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Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China

Yuebing Sun[a,b], Qixing Zhou[a,c,*], Xiaokui Xie[a,b], Rui Liu[a]

[a] Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, China
[c] Key Laboratory of Pollution Process and Environmental Criteria (Ministry of Education), College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

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ABSTRACT

Surface soil samples from 36 sampling sites including different functional areas in seven districts of Shenyang, China were collected and analyzed. The results showed that the average concentrations of Cd, Cu, Pb and Zn in soil of Shenyang were up to 0.42, 51.26, 75.29 and 140.02 mg/kg, respectively, which are much higher than their natural background values. Among the functional areas and administrative regions, the industrial regions and the Tiexi District displayed the highest metal concentrations. Pearson's correlation analysis showed that there existed close correlations among Cd, Cu, Pb and Zn (except for Cd–Cu) at 1% level. Principal Component Analysis (PCA) coupled with correlation between heavy metals revealed that heavy metal contamination might originate from traffic and industrial activities. The values of pollution index (PI) and integrated pollution index (IPI) indicated that metal pollution level was Pb > Cd > Zn > Cu, and Cd, Cu, Pb and Zn belong to moderate or high pollution level. Potential ecological risk indexes (RI) further indicated that Shenyang was suffering from serious metal contamination. These results are important for the development of proper management strategies to decrease non-point source pollution by various remediation practices in Shenyang, China.

1. Introduction

In recent years much concern has been addressed over the problem of urban soil contamination with heavy metals due to rapid industrialization and urbanization. The modernization of industry and the presence of intensive human activities in urban areas have exacerbated the problem of heavy metal contamination in urban soils. The pollutants are discharged in many ways such as vehicle emission [1,2], industrial wastes, the sedimentation of dust and suspended substances in the atmosphere, the combustion of coals and the dry and wet precipitation of other pollutants [2]. The soil environment is interfacial, heterogeneous, and changing, and the basic characteristics of soil contamination are different from those of air and water, such as concealment and hysteresis, accumulation, and irreversibility [3,4]. The high concentrations of heavy metals in urban soils have posed adverse effect on human health because it can be easily transferred into human bodies from suspended dust or by direct contact [5,6]. Moreover, the long-term input of metals could result in decreased buffering capacity of soil [7] and groundwater contamination [7,8]. Thus, trace metal contamination of the urban environment can have long-term and far-reaching environmental and health implications [9].

Soil serves as both a sink and a source for trace metal contaminants in the terrestrial environment. Excessive accumulation of heavy metals in urban soils may result not only in heavy metal contamination of the soils but also in increased human exposure to heavy metals due to their close proximity to human activities. The investigation of soil metal distribution and their influencing factors in topsoil could offer an ideal means to monitor and assess the pollution of soil itself and the overall environmental quality as reflected in soils [10,11]. Therefore, numerous extensive investigations of heavy metal contamination in urban soils have been carried out in many regions such as Ibadan [12], Cartagena [13], Hyderabad [11], Uppsala [7], Guangzhou [14], Yixing [15] and Xuzhou [16].

Shenyang, the biggest city and a major political, industrial and economic center in northeastern China, has an area of 13,000 km^2 and a population over 7.2 million. Shenyang is a traditional industrial base and an emphatically constructed city in China. It has formed an industrial system complete with all necessary departments, giving priority to mechanical processing, embracing automobile, petrochemical industry, aviation, pharmacy, building materials, metallurgy, electronic industry, coal industry, and so on (see the Shenyang Government webpage; http://www.shenyang.gov.cn). The growth rate of gross domestic

* Corresponding author at: Key Laboratory of Terrestrial Ecological Process, Chinese Academy of Sciences, Institute of Applied Ecology, Shenyang 110016, China. Tel.: +86 24 83970373; fax: +86 24 83970436.
E-mail addresses: zhouqx@iae.ac.cn, zhouqx523@yahoo.com (Q. Zhou).

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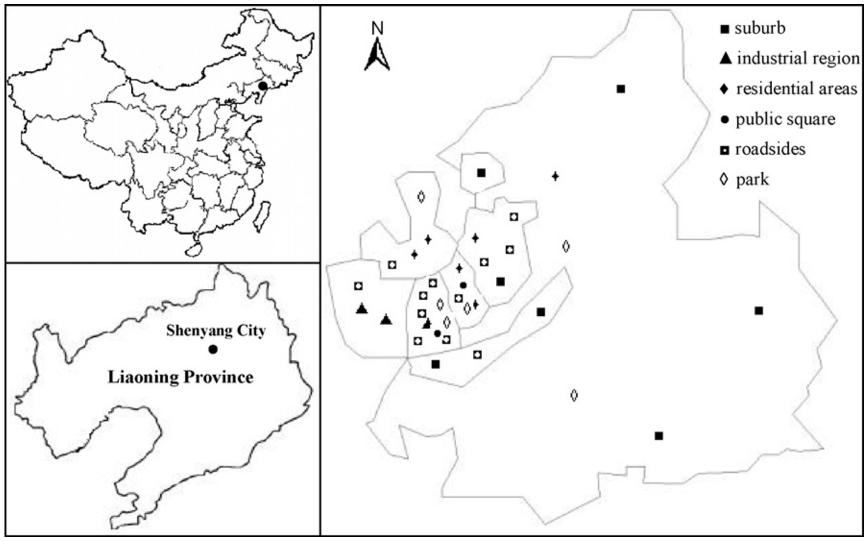

Fig. 1. Map of sampling sites in Shenyang City.

product (GDP) grew over 16.0% over the previous year, and with an increase of approximately 90.5% over that of the year 2000 (Economic and Social Development Statistical Bulletin of shenyang; http://www.sysinet.gov.cn/). With rapid economic development, the environmental quality has been severely deteriorated. According to the research by Wang et al. [17], the concentrations of Pb in urban soils of Shenyang ranged from 22.02 to 2910.60 mg/kg, with a mean concentration of 138.59 mg/kg. In the Tiexi District of Shenyang, the average concentrations of total Cu, Zn, Pb and Cd were up to 209.06, 599.92, 407.19 and 8.59 mg/kg, respectively [10]. However, little literature exists about the concentration and distribution of heavy metals in the typical areas of Shenyang. The main objectives of this study were (1) to determine the concentration and distribution of heavy metals in soils of Shenyang; (2) to identify the possible sources of heavy metals; and (3) to assess the heavy metal contamination in urban soils.

2. Materials and methods

2.1. Sampling and preparation

Thirty-six surface (0–5 cm) soil samples were collected from different main functional sections in six districts of Shenyang, Liaoning Province, China (Fig. 1), and each main soil sample consisted of 5–10 subsamples collected randomly from the surroundings of each site, pooled and homogenized to form a representative sample [3,18]. Among 36 soil samples, 7 were collected from suburbs, 3 from industrial regions, 7 from parks, 2 from public squares, 11 from main roadsides and 6 from residential areas. These sites are very famous places in Shenyang, to same extent as landmark areas. For example, Youth Park, Wulihe Park, Shenhai Power Plant, Shenyang Smelting Plant, Youth Avenue, and Wenhua Road, etc. The coordinates of sampling locations were recorded with a GPS. The composite soils were stored in glass jars at 4 °C after being air-dried at room temperature for 10 days and sieved through a 1 mm mesh. The soil samples were digested with a solution of 3:1 HNO_3:$HClO_4$ (v/v) [19]. The concentrations of Cd, Cu, Pb and Zn in digested solutions were determined by a flame atomic absorption spectrophotometer (WFX-120, Beijing Rayleigh Analytical Instrument Corp., China).

2.2. Data treatment with computer software and analysis

The descriptive statistical parameters were calculated with SPSS10.0 package, and the correlations between heavy metals were assessed by using Pearson correlation analysis. The difference was investigated using one-way ANOVA analysis. The positions of soil sample locations were recorded as a coordinate system using a GPS receiver. The kriging interpolations of the contaminant concentrations were computed with the ArcView 3.2.

3. Results and discussion

3.1. Heavy metal contamination

As shown in Table 1, there was a distinct change in the contents of heavy metals among the sampling soils, the concentrations of Cd, Cu, Pb and Zn varied between 0 and 2.08, 0 and 274.61, 0.12 and 533.29, and 61.05 and 403.43 mg/kg, respectively, with an average concentration of 0.42, 51.26, 75.29 and 140.02 mg/kg, respectively. Based on the mean concentration, the components in soils were arranged in the following decreasing order: Zn > Pb > Cu > Cd. According to the environmental quality standard for soils (GB 15618–1995), which are considerably higher than the corresponding natural background value of soils in China, these components are about 1.4-, 2.2-, 1.6- and 2.5-fold, respectively, and reach 2.63-, 2.09-, 3.56- and 2.37-fold, respectively, when compared with the corresponding natural background value of soils in Shenyang, clearly demonstrating an anthropogenic contribution. Compared with the documented studies in other urban soils, it was shown that the metal concentrations in the present study were higher than those from Hong Kong (0.36 ± 0.16 mg Cd kg^{-1}, 16.2 ± 5.92 mg Cu kg^{-1} and 103 ± 91.3 mg Zn kg^{-1}) [20], the Thrace region (0.2 mg Cd kg^{-1}, 20 mg Cu kg^{-1}, 33 mg Pb kg^{-1} and 45 mg Zn kg^{-1}) [21], the Zagreb region (20.8 mg Cu kg^{-1}, 25.9 mg Pb kg^{-1} and 77.9 mg Zn kg^{-1}) [22] and the world average. But it was lower than other cities, such as Ibadan (8.4 ± 19.78 mg Cd kg^{-1}, 95.1 ± 126.68 mg Pb kg^{-1} and 228.6 ± 366.28 mg Zn kg^{-1}) [12] and Mortagne du Nord (1.92 ± 0.81 mg Cd kg^{-1} and 230.8 ± 146.3 mg Pb kg^{-1}) [23] (Table 2).

3.2. Spatial distribution of heavy metals

Regionalized variables are characterized by the spatial features of randomness and structure which can be represented by a variable function [15]. The spatial distributions of heavy metals in 6 districts of Shenyang are shown in Fig. 2. The con-

Table 1
Heavy metal concentrations in the soils of Shenyang (mg/kg).

Location	Cd	Cu	Pb	Zn
Shenhe District				
11-PS	0.08 ± 0.04	19.88 ± 18.08	34.68 ± 28.15	98.27 ± 6.19
20-RA	0.06 ± 0.00	28.80 ± 0.86	23.35 ± 3.35	89.13 ± 12.94
21-P	1.40 ± 0.05	274.61 ± 64.06	340.17 ± 129.12	112.72 ± 16.74
23-RA	0.16 ± 0.01	28.07 ± 2.09	42.64 ± 2.01	114.85 ± 7.38
30-MR	0.44 ± 0.11	41.24 ± 1.28	61.89 ± 0.73	148.55 ± 2.41
Mean ± S.D.	0.43 ± 0.56	78.52 ± 109.89	100.55 ± 134.69	112.70 ± 20.27
Heping District				
7-P	0 ± 0	60.83 ± 1.77	49.84 ± 2.17	118.34 ± 8.16
8-MR	0.04 ± 0.02	57.11 ± 2.34	56.43 ± 4.84	180.35 ± 20.63
10-MR	0.21 ± 0.14	64.41 ± 3.10	98.46 ± 1.18	169.38 ± 4.62
19-P	0.31 ± 0.11	23.62 ± 1.21	36.86 ± 5.87	75.07 ± 2.05
22-MR	0.41 ± 0.10	260.43 ± 105.45	98.01 ± 27.90	261.50 ± 71.01
27-MR	0.44 ± 0.13	28.80 ± 1.48	46.56 ± 1.06	117.91 ± 8.83
33-IR	1.19 ± 0.03	57.45 ± 1.99	115.42 ± 1.50	264.70 ± 19.92
35-PS	0.56 ± 0.01	28.05 ± 2.36	51.40 ± 1.69	132.36 ± 18.09
36-MR	0.41 ± 0.06	47.99 ± 1.69	97.84 ± 14.01	140.97 ± 32.04
Mean ± S.D.	0.51 ± 0.49	69.85 ± 73.14	72.31 ± 29.52	162.29 ± 64.77
Dongling District				
13-S	0 ± 0	18.56 ± 0.65	25.70 ± 1.39	61.05 ± 4.23
17-S	0.35 ± 0.03	74.26 ± 20.19	33.76 ± 0.78	115.15 ± 9.77
26-RA	0.10 ± 0.07	0.00 ± 0.00	0.09 ± 0.11	94.04 ± 21.35
32-P	0.15 ± 0.09	26.75 ± 0.49	48.37 ± 1.08	110.43 ± 5.20
34-P	0.28 ± 0.14	16.63 ± 0.29	25.12 ± 2.77	89.60 ± 8.46
Mean ± S.D.	0.18 ± 0.14	27.24 ± 28.02	26.61 ± 17.54	75.38 ± 47.17
Tiexi District				
3-MR	1.52 ± 0.76	24.80 ± 3.73	35.31 ± 1.26	403.43 ± 21.34
9-IR	2.08 ± 0.03	58.23 ± 2.76	533.29 ± 28.57	222.74 ± 3.61
28-IR	0.99 ± 0.42	86.83 ± 17.91	124.97 ± 12.15	156.99 ± 8.50
Mean ± S.D.	1.53 ± 0.54	56.62 ± 31.04	231.19 ± 265.44	261.05 ± 127.61
Dadong District				
1-S	0.00 ± 0.00	26.51 ± 0.51	28.09 ± 0.50	89.73 ± 11.68
2-S	0.64 ± 0.01	58.93 ± 5.81	92.89 ± 1.39	183.54 ± 5.52
12-MR	0.89 ± 0.04	119.80 ± 1.79	191.46 ± 14.32	221.31 ± 1.04
14-MR	0.03 ± 0.03	31.10 ± 15.22	36.89 ± 1.27	98.87 ± 17.07
15-RA	0.40 ± 0.15	27.00 ± 0.77	42.07 ± 3.53	168.70 ± 19.81
31-P	0.02 ± 0.00	26.76 ± 2.82	26.34 ± 2.27	143.53 ± 14.52
Mean ± S.D.	0.38 ± 0.48	48.35 ± 37.18	69.62 ± 64.52	150.95 ± 50.68
Huanggu District				
4-P	0.10 ± 0.0	18.73 ± 1.89	69.14 ± 1.17	76.48 ± 3.45
5-RA	0.48 ± 0.03	31.44 ± 0.51	45.63 ± 3.44	105.18 ± 12.73
6-RA	0.11 ± 0.03	43.05 ± 1.55	53.32 ± 1.01	118.94 ± 3.99
25-MR	0.32 ± 0.12	47.93 ± 9.28	56.89 ± 2.42	125.01 ± 23.46
Mean ± S.D.	0.25 ± 0.18	35.29 ± 13.03	56.24 ± 9.80	106.40 ± 21.60
Hunnan New District				
16-S	0.18 ± 0.02	23.45 ± 0.81	24.65 ± 0.55	81.67 ± 23.05
18-S	0.36 ± 0.02	35.08 ± 4.79	34.39 ± 0.86	94.48 ± 11.99
24-S	0.08 ± 0.05	0.00 ± 0.00	0.12 ± 0.00	89.71 ± 51.23
29-MR	0.47 ± 0.04	28.38 ± 6.76	28.47 ± 0.89	93.03 ± 13.07
Mean ± S.D.	0.27 ± 0.18	21.73 ± 15.25	21.91 ± 15.06	89.72 ± 5.73
Shenyang City				
Range	0–2.08	0–274.61	0.12–533.29	61.05–403.43
Mean ± S.D.	0.42 ± 0.49	51.26 ± 20.12	75.29 ± 99.22	137.99 ± 68.09

PS, RA, P, MR, S and IR refer to public square, residential area, park, main roadside, suburb and industrial region, respectively.

Table 2
A summary of heavy metal concentrations in various cities of the world (mg/kg).

Cities	Cd	Cu	Pb	Zn	References
Chennai, India		154.4 ± 103.9	41.8 ± 38.8	128.2 ± 43.4	[8]
Ibadan, Nigeria	8.4 ± 19.78	46.8 ± 44.12	95.1 ± 126.68	228.6 ± 366.28	[12]
Hong Kong, China	0.36 ± 0.16	16.2 ± 5.92		103 ± 91.3	[20]
Thrace, Turkey	0.2	20	33	45	[21]
Zagreb, Croatian	0.66 ± 0.51	20.8 ± 16.2	25.9 ± 16.3	77.9 ± 30.9	[22]
Mortagne du Nord, France	1.92 ± 0.81		230.8 ± 146.3		[23]
This study	0.42 ± 0.49	51.26 ± 20.12	75.29 ± 99.22	137.99 ± 68.09	
Xuzhou, China	0.54 ± 0.6	38.2 ± 16.2	43.3 ± 26.1	144.1 ± 90.1	[24]
Creswick-Ballarat, Australia		13.95 ± 22.97	16.58 ± 13.71	273.17 ± 191.47	[25]

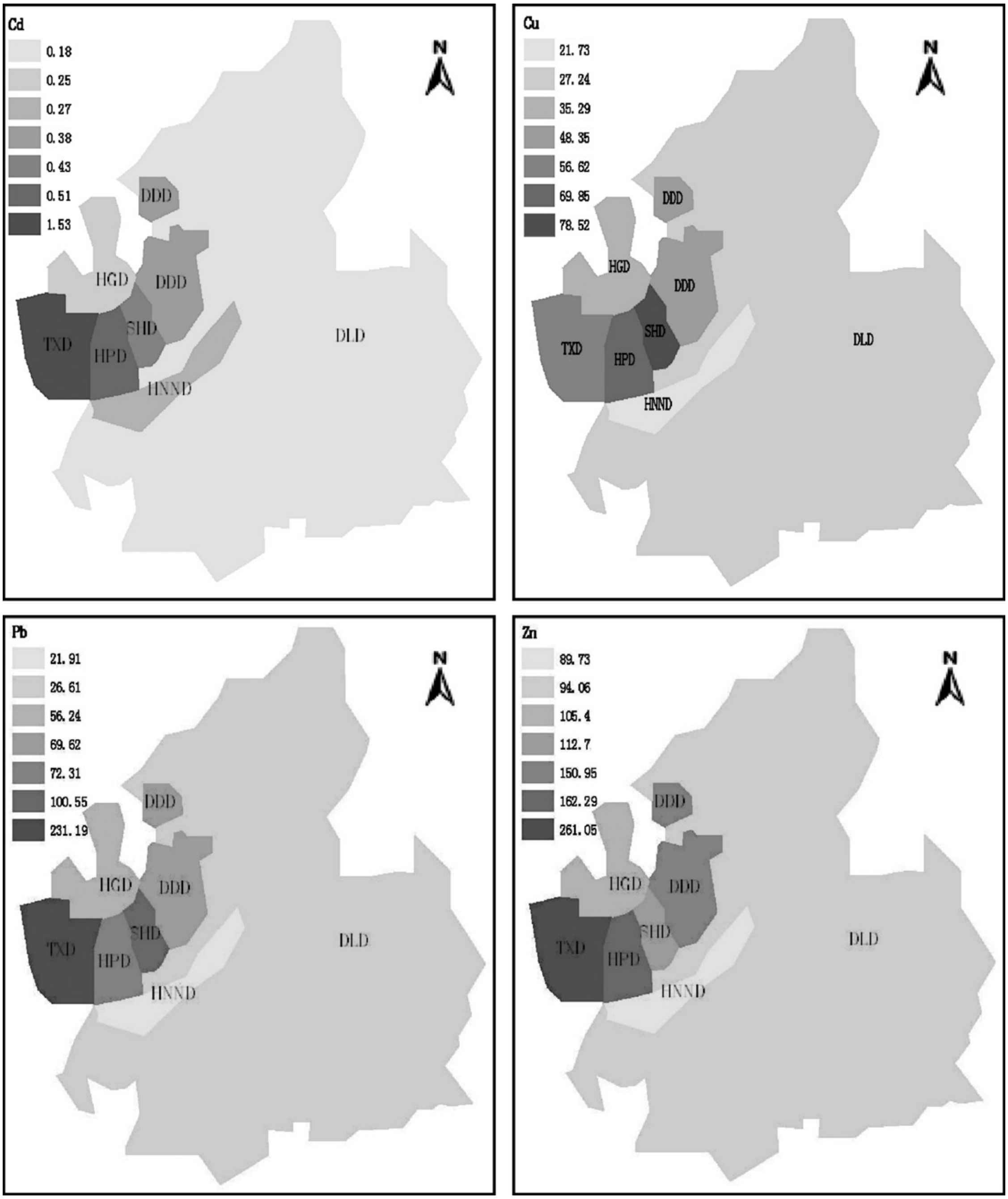

Fig. 2. The spatial distribution of heavy metals in different administrative regions of Shenyang.

centrations of total metals were in the following decreasing order:

Cd: Tiexi District > Heping District > Shenhe District > Dadong District > Hunnan New District > Huanggu District > Dongling District;
Cu: Shenhe District > Heping District >Tiexi District > Dadong District > Huanggu District > Dongling District > Hunnan New District;
Pb: Tiexi District > Shenhe District > Heping District > Dadong District > Huanggu District > Dongling District > Hunnan New District; and
Zn: Tiexi District > Heping District > Dadong District > Shenhe District > Huanggu District > Dongling District > Hunnan New District.

Similar spatial distributions of Cd, Pb and Zn were found in the geochemical maps, the most serious metal contamination was found in the Tiexi District, which was consistent with the report by An et al. [26] and Li et al. [10]. The maximum value of Cd and Pb concentrations in snow were found in the Tiexi District, which reached 2.2 and 850.0 μg/kg, respectively [26]. The average concentrations of total Cu, Zn, Pb, and Cd in the Tiexi District were 209.06, 599.92, 470.19 and 8.59 mg/kg, respectively [10]. The Tiexi District is the oldest and largest industrial zone in Northeast China. About 1200 industrial factories and plants such as machinery, metal casting, smelter, textile processing, chemical industry, and rubber manufacturing were located in the industrial district by the end of 1998 [2]. Furthermore, the Cu, Pb and Zn contents in the Tiexi District were higher than those in other districts [10]. The spatial distribution of these elements indicates the dominant role of industrial activities as the pollutant source.

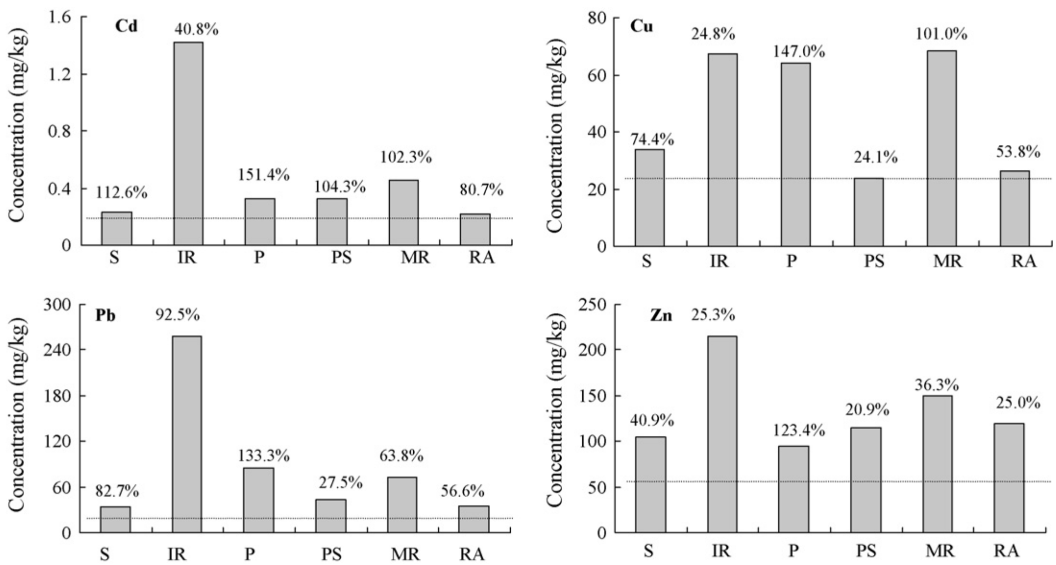

Fig. 3. Heavy metal concentrations in soils of different functional areas of Shenyang. PS, RA, P, MR, S and IR refer to public square, residential area, park, main roadside, suburb and industrial region, respectively. Horizontal lines represent the natural background of Cd, Cu, Pb and Zn in soils of Shenyang, respectively. RSD% of heavy metals for each region is listed above the bar diagram.

The concentrations of Cd, Cu, Pb and Zn in different functional areas were higher than the corresponding natural background heavy metals in the soil of Shenyang (Fig. 3). Heavy metal concentrations in the industrial areas were relatively higher (the concentrations of Cd, Cu, Pb and Zn varied from 0.99 to 2.08, 57.45 to 86.83, 115.42 to 533.29 and 156.99 to 264.70 mg/kg, respectively, and the average concentrations were 1.42, 67.50, 257.89 and 214.81 mg/kg, respectively) than those of other functional areas in Shenyang. Industrial activities, coal combustion, and refuse incineration were the main reasons for heavy metal emission in those industrial areas and high metal concentrations [5,16,18]. The lowest concentrations of Cd, Cu, Pb and Zn were found in residential areas, public squares, suburbs and parks, respectively, only about 0.22, 23.96, 34.23 and 94.70 mg/kg, respectively. Main roads contained rather higher concentrations of heavy metals than residential areas, public squares, suburbs and parks, which were 0.45, 68.36, 73.47 and 149.98 mg/kg, respectively. Main roadsides are always jammed with motor vehicles which brought heavy metal emission and heavy metal pollution. Liu and Bao [27] reported that roadside soils near motorways were polluted with Pb and other heavy metals by automobile exhausts, and there was the potential for exposure to high levels of heavy metals for road users and those living in those areas [28]. The distribution of heavy metals in different functional areas was similar to Wong et al. [29] who reported that within the urban areas, industrial areas have the highest heavy metal concentration, followed by commercial and residential districts. Wang and Qin [16] also found that Pb concentration varied in different functional areas in Shenyang with the order of industrial area > commercial area > residential area > suburb. The results above indicated that industrial and traffic activities were the main sources of heavy metal pollution in urban soils of Shenyang.

3.3. Correlation between heavy metals

Heavy metals in soil usually have complicated relationships among them. It was noted that numerous factors control their relative abundance, e.g., original contents of heavy metals in rocks and parent materials, various processes of soil formation, and anthropogenic factors such as the contamination by human activities [2]. Table 3 depicted the correlation coefficient matrix, listing the Pearson's product moment correlation coefficient. A very significant correlation was found between Cd and Pb (r = 0.76), Cd and Zn (r = 0.56), Pb and Cu (r = 0.49), Cu and Zn (r = 0.83), and Pb and Zn (r = 0.69) at 0.01 level, but Cd values showed weak positive correlation with Cu. The high correlations between soil heavy metals may reflect that these heavy metals had similar pollution level and similar pollution sources [10]. Overall, all the elements, Cd, Cu, Pb and Zn, are grouped together, indicating that the anthropogenic sources of these heavy metals are closely related in the soil of the study area, which was consistent with the research reported by Romic and Romic [22] and Li et al. [10].

Table 3
Correlation coefficients between different heavy metal elements (n = 36).

	Cd	Cu	Pb	Zn
Cd	1			
Cu	0.34	1		
Pb	0.76**	0.49**	1	
Zn	0.56**	0.83**	0.69**	1

Levels of significance: *P < 0.05; **P < 0.01.

3.4. Principal Component Analysis (PCA)

PCA has been applied to indicate the degree of pollution by heavy metals from lithogenic action and anthropogenic sources [1,30,31]. The results of PCA for heavy metal contents are listed in Table 4. According to these results, Cd, Cu, Pb and Zn concentrations could be grouped into a two-component model, which accounted for 91.04% of all the data variation. The initial component matrix that Cd, Cu, Pb and Zn were associated, displaying high values in the first component (PC1), while for in the second component (PC2), Cd and Cu also showed high values. The rotation of the matrix revealed that Cu and Zn were associated because of high values of PC1. Cd and Pb showed greater values of PC2 and were also partially represented in PC1. The results imply that Cd, Cu, Pb and Zn can be defined as anthropogenic components and may originate from similar pollution sources such as the precipitation of aerosol particles released by traffic and industrial activities [1,32].

Table 4
Total variance explained and component matrices for the heavy metals.

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	2.82	70.52	70.52	2.82	70.52	70.52	1.83	45.64	45.64
2	0.82	20.52	91.04	0.82	20.52	91.04	1.82	45.40	91.04
3	0.23	5.77	96.81						
4	0.13	3.20	100.00						

Elements	Component matrix		Rotated component matrix	
	PC1	PC2	PC1	PC2
Component matrix				
Cd	0.78	0.55	0.17	0.94
Cu	0.79	−0.57	0.96	0.16
Pb	0.87	0.34	0.38	0.85
Zn	0.91	−0.30	0.86	0.44

Extraction method: Principal Component Analysis (PCA).

3.5. Assessment of potential ecological risk

Potential ecological risk index (RI) was introduced to assess the degree of heavy metal pollution in soil, which was originally introduced by Hakanson [33], according to the toxicity of heavy metals and the response of the environment :

$$\mathrm{RI} = \sum E_i \quad (1)$$

$$E_i = T_i f_i \quad (2)$$

$$f_i = \frac{C_i}{B_i} \quad (3)$$

where RI is calculated as the sum of all four risk factors for heavy metals in soils, E_i is the monomial potential ecological risk factor, T_i is the metal toxic factor. Based on the standardized heavy metal toxic factor developed by Hakanson [33], the order of the level of heavy metal toxicity is Cd > Pb = Cu > Zn. The toxic factor for Pb and Cu is 5, 30 for Cd, and 1 for Zn. f_i is the metal pollution factor, C_i is the concentration of metals in soil, and B_i is a reference value for metals. In this study, the adjustment of factor standards was made according to Zhu et al. [34]. Four categories of metal pollution were low contamination ($\mathrm{RI} \leq 50$), moderated contamination ($50 < \mathrm{RI} \leq 100$), considerable contamination ($100 < \mathrm{RI} \leq 200$), and high contamination ($\mathrm{RI} > 200$).

RI represents the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk caused by heavy metals. As listed in Table 5, Cd posed a medium potential risk to the local, while for other metals the potential ecological risk was low. The ecological risk index, accounting for the contamination caused by Cd, Cu, Pb and Zn indicated that Shenyang was suffering from considerable contamination. Among different functional areas, the RIs were potentially posed high risk in industrial regions, considerable pollution in main roadsides, and moderate contamination in other regions. As for different administrating regions, there is a sharp boundary in Shenyang where the RI values decreased from high ecological risk in the Tiexi District (353.07) to considerable contamination in the Heping District (128.51), the Shenhe District (119.35) and the Dadong District (100.13), to medium pollution in the Huanggu District (69.12) and the Hunan New District (61.94), and to low ecological risk in the Dongling District (46.38).

Assessment of soil contamination degrees is performed by the quantification of an accumulation factor (pollution index, PI) and integrated pollution index (IPI). In general, the pollution index was defined as the ratio of the heavy metal concentration to the geometric means of background concentration of the corresponding metal [1]:

$$\mathrm{PI} = \frac{C_i}{S_i} \quad (4)$$

where PI is the evaluation score corresponding to each sample, C_i is the measured concentration of the examined metals in the soils, and S_i is the geochemical background concentration of the metals. The background values (mg/kg) utilized were 0.16 for Cd, 24.57 for Cu, 22.15 for Pb, and 59.04 for Zn, respectively. The PI value of each metal was calculated and classified as either low contamination ($\mathrm{PI} \leq 1.0$), moderate contamination ($1.0 < \mathrm{PI} \leq 3.0$) or high contamination ($\mathrm{PI} > 3.0$).

Table 5
The heavy metal potential ecological risk indexes in Shenyang.

Region	E_i				RI	Pollution degree
	Cd	Cu	Pb	Zn		
Suburb	43.17	6.88	7.73	1.73	59.51	Moderate
Park	60.51	13.02	19.21	2.45	95.20	Moderate
Residential area	40.98	5.37	7.79	1.95	56.09	Moderate
Main roadside	110.88	13.91	16.59	2.54	143.92	Considerable
Industrial region	266.14	13.74	58.22	3.64	341.73	High
Public square	60.33	4.88	9.72	1.95	76.87	Moderate
Shenhe District	78.99	15.64	21.99	2.73	119.35	Considerable
Heping District	95.22	14.22	16.32	2.75	128.51	Considerable
Dadong District	72.02	9.84	15.72	2.56	100.13	Considerable
Dongling District	33.24	5.54	6.01	1.59	46.38	Low
Huanggu District	47.46	7.18	12.70	1.79	69.12	Moderate
Hunnan New District	51.06	4.42	4.95	1.52	61.94	Moderate
Tiexie District	286.69	11.52	52.19	2.67	353.07	High
Shenyang City	94.90	9.77	18.55	2.23	125.45	Considerable

Table 6
Pollution index (PI) and integrated pollution index (IPI) of heavy metals in urban soil of Shenyang.

	NBVS	PI			Number of samples			IPI			Number of samples		
		Min	Max	Mean	Low	Middle	High	Min	Max	Mean	Low	Middle	High
Cd	0.16	0	12.99	2.88	13	13	10						
Cu	24.57	0	11.18	2.09	8	23	5	0.50	10.80	2.67	4	14	18
Pb	22.15	0.00	24.08	3.40	2	24	10						
Zn	59.04	1.03	6.83	2.33	0	29	7						

NBVS refers to the natural background value of soil in Shenyang.

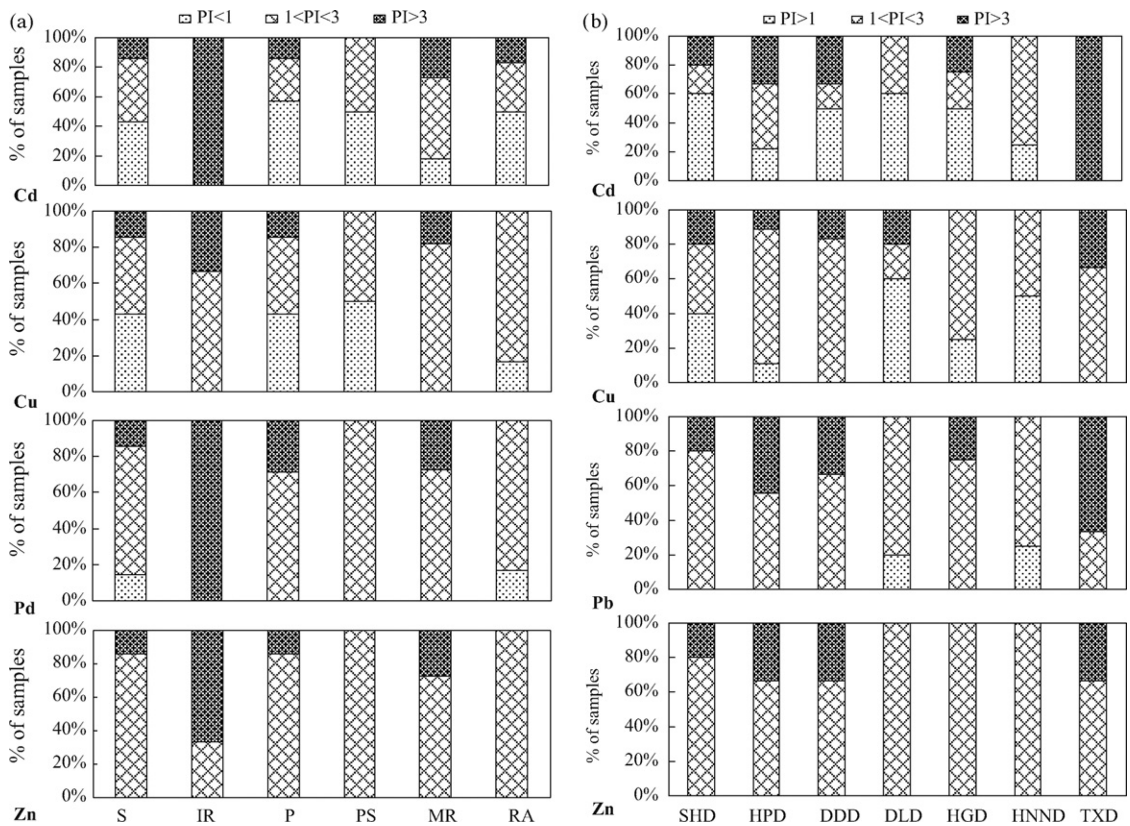

Fig. 4. Pollution characteristics of heavy metals in typical regions of Shenyang: (a) functional areas and (b) administrative regions. PS, RA, P, MR, S and IR refer to public square, residential area, park, main roadside, suburb and industrial region, respectively. Furthermore, SHD, HPD, DDD, DLD, HGD, HNXD and TXD refer to Shenhe District, Heping District, Dadong District, Dongling District, Huanggu District Hunnan New District and Tiexi District, respectively.

The PIs, calculated according to the natural background values of heavy metals in soils of Shenyang, varied considerably across the different metals and different typical soils (Table 6). The PI value of Zn in urban soils varied from 1.03 to 2.83 with an average of 2.33 and all soil samples had middle or high level PI. The PI value of Cd ranged from 0 to 12.99 and more than 63.89% of soil samples were moderately or heavily contaminated by Cd. All soil samples in the industrial regions and the Tiexi District were heavily polluted by Cd, but for other functional areas and administrative regions about 72.73–100% and 25–60% soil samples were classified as low and middle pollution, respectively (Fig. 4). The mean PI value for Cu was 2.09 and more than 77.78% of soil samples were moderately or heavy contaminated by Cu. The PI value for Pb varied from 0.00 to 24.08 with an average of 3.04, indicating that urban soils were seriously contaminated by Pb, which was consistent with the report by Wang et al. [17]. All soil samples in industrial regions, parks, public squares, main roadsides, the Shenhe District, the Heping District, the Dadong District, the Huanggu District and the Tiexi District got middle or high PIs, while for suburbs and residential areas, including the Dongling District and the Hunnan New District soil samples were classified as low-middle PIs. Cd, Pb and Zn pollution in urban soils followed the order of industrial region > main roadside > park > public square > residential area > suburb, while the decreasing sequence for Cu was main roadside > industrial region > park > suburb > residential area > public square.

Another commonly used criterion to evaluate the heavy metal pollution in soils is the integrated pollution index which is defined as the mean values for all the PIs of all considered metals, and was then classified as low contamination ($IPI \leq 1.0$), middle contamination ($1.0 < IPI \leq 2.0$) or high contamination ($IPI > 2.0$). The IPI value of urban soils varied from 0.50 to 10.80 with an average of 2.67 (Table 5). There were 4 samples with $IPI < 1.0$, 14 samples with IPI between 1.0 and 2.0, and 18 samples with $IPI > 2.0$. Thus, it is very likely that many urban soils in Shenyang are moderately or highly polluted with heavy metals.

4. Conclusion

The investigation of 36 soil samples from different functional areas in 7 districts of Shenyang revealed a clear accumulation of Cd, Cu, Pb and Zn. The concentrations of Cd, Cu, Pb and Zn varied between 0 and 2.08, 0 and 274.61, 0.12 and 533.29, and 61.05 and

403.43 mg/kg, respectively, with an average of 0.42, 51.26, 75.29 and 140.02 mg/kg, respectively. 63.89%, 77.78%, 94.44% and 100% of the soil samples were moderately or heavily contaminated by Cd, Cu, Pb and Zn, respectively. Among the functional areas and administrative regions, the industrial regions and the Tiexi District suffered from the most serious metal contamination. Heavy metals between Cd–Pb, Cd–Zn, Cu–Pb, Cu–Zn and Pb–Zn showed a significant correlation at level 0.01. PCA and correlation between heavy metals indicated that heavy metal pollution in Shenyang may originate from traffic and industrial activities.

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References

[1] T.B. Chen, Y.M. Zheng, M. Lei, Z.C. Huang, H.T. Wu, H. Chen, K.K. Fan, K. Yu, X. Wu, Q.Z. Tian, Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China, Chemosphere 60 (2005) 542–551.
[2] C. Li, F.Y. Lu, Y. Zhang, T.W. Liu, W. Hou, Spatial distribution characteristics of heavy metals in street dust in Shenyang city, Ecol. Environ. 17 (2008) 560–564.
[3] Q.X. Zhou, Research progress on in-situ remediation of polluted land, Pollut. Control Technol. 11 (1998) 207–211.
[4] Q.X. Zhou, Y.F. Song, Remediation of Contaminated Soils: Principles and Methods, Science Press, Beijing, 2000.
[5] L. Madrid, E. Diaz-Barrientos, F. Madrid, Distribution of heavy metal contents of urban soils in parks of Seville, Chemosphere 49 (2002) 1301–1308.
[6] S.X. Wang, Y. Qin, Correlation between magnetic susceptibility and heavy metals in urban topsoil: a case study from the city of Xuzhou, China, Environ. Geol. 49 (2005) 10–18.
[7] K. Ljung, E. Otabbong, O. Selinus, Natural and anthropogenic metal inputs to soils in urban Uppsala, Sweden, Environ. Geochem. Health 28 (2006) 353–364.
[8] A.K. Krishna, P.K. Govil, Assessment of heavy metal contamination in soils around Manali industrial area, Chennai, Southern India, Environ. Geol. 54 (2008) 1465–1472.
[9] C.S.C. Wong, X.D. Li, I. Thornton, Urban environmental geochemistry of trace metals, Environ. Pollut. 142 (2006) 1–16.
[10] F.Y. Li, Z.P. Fan, P.F. Xiao, K. Oh, X.P. Ma, W. Hou, Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China, Environ. Geol. 54 (2009) 1815–1823.
[11] P.K. Govil, J.E. Sorlie, N.N. Murthy, D. Sujatha, G.L.N. Reddy, K. Rudolph-Lund, R.A.K. Krishna, K. Mohan, Soil contamination of heavy metals in the Katedan Industrial Development Area, Hyderabad, India, Environ. Monit. Assess. 140 (2008) 313–323.
[12] A.A. Odewande, A.F. Abimbola, Contamination indices and heavy metal concentrations in urban soil of Ibadan metropolis, southwestern Nigeria, Environ. Geochem. Health 30 (2008) 243–254.
[13] M.J.M. García, S. Moreno-Grau, J.J.M. Garcí, J. Moreno, J. Bayo, J.J.G. Pérez, J. Moreno-Clavel, Distribution of the metals lead, cadmium, copper, and zinc in the top soil of Cartagena, Spain, Water Air Soil Pollut. 131 (2001) 329–347.
[14] N.S. Duzgoren-Aydin, C.S.C. Wong, A. Aydin, Z. Song, M. You, X.D. Li, Heavy metal contamination and distribution in the urban environment of Guangzhou, SE China, Environ. Geochem. Health 28 (2006) 375–391.
[15] S.H. Wu, S.L. Zhou, D.Z. Yang, F.Q. Liao, H.F. Zhang, K. Ren, Spatial distribution and sources of soil heavy metals in the outskirts of Yixing City, Jiangsu Province, China, Chin. Sci. Bull. 53 (2008) 188–198.
[16] X.S. Wang, Y. Qin, Spatial distribution of metals in urban topsoils of Xuzhou (China): controlling factors and environmental implications, Environ. Geol. 49 (2006) 905–914.
[17] J.D. Wang, H.M. Ren, J.S. Liu, J.B. Yu, X.L. Zhang, Distribution of lead in urban soil and its potential risk in Shenyang city, China, Chin. Geogr. Sci. 16 (2006) 127–132.
[18] X.J. Li, P.J. Li, X. Lin, Z.Q. Gong, S.X. Fan, L. Zheng, E.A. Verkhozina, Spatial distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in soils from typical oil-sewage irrigation area, Northeast China, Environ. Monit. Assess. 143 (2008) 257–265.
[19] Y.B. Sun, Q.X. Zhou, L.P. Ren, Growth responses of *Rorippa globosa* and its accumulation characteristics of Cd and As under the Cd–As combined pollution, Environ. Sci. 28 (2007) 1355–1360.
[20] C.S.L. Lee, X.D. Li, W.Z. Shi, S.C.N. Cheung, I. Thornton, Metal contamination in urban, suburban, and country park soils of Hong Kong: A study based on GIS and multivariate statistics, Sci. Total Environ. 356 (2006) 45–61.
[21] M. Coşkun, E. Steinnes, M.V. Frontasyeva, T.E. Sjobakk, S. Demkina, Heavy metal pollution of surface soil in the Thrace Region, Turkey, Environ. Monit. Assess. 119 (2006) 545–556.
[22] M. Romic, D. Romic, Heavy metals distribution in agricultural topsoils in urban area, Environ. Geol. 43 (2003) 795–805.
[23] F. Douay, H. Roussel, H. Fourrier, C. Heyman, G. Chateau, Investigation of heavy metal concentrations on urban soils, dust and vegetables nearby a former smelter site in Mortagne du Nord, Northern France, J. Soils Sediments 7 (2007) 143–146.
[24] X.S. Wang, Y. Qin, Some characteristics of the distribution of heavy metals in urban topsoil of Xuzhou, China, Environ. Geochem. Health 29 (2007) 11–19.
[25] K. Sultan, Distribution of metals and arsenic in soils of central Victoria (Crewick–Ballarat), Australia, Arch. Environ. Contam. Toxicol. 52 (2007) 339–346.
[26] J. An, Q.X. Zhou, W.T. Liu, L.P. Ren, Horizontal distribution and levels of heavy metals in the biggest snowstorm in a century in Shenyang, China, J. Environ. Sci. 20 (2008) 846–851.
[27] S.G. Liu, S.Q. Bai, Study on the correlation of magnetic properties and heavy metals content in urban soils of Hangzhou City, China, J. Appl. Geophys. 60 (2006) 1–12.
[28] D.K. Essumang, D.K. Dodoo, S. Obiri, A.K. Oduro, Analysis of polycyclic aromatic hydrocarbons in street soil dust in Kumasi metropolis of Ghana, Environ. Monit. Assess. 121 (2006) 401–408.
[29] M.H. Wong, T.B. Chen, J.W.C. Wong, Trace metal contamination of the Hong Kong soil environment: a review, in: R. Naidu, R.S. Kookuna, D.P. Oliver, S. Rogers, M.J. McLaughlin (Eds.), Contaminants and the Soil Environment in the Australasia—Pacific Region, Kluwer, Dordrecht, 1996, pp. 501–551.
[30] F. Zhou, H.C. Guo, Z.J. Hao, Spatial distribution of heavy metals in Hong Kong's marine sediments and their human impacts: A GIS-based chemometric approach, Mar. Pollut. Bull. 54 (2007) 1372–1384.
[31] J.A. Rodríguez, N. Nanos, J.M. Grau, L. Gil, M. López-Arias, Multiscale analysis of heavy metal contents in Spanish agricultural topsoils, Chemosphere 70 (2008) 1085–1096.
[32] C. Micó, L. Recatalá, M. Peris, J. Sánchez, Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis, Chemosphere 65 (2006) 863–872.
[33] L. Hakanson, An ecological risk index for aquatic pollution control—A sediment ecological approach, Water Res. 14 (1980) 975–1001.
[34] W. Zhu, B. Bian, L. Li, Heavy metal contamination of road-deposited sediments in a medium size city of China, Environ. Monit. Assess. 147 (2008) 171–181.