

Original Research

Spatial Distribution and Pollution Assessment of Potentially Toxic Elements in Urban Forest Soil of Nanjing, China

Junye Zhang^{1,2}, Fei Yu³, Shadong Pang¹, Yuanchun Yu^{1*}

¹Co-Innovation Center for Sustainable Forestry in Southern China, College of Biology and the Environment, Nanjing Forestry University, Nanjing, P.R. China

²Henan Polytechnic, Zhengzhou, P.R. China

³Jiangsu Polytechnic College of Agriculture and Forestry, Jurong, P.R. China

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Abstract

Our study aimed to assess the pollution levels and ecological risk of potentially toxic elements (PTEs): Pb, Cd, Cu, Cr, Zn, Ni, and As in the urban forest soil of Nanjing, China. A total of 180 topsoil (0~20cm) samples were collected with the aid of GPS according to 1 × 1 km grid cells in six different function zones: road green belt (RGB), urban square (US), urban garden (UG), institution greenland (IG), residential greenland (RG), and urban rural forest (URF). The concentrations of seven PTEs in study areas were higher than their background values (BVs), and three anthropogenic origins were identified: industrial origin, traffic origin, and agricultural origin by principle analysis (PCA), coupled cluster analysis (CA), and kriging interpolation. The potential ecological risk index (PERI) in the Nanjing urban forest soils was 305.62, in a state of significant pollution, which was mainly due to high contents of Pb, Cd, As, and Zn by correlation analysis. There were three distribution patterns for seven PTEs and PERI: Pb, Cd, As, and PERI presented similar island pattern which took traffic and commercial center as a hot spot (TCIP), while Cr and Ni presented an island pattern that took chemical plants as hotspot (CPIP), and Cu and Zn presented a scattered point pattern (SPP).

Keywords: urban forest soil, potentially toxic elements, spatial distribution, pollution assessment, potential ecological risk index

Introduction

With rapid development of industrialization and urbanization, potentially toxic elements (PTEs) contamination has become a popular problems in

China. Many researchers have studied the effects of PTE contamination in agricultural soils [1-2]. Some elements are necessary or beneficial to plants at certain levels, such as Cu, Zn, and Ni. Fertilization with Zn improves water use efficiency, grain yield, and content of seed Zn in chickpea [3], and the experiments conducted at a total of 23 experimental site-years in China, India, Kazakhstan, Mexico, Pakistan, Turkey,

*e-mail: 122418810@qq.com

and Zambia also showed foliar Zn application alone or in combination with soil application, significantly increasing the concentration of grain Zn from 27 to 48 mg·kg⁻¹ across all the 23 site-years, which resulted in an increase in grain Zn by 84% and 90%, respectively [4]. Field experiments conducted in soil on Cu-deficient soil near the Porcupine Plain in northeastern Saskatchewan showed that the increase in concentration and uptake of Cu in grain from Cu fertilization usually showed a similar trend to grain yield [5]. Nikoli used five methods to extract Ni from cultivated soils, the result showed that sufficiency critical levels of Ni in soil were approximately 2 mg·kg⁻¹, which was probably a good guide to indicate soils that will respond to Ni fertilization [6]. Also, excessive amounts of Cu, Zn, and Ni retard plant growth [7-9]. Some elements are not essential for plant growth, and are poisoning plants when contents accumulated to a certain degree. Pb, Cd, and Cr are common heavy metals, and their stress will produce different degrees of damage. PTEs have strong influence on nutrition values, therefore plants grown on metal-contaminated soil were nutrient deficient, and consumption of such vegetables may lead to nutritional deficiency in the population – particularly when living in developing countries that are already facing nutrition problems [3]. Pot culture experiments of *Zea mays* L. showed that growth response of *Zea mays* L. was considerably influenced by interaction of Cd and PCP, significantly declining with either Cd or PCP additions [10]. Research about *Hibiscus Sabdarifa* showed that beyond 10 mg·kg⁻¹ of Cr in soil was toxic to the plants and resulted in a significant a reduction in the growth of plants [11]. Arsenic is a carcinogenic metalloid that occurs in the environment in a variety of chemical forms, showing different mobility, bioavailability, and toxicity [12], and a global data analysis shows that rice grain arsenic concentrations increase with increasing

soil arsenic concentration until about 60 mg·kg⁻¹ and then decrease [13]. The PTEs in agricultural soil also accumulate in plants, absorbed by human body through food chain and harm human health [14-16]. All seven of these PTEs are common in urban environments for traffic pollution [17], industrial discharge [18], extensive use of fertilizers and pesticides [19], and soil parent materials [20]. The PTEs accumulated in urban soil affect the growth of urban plants [21] and weaken the regulating function of urban ecological environment on one hand [22], while on the other hand they enter and harm the human body through road dust and by rainfall into the atmosphere and underground water [23].

Here we aimed to assess the pollution levels of seven PTEs in the urban forest soils in Nanjing, China. Pb, Cd, Cr, Zn, Cu, Ni, and As concentrations in the different function zones and their spatial distribution were discussed in relation to possible influence of land use. We used three indexes to assess the potential ecological risk level.

Material and Method

Soil Sampling

The study was conducted in Nanjing (118°22'E-119°14'E, 31°14'N-32°37'N), Jiangsu Province – a rapidly urbanizing city in eastern China near the Yangtze river. The soil for analysis PTEs was sampled in 2015 from urban forest encircled by the NingLuo Highway, the HuRong Highway, and Jiangbei Avenue in the center of Nanjing. 180 topsoil samples (0~20cm) were collected across the area with the aid of GPS, distributed in downtown Nanjing (Fig. 1) with grid cells of 1×1 km. Each composition sample from the sampling sites consisted of five subsamples. The soils

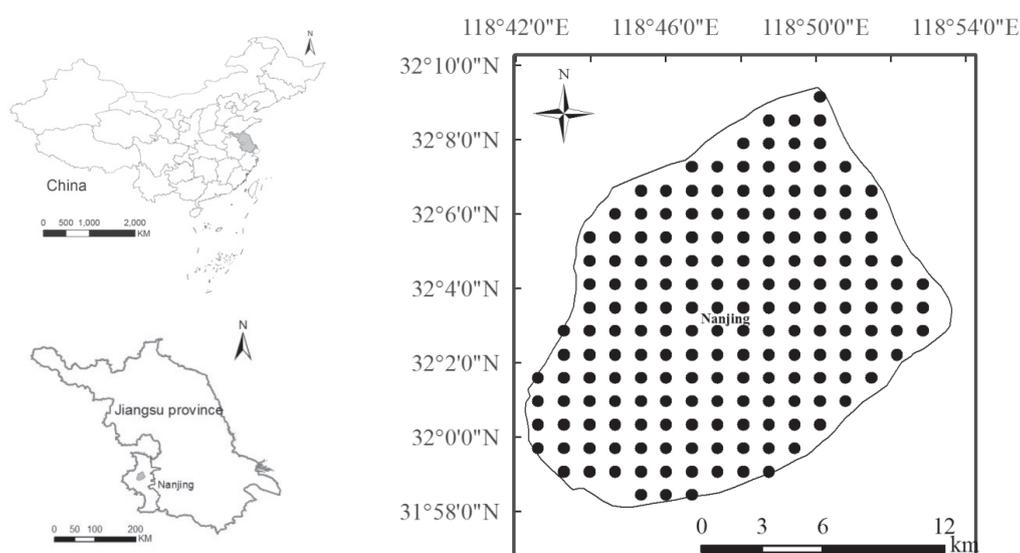


Fig. 1. Study area location and sampling sites in Nanjing.

Table 1. Three indexes to assess PTE pollution.

Index	Formula	Meanings of each letter	Assess
P_{in}	$P_{in} = \sqrt{\frac{(\frac{1}{n} \sum_{i=1}^n P_i)^2 + P_{i\max}^2}{2}}$ $P_i = \frac{C_i}{S_i}, P_{i\max} = \frac{C_{i\max}}{S_i}$	P_i : environmental quality index of pollutant; C_i : measured mass fraction of pollutant ($mg \cdot kg^{-1}$); S_i : background value of pollutant ($mg \cdot kg^{-1}$);	$P_{in} < 0.7$, Safe $0.7 \leq P_{in} < 1$, vigilance $1 \leq P_{in} < 2$, clean-light pollution $2 \leq P_{in} < 3$, moderate pollution $P_{in} > 3$, strong pollution
I_{geo}	$I_{geo} = \log_2\left(\frac{C_i}{1.5B_i}\right)$	C_i : measured value of the heavy metal i ($mg \cdot kg^{-1}$); B_i : background value of PTE i ($mg \cdot kg^{-1}$);	$I_{geo} < 2$, clean-light pollution $2 \leq I_{geo} < 5$, moderate pollution $5 \leq I_{geo} < 20$, significant pollution $20 \leq I_{geo} < 40$, strong pollution $I_{geo} \geq 40$, extreme pollution
PERI	$PERI = \sum E_i$ $E_i = T_i \frac{C_i}{B_i}$	E_i : ecological risk of single heavy metal i; T_i : toxic-response factor for heavy metal i; C_i : measured value of PTE i ($mg \cdot kg^{-1}$); B_i : background value of PTE i ($mg \cdot kg^{-1}$);	$RI < 150$, clean-light pollution $150 \leq RI < 300$, moderate pollution $300 \leq RI < 600$, significant pollution $RI \geq 600$, extreme pollution

were collected from neighboring areas once there were buildings or water on the designated position. Each soil sample was obtained with a wooden shovel and packed into polyethylene. The locations of sampling sites were recorded, including environmental information and land use, which were divided into 6 function zones according to their land use: road green belt (RGB), urban square (US), urban garden (UG), institution greenland (IG), residential greenland (RG), and urban rural forest (URF).

Determination of PTEs

Soil samples were placed on a wooden plate and air-dried at room temperature. Root, stem, leaf, worm and stones, and tuberculosis (lime, iron, manganese) were picked up. Dried soil samples in wooden discs were crushed, sieved through a 100-mesh nylon sieve, and loaded in a brown paper bag for analysis.

The sample digestion method was as follows: accurately weighing 0.5000 g (accurate to 0.0001 g, the same as below) dry soil samples in the Teflon crucible, plus 20 mL HNO_3 , then heating to being almost sticky on an electric heating plate, added 20 mL HF and continue heating, often shaken in a crucible to almost sticky, with added 20 mL $HClO_4$, heated to no longer making white smoke, with added water to rinse the lining and the crucible lid, tepid digestion residue, after cooling, added water up to 100 mL. HNO_3 , HF, and $HClO_4$ are guaranteed reagents, and the water used in the experiment is ultra pure.

Determining Pb, Zn, Cu, Cr, Cd, Ni, and As in soil was carried out by ICP-OES analysis, and recommended wavelengths of seven elements were 216.9, 213.8, 324.7, 267.7, 228.8, 231.6, and 189.0 nm for Pb, Zn, Cu, Cr, Cd, Ni, and As, respectively. Method detection limit

(MDL) was 0.0101, 0.0003, 0.0003, 0.0006, 0.0003, 0.0003, and 0.0004 $mg \cdot L^{-1}$ for Pb, Zn, Cu, Cr, Cd, Ni, and As, respectively. Take two soil samples, one was added with standard, the other not. Seven elements were continuously determined for six times, then recovery rate was calculated, taking soil standard sample GSS-6 as quality control sample. The results show that the recovery rate of Pb, Zn, Cu, Cr, Cd, Ni, and As was 101.2%, 101.1%, 93.3%, 96.1%, 96.2%, 94.7%, and 99.4%, respectively.

Assessment Index of PTEs

Three indexes were used to assess the pollution level (calculation methods and evaluation indicators were listed in Table 1) [24]. In order to evaluate the pollution status of a single element we used the Nemerow pollution index (PI_N), which takes both mean and maximum values into consideration, hence this index reflects environmental quality conditions scientifically and comprehensively [25]. The index of geo-accumulation (I_{geo}) was also used to assess the pollution level of a single element. This method not only considers anthropogenic factors and environmental geochemistry background value, but also considers the influence of natural activities on the background values [26]. The comprehensive pollution of 7 PTEs in soils was evaluated by the potential ecological risk index (PERI) [27].

Statistical Analysis

Basic statistics of the raw data were carried out using SPSS 23.1 software. One-way analysis of variance (ANOVA) was carried out to determine the significant differences of PTEs among the different zones.

Table 2. Descriptive statistics of soil PTE concentrations.

Metal	Mean (mg·kg ⁻¹)	Min (mg·kg ⁻¹)	Max (mg·kg ⁻¹)	SD	BV (mg·kg ⁻¹)	S (mg·kg ⁻¹)	CV (%)
Pb	111.13	20.53	356.45	64.22	24.8	500	57.79
Cd	1.11	0.10	3.75	0.85	0.19	1.0	76.46
Cu	76.50	51.80	200.55	17.56	32.2	400	22.95
Cr	89.52	25.78	659.95	67.96	59	400	75.92
Zn	196.33	113.69	785.91	72.78	76.8	500	37.07
Ni	53.13	29.63	234.95	28.13	35.00	200	52.94
As	88.28	4.56	617.39	101.83	10.60	40	115.35

Note: BV - background value; S - soil environmental quality standards of the People's Republic of China (grade III)

Comparisons of means were carried out by the least significant difference (LSD) at the 5% level. Principle component analysis (PCA), Cluster analysis (CA) were used to identify the source of elements.

Kriging interpolation was applied to the data set for describing the spatial distribution of PTEs. Ordinary kriging with a proper correction from smoothing effect can be revitalized as a reliable estimation method that allows for better use of the available information [28]. This method provides a best linear unbiased estimation (points of certain value) method in mathematics for the object. Its plug has higher credibility when the data points were more [29].

Results and Discussion

Concentrations of PTEs in the Study Area

The descriptive statistics of the concentrations of PTEs in soils are listed in Table 2. The total concentrations of As in soils were extremely variable, ranging from 4.56 to 617.39 mg·kg⁻¹, with an average concentration of 88.28 mg·kg⁻¹. The As concentration in some soil sampling sites exceeded the background value (BV) [30], which indicated that As was mainly derived from an anthropological source. The total concentrations of Cd and Cr in soils were also very variable, ranging from 0.10 to 3.75 mg·kg⁻¹ and 25.78 to 659.95 mg·kg⁻¹, respectively, with average concentrations of 1.11 mg·kg⁻¹ and 89.52 mg·kg⁻¹, respectively. Maximum concentrations of Cd and Cr were about 20 and 11 times their BVs, which derived from an anthropological source. The concentrations of Pb and Zn in soils ranged from 20.53 to 356.45 mg·kg⁻¹, and 113.69 to 785.91 mg·kg⁻¹, respectively, with average values of 111.13 mg·kg⁻¹ and 196.33 mg·kg⁻¹. The concentrations of Pb and Zn in the soils also exceeded their BVs, and maximum concentrations of Pb and Zn were about 14 and 10 times their BVs. Highest concentrations of Ni and Cu were about 7 and 6 times their BVs, respectively, which indicated that the soils in the local area mainly derived from an anthropogenic source.

Sources of PTEs in the Study Area

The results of PTE concentrations in different function zones were presented in Table 3. The higher concentrations of Pb, Cd, Cr, Ni, and As were all distributed in RGB and US. These two function zones were mainly polluted by vehicle exhaust emissions and industrial dust. Pb and Cd were mainly controlled by traffic activities (e.g., brake wear, tire wear, automobile exhaust) with high contamination levels found near traffic-intensive areas [31]. The Yu et al. report on the Mukal et al. also revealed that the sources of urban lead pollution in China were mainly leaded gasoline, industrial emissions, and coal dust [34]. The research on heavy metals in Zhangzhou city showed that Pb and Cd elements were disturbed by anthropogenic contributions [35]. Extreme sediment contamination in As was observed in industrial mining areas at Afrma [36], while Cr and Ni may also originate from industrial dust, since maximum values were much higher than their BVs. Tume et al. had the same conclusion [37]. On the other hand, Vince et al. and Manta et al. reported that Cr and Ni were primarily of lithogenic origin [38, 39]. The higher concentration of Zn distributed in RG expect RGB and US, which indicated that daily life emissions may also lead to Zn accumulation in topsoil. Although there were no significant difference between 6 function zones, the highest concentration was distributed in UG, RG, and IG, therefore fertilizer and sewage irrigation may be the cause of the accumulation of copper in the soil. Because concentrations of 7 PTEs were higher than their BVs, PTE pollution of this area was caused by anthropogenic input.

The results of PCA for total metal concentration in soil were shown in Fig. 2. Three principal component (PC) with eigenvalues higher than 1 were extracted. The associations between metals were displayed in Fig. 2. PCA leads to a reduction of the initial dimension of the dataset to three components, which explained 72.79% of the data variation.

The initial component matrix showed that Ni and Cr were associated with the first component (PC1), which explained 34.99% of the variance (Fig. 2). Industrial

Table 3. PTE concentrations in different function zones ($\text{mg}\cdot\text{kg}^{-1}$).

Function zones	Pb (M \pm SD)	Cd (M \pm SD)	Cu (M \pm SD)	Cr (M \pm SD)	Zn (M \pm SD)	Ni (M \pm SD)	As (M \pm SD)
RG	91.76 \pm 34.28b	1.05 \pm 0.96b	78.03 \pm 18.90a	74.07 \pm 13.25ab	197.36 \pm 85.94b	48.17 \pm 10.07ab	61.71 \pm 41.66b
UG	154.05 \pm 59.63a	1.20 \pm 0.67ab	79.72 \pm 14.42a	82.86 \pm 27.24ab	189.30 \pm 26.70b	47.15 \pm 6.88ab	74.81 \pm 116.72b
US	157.34 \pm 82.31a	1.52 \pm 0.80a	75.50 \pm 22.42a	86.93 \pm 16.74ab	243.70 \pm 104.63a	55.80 \pm 21.07ab	179.61 \pm 138.31a
RGB	167.53 \pm 86.90a	1.68 \pm 0.89a	73.00 \pm 18.30a	111.12 \pm 99.26a	202.54 \pm 56.01ab	61.02 \pm 40.11a	138.80 \pm 45.04ab
URF	91.09 \pm 51.20b	1.01 \pm 0.80b	70.25 \pm 4.00a	65.79 \pm 24.95b	167.95 \pm 23.08b	46.85 \pm 9.98b	50.56 \pm 17.10b
IG	107.77 \pm 62.82b	0.77 \pm 0.69b	77.96 \pm 18.36a	73.82 \pm 6.92b	186.52 \pm 46.05b	41.72 \pm 4.55b	88.18 \pm 82.69b

Note: Data in the table are the Means \pm SD; the different normal letters in the same column indicate significant difference among different function zones ($P < 0.05$). RGB: road green belt; US: urban square; UG: urban garden; IG: institution greenland; RG: residential greenland; UF: urban rural forest.

origin could be presumed for these two elements, since the highest concentration of Cr and Ni was found in the northern industrial zones. This result was consistent with Chen et al., who found that Cr and Ni were mainly from industrial activities [40], and Cr and Ni in soils of industrial townships also originated from industrial emissions [41].

Another component (PC2), which included Cd, Pb, and As and explained 22% of the variance, was identified according to their coefficients in component matrix (Fig. 2). Traffic origin was deduced for these elements, since the highest concentrations of Cd, Pb, and As were found in the central business zones with heavy traffic. The concentrations of Pb and Cd were higher in roadside areas than other areas in Beijing, which indicated that Pb and Cd were mainly from traffic

sources [42]. Acosta et al. used multivariable analysis to identify the sources of Pb and Cd in soils, which were anthropogenic activities – specifically industrial activities and traffic [43].

The third component (PC3) which included Cu and Zn and explained 15.8% of the variance, was identified, according to their coefficients in component matrix (Fig. 2). Fertilizer origin was speculated for these two metals, since the highest concentrations of Cu and Zn were found scattered in all areas, and the anthropogenic source of Cu and Zn were pesticides and fertilizer [44], the green rate of Nanjing is as high as 45%, with many green areas scattered across the city, and large amounts of fertilizer and pesticides are put into the soil every year, which may lead to the accumulation of Cu and Zn.

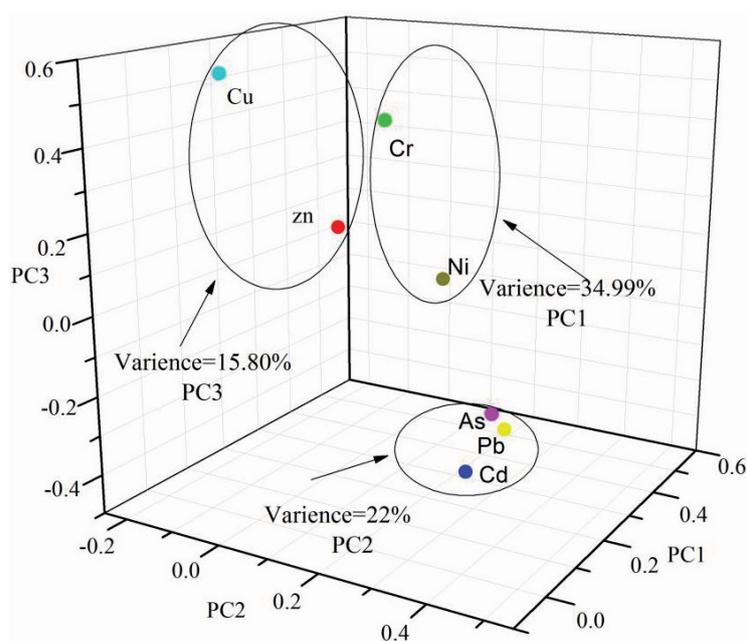


Fig. 2. 3-D plot of PCA loading for 7 PTEs in urban forest soils of Nanjing. Note: The numbers represent the variations explained by each principle component.

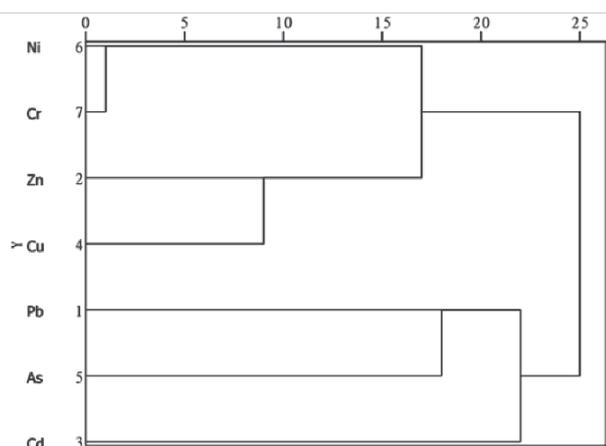


Fig. 3. Cluster analysis of 7 PTEs in urban forest soils of Nanjing.

Cluster analysis (CA) was often coupled with PCA to confirm results and provide grouping of variances (Fig. 3). In total, three clusters were observed: Ni-Cr, Pb-As-Cd, and Cu-Zn. Thus, CA suggested at least

three different sources of heavy metals in urban forest soils, which was in agreement with the PCA results.

Pollution Assessment of PTEs in the Study Area

PIN, I_{geo} , and PERI were used to evaluate the pollution status of 7 heavy metals and the results are shown in Table 4. PI_N using background value for reference showing the pollution conditions in the order of $As > Cd > Pb > Cr > Zn > Ni > Cu$, with I_{geo} indicating that As was in moderate pollution level with a value of 2.47, whereas the other 6 metals were in clean-light pollution level. PERI showed that the study area was in significant pollution level with value of 305.62. From Table 5 we found that Pb was in significant correlation with As ($P < 0.01$), and Ni and Cr were also in significant correlation with As ($P < 0.01$) when Cu was significantly correlated with Zn ($P < 0.01$). RI was in significant correlation with Cd, As, Pb, and Zn ($P < 0.01$), which means that the pollution source of this study area was mainly traffic origin.

Table 4. The result of pollution indices of 7 PTEs in the sampling sites.

Element	P_{in}		I_{geo}		PERI			
	Use BV as reference	Use S as reference	Value	Pollution level	Ti	Ei	PERI	Level
Pb	10.65	0.53	1.58	Clean-light pollution	5	22.41	305.62	Significant pollution
Cd	14.55	2.77	1.96	Clean-light pollution	30	174.88		
Cu	4.71	0.38	0.66	Clean-light pollution	5	11.88		
Cr	7.98	1.57	1.17	Clean-light pollution	2	3.03		
Zn	7.46	1.15	0.77	Clean-light pollution	1	2.56		
Ni	4.87	0.85	0.17	Clean-light pollution	5	7.59		
As	41.60	11.03	2.47	Moderate pollution	10	83.28		

Note: P_{in} - Nemerow pollution index; I_{geo} - geo-accumulation index; PERI - potentially ecological risk index. BV - background value of PTEs; S - soil environmental quality standards of the People's Republic of China (grade III). T_i - toxic-response factor for PTE i.

Table 5. Correlative coefficient matrix of 7 PTEs and RI.

Variate	Pb	Zn	Cd	Cu	As	Ni	Cr	RI
Pb	1							
Zn	.162*	1						
Cd	.125	.000	1					
Cu	-.036	.595**	-.121	1				
As	.257**	.374**	.115	-.095	1			
Ni	-.156*	.346**	-.031	.336**	.000	1		
Cr	-.170*	.333**	-.027	.281**	.038	.916**	1	
RI	.302**	.242**	.825**	-.116	.650**	.007	.028	1

Note: * means 2 elements had significant correlation at 0.01 level (1-tailed); ** means 2 elements had significant correlation at 0.01 level (2-tailed).

Spatial Distribution of PTEs and PERI in the Study Area

Kriging interpolation showed different spatial distribution patterns of PETs and PERI in the study area, and the results are presented in Fig. 4. There were 3 patterns for PETs and PERI. Pb, Cd, As, and PERI presented a similar island pattern that took traffic and the commercial center as a hot spot (TCIP), while Cr and Ni presented an island pattern that took chemical plants as a hotspot (CPIP), with Cu and Zn presenting a scattered

point pattern (SPP). TCIP covered Nanjing Railway Station, Gulou-Xinjiekou District, and Xinzhuang overpass, where there was an urban commercial and cultural center with busy traffic and dense population, with high concentrations of Pb, Cd, and As in this region's soils derived from fuel combustion, road dust, and tire wear. Wang et al. found that soil concentration of As was the highest in Beijing urban soils [45]. Xu et al. pointed out that As and Cd contamination were significantly correlated with landscape patterns [46]. CPIP covered NingLuo Highway, Qixia Avenue, and

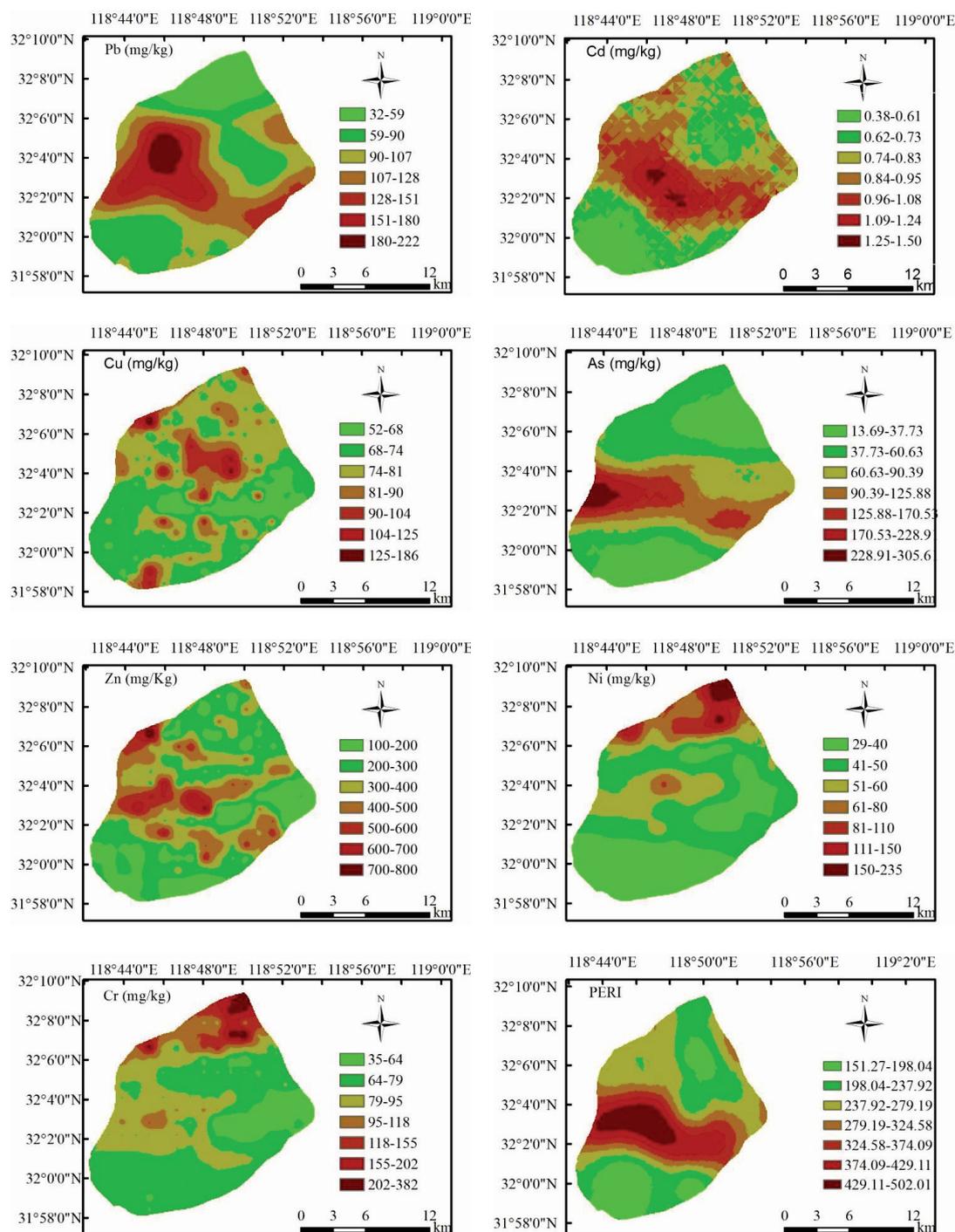


Fig. 4. Spatial distribution of PTEs and PERI in study area.

Liutang overpass with many large chemical plants and gas stations in addition to heavy traffic. There were large numbers of equipment, instruments, and machinery production factories mainly producing electronic equipment and steel products, which were using Cr and Ni as raw materials. Cr and Ni in soil minerals were associated with a high correlation coefficient of 0.916 ($P < 0.01$), content of two elements affected by the common soil minerals. Hence, spatial structure and distribution of two elements had certain similarity. SPP was distributed widely in the area of the city, especially in the central and northern parts of the city, presented by an irregular dot. Therefore, zinc and copper pollution were caused not only by traffic and industrial origin, but also by pesticide, fertilizer, and sewage irrigation widely used in greening and daily life waste. Many researchers revealed that fertilizer with high content of Cu and Zn was a source of long-term soil contamination [47-49]. Spatial distribution characteristics of metals in the study area suggested that seven elements in urban forest soils of Nanjing were anthropogenic sources: industrial origin, traffic origin, fertilizer and pesticides, which were in total agreement with the PAC and CA results.

Conclusions

Concentrations of 7 PTEs in Nanjing urban forest soils were heterogeneity and all higher than their BVs, especially for As and Cd, whose mean values were 8.7 and 5.8 times their BVs, respectively. Land type of the urban forest soils affected the metals accumulation in Nanjing. High concentrations of all elements were measured in RGB, US, and UG. PCA and CA identified Pb, As, and Cd as being mainly derived from traffic, Ni and Cr mainly from industrial origin, and Zn and Cu mainly from three spatial distribution patterns of seven metals (CCIP, CNIP, and SPP) confirm the anthropogenic sources of Nanjing urban forest soils. As pollution was most serious in the study area, PERI of seven elements was 305.62 – in a state of significant pollution. High PERI value was mainly due to the high concentrations of Pb, Cd, As, and Zn in the urban forest soils. Hence, pollution of PTEs in Nanjing urban forest soil were mainly due to traffic emissions.

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Conflict of Interest

The authors declare no conflict of interest.

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