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Spatial Patterns of Potentially Hazardous Metals in Soils of Lin'an City, Southeastern China

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Abstract: Urban soils are strongly related to human health. In this study, Lin'an city was chosen as a typical small-scale city with which to study the spatial variation of potentially hazardous metals (PHMs) in urban soils and their potential ecological risks using multivariate analysis, geostatistics and GIS techniques. A total of 62 soil samples were collected from the study area. The results showed that the average concentrations of total soil Mn, Cu, Zn, Pb, Cr, Cd were 439.42, 42.23, 196.80, 62.55, 63.65, 0.22 mg·kg^{-1}, respectively. Compared with the background values and the environmental quality standards, these PHMs were accumulated in urban soils to some extent. The single potential ecological risk indices of PHMs indicated that Pb and Cd had relatively high ecological risks. The pH and most of the PHMs had significant correlations ($p < 0.05$). The principle components analysis (PCA) showed that Pb, Zn and Cu had similar pollution sources related to the vehicles' exhaust emission; Mn and Cr were mainly from the parent materials; while Cd was from the emission of industrial manufactories. The spatial structures and distributions of PHMs and their corresponding available fractions had strong/moderate spatial autocorrelation, which were influenced by human activities.

Keywords: urban soil; geostatistical analysis; potentially hazardous metals; spatial distribution; ecological risk

1. Introduction

Due to economic globalization, human activities continue to increase in the cities, causing the urban population to increase and urban expansion. From 2000 to 2010, urbanization rate in China increased by 15% [1]. However, the rapid process of urbanization is accompanied by unprecedented environmental problems. For example, vehicle exhaust emission, industrial waste disposal and coal combustion led to the enrichment of potentially hazardous metals (PHMs) in urban soils [2]. These PHMs could directly affect the physico-chemical properties of soil and impede the activity of soil microorganisms. The PHMs could also threaten human health by dust inhalation and food ingestion [3]. In addition, urbanization reduces the city wind speed, which is detrimental to the transportation of urban pollutants [4]. Meanwhile, municipal solid waste contains a large amount of

abandoned batteries, plastic products, metals, toxic organic compounds and so forth, which can cause serious damage to the soil environment and the growth of crops [5–8].

In recent years, soils have been used as a diagnostic tool of environmental conditions that influence human health [9,10]. Urban soils are the basic site condition for urban green spaces [11]. Therefore, the research related to urban soil pollution has attracted increasing attention. Manta reported that the vehicle emission was the major source of PHMs pollution in urban soils in Palermo of Italy [12]. Moller et al. [13] found that the discharge of municipal domestic sewage combined with industrial wastewater was an important factor for the increase of PHM contents in urban soils of Damascus, Syria and direct ingestion of soil and inhalation of dust could contribute largely to the accumulation of heavy metal in human and livestock. A study showed that anthropogenic inputs (used oil) could lead to organic pollution of urban soils [14]. In China, much work has been carried out on soils of cities such as Beijing, Guangzhou, Shenyang, Nanjing, Guiyang [15–18]. However, most of these researches focused on large cities or cities with high-intensity of industrialization. Little information could be found related to PHMs pollution in smaller cities. This is now important as more and more people prefer to live in such cities.

Over the last 35 y, geostatistical techniques such as semivariogram and kriging have been extensively applied to investigate the spatial distribution of continuously varying environmental variables and to incorporate this information into mapping [19–21]. Geostatistics has provided an effectively advanced method, which could guarantee high accuracy of the spatial features of soil variables and subsequent spatial interpolation [22,23].

Lin'an, located in southeastern China, is a typical small city in China. In recent years, the normal life of residents have been affected by the rapid development of urbanization [24]. Therefore, detailed information is necessary to provide the basis for urban planning, which could also further be used by other small cities in China. The main objectives of this study were to reveal the spatial variation of PHMs in soils and to identify the PHMs pollution characteristics in the study area using the geostatistics, geographic information system (GIS) technology and multivariate analysis.

2. Materials and Methods

2.1. Study Area

Lin'an city is located in southeastern China (118°51′~119°52′ E; 29°56′~30°23′ N). It has a subtropical monsoon climate with an average annual temperature of 15.8 °C and an average annual precipitation of 1613.9 mm. The main soil types include yellow soils, red soils, fluvo-aquic soils, paddy soils and saline soils. Lin'an is adjacent to the large city of Hangzhou. It has an urban population of 200,000 and an annual GDP of 95,500 Yuan per person, which is a the moderately developed small-city in Zhejiang Province, China. The main industries of Lin'an include electronics, pharmacy and agricultural products processing. Lin'an is a typical small city in southeastern China.

2.2. Soil Sampling and Analysis

The urban area of Lin'an city was chosen as the study area (Figure 1). A total of 62 top soil samples (0–20 cm) were collected based on a grid sampling scheme of 1 sample per 0.25 km^2, covering the main urban area of Lin'an city. Among which 20, 15, 12, 8, 7 samples were taken from residential areas, roadsides, public park, schools and agricultural areas, respectively. The sampling location of each sample point was recorded with a portable GPS. The positioning data of GPS was imported into the computer to produce the spatial soil sampling map (Figure 1).
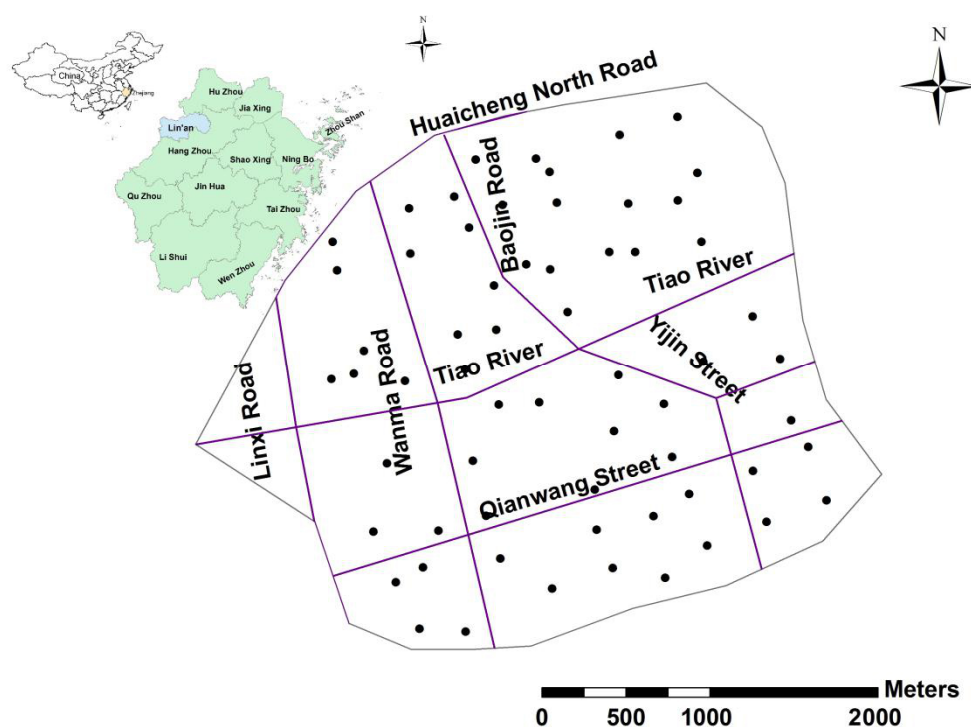
Figure 1. Spatial distribution map of soil sampling sites.

The soil samples were air-dried in laboratory and then sieved through a 2-mm nylon mesh for soil chemical and physical analyses. A portion of the prepared soil samples were ground in an agate mortar to pass through a 0.1 mm pore size sieve and stored in polyethylene bottles.

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 [25]. The available concentrations of Mn, Cu, Zn, Pb, Cr, Cd for the soil samples (<2 mm) were extracted using 0.1 mol·L^{-1} HCl. The milled samples (<0.1 mm) of 0.25 g were digested to dryness with the mixture of HF, HNO$_3$ and HClO$_4$ for measurements of the concentrations of PHMs. Total and available Mn, Cu, Zn, Pb, Cr, Cd concentrations were determined by ICP-OES (Optima 7000 DV, PerkinElmer, Waltham, MA, USA).

For quality assurance of the experiments, the samples were measured in duplicate and the quality control was carried out using the Chinese standardized reference materials (GSS-4 and GSS-15 for soil samples). The analytical quality control showed satisfactory precision throughout.

2.3. Pollution Assessment Methods for PHMs

In this study, the single factor pollution index (SFPI) and Nemerow multi-factor pollution index were adopted to evaluate the PHM pollution in urban soils. The formula of single factor contaminant index was as follows [26]:

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

Where P_i is the single pollution index of pollutant i; C_i is the measured total concentration of pollutant i; S_i is the background value in soils of Zhejiang Province [27].

The Nemerow multi-factor pollution index takes into account the average and maximum of the SFPI, which could reflects the overall PHMs pollution. The formula was as follows [28]:

$$P_N = \sqrt{\frac{1}{2}\left[\left(\frac{C_i}{S_i}\right)^2_{max} + \left(\frac{C_i}{S_i}\right)^2_{ave}\right]} \tag{2}$$

where P_N is the multiple pollution index; $(C_i/S_i)_{max}$ and $(C_i/S_i)_{ave}$ represent the maximum and average value of the SFPI, respectively.

According to the Nemerow multi-factor pollution index, the urban soil quality is divided into five levels, including Clean level ($P_N \leq 0.7$), Precaution level ($0.7 < P_N < 1.0$), Slightly polluted level ($1.0 < P_N \leq 2.0$), Moderately polluted level ($2.0 < P_N \leq 3.0$), Heavily Polluted level ($P_N > 3.0$).

2.4. Potential Ecological Risk Assessment

The potential ecological risk index proposed by Hakanson [29] was used to evaluate PHMs in soils. According to the toxicity of PHMs and their environmental behavior, this method has been widely used by researchers [30–32]. The formula is as follows [29]:

$$E_f^i = T_f^i \times \frac{C_i}{C_0} \tag{3}$$

$$RI = \sum_{i=1}^{n} E_f^i \tag{4}$$

where C_i is the measured concentration of an element in the sample i, C_0 is the soil background value of the element in the study area, E_f^i is the potential individual ecological risk index for PHM, T_f^i is the toxicity response factor of PHMs (Pb = Cu = 5; Cr = 2; Zn = Mn = 1; Cd = 30) [29], RI is the comprehensive index of potential ecological risk of the study area. In this study, the soil background value of Zhejiang province was used as the guideline value for calculation.

$E_f^i < 40$; $RI < 150$ means low potential ecological risk;

$40 \leq E_f^i < 80$; $150 \leq RI < 300$ means moderate potential ecological risk;

$80 \leq E_f^i < 160$; $300 \leq RI < 600$ means considerable potential ecological risk;

$160 \leq E_f^i < 320$; $RI > 600$ means very high potential ecological risk;

$E_f^i \geq 320$ means extremely potential ecological risk.

2.5. Geostatistical Analysis

Geostatistics is based on the theory of regionalized variables [33]. A semi-variogram is chosen to quantify the spatial variation of an environmental variables and derives essential input parameters for kriging interpolation [34,35]. Geostatistics is widely applied to study environmental variables, which contain both random and structural features in their spatial distributions [36]. In this study, the ordinary kriging interpolation is used to map the spatial distribution and to identify the spatial patterns of studied variables. Ordinary kriging requires that the data should be subject to the normal distribution [37]. Therefore, Kolmogorov-Smirnov (K-S) test combined with kurtosis and skewness values [38,39], are widely applied and considered conservative for normality test. A logarithmic transformation was performed if the raw data did not follow the normal distribution as the highly skewed data can endanger the spatial structure as well as influence the prediction accuracy [21,40].

2.6. Data Analysis with Computer Software

The SPSS® for windows (version 22.0) (IBM, Armonk, NY, USA) and Microsoft Excel® statistical software packages were used to calculate descriptive parameters of data and to carry out multi-variates analyses, such as correlation and principal components analyses. Geostatistical analyses were performed with GS+ (v. 7.0) software (Gamma Design, Plainwell, MI, USA). All maps were produced using ArcGIS (v. 10.2) software (ESRI, Redlands, CA, USA).

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3. Results and Discussion

3.1. Descriptive Statistics of the Raw-Data Sets

Descriptive statistics of soil physico-chemical properties and PHMs are shown in Table 1. Soil pH values ranged from 4.64 to 7.33, with an average of 5.66, indicating that the soils were mainly acidic in the study area [41,42]. The mean value of electrical conductivity (EC) was 166.72 μS·cm^{-1}, with a wide range of 10.00 to 460.00 μS·cm^{-1}, which was related to the variety of soil types in the study area. For example, the high soil EC values were mainly from saline soils. Compared to soil background values of Zhejiang province, all the mean concentrations of total Cu, Zn and Pb were higher than their corresponding background values. Especially for total Pb, its mean value was twice higher than its background value. The average available concentrations of Mn, Cu, Zn, Pb, Cr and Cd were 439.42, 42.23, 196.80, 62.55, 63.65, 0.22 mg·kg^{-1}, respectively. Among them, the activation rate of Cd (available fraction/total amount) was the highest, while Cr was the lowest in the soils.

Table 1. Descriptive statistics of physical-chemical properties and PHMs in soils (mg·kg^{-1}; EC: μS·cm^{-1}).

Variable	Min	Max	Median	Mean	SD	CV/%	Skew	Kurt	Geometric Mean	Background Value [a]
Mn$_{Total}$	88.16	2248.31	397.33	439.42	305.37	69.49	3.61	20	371.99	555.48
Cu$_{Tota}$	11.73	123.63	37.47	42.23	21.66	51.29	1.73	4.13	37.8	30.54
Zn$_{Total}$	67.49	872.19	158	196.8	142.76	72.54	2.59	8.46	165.73	107.79
Pb$_{Total}$	7.61	1259.62	30.94	62.55	167.95	268.51	6.55	45.27	34.44	30.46
Cr$_{Total}$	18.87	311.37	51.13	63.65	53.89	84.67	3.78	14.61	54.11	55.99
Cd$_{Total}$	0.02	1.12	0.09	0.22	0.15	68.2	5.1	33.1	0.09	0.13
pH	4.64	7.33	5.81	5.66	0.94	16.61	-0.83	0.67	5.57	—
EC	10	460	0.16	166.72	71.83	43.08	1.49	4.63	150.64	—
Mn$_{avai}$	4.59	102.95	34.53	38.41	24.4	63.53	0.83	0.11	30.63	—
Cu$_{avail.}$	0.01	14.97	1.89	2.57	2.6	91.17	2.38	7.82	1.49	—
Zn$_{avail.}$	0.11	66.55	9.43	13.46	12.81	95.17	1.94	4.4	8.89	—
Pb$_{avail.}$	0.07	98.25	2.91	6.01	13.47	224.13	5.83	37.85	2.35	—
Cr$_{avail.}$	0.04	0.67	0.16	0.17	0.13	76.47	1.76	3.49	0.14	—
Cd$_{avail.}$	0.01	0.84	0.07	0.09	0.11	122.22	5.12	33.47	0.07	—

—: No relevant data, Min: minimum, Max: maximum, SD: standard deviation, CV: coefficient of variation, Skew: skewness, Kurt: kurtosis, Mn$_{Total}$, Cu$_{Total}$, Zn$_{Total}$, Pb$_{Total}$, Cr$_{Total}$, Cd$_{Total}$: total Mn, Cu, Zn, Pb, Cr, Cd in soils, respectively; Mn$_{avail.}$, Cu$_{avail.}$, Zn$_{avail.}$, Pb$_{avail.}$, Cr$_{avail.}$, Cd$_{avail.}$: the availability of Mn, Cu, Zn, Pb, Cr, Cd refers to the acid extractables form in soils, respectively. [a] The background value of potentially hazardous metals of soil in the Zhejiang Province [27].

The coefficients of variation (CV) of soil PHMs in study area ranged from 51.29% to 268.51%, which belonged to the medium and strong variation level [43]. The CV values of total Pb, available Pb and available Cd were higher than 100%, which indicated that there was a significant difference between the maximum and minimum values of these two elements. The maximum value of Pb is 40 times higher than its background value in Zhejiang province, indicating that the element Pb was highly enriched in some areas of the study area. Meanwhile, both the kurtosis and skewness values of the soil total Pb and its available fraction were high. Such high positive skewness was likely related to anthropogenic activities [44]. Compared with the large cities of Beijing [16] and Guangzhou [45], some PHMs (Pb, Cu and Cd) in the soils of Lin'an city were at a higher level. Compared with the old industrial city of Xi'an [15], all the PHMs concentrations in the soil of Lin'an city were relatively low. While compared with less developed areas such as Hohhot [46], the PHMs in the study area were high.

3.2. Assessment of PHMs Pollution in Soils

In this study, the background values of PHMs in soils of Zhejiang Province were used as evaluation criteria for metal pollution in the soils. The average SFPI values of Pb, Zn, Cu and Cr were higher than 1 (2.05, 1.83, 1.38, 1.14, respectively) (Table 2), among which the Pb had the highest average SFPI, indicating that these metals were enriched in the soils of the study area. The pollution ratio followed the order of Zn > Cu > Pb > Cr > Cd > Mn. The average values of SFPI of Mn and Cd were less than

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1 but the concentrations of Mn and Cd in some samples were still higher than the corresponding background values, respectively.

Table 2. The evaluated results of single factor pollution index for soil PHMs in Lin'an.

Elements	Background Values as Critical Value in Zhejiang Province			
	Mean	Minimum	Maximum	Pollution Ratio (%)
Mn	0.71	0.14	3.62	16.39
Cu	1.38	0.38	4.05	67.21
Zn	1.83	0.63	8.09	78.69
Pb	2.05	0.25	41.35	52.46
Cr	1.14	0.34	5.56	37.70
Cd	0.96	0.12	8.62	32.79

The Nemerow multi-factor index results indicated that no samples belonged to the clean level, while there were 12, 34, 9 and 7 samples belonged to the precaution level, light, moderate and heavy pollution, respectively (Table 3). The corresponding percentages followed the order of light pollution > precaution level > moderate pollution > heavy pollution > clean. About 80% of the soil sampling points were polluted, indicating that the overall pollution status of soils in Lin'an was serious. Some of the samples belong to the heavy pollution level, requiring attention for management.

Table 3. Evaluated results of PHMs pollution in soils (%).

Degree of Pollution	Clean $P_N < 0.7$	Precaution Level $0.7 < P_N < 1$	Light Pollution $1 < P_N < 2$	Moderate Pollution $2 < P_N < 3$	Heavy Pollution $P_N > 3$
Number of samples	0	12	34	9	7
Percentage (%)	0	20	55	15	11

P_N is Nemerow multi-factor pollution index.

3.3. Ecological Risk Assessment

The average E_f^i of Mn, Cu, Zn, Pb, Cr and Cd in soils were 0.71, 6.91, 1.83, 10.27, 2.27, 28.73, respectively. They were all less than 40, indicating that these metals posed a low ecological risk. The mean E_f^i values decreased in the order Cd > Pb > Cu > Cr > Zn > Mn (Table 4). The Pb and Cd posed a higher individual potential ecological risk than the other studied elements in some specific locations such as roadsides. The average *RI* value of the soil in Lin'an was 50.72, indicating that the average pollution degree of PHMs in soils of Lin'an City was relatively low. Ma et al. [47] reported that the urban soils of Changsha city had a moderate potential ecological risk with an average *RI* value of 151.7. The relatively low average *RI* values in Lin'an city may be related to less toxic elements, such as As and low average Cd values.

Table 4. Ecological Risk index of PHMs in the soils of Lin'an.

Elements	E_f^i	Ratio of Samples with Different Degree of Risk (%)				
		Slight	Moderate	Strong	Very Strong	Extremely Strong
Mn	0.71	100	0	0	0	0
Cu	6.91	100	0	0	0	0
Zn	1.83	100	0	0	0	0
Pb	10.27	98.36	0	1.64	0	0
Cr	2.27	100	0	0	0	0
Cd	28.73	78.69	19.67	0	1.64	0

3.4. Correlation and Principal Component Analyses

The correlation between studied variables was analyzed based on Spearman correlation coefficient analysis. The results (Table 5) showed that soil pH was significantly correlated with most of the total PHMs and the available fractions of Mn and Pb, which was consistent with other studies that soil pH was an important factor affecting the activity of metals in soil [43,48]. There was a significant correlation between the total PHMs and their available fractions, among which the total Cd and available Cd had the highest correlation coefficient, indicating that the activity of soil Cd was much stronger than others [48]. Significant correlations between most PHMs were also found, indicating that the sources of PHMs may be similar [5].

Table 5. Spearman's correlations between heavy metals in soil.

Variable	Mn_{Total}	Cu_{Total}	Zn_{Total}	Pb_{Total}	Cr_{Total}	Cr_{Total}	pH	CEC	Mn_{avail}	Cu_{avail}	Zn_{avail}	Pb_{avail}	Cr_{avail}
Cu_{Total}	0.47 **												
Zn_{Total}	0.48 **	0.75 **											
Pb_{Total}	0.34 *	0.85 **	0.68 **										
Cr_{Total}	0.18	0.35 **	0.39 **	0.13									
Cd_{Total}	0.35 **	0.58 **	0.64 **	049 **	0.10								
pH	0.27 *	0.25 *	0.39 **	0.41 **	−0.15	0.26 *							
CEC	0.06	0.13	0.26 *	0.20	−0.12	0.16	0.31 *						
Mn_{avail}	0.26 *	−0.02	0.06	0.12	−0.06	0.45 **	0.26 *	−0.01					
Cu_{avail}	−0.04	0.24 *	0.09	0.27 *	0.04	0.33 *	−0.04	0.11	0.38 **				
Zn_{avail}	0.35 **	0.26 *	0.29 *	0.46 **	−0.09	0.79 **	0.25	0.25	0.49 **	0.55 **			
Pb_{avail}	−0.28 *	−0.12	−0.16	0.28 *	0.01	0.34 **	−0.31 *	−0.11	0.31 *	0.34 **	0.39 **		
Cr_{avail}	0.10	0.15	0.09	0.26 *	0.25 *	−0.10	0.20	0.18	0.47 **	0.33 **	0.45 **	0.46 **	
Cd_{avail}	0.13	0.12	0.21	0.14	0.10	0.36 **	−0.10	0.10	0.03	0.23	0.24	0.05	0.09

* Significant at 0.05 level; ** Significant at the 0.01 level; Mn_{Total}, Cu_{Total}, Zn_{Total}, Pb_{Total}, Cr_{Total}, Cd_{Total}: total Mn, Cu, Zn, Pb, Cr, Cd in soils, $Mn_{avail.}$, $Cu_{avail.}$, $Zn_{avail.}$, $Pb_{avail.}$, $Cr_{avail.}$, $Cd_{avail.}$: the availability of Mn, Cu, Zn, Pb, Cr, Cd refers to the acid extractables form in soils.

The principal component analysis results showed that the first principal component (PC1) explained 50.32% of the total variation, with positive and high loading values of the total Cu, Zn and Pb (>0.8) (Table 6). The strong correlations between the three elements may be related to the same anthropogenic activity [22]. Over the past 50 years, the main source of Pb in urban soils was from vehicle exhaust emission [5,49,50]. Although the use of leaded petrol has been controlled since 2000, the deposited Pb in soils has a long half-life [51]. Therefore, Pb has always been regarded as an important contaminant in urban soils. Copper and Zn were also released into the environment from the emissions of vehicles, tire wear and the loss of automotive components [52,53]. The second principal component (PC2) explained 28.45% of the total variation and showed the high loading values of Mn and Cr (>0.7), indicating that the soil parent materials were their main source [47]. Cadmium alone occupied the third main component, which may be caused by the discharge of "wastes" from electroplating, metallurgy and other industries in urban areas [54].

Table 6. Matrix of the principal component analysis loadings of soil PHMs.

Elements	Principal Component Loading Factor		
	PC1 (50.32%)	PC2 (28.45%)	PC3 (16.53%)
Mn	0.168	0.782	0.215
Cu	0.895	0.283	0.138
Zn	0.821	0.196	0.241
Pb	0.839	0.251	0.169
Cr	0.287	0.756	0.184
Cd	0.282	0.179	0.786

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3.5. Spatial Structures of PHMs

The semivariance models and their key parameters are presented in Table 7. The best-fitted theoretical variogram models were based on the mean standardized (MS) and root-mean-square standardized (RMSS) [55,56]. When the MS value is closer to 0 and the RMSS values are closer to 1, the fitted model is optimal [57]. The total Mn, Cd, Pb, Zn, Cr and available Mn, Zn, Cd in soils were all satisfactorily fitted with Gaussian models. Total Cu, available Pb, Cr and pH in soils were well fitted with exponential models, while the available Cu and soil EC were fitted with spherical models. "Nugget/sill" ratio ($[C_0/(C_0+C)]$) is used to measure the strength of the spatial autocorrelation of the studied variables [58]. If the "nugget/sill" ratio is <25%, the variable is considered to have a strong spatial dependence and the spatial variability is mainly caused by natural factors such as soil parent material, topography and climate. A ratio is between 25% and 75% indicates that the variable has moderate spatial dependence and its spatial variability is affected by the combination of soil properties and human activities [21,36]. When the ratio is >75%, the spatial dependence of variable is very weak. The "nugget/sill" ratio of pH, CEC and available Mn, Cu, Zn and Cr in soils ranged from 25% to 75% (Table 7), indicating that random and structural factors were the important factors causing variation. The ratios of other variables were less than 25%, indicating that they were affected by structural factors, whereas the spatial structures of Pb and Cd were strong, which might be related to the influences of long-term anthropogenic activities. Such influences could become part of the structural factors [43]. According to the low "nugget/sill" ratio values, clear spatial patterns of PHMs could be revealed by kriging interpolation [23]. Similar moderate and strong spatial structures of PHMs were also found in Galway city, a small tourist city in Western Ireland [22].

Table 7. The theoretical semivariogram models and the corresponding parameters for PHMs in soils.

Variable	Model	Nugget (C_0)	Sill ($C_0 + C$)	Nugget/Sill [$C_0/(C_0 + C)$]	Range (km)	MS	RMSS
Mn_{Total}	Gaussian	124.544	124,668.444	0.10%	0.005	−0.072	1.015
Cd_{Total}	Gaussian	0.076	0.684	11.11%	0.004	−0.152	1.039
Cu_{Total}	Exponential	75.479	553.778	12.63%	0.006	0.021	1.084
Pb_{Total}	Gaussian	42.554	42,596.924	0.10%	0.007	−0.072	1.073
Zn_{Total}	Gaussian	238.042	23,034.992	1.03%	0.004	0.010	1.032
Cr_{Total}	Gaussian	3.296	3299.030	0.09%	0.004	−0.021	1.093
pH	Exponential	0.018	0.038	47.38%	0.017	−0.005	0.900
CEC	Spherical	0.168	0.278	56.40%	0.038	0.003	0.765
Mn_{avail}	Gaussian	0.201	0.588	34.18%	0.011	−0.001	0.739
Cu_{avail}	Spherical	5.854	7.496	46.09%	0.006	0.010	0.960
Zn_{avail}	Gaussian	0.540	1.275	42.35%	0.007	−0.001	0.939
Pb_{avail}	Exponential	0.529	2.540	20.83%	0.006	0.010	0.908
Cd_{avail}	Gaussian	0.076	0.684	11.11%	0.004	−0.151	1.039
Cr_{avail}	Exponential	0.291	0.592	49.15%	0.012	−0.013	0.880

Mn_{Total}, Cu_{Total}, Zn_{Total}, Pb_{Total}, Cr_{Total}, Cd_{Total}: total Mn, Cu, Zn, Pb, Cr, Cd in soils, $Mn_{avail.}$, $Cu_{avail.}$, $Zn_{avail.}$, $Pb_{avail.}$, $Cr_{avail.}$, $Cd_{avail.}$: the availability of Mn, Cu, Zn, Pb, Cr, Cd refers to the acid extractables form in soils. MS: mean standardized, RMSS: root-mean-square standardized.

3.6. Spatial Distribution Pattern of PHMs and Physicochemical Properties in Soils

Figures 2 and 3 describe the spatial distributions of total PHMs, their available fractions, pH and EC based on ordinary Kriging interpolation. The spatial distribution characteristics of total Cu, Zn and Pb in soils had strong similarity. The concentrations of total Cu, Zn and Pb in the central and southeast parts of Lin'an City were high, while they were low in the northwest and southwest of City. The concentrations of total Cr was high in the eastern part of the study area and low in the western part, showing an increasing trend from west to east. Total Cd in soil was high in the central part of the study area, while it was low in the northern part and the southern part, indicating an increasing trend from south to north. The high values of total Cu, Zn and Pb in soils were mainly distributed in Wanma Road and Qianwang Street, which was related to a large number of automobile fitting factories and shops, as well as the heavy traffic and transportation of these two main traffic routes, indicating that

transportation and relevant industry were the main factors affecting Cu, Zn and Pb concentrations in soils [22,31].
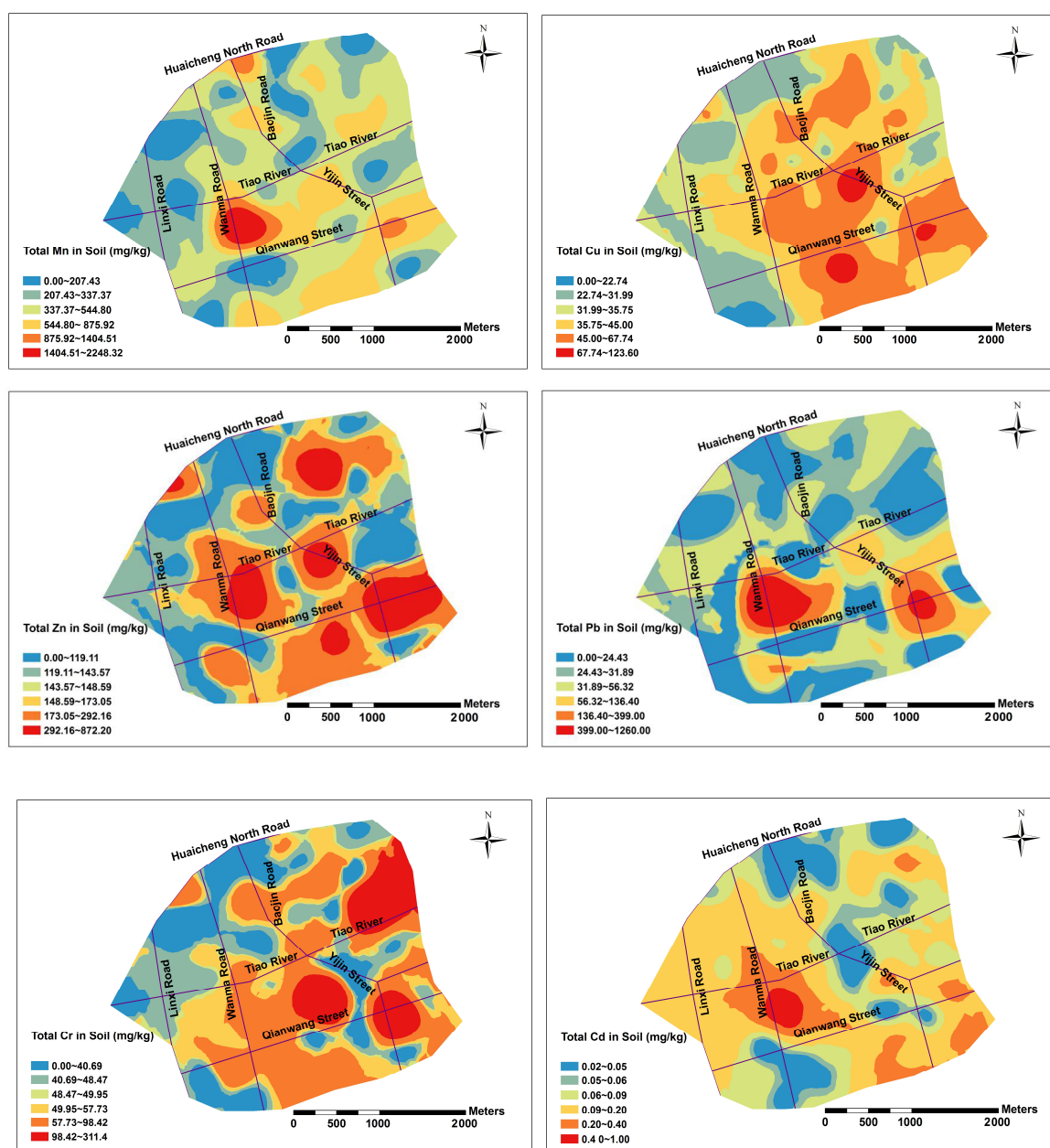

Figure 2. Spatial distribution maps of the total PHMs.

The pH values were low in the western part of the study area and increased gradually from west to east. Soil CEC showed a decreasing trend from south to north in the study area. The spatial distribution of available Cd in soils was consistent with total Cd in soils, especially the spatial patterns of high values were basically the same, indicating that the available Cd was mainly related to total Cd, while the spatial patterns of available Mn and Cr in soils and total Mn and Cr were quite different, respectively. The concentrations of available Mn was high in the western and eastern parts of the study area and relatively low in the southern and northern parts. The available Cr values were high in the western and southeast parts of the study area and low in the northern part of the study area. The available fractions of PHMs is affected not only by the total amount of corresponding PHMs but also influenced by other factors [59,60].
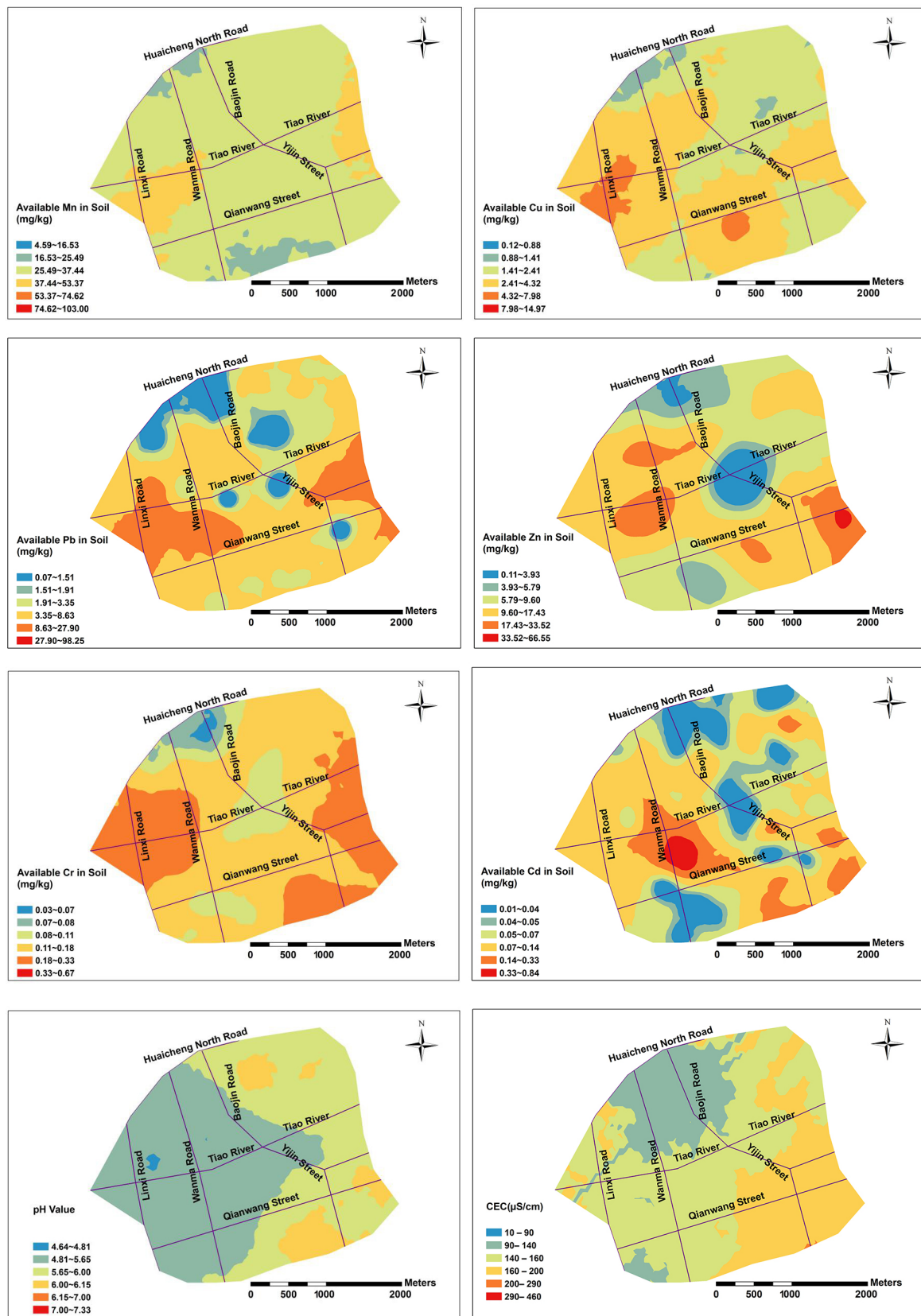
Figure 3. Spatial distribution maps of available fractions of PHMs, pH and CEC.

4. Conclusions

The average concentrations of total Mn, Cu, Zn, Pb, Cr and Cd in the soils were 439.42, 42.23, 196.66, 62.55, 63.65 and 0.22 mg·kg^{-1}, respectively. Compared with the background values of PHMs in Zhejiang Province, the total Mn, Cu, Zn, Pb, Cr and Cd in soils of Lin'an city were enriched to some extent. There was a significant correlation between soil PHMs metals and pH, indicating that pH had an important effect on the activity and accumulation of PHMs in soils. Soil PHMs in the study area had clear spatial patterns, as the high concentrations of PHMs mainly located in the industrial areas and along traffic routes. The main sources of Cu, Zn and Pb were related to the automobile exhaust emissions, tire wear and the loss of automobile parts, while Cd might be related to the industrial activities. Necessary pollution control measures should be considered with the rapid development of small cities in China.

References

1. You, Z. The past, present and future of the city scale and urbanization level in China. *Geogr. Sci. Res.* **2016**, *5*, 275–284. (In Chinese)
2. Yekeen, T.A.; Onifade, T.O. Evaluation of some heavy metals in soils along a major road in Ogbomoso, South West Nigeria. *J. Environ. Earth Sci.* **2012**, *8*, 71–79.
3. Kabata-Pendias, A. *Heavy Metals in Soils*; Chapman and Hall: London, UK, 1955.
4. Zhou, J.F.; Fan, S.J.; Li, H.W.; Fan, Q. Impact of urbanization on meteorological factors in Pearl River delta. *China Environ. Sci.* **2012**, *32*, 1153–1158. (In Chinese)
5. Li, X.D.; Lee, S.L.; Wong, S.C.; Shi, W.Z.; Thornton, I. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. *Environ. Pollut.* **2004**, *129*, 113–124. [CrossRef]
6. Wang, L.A.; Yue, J.H.; Huang, C.; Liu, Y.Y. Contamination characteristic analysis of heavy metals in MSW dumped in three gorges region. *Acta Sci. Circumst.* **2006**, *26*, 246–251. (In Chinese)
7. Deng, H.G.; Zhang, J.; Chen, Z.L.; Wang, D.Q. Pollution and assessment of heavy metals in the tidal flat sediment near Laogang garbage landfill of Shanghai. *Chin. J. Soil Sci.* **2007**, *38*, 141–145. (In Chinese)
8. Wang, J.F.; You, W.H.; Zhao, W.B.; Tang, X.L.; Zhang, Y. Study on the relationship between soil animal communities environmental factors in landfill reclamation soil. *Res. Environ. Sci.* **2010**, *23*, 80–84. (In Chinese)
9. Abrahams, P.W. Soils: Their implications to human health. *Sci. Total Environ.* **2002**, *291*, 1–32. [CrossRef]
10. Davydova, S. Heavy metals as toxicants in big cities. *Microchem. J.* **2005**, *79*, 133–136. [CrossRef]
11. Li, Y.M.; Ma, J.H.; Liu, D.X.; Sun, Y.L. Assessment of heavy metal pollution and potential ecological risks of urban soils in Kaifeng city, China. *Environ. Sci.* **2015**, *36*, 1037–1044. (In Chinese)
12. Manta, D.S.; Angelone, M.; Bellanca, A.; Neri, R.; Sprovieri, M. Heavy metals in urban soils: A case study from the city of Palermo (Sicily), Italy. *Sci. Total Environ.* **2002**, *300*, 229–243. [CrossRef]
13. Moller, H.W.; Muller, A.; Abdullah, A.; Abdelgawad, G.; Utermann, J. Urban soil pollution in Damascus, Syria: Concentrations and patterns of heavy metals in the soils of the Damascus Ghouta. *Geoderma* **2005**, *124*, 63–71. [CrossRef]
14. Kelome, N.C.; Faure, P.; Mathieu, O.; Leveque, J.; Oyede, L.M. Evidence of organic contamination in urban soils of Cotonoutown (Benin). *Br. J. Environ. Clim. Chang.* **2012**, *2*, 99–112. [CrossRef]
15. Wu, X.M.; Li, L.Q.; Pan, G.X.; Ju, Y.F.; Jiang, H.Y. Soil pollution of Cu, Zn, Pb and Cd in different city zones of Nanjing. *Environ. Sci.* **2003**, *24*, 105–111. (In Chinese)

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16. Xia, X.H.; Chen, X.; Liu, R.M.; Liu, H. Heavy metals in urban soils with various types of land use in Beijing, China. *J. Hazard. Mater.* **2011**, *186*, 2043–2050. [CrossRef] [PubMed]

17. Zhang, Y.X.; Wang, J.; Qin, F.X.; Zhang, H. Comparison of source of metals in road-dust and soil in Guiyang. *Environ. Sci.* **2012**, *32*, 204–212. (In Chinese)

18. Li, X.Y.; Liu, L.J.; Wang, Y.G.; Luo, G.P.; Chen, X.; Yang, X.L.; Myrna, H.P.; Guo, R.C.; Wang, H.J.; Cui, J.H.; et al. Heavy metal contamination of urban soil in an old industrial city (Shenyang) in Northeast China. *Geoderma* **2013**, *192*, 50–58. [CrossRef]

19. Burrough, P.A.; Mc Donnell, R.A. *Principles of Geographical Information Systems*; Oxford University Press: Oxford, UK, 1998.

20. Carlon, C.; Critto, A.; Marcomini, A. Risk based characterisation of contaminated industrial site using multivariate and geostatistical tools. *Environ. Pollut.* **2001**, *111*, 417–427. [CrossRef]

21. Fu, W.J.; Zhao, K.L.; Zhang, C.S.; Tunney, H. Using Moran's I and geostatistics to identify spatial patterns of soil nutrients in two different long-term phosphorus-application plots. *J. Plant Nutr. Soil Sci.* **2011**, *174*, 785–798. [CrossRef]

22. Zhang, C.S. Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. *Environ. Pollut.* **2006**, *142*, 501–511. [CrossRef]

23. Fu, W.J.; Zhao, K.L.; Zhang, C.S.; Tunney, H. Using GIS and geostatistics to optimize soil phosphor and magnesium sampling in temperate grassland. *Soil Sci.* **2013**, *178*, 240–247. [CrossRef]

24. Wang, H.T.; Zheng, G.Q.; Shen, B.L.; Dong, T. Analysis on current industrial carbon emissions and low carbon strategy in Lin'an city. *J. Chin. Urban For.* **2015**, *13*, 23–27. (In Chinese)

25. Agricultural Chemistry Committee of China. *Conventional Methods of Soil and Agricultural Chemistry Analysis*; Science: Beijing, China, 1983. (In Chinese)

26. Brady, J.P.; Ayoko, G.A.; Martens, W.N.; Goonetilleke, A. Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. *Environ. Monit. Assess.* **2015**, *187*, 1–14. [CrossRef] [PubMed]

27. Zhejiang Soil Survey Office. *Zhejiang Soils*; Zhejiang Technology Press: Hangzhou, China, 1994; pp. 556–562. (In Chinese)

28. Zhao, K.L.; Fu, W.J.; Ye, Z.Q.; Zhang, C.S. Contamination and spatial variation of heavy metals in the soil-rice system in Nanxun County, Southeastern China. *Int. J. Environ. Res. Public Health.* **2015**, *12*, 1577–1594. [CrossRef] [PubMed]

29. Hakanson, L. An ecological rish index for aquatic pollution control a sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]

30. Wang, H.Y.; Lu, S.G. Spatial distribution, source identification and affecting factors of heavy metals contamination in urban-suburban soils of Lishui city, China. *Environ. Earth Sci.* **2011**, *64*, 1921–1929. [CrossRef]

31. Li, J.H.; Wang, S.; Fang, J.; Huang, J.L.; Lu, F.H.; Lu, Y.H.; Zhang, H.M. Heavy metal pollution characteristics and ecological risk analysis for soil around Haining electroplating industrial park. *Environ. Sci.* **2014**, *35*, 1509–1515. (In Chinese)

32. Zhao, W.T.; Ding, L.; Gu, X.W.; Luo, J.; Liu, Y.L.; Guo, L.; Shi, Y.; Ting, H.; Cheng, S.G. Levels and ecological risk assessment of metals in soils from a typical e-waste recycling region in southeast China. *Ecotoxicology* **2015**, *24*, 1947–1960. [CrossRef]

33. Dai, W.; Fu, W.J.; Jiang, P.K.; Zhao, K.L.; Li, Y.H.; Tao, J.X. Spatial pattern of carbon stocks in forest ecosystems of a typical subtropical region of southeastern China. *For. Ecol. Manag.* **2018**, *409*, 288–297. [CrossRef]

34. Fu, W.J.; Zhao, K.L.; Zhang, C.S.; Wu, J.S.; Tunney, H. Outlier identification of soil phosphorus and its implication for spatial structure modeling. *Precis. Agric.* **2016**, *17*, 121–135. [CrossRef]

35. Dai, W.; Li, Y.H.; Fu, W.J.; Jiang, P.K.; Zhao, K.L.; Li, Y.F.; Penttinen, P. Spatial variability of soil nutrients in forest areas: A case study from subtropical China. *J. Plant Nutr. Soil Sci.* **2018**, *181*, 827–835. [CrossRef]

36. Webster, R.; Oliver, M.A. *Geostatistics for Environmental Scientists*; John Wiley & Sons Ltd.: Chichester, UK, 2001.

37. Zhao, K.L.; Liu, X.M.; Zhang, W.W.; Xu, J.M.; Wang, F. Spatial dependence and bioavailability of metal fractions in paddy fields on metal concentrations in rice grain at a regional scale. *J. Soils Sediments* **2011**, *11*, 1165–1177. [CrossRef]

38.	Fu, W.J.; Fu, Z.J.; Zhao, K.L.; Tunney, H.; Zhang, C.S. Variation of soil P and other nutrients in a long-term grazed grassland P experiment field. *Arch. Agron. Soil Sci.* **2014**, *60*, 1459–1466. [CrossRef]

39.	Dai, W.; Zhao, K.L.; Fu, W.J.; Jiang, P.K.; Li, Y.F.; Zhang, C.S.; Gielen, G.; Gong, X.; Li, Y.H.; Wang, H.L.; et al. Spatial variation of organic carbon density in topsoils of a typical subtropical forest, southeastern China. *Catena* **2018**, *167*, 181–189. [CrossRef]

40.	Fu, W.J.; Tunney, H.; Zhang, C.S. Spatial variation of soil nutrients in a dairy farm and its implications for site-specific fertilizer application. *Soil Till. Res.* **2010**, *106*, 185–193. [CrossRef]

41.	Zhao, K.L.; Fu, W.J.; Liu, X.M.; Huang, D.L.; Zhang, C.S.; Ye, Z.Q.; Xu, J.M. Spatial variations of concentrations of copper and its speciation in the soil-rice system in Wenling of southeastern China. *Environ. Sci. Pollut. Res.* **2014**, *21*, 7165–7176. [CrossRef] [PubMed]

42.	Fang, X.H.; Zhang, J.C.; Meng, M.J.; Guo, X.P.; Wu, W.Y.; Liu, X.M.; Zhao, K.L.; Ding, L.Z.; Shao, Y.F.; Fu, W.J. Forest-type shift and subsequent intensive management affected soil organic carbon and microbial community in southeastern China. *Eur. J. For. Res.* **2017**, *136*, 689–697. [CrossRef]

43.	Zhao, K.L.; Fu, W.J.; Qiu, Q.Z.; Ye, Z.Q.; Li, Y.F.; Tunney, H.; Dou, C.Y.; Zhou, K.N.; Qian, X.B. Spatial patterns of potentially hazardous metals in paddy soils in a typical electrical waste dismantling area and their pollution characteristics. *Geoderma* **2019**, *337*, 453–462. [CrossRef]

44.	Lv, J.S.; Zhang, Z.L.; Liu, Y. Sources identification and hazardous risk delineation of heavy metals contamination in Rizhao city. *Acta Geogr. Sin.* **2012**, *67*, 971–983. (In Chinese)

45.	Chen, H.Z.; Gong, C.S.; Li, W.L. Characteristic and evaluation of soil pollution by heavy metal in different functional zones of Guangzhou. *J. Environ. Health* **2010**, *27*, 700–703.

46.	Guo, W.; Sun, W.H.; Zhao, R.X.; Fu, R.Y.; Zhang, J. Characteristic and evaluation of soil pollution by heavy metal in different functional zones of Hohhot. *Environ. Sci.* **2013**, *34*, 1564–1567.

47.	Ma, L.; Yang, Z.G.; Li, L.; Wang, L. Source identification and risk assessment of heavy metal contaminations in urban soils of Changsha, a mine-impacted city in Southern China. *Environ. Sci. Pollut. Res.* **2016**, *23*, 17058–17066. [CrossRef] [PubMed]

48.	Kirkham, M.B. Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. *Geoderma* **2006**, *137*, 19–32. [CrossRef]

49.	Wong, C.S.C.; Li, X.D.; Zhang, G.; Qi, S.H.; Peng, X.Z. Atmospheric deposition of heavy metals in the Pearl River Delta, China. *Atmos. Environ.* **2003**, *37*, 767–776. [CrossRef]

50.	Ma, J.H.; Gu, L.; Li, W.J. Accumulation and potential risk of heavy metals in roadside soils along the section of Zhengzhou-Shangqiu, Lianyungang-Huoerguosi highway. *Environ. Sci.* **2009**, *30*, 894–899. (In Chinese)

51.	Guney, M.; Onay, T.T.; Copty, N.K. Impact of overland traffic on heavy metal levels in highway dust and soils of Istanbul, Turkey. *Environ. Monit. Assess.* **2010**, *164*, 101–110. [CrossRef]

52.	Adachi, K.; Tainosho, Y. Characterization of heavy metal particles embedded in tire dust. *Environ. Int.* **2003**, *30*, 1009–1017. [CrossRef] [PubMed]

53.	Yang, Z.P.; Lu, W.X.; Long, Y.Q.; Bao, X.H.; Yang, Q.C. Assessment of heavy metals contamination in urban topsoil from Changchun City, China. *J. Geochem. Explor.* **2011**, *108*, 27–38. [CrossRef]

54.	Cai, L.M.; Ma, J.; Zhou, Y.Z.; Xu, Z.C.; Peng, X.C.; Yao, L.A.; Zhou, Y.; Peng, P.A. Heavy metal concentrations of agricultural soils and vegetables from Dongguan, Guangdong Province, China. *Acta Geogr. Sin.* **2008**, *63*, 994–1003. (In Chinese)

55.	Guan, F.Y.; Xia, M.P.; Tang, X.L.; Fan, S.H. Spatial variability of soil nitrogen, phosphorus and potassium contents in Moso bamboo forests in Yong'an City, China. *Catena* **2017**, *150*, 161–172. [CrossRef]

56.	Franklin, R.B.; Mills, A.L. Multi-scale variation in spatial heterogeneity for microbial community structure in an Eastern Virginia agricultural field. *FEMS Microbiol. Ecol.* **2003**, *44*, 335–346. [CrossRef]

57.	Tang, G.A.; Yang, X. *The Experiments Tutorial of ArcGIS Geographic Information Systems Spatial Analysis*; Science Press: Beijing, China, 2006; p. 356.

58.	Cambardella, C.A.; Moorman, T.B.; Novak, J.M.; Parkin, T.B.; Karlen, D.L.; Turco, R.F.; Konopka, A.E. Field-scale variability of soil properties in central Iowa soils. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1501–1511. [CrossRef]

59. Zhao, K.L.; Liu, X.M.; Xu, J.M.; Selim, H.M. Heavy metal contaminations in a soil-rice system: Identification of spatial dependence in relation to soil properties of paddy fields. *J. Hazard. Mater.* **2010**, *181*, 778–787. [CrossRef] [PubMed]

60. Fu, W.J.; Zhao, K.L.; Jiang, P.; Ye, Z.; Tunney, H.; Zhang, C. Field-scale variability of soil test phosphorus and other nutrients in grasslands under long-term agricultural managements. *Soil Res.* **2013**, *51*, 503–512. [CrossRef]