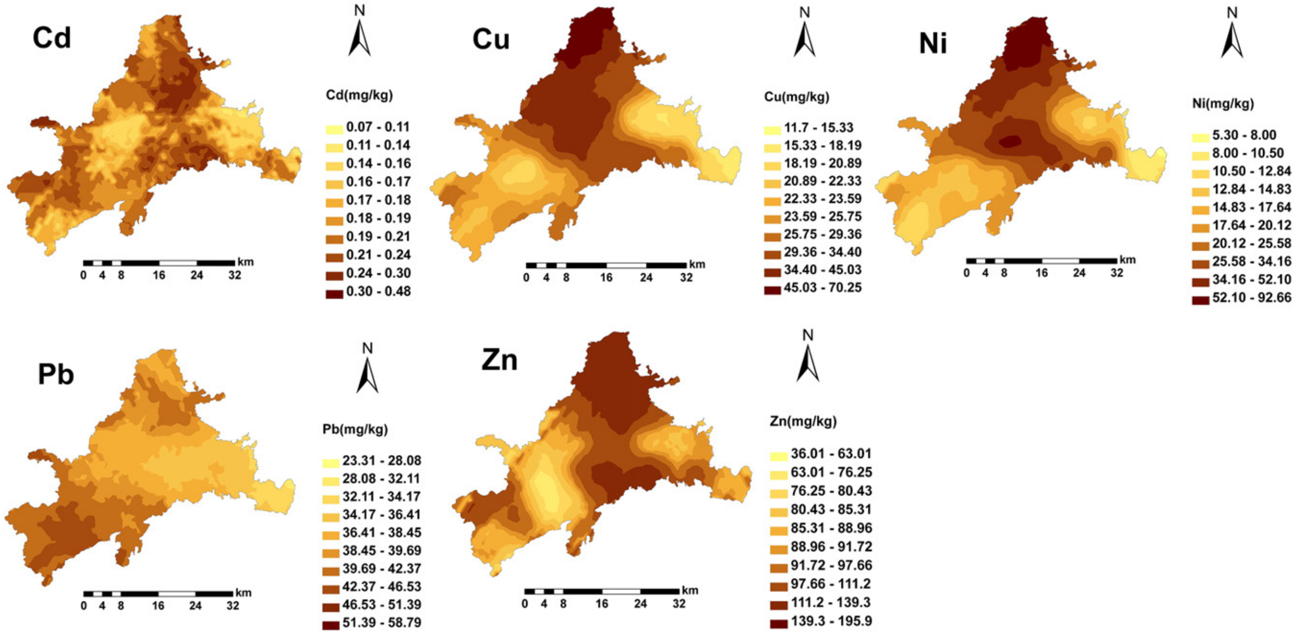

Fig. 3. Spatial distribution maps of the total concentrations of potentially hazardous metals in soil.

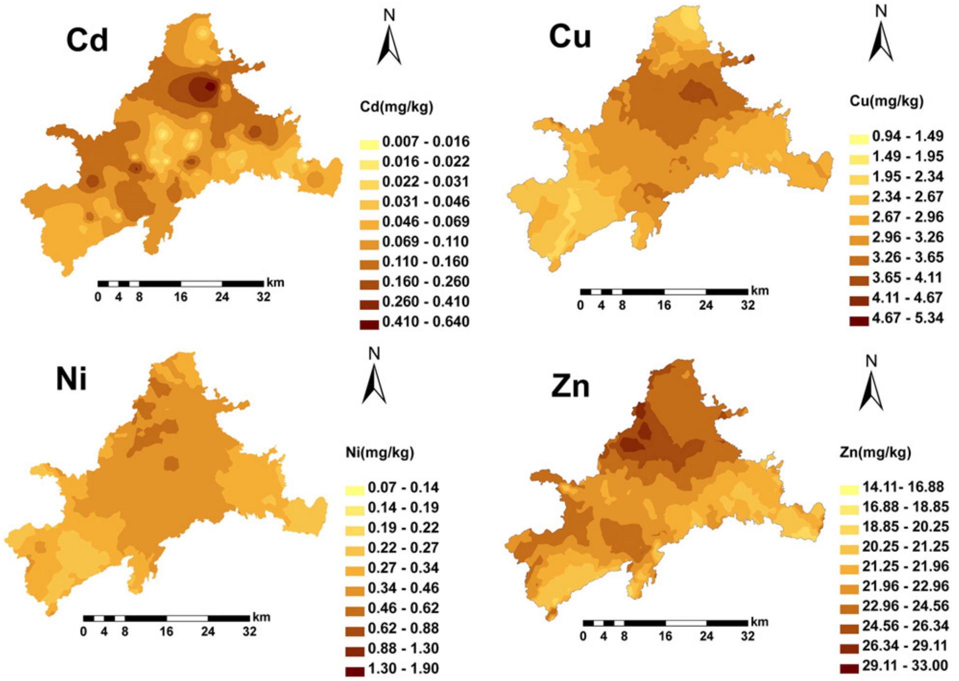

Fig. 4. Spatial distribution maps of the concentrations of potentially hazardous metals in rice.

of the study area, and high concentrations in the center. The spatial distribution map of total concentrations of Cd in soils was formed by a large number of small patches, due to its short range. Based on our survey, it was found that many industries are distributed in the region, which included hardware production, automobile and motorcycle accessories, machinery manufacturing, among others. These industries are the likely sources for the extrinsic factors leading to the pollution of the soils by potentially hazardous metals. Compared to other potentially hazardous metals, the concentration of Pb in soils showed a different spatial pattern. Its high concentration values were observed in the west of Shengzhou, with low concentration in the east.

Compared with the spatial distribution of potentially hazardous metals in soils, spatial differences were found for the corresponding potentially hazardous metals in rice. The spatial distribution of concentrations of Cd in rice showed high concentrations located in the north and low concentrations in the southeast (Fig. 4). Copper and Ni in rice shared similar spatial patterns with high values in center and low values in southwest and southeast part. Zinc in rice showed high concentrations in the north, indicating that other factors, such as human activities, had an important effect on the metals transfer from soils to rice.

Meanwhile, the estimated probability of excess for the concentrations of Cd, Cu, Ni and Zn, defined by the thresholds in Table 1, was kriged by disjunctive kriging and shown in Fig. 5 (Cd and Cu as examples). For total concentrations of Cd in soil, the map showed that the areas with high risk were mainly located in north of Shengzhou county, where the estimated probability $\Omega[\mathrm{Cd} \geq 0.3\ \mathrm{mg\ kg}^{-1}]$ reached 0.102–0.107. The probability map of Cu exceeding the guide value 100 mg kg^{-1} exhibited many risk patches. Especially, the highest risk areas were distributed towards the center of the study area. Therefore, the high risk areas should be taken seriously, to strengthen the prevention and management, to ensure the safety of crop growth. Compared to Cd and Cu, the probability of excess soil in Ni and Zn were relatively low (not shown).

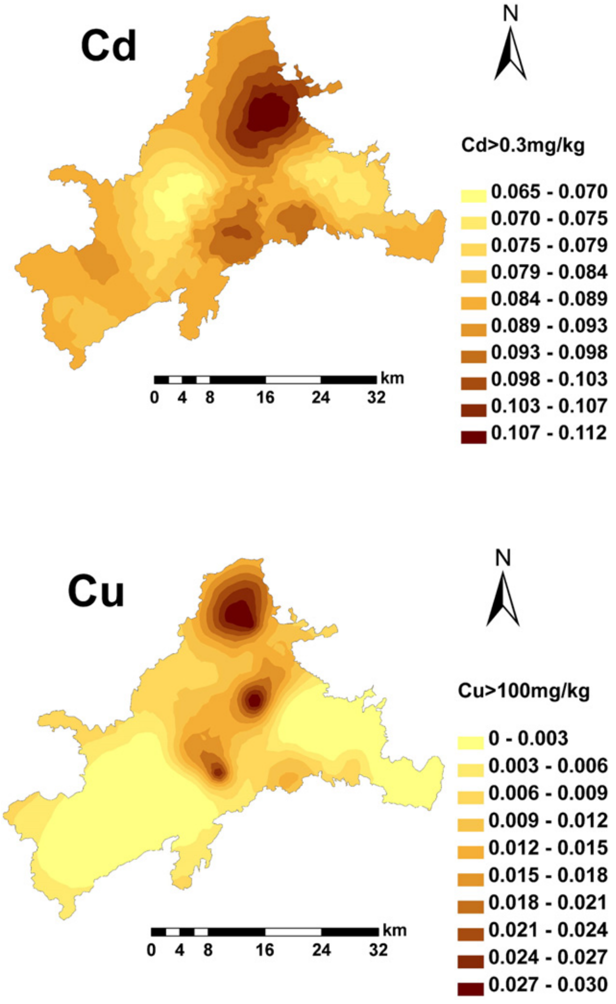

Fig. 5. The estimated probability map of Cd and Cu in soil.

4. Conclusions

Compared with the background values of Zhejiang Province, the paddy fields of Shengzhou city showed Cd, Cu, Ni, Pb, and Zn accumulation to some degree. Compared with second grade standardized value of

EQSS in China, the environmental quality of the paddy fields in the study area remained at a safe level, however, the concentrations of potentially hazardous metals enriched in some parts of the study area. The long-term application of fertilizers and pesticides, and industrial activities affected the accumulation of potentially hazardous metals in both soils and rice.

The concentrations of potentially hazardous metals and physicochemical properties of soils played an important role in the accumulation of most potentially hazardous metals in the rice grain. Moran's I combined with geostatistics proved to be an effective way to describe the spatial pattern of potentially hazardous metals in paddy soils. Kriging maps of metal concentration indicated that many areas in Shengzhou were polluted by potentially hazardous metals and pollution hotspots were mostly distributed in the center of the study area. As a result, environmental measures should be taken to control soil pollution and to curtail metal contamination of the food chain.

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