

Heavy metal contamination of urban topsoil in a petrochemical industrial city in Xinjiang, China

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Abstract: Heavy metal pollution is a widespread phenomenon in many countries of the world. In this study, we conducted a field investigation to assess the status of heavy metal pollution in urban soils of Dushanzi, a district of Karamay city in Xinjiang, China. A total of 56 soil samples in the topsoil layer of 0–15 cm were collected within the urban area and seven elements (Cu, Zn, Cd, Pb, Cr, As and Ni) were analyzed. The mean concentrations of these metals were all higher than their corresponding background values of soils in Xinjiang. We used the pollution index and ecological risk index to assess the degree of heavy metal pollution and the potential ecological risk of urban soils. The pollution index values of Cu, Zn, Cd, Pb, Cr, As and Ni were 1.81, 1.35, 4.64, 1.27, 1.80, 1.39 and 1.22, respectively; and the potential ecological risk index values for them were 12.03, 1.79, 185.05, 8.39, 4.78, 18.44 and 1.79, respectively. These results indicated that urban soils in Dushanzi were polluted by heavy metals to some extent and demonstrated a high ecological risk, as influenced by industrial activities. Cd was the key element for the metal pollution of urban soils in the study area. Correlation analyses, principal component analysis coupled with the spatial distribution maps of element concentrations further revealed that heavy metal pollution of urban soils can be mainly attributed to petrochemical industry, coal chemical industry, traffic and commercial activities.

Keywords: heavy metal; urban soils; source identification; ecological risk; pollution index

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Favorable soil conditions are essential for the human health and well-being (Shi et al., 2008; Wang et al., 2012a). However, soil environment is interfacial, heterogeneous and changing. Soil becomes contaminated with the development of economic society, and the contamination is characterized by hysteresis, accumulation, concealment and irreversibility (Sun et al., 2010). With industrialization and urbanization, heavy metal pollution of soils is exacerbated; as a consequence, ecosystems, water bodies, food safety and human health are threatened (Chen et al., 2005).

According to World Urbanization Prospects, urban population in the world is expected to reach 6.3×10^9 in 2050, which is likely similar to the world's total population in 2002. With industrial and human activities, the amount of contaminants released into the urban environments has increased (Shi et al., 2008; Li, 2014). Soil contamination can be broadly classified into three types according to the pollution sources: point sources, such as industrial sites; line sources, such as

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road traffic emissions; and non-point sources usually due to atmospheric deposition throughout urban areas (Luo et al., 2012). Heavy metals, which are typical contaminants in urban environments, are important indicators of environment pollution (Manta et al., 2002). Heavy metals in urban soils may originate directly from industrial activities, municipal wastes, traffic emissions and domestic activities (Li et al., 2014). They can easily enter human bodies through ingestion of soil and inhalation of dust (Meyer et al., 1999; Mielke et al., 1999). Human exposure to heavy metal contaminated environments can elicit various effects, such as carcinogenic effects and nervous or digestive system disturbances (Maas et al., 2010). For this reason, concentrations of heavy metals in urban soils should be evaluated through environment and human risk assessments. Moreover, the assessment of heavy metal concentrations in urban soils will be beneficial for the protection of local environment and will provide scientific guidance for policy making to reduce heavy metal contamination (Micó et al., 2006).

Heavy metal contamination of urban soils in many countries, especially in China, has been extensively investigated. Previous studies mainly focused on heavy metal contamination in the south and northeast parts of China (Sun et al., 2010; Ren et al., 2014). However, few investigations were conducted in Northwest China, especially in Xinjiang (Wei et al., 2010). Dushanzi District, located in Karamay city of Xinjiang, is a widely known petrochemical base and an original region of oil industry in China. The disposal of petrochemical wastes may pollute the soils with heavy metals, such as Cd (cadmium), Cr (chromium), Cu (copper), Pb (lead), Zn (zinc) and Ni (nickel) (Nadal et al., 2004). With the development of Dushanzi for almost 60 years, huge petroleum refineries, thermal power plants and other important petrochemical and chemical industries are developed in the industrial region of Dushanzi. The petrochemical industries release heavy metals that have been accumulated in the environment. The heavy metals could affect the health of inhabitants living near these facilities (Zhao et al., 2010). In past years, numerous residents in Dushanzi showed great concern for the environment because the petrochemical industries have negatively affected humans through heavy metal contamination in soils. Thus, the degree of soil pollution should be assessed and the possibility of heavy metal contamination in soils of Dushanzi should be predicated.

This study aimed to: (1) determine the concentrations of seven heavy metals (Cu, Zn, Cd, Cr, Pb, As (arsenic) and Ni) in urban soils; (2) evaluate the degree of heavy metal pollution in urban soils on the basis of pollution indices; (3) identify the sources of heavy metals through Pearson correlation analysis, principal component analysis (PCA) and spatial distribution maps of heavy metals; and (4) examine the potential ecological risk of heavy metal pollution in urban soils.

1 Materials and methods

1.1 Study area

This study was conducted in the urban areas of Dushanzi district (44°18'42"–44°23'22"N, 84°47'28"–84°55'39"E; Fig. 1), Karamay city, Xinjiang, Northwest China. Dushanzi has a total area of 448 km² and a total population of 6.9×10^4 . It is characterized by a typical continental climate, with an average annual precipitation of 108.9 mm and an annual average temperature of 8.1°C. The terrain of Dushanzi appears a slanted bar, i.e. long from south to north and narrow from east to west. In addition, the elevation in the northwest part is higher than that in the southeast part. Most regions in Dushanzi are characterized by Gobi deserts and are elevated down to less than 500 m asl. Dushanzi is an origin region of oil industry in China begun in 1936, and also an important petrochemical base in western China. In this region, oil refinery, chemical and petrochemical project construction and maintenance are integrated. The largest refining-chemical integration project in China is also located in Dushanzi. With this project, fuel oil, polyolefin, rubber, aromatic and 26 other major categories of 600 types of refined products are generated.

1.2 Soil sampling and chemical analyses

In October 2014, 56 samples from the topsoil layer (0–15 cm) were collected in the urban areas of Dushanzi. The sampling points were designed in regular grids with 1 km×1 km each, and every

grid contained at least one point (Fig. 1). A total of 14 samples were collected from the residential region, 30 samples from the area near the industrial region and 12 samples from the area between the residential and industrial regions. We collected 3–5 replicated samples at each sampling point and mixed them into one sample to reduce deviation. All samples were collected using a stainless steel spatula, kept in sealed polyethylene bags to avoid contamination, transported into the laboratory and then stored until use.

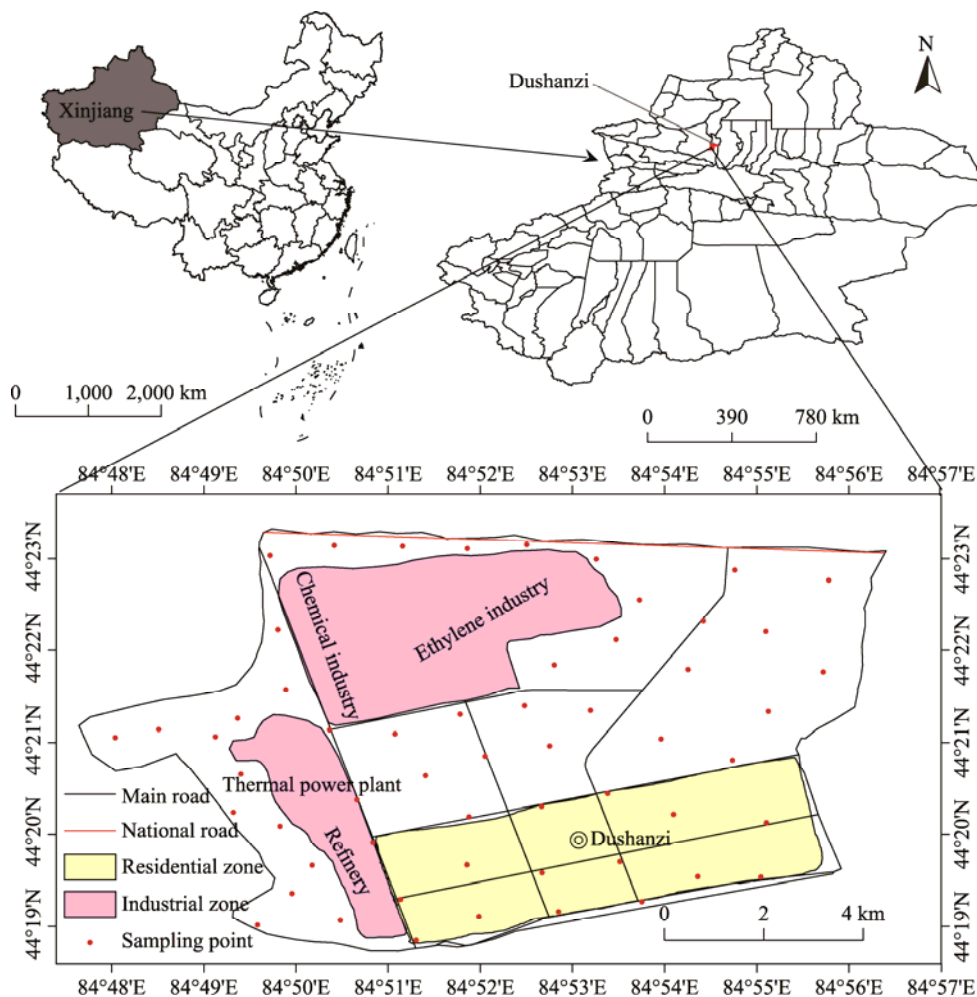


Fig. 1 Location of Dushanzi and soil sampling points in the urban areas of Dushanzi

Soil samples were dried at room temperature in the laboratory for at least 3 d. Debris, including stones and tree leaves, were removed from the soil samples. Then, soil samples were passed through a 2-mm nylon sieve for pH measurement. Soil pH was measured in 1:2.5 soil:deionized water suspension by using a standard pH meter (PHS-25, Shanghai Electronics Science Instrument Co. Ltd., Shanghai, China). For each sample, a small portion (approximately 0.2 g) was passed through a 100-mesh nylon sieve and digested with 8 mL of HNO_3 and 2 mL of H_2O_2 in a microwave oven at 120°C for 10 min and 180°C for 60 min. After cooled, 2 mL of HF and 1 mL of HClO_4 were added; the mixture was placed into a PTFE beaker and then heated on a heating plate at 180°C until HClO_4 disappeared. Subsequently, the mixture was transferred into a volumetric flask (50 mL) and the solutions were diluted with 5% HNO_3 up to the mark. The heavy metal concentrations were determined with the ICP-OES (ICAP 6300, Thermo Fisher Scientific, Massachusetts, United States).

We conducted quality assurance and quality control based on standard reference materials

(GBW(E)070008). The recoveries for the observed metals by adding standard sample were 93% to 110%. The accuracy of our analysis was verified by using duplicated samples, and the standard deviation ranged within $\pm 5\%$. In addition, blank samples were used as controls in all experiments.

1.3 Analysis methods

We analyzed the data by using SPSS 20.0 and EXCEL 2010 to determine the statistical indicators (means, ranges and standard deviations (SDs)) and to perform the Pearson correlation analysis and PCA. In PCA, the principal components were calculated by correlation matrix and eigenvalues greater than 1 were accepted, and varimax normalized rotation was also used. We used the single factor pollution index (P_i) and the integrated Nemerow pollution index (IP_i) to assess the degree of heavy metal pollution, and also used the comprehensive potential ecological risk index (RI) proposed by Hakanson (1980) to assess the ecological risk caused by heavy metal pollution.

P_i is the ratio of the measured element concentration to the corresponding background value:

$$P_i = C_i / S_i. \quad (1)$$

Where, C_i is the measured concentration of each metal (Cu, Zn, Cd, Cr, Pb, As and Ni) in the examined environment, and S_i is the background value of each metal in soils of Xinjiang (China National Environmental Monitoring Centre, 1990). If $P_i \leq 1$, the soils are not polluted with metals; by contrast, if $P_i > 1$, the soils are polluted with metals. Moreover, higher P_i values indicate higher degree of soil pollution.

IP_i assesses the overall heavy metal pollution in soils and can be calculated by using the following equation:

$$IP_i = \sqrt{IP_{i\max}^2 + IP_{iave}^2}. \quad (2)$$

Where, $IP_{i\max}$ is the maximum value of IP_i and IP_{iave} is the mean value of all IP_i values. IP_i is used as an indicator for assessing the element pollution as follow: $IP_i \leq 0.7$, safety; $0.7 < IP_i \leq 1$, warning; $1 < IP_i \leq 2$, light pollution; $2 < IP_i \leq 3$, moderate pollution; and $IP_i > 3$, heavy pollution.

The comprehensive potential ecological risk index (RI) was applied to assess the ecological risk of heavy metal pollution, and it was calculated by the following equations:

$$C_f = C_s / C_n. \quad (3)$$

$$E_R^i = T_R^i \times C_f. \quad (4)$$

$$RI = \sum_{i=1}^n E_R^i. \quad (5)$$

Where, C_s is the measured heavy metal concentration in the sampling points; C_n is the background value of corresponding heavy metal in soils of Xinjiang; T_R^i is the biological toxic response factor for heavy metals and can be determined as follows: Cu=5, Zn=1, Cd=30, Cr=2, Pb=5, As=10 and Ni=5 (Hakanson, 1980); C_f is the contamination factor; and E_R^i is the potential ecological risk index of heavy metal i . According to the study of Jiang et al. (2014), the comprehensive potential ecological risk index (RI) is classified as follows: $RI \leq 60$, low ecological risk; $60 < RI \leq 120$, moderate ecological risk; $120 < RI \leq 240$, high ecological risk; and $RI > 240$, significant ecological risk.

The map of the study area (Fig. 1) was obtained from Google Earth. Moreover, the maps of the spatial distribution of metal concentrations were prepared through inverse-distance weighted (IDW) interpolation by using ArcGIS 10.2.

2 Results and discussion

2.1 Soil pH values

Table 1 shows the minimum, maximum, mean and standard deviation of soil pH values in the

study area. Soil pH values ranged from 7.58 to 9.50 (alkalinity), and the mean value was generally equal to the background value of soils in Xinjiang. Soil pH can affect heavy metal mobilization in soil. Some studies have demonstrated that soil alkalinity limits heavy metal mobilization and reduces heavy metal uptake by plants (Hu et al., 2014).

Table 1 Statistics for pH value in urban soils of the study area

Parameter	Minimum	Maximum	Mean	SD	CV (%)	Background value of soils in Xinjiang
pH	7.58	9.50	8.13	0.43	5.29	8.10

Note: SD, standard deviation; CV, coefficient of variation.

2.2 Heavy metal concentrations

Table 2 shows the descriptive statistics of heavy metal concentrations in urban soils of Dushanzi, and the corresponding background values of soils in Xinjiang and the second class standard of Chinese Environmental Quality Standard for Soils (GB 15618-1995; State Environmental Protection Administration of China, 1995). The average concentrations of Cu, Zn, Cd, Cr, Pb, As and Ni in urban soils were higher by approximately 2.40, 1.79, 6.17, 2.39, 1.68, 1.84 and 1.61 times than the corresponding background values of soils in Xinjiang, respectively. Specifically, the average concentrations of As, Cr, Cu and Zn in all samples were higher than their corresponding background values, while 96%, 93% and 71% of the samples contained higher concentrations of Cd, Ni and Pb than their corresponding background values, respectively.

Table 2 Statistics for heavy metal concentrations in urban soils

Item	Cu	Zn	Cd	Pb	Cr	As	Ni
	(mg/kg)						
Minimum	52.60	84.73	0.07	10.48	100.37	12.37	6.15
Maximum	90.90	233.49	1.74	126.61	141.59	31.01	60.51
Mean	64.22	123.32	0.74	32.56	117.86	20.65	42.70
SD	7.90	29.57	0.36	21.68	9.44	4.63	12.23
CV (%)	12.30	23.98	48.65	66.58	8.00	22.42	28.64
Background value of soils in Xinjiang	26.70	68.80	0.12	19.40	49.30	11.20	26.60
Chinese Environmental Quality Standard for Soils (GB15618-1995)	100	300	0.6	350	250	25	60

As shown in Table 3, the mean concentrations of Cu, Zn, Cd, Ni, Cr and As in our study area were higher than the corresponding average values in Beijing, Shanghai and Zhangzhou. The high values were possibly caused by industrial activities, such as electroplating, power generation, industrial waste production and smelting. Emissions from vehicular traffic and coal burning for heating are the main sources of Pb in urban soils. Pb concentration in our study area was lower than that in other cities, except in Beijing. Lower traffic volume in our study area should be the possible reason.

2.3 Assessment of heavy metal pollution

More than 70% of the P_i values for each metal were higher than 1 (Table 1), indicating a certain accumulation of heavy metals in urban soils. The decreasing order of the degree of heavy metal pollution in our study area was as $Cd > Cu > Cr > As > Zn > Pb > Ni$. For Cd, 96.43% of the P_i values were higher than 1 and the mean was 6.17, demonstrating the widespread and severe Cd pollution in the study area. The main sources of Cd in urban soils are the use of vehicle lubricating oil, incineration of some solid wastes, burning of fossil fuels and application of Cd-contaminated phosphate fertilizers (Yesilonis et al., 2008). For Pb, 71.43% of the P_i values were higher than 1 and the mean was 1.68. Combustion of gasoline is the main source of Pb, and wastes from commodities may also contribute to Pb contamination in soils (Wu et al., 2003). Chemically and environmentally, previous study has demonstrated that Cd, Cu, Pb and Zn belong

Table 3 Mean concentrations of heavy metals in urban soils of different cities in China

City	Cu	Zn	Cd	Pb	Cr	As	Ni	Reference
	(mg/kg)							
Dushanzi	64.22	123.32	0.74	32.56	117.86	20.65	42.70	This study
Beijing	23.70	65.60	0.15	28.60	35.60	–	27.80	Zheng et al. (2008)
Shenyang	95.50	265.00	1.32	115.00	0.89	21.30	64.50	Ren et al. (2014)
Jinchang	1,226.00	118.00	1.11	40.30	197.00	30.90	910.00	Liao et al. (2006)
Baoji	112.14	1,964.12	–	25,380.55	102.40	–	72.10	Li and Huang (2007)
Shanghai	59.25	301.40	0.52	70.69	107.90	–	31.14	Shi et al. (2008)
Zhangzhou	32.60	107.00	0.35	75.90	29.70	6.86	12.80	Qiao et al. (2005)
Urumqi	94.54	294.47	1.17	53.53	54.28	–	43.28	Wei et al. (2010)

Note: “–” means no data.

to a group (Wang et al., 2012b). High concentrations of Cu and Zn in urban soils can be attributed to human activities, such as house construction, electric energy transport, industrial wastes and so on (Hu et al., 2014).

The mean IP_i value in the study area was 4.80, indicating heavy pollution of urban soils. The IP_i values were higher than 2 in all sampling points and 82.14% of which displayed heavy pollution whereas 17.86% exhibited moderate pollution. The sampling points with larger IP_i values were concentrated around the industrial region and in the center of Dushanzi.

Table 4 Pollution index (P_i) and integrated Nemerow pollution index (IP_i) for heavy metals in urban soils

Metal	P_i			IP_i
	Mean	Maximum	Minimum	
Cu	2.41	3.40	1.97	4.80
Zn	1.79	3.39	1.23	
Cd	6.17	14.48	0.62	
Pb	1.68	6.52	0.54	
Cr	2.39	2.87	2.04	
As	1.84	2.77	1.10	
Ni	1.61	2.27	0.23	

2.4 Spatial distribution of heavy metal pollution

Spatial distribution of heavy metal concentrations in urban soils can reveal the potential sources of metals in the city (Li et al., 2004). The spatial distributions of Cu, Cd, Zn and Pb concentrations were generally similar, with high concentrations in the southern (residential region) and northern parts of the study area (Fig. 2). The concentrations of these four metals may be affected by industrial activities. Emission of sulfur oxides and nitrogen oxides from oil industries not only pollutes the air, but also leaches into the soil and results in heavy metal pollution in soil. Crude oil contains a certain amount of heavy metals, such as Cu, Zn and Pb. Moreover, catalysts used in oil refining also contain heavy metals, including Cd and Cu (Zhao et al., 2010). The concentrations of these four metals were higher in the northeast region near the intersection of two national roads where some industries are located, suggesting that traffic and industrial emissions contribute to the contamination of these four metals in urban soils. Vehicle exhaust and tire wear are also the main sources of heavy metals.

Concentrations of As and Cr generally showed a similar spatial distribution pattern with the four metals mentioned above, except that their highest concentrations were found in the residential region, suggesting that the contamination of this two metals mainly originated from industrial wastes and human activities. Element As in soils may come from coal combustion (Luo et al.,

2012), because coal is the main energy source for heating activities in the study area. The major source of Cr is possibly the industrial wastewater (Yang et al., 2011). Previous studies have demonstrated that heavy metals originate from fossil fuel combustion mainly contaminate the soils through atmospheric deposition (Zhao et al., 2010). Considering the dominant wind direction in this study area (northwest), we concluded that the concentrations of As and Cr in the residential region were mainly affected by the emissions from the thermal power plants and oil refineries. Spatial distribution of Ni concentration differed from the other metals. Nearly two-thirds of the study area had high Ni concentrations and the highest value was observed in the northeast region. In addition to weathering of parent rock, smelting is likely another major source of Ni (Ren et al., 2014) because a large ore processing region is found close to the study area.

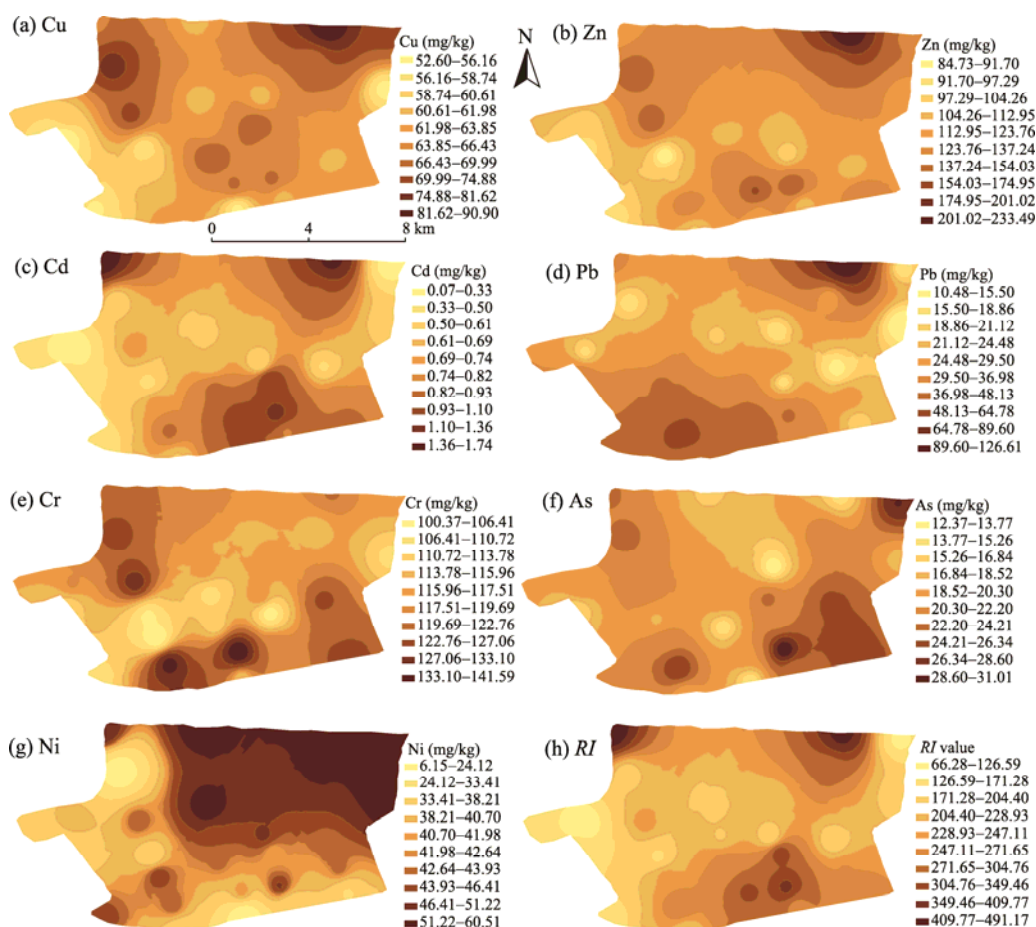


Fig. 2 Spatial distributions of heavy metal concentrations (a–g) and comprehensive potential ecological risk index (*RI*; h) in urban soils

2.5 Correlations between heavy metals

Heavy metal concentrations in soils show complicated relationships (Rodríguez et al., 2008). Positive correlations between metals in soils indicate that these metals are come from the similar sources, whereas negative correlations indicate that these metals do not share the same traits. Table 5 shows the results of the Pearson correlation analysis for heavy metals. Cd concentration showed a significant positive relationship with Cu, Zn and Pb concentrations at the $P < 0.01$ level. As and Cr, as well as Cr and Zn, demonstrated a positive relationship at the $P < 0.05$ level. Ni concentration had a very weak correlation with the concentrations of other metals. These results showed that, Cu, Zn, Pb and Cd were came from the similar sources, while As and Cr were came from the similar sources.

Table 5 Correlations between seven metal concentrations in urban soils

	Cu	Zn	Cd	Pb	Cr	As	Ni
Cu	1.000						
Zn	0.819**	1.000					
Cd	0.380*	0.482**	1.000				
Pb	0.492**	0.627**	0.480**	1.000			
Cr	0.315	0.470*	0.187	0.159	1.000		
As	0.136	0.042	-0.015	-0.212	0.501*	1.000	
Ni	0.146	0.200	0.122	0.046	-0.059	0.122	1.000

Note: * and ** mean significance at $P < 0.05$ and $P < 0.01$ levels, respectively.

2.6 Principal component analysis (PCA)

In multivariate statistical analysis, we often hope to obtain more information with less variables. Because of the superposition of variables, some repeated variables can be deleted in the statistical analysis. As a popular statistical method, PCA is successful for data dimension reduction. In this study, because of the correlations between heavy metals, less heavy metals can be collected to evaluate the pollution level and ecological risk of the study area.

In this study, results of PCA for heavy metal concentrations in soils are shown in Table 6. The results showed that the heavy metal concentrations could be represented by three principal components, which accounted for about 75.13% of the total variance. The varimax-rotated component matrix indicated that Cd, Cu, Pb and Zn were associated with the first principal component (PC1), which accounted for 39.43% of the total variance; As and Cr were associated with the second principal component (PC2), which accounted for 20.42% of the total variance; and the third principal component (PC3) accounted for 15.28% of the total variance, which was dominated by Ni. Moreover, some metals may be distributed in two or more components (Li et al., 2013). For instance, Cr was mostly distributed in PC2, and partially in PC1. This phenomenon demonstrated that each metal can possibly be distributed in several principal components. The metals in PC1, PC2 and PC3 mostly came from different sources.

Table 6 Varimax-rotated component matrix for seven metals of urban soils

Item	Principal component		
	1	2	3
Cu	0.787	0.281	0.151
Zn	0.894	0.253	0.117
Cd	0.694	-0.033	-0.014
Pb	0.833	-0.218	-0.048
Cr	0.363	0.726	-0.268
As	-0.152	0.843	0.211
Ni	0.694	0.027	0.956
Percentage of variance (%)	39.43	20.42	15.28
Cumulative percentage of variance (%)	39.43	59.85	75.13

2.7 Assessment of potential ecological risk in urban soils

The average value of the potential ecological risk index for Cd was the highest (185.05; Table 7), thus Cd was the key factor that causes the potential ecological risk in urban soils. By contrast, the other metals demonstrated a low potential ecological risk, and their potential ecological risk index values ranged from 1.79 to 18.44. Therefore, Cd is the main pollutant in urban soils. The comprehensive potential ecological risk index values in the study area ranged from 66.28 to 491.17, and the mean value was 238.51. The proportions of the sampling points showing moderate, high and significant high ecological risk were 7.14%, 46.43% and 46.43%, respectively.

Figure 2h showed the spatial distribution of the comprehensive potential ecological risk index, which was similar to that of Cd (Fig. 2c). The sampling points which demonstrated high and significant high ecological risk were located in the central and northern parts of the study area. This research revealed that the urban soils of Dushanzi are severely polluted. Some measures, such as ecological restoration and limitation of industrial emissions, should be implemented to reduce heavy metal contamination of urban soils.

Table 7 Statistics of potential ecological risk index of each heavy metal (E_R^i) and comprehensive potential ecological risk index (RI)

Item	E_R^i							RI
	Cu	Zn	Cd	Cr	Pb	As	Ni	
Minimum	9.85	1.23	18.66	4.07	2.70	11.04	1.16	66.28
Maximum	17.02	3.39	434.46	5.74	32.63	27.69	3.39	491.17
Mean	12.03	1.79	185.05	4.78	8.39	18.44	1.79	238.51

3 Conclusions

Urban soils in Dushanzi is alkaline with soil pH values ranging from 7.58 to 9.50. The concentrations of the seven heavy metals (Cu, Zn, Cd, Pb, Cr, As and Ni) in urban soils all exceeded the corresponding background values of soils in Xinjiang. Pollution index and potential ecological risk index were used to evaluate the degree of heavy metal contamination. Approximately 17.86% and 82.14% of the sampling points were moderately and heavily polluted, respectively. Moreover, 7.14%, 46.43% and 46.43% of the sampling points demonstrated moderate, high and significant high ecological risk. The results showed that urban soils in Dushanzi were highly polluted with multiple heavy metals and Cd was the major soil pollutant.

The spatial distribution maps, correlation analysis and principal component analysis of heavy metal concentrations revealed that Pb, Cu, Cd and Zn were strongly associated with one another and showed similar distribution pattern. Thus, the sources of these metals are similar, and they possibly originate from traffic and industrial emissions. Distribution of Ni concentration in urban soils was probably influenced by smelting. As and Cr, as a group, had different sources from the other five metals. The concentrations of this two metals may be affected by the emissions from thermal power plants and oil refineries. Because the residential region is very close to the industrial region, most of the emissions from industrial activities pollute the residential region through atmospheric deposition. Moreover, human activities, such as house constructions, electric energy transport and battery disposal, also caused heavy metal pollution in urban soils. The residential region and the northern half of the study area were also severely polluted with heavy metals. Therefore, effective measures, such as enhancing the standards of industrial and vehicle emissions, should be implemented.

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