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Spatial distribution of hazardous elements in urban topsoils surrounding Xi'an industrial areas, (NW, China): Controlling factors and contamination assessments

Xiaoping Li[a,b,*], Linna Feng[c]

[a] Department of Environmental Science, College of Tourism and Environment, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China
[b] Department of Chemistry, Jackson State University, Jackson, MS 39217, United States
[c] Department of Law and Foreign Language, Shaanxi Police Professional College, Xi'an, Shaanxi 710043, PR China

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ABSTRACT

Understanding of the hazardous in urban soil and their anthropogenic effect from urban industrial areas is important for urban environmental management and protection. In this study, a total of 44 soil samples were collected from Xi'an western industrial areas, NW, China, and the concentrations of 29 elements were measured by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry. The sources of hazardous metals were conducted through multivariate statistical methods (principal component analysis, clustering analysis, and correlation analysis). The dangerous metals' influences on the environment were evaluated from Nemero Synthesis Index Method and Geostatistical Analysis. All the results indicated the multivariate statistical methods had successfully classified three factors of heavy metals from different sources, of which 36.40% accounted for industrial activities and exhaust emissions, 32.09% for agricultural as well as the precipitant of gas stream, and 31.51% for coal combustion factor. Through the pollution evaluation and the further spatial analysis, the hazardous metals distributed consistently with prevailing NW–SE local wind direction, strongly polluted the urban soil and potentially affected environmental quality and health of Xi'an urban city, especially Bi, Pb, Zn, Sb, and Sn. The results advocated the future tactics for Xi'an environment quality control on a local scale had to concern not only the levels of hazardous but also the industrial emission abatement techniques and urban setting and plan.

1. Introduction

Soil, composed of mineral constituents, organic matter (humus), living organisms, air and water, regulates the natural cycles of these components. Heavy metals, formed by geology, such as alteration and erosion, occur naturally in soil. However, the sources of contaminants in soil are multifarious, including agricultural and industrial emissions pollution [1].

Recently, known for peculiar characteristics such as unpredictable layering, poor structure, and high concentrations of trace elements [2,3], urban soil is regarded as 'recipients' of large amounts of element variables from a variety of sources. In general, anthropogenic activities, such as industrialization and urbanization, make a significant contribution to the potential accumulations of hazardous metal in urban soil. Therefore, the study of hazardous in urban soil is important for determining the origin, distribution and contamination level of toxic metals in urban environments.

Nowadays, numerous studies on the trace element contamination in soil, plants, water and sediments in city have been performed [4–14] and are well documented in developed countries (for example U.S.A., Germany, Japan), while only limited information is available in developing countries, including China [10,14–16]. Therefore, more attention will be emphasized on the trace metal pollutants caused by human activities in the developing countries [15].

Xi'an, one important city in northwest China, has experienced a rapid urbanization and industrialization process in the previous decades. The rapid growth of high-tech industry and population exerts a heavy pressure on its urban environment. For example, the total amount of hazardous precipitation (including the waste water, waste gas as well as waste solid discharge) from Xi'an western industrial areas has reached to at least 4000 ton a year. The dangerous elements are usually absorbed onto the surface of suspended particulates, consequently, these risky particulates will be flowed to the urban center with local prevailing wind. Thus, the environment of Xi'an city will be highly susceptible to pollution due to industry-generated and urbanization-generated hazardous discharges (metals and toxic wastes). The present study is designed to highlight and identify the hazardous elements concentrations, contaminated level and sources of the risky contaminations in urban

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* Corresponding author at: Department of Environmental Science, College of Tourism and Environment, Shaanxi Normal University, No. 1 ShiDa Street, Xi'an, Shaanxi 710062, PR China. Tel.: +86 29 85310525.
E-mail addresses: lixiaoping@snnu.edu.cn, leexpok@yahoo.com.cn (X. Li).

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soil. Therefore this investigation will assist in developing strategies to protect urban environment against long-term hazardous accumulation, which can ensure that hazardous contaminants will not become a serious problem in Xi'an city in the future.

2. Materials and methods

2.1. Background of study area

Xi'an, the capital of the Shaanxi province, locates in E108°09′ N34°02′, northwest of China. It has about 9983 km^2 of areas with the urban population of approximately 8,000,000. The climate is a continental monsoon climate (hot rainy summers and cold dry winters). With the rapid industrialization, urbanization and high-tech development in previous decades, the city has become the center of the economy, culture, education, manufactory, as well as high-tech industries in the northwest of China.

The investigation area comprises typical urban land use types, such as rivers, traffic, farming lands, residential settlements and industrials (such as metallurgy, chemical industry, ceramics, textile, construction, cement manufacturing plants, alcohol production plant, mechanics industries, electrics and electronics, coal-fired power plant, and others). Compared with western developed countries, the industrial layout in this area apparently lacks planning, posing a potential risk of multiple pollutant sources.

2.2. Soil sampling location

Soil samples were taken at 44 locations distributed across the investigation area of about 25 km^2 (Fig. 1) during the dry season in March 2007. The soil sampling sites were chosen carefully to guarantee minimal disturbance, and the soil samples were collected as regularly as possible across the investigation area. The detail sampling procedure was as follows: first, the whole investigation area was divided into four quadrants, then, at every quadrant grid, the corresponding 11 samples were chosen from the upper 10 cm layer of the soil. All 11 subsamples collected from every quadrant grid were mixed to get a bulk sample; this strategy would minimize local in-homogeneity. Next, one representative sample was singled out by repeated quartering. Similarly, other representative samples would be chosen in the other three quadrant grids with the same strategy and labeled by XS001, XS002, XS003 and XS004, respectively. Finally, all the samples were collected with a stainless steel spatula and kept in PVC packages at room temperature for 2 weeks.

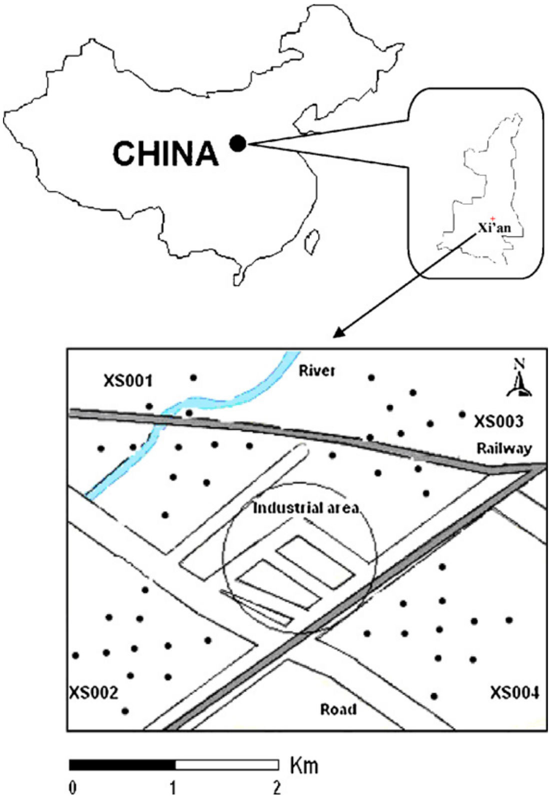

Fig. 1. Map location of the study area and distributions of sampling sites from Xi'an western industrial areas, China.

2.3. Preparation of the samples, analysis and quality control

At first, each sample was allowed to air-dry at Soil Environmental Chemistry Laboratory (SECL), Shaanxi Normal University. Before grinding with agate mortar stones, coarse materials and other woody debris were removed by 0.2 mm sieve (70 mesh), then sieved step-by-step through 7 plastic mesh sieves (80, 100, 120, 140, 160, 180, and 200 mesh) and homogenized with cut sizes of 0.075 mm. All procedures of handling were carried out without contacting with any metals in order to avoid potential cross-contamination of the samples. Next, 4.0 g of each milled soil sample and 2.0 g of boric acid were added in the mold synchronously, and pressed into a 32-mm diameter pellet by 9.5×10^6 Pa pressure. The pellets were stored in a desiccator. Finally, The concentrations of trace elements As, Bi, Br, La, Ce, Cl, Co, Cr, Cs, Cu, Ni, Pb, Rb, S, Sb, Sn, Sr, V, Zn, Zr, N, P and heavy metal oxides Al_2O_3 (%), $CaCO_3$ (%), Fe_2O_3 (%), K_2O (%), SiO_2 (%), MgO (%), Na_2O (%) were directly determined by wavelength dispersive X-ray fluorescence spectrometry (XRF, PANalytical PW2403 apparatus), and the relative proportions of soils were measured according to methods [17–20].

A series of soil and rock standards were used to calibrate and check the accuracy. These were the GSS-, GRS-, and GSD-series certified standard reference materials (Institute of Geophysical and Element Prospecting, People's Republic of China), together with NIST-2709, NIST-2710, NIST-2711 (National Institute of Standards and Technology, USA) and soil standards SO-1, SO-2, SO-3 and SO-4 (Canadian Certified Reference Materials Project) were also used as described in the previous paper [18–20]. The total organic carbon (TOC) was determined using High-TOCII Elementar (Germany) [21], and soil pH was determined by mixing fresh soil with deionized water (1:2, w/v) [22].

The analytical precision, measured as relative standard deviation (R.S.D.), routinely ranged from 3% to 5%, and was never higher than 8%. All of the trace element concentrations were not below the instrument detection limit of 2 mg/kg. Accuracy of analyses was checked using standard and duplicate samples. The quality control results agreed within ±5% (S.D.) of the certified values.

2.4. Environmental impact assessment

To quantify the pollution risk and gain the potential contaminated region, the Single Factor Index and the Nemero Synthesis Index evaluation method are calculated. The Single Factor Index is expressed as follows (Eq. (1)):

$$PI_j = \frac{C_i}{S_{ij}} \qquad (1)$$

where PI_j is the evaluation score corresponding to each sample, C_i is the measured value of an element at each sample point, i is some element, and S_{ij} is the geochemical background value of the ith kind of element. The integrated index can be computed by Eq. (2):

$$PN = \sqrt{\frac{(\max(C_i/S_{ij}))^2 + \left((1/n)\sum_{i=1}^{n} C_i/S_{ij}\right)^2}{2}} \tag{2}$$

where, the PN_j is the integrated evaluation score corresponding to each site. In this study, the geochemical background value refers from Chinese soil background value [23,24]. The following classification is given according to the integrated index [23]: practically unpolluted ($PN_j \leq 0.7$), unpolluted to moderately polluted ($0.7 < PN_j \leq 1.0$), moderately polluted ($1.0 < PN_j \leq 2.0$), moderately to strongly polluted ($2.0 < PN_j \leq 3.0$), severe or strongly polluted ($PN_j > 3$). This method has been successfully applied to evaluate the environmental impact of the risk metals on the urban soil [18,25].

2.5. Statistical analysis

Cluster analyses (CAs) and factor analyses (FAs) are used to distinguish different groups of elements according to close element behavior. A principal component analysis (PCA) by means of varimax rotation with kaiser normalization was carried on the base of the natural log-transformed data. All statistical data processing in this work were carried out using the SPSS.12 software packages (SPSS Inc., Chicago, IL, USA). The geostatistical analysis was performed with the extension Geostatistical Analyst of the GIS software ArcGIS (version 9.0) and Arcview 3.2 (ESRI Inc., CA, USA).

3. Results and discussion

3.1. Soil properties

Summary statistics of soil properties were listed in Table 1. The pH of the soils varied around 8.27, which appeared subalkaline in all cases. The concentrations of Ca ($CaCO_3$%) varied greatly from 8.21% to 13.21%, whereas other oxide concentrations changed slightly, Al_2O_3 (%) arranged from 12.27% to 12.85%, K_2O (%) from 2.39% to 2.56%, MgO (%) from 2.10% to 2.32%, Na_2O (%) from 1.56% to 1.77%, and so on. The proportion of TOC also changed slightly from 11.30% to 11.94%, which indicated the main soil type was cinnamon soil. However, the N and P element contents changed greatly because of agriculture activities or related influences, which suggested the soil was loamy.

3.2. Spatial distributions of elements in soil

The elements concentrations and distributions in investigation locations, as well as other different urban environments and background values of Chinese soils, were shown in Table 2. The Table 2 marked that in this study the concentrations of Cl and S in XS002 were significantly higher, accounted for 525.10 and 510.2 mg kg^{-1} respectively. On the other hand, Sr and Zr contents kept slight change across the XS001, XS002, XS003 and XS004. In addition, the contents of trace elements As, Bi, Br, Co, Cs, Sb and Sn were relatively lower in all samples, and other heavy metals elements kept a moderate extent. However, all the elements concentrations almost went beyond the soil background values of China.

It is a common practice to compare average concentrations of metals in different surveyed cities, although there are no universally accepted sampling and analytical procedures for geochemical studies of urban deposits. Comparing with the other cities' reported data [4,26–31], it was easy to find out the concentrations of Ni, Cu, Cr, La, Sn, Co, Sr, V, Zr, Ce, Rb and S in Xi'an were higher than those in Aegean (Turkey), Aragon (Spain), Aviles (Spain) and in Ireland. While the values of Pb, La, As, Sb and Cu, Cr, V, Sn in Xi'an were greatly lower than those in Linares (Spain) and Lancashire (UK)

Table 1
Selected soil chemical characteristics.

Sample label (sample amount)	pH (H_2O)	N (mg/kg)	P (mg/kg)	$CaCO_3$ (mass%)	Fe_2O_3 (mass%)	K_2O (mass%)	MgO (mass%)	Na_2O (mass%)	SiO_2 (mass%)	Al_2O_3 (mass%)	Total organic carbon (mass%)
XS001 (11)	8.27 ± 0.06	1785.40 ± 1.24	1585.40 ± 2.22	8.76 ± 0.06	4.71 ± 0.08	2.52 ± 0.03	2.10 ± 0.02	1.66 ± 0.03	58.78 ± 0.01	12.63 ± 0.02	11.64 ± 0.37
XS002 (11)	8.06 ± 0.05	2205.60 ± 1.82	1655.80 ± 2.95	8.23 ± 0.04	5.03 ± 0.05	2.56 ± 0.03	2.24 ± 0.01	1.57 ± 0.04	58.55 ± 0.02	12.79 ± 0.06	11.49 ± 0.46
XS003 (11)	8.34 ± 0.06	1537.30 ± 1.13	1060.80 ± 1.89	8.21 ± 0.05	5.04 ± 0.04	2.53 ± 0.06	2.18 ± 0.02	1.77 ± 0.03	58.77 ± 0.01	12.85 ± 0.04	11.30 ± 0.59
XS004 (11)	8.41 ± 0.03	1348.50 ± 1.01	808.60 ± 2.00	13.21 ± 0.07	4.73 ± 0.06	2.39 ± 0.04	2.32 ± 0.05	1.56 ± 0.02	56.49 ± 0.01	12.27 ± 0.05	11.94 ± 0.66

Data in the table stand for mean ± S (standard deviation), $S = \sqrt{\sum_{i=1}^{n}(X_i - \bar{X})^2/(n-1)}$

Table 2
Hazardous elements in soil samples in different city and soil background contents (mg kg^{-1}).

Soil location	Soil sample (sample amount)	Ni	Pb	Cu	Zn	Cr	La	As	Bi	Reference
Xi'an, China	XS001 (11)	26.00	38.30	27.70	106.60	88.10	54.20	11.30	1.70	In this study
	XS002 (11)	32.40	62.90	44.00	216.40	93.70	36.90	12.90	0.20	
	XS003 (11)	29.80	34.80	32.50	134.20	92.20	43.80	11.40	1.60	
	XS004 (11)	31.20	109.60	34.80	82.50	76.50	31.40	8.00	0.50	
Aegean region nearby Mugla City, Turkey	9	29.78	8.89	19.11	43.22	58.89	14.56	13.33	<5	[4]
Pforzheim, Germany	6		52.50	48.20	98.50			11.90		[26]
Aragon, Spain	133	19.30	8.30	10.30	55.60	21.00		11.80		[27]
Halsall Moss and Downholland Moss, Lancashire, UK	28	76.00	718.00	249.00	453.00	150.00				[28]
Avileĩs, Spain	33	11.40	106.67	19.97	476.58	18.15	14.3	14.73		[29]
Ireland	1310	17.50	24.80	16.20	62.60	42.6	20.00	7.25		[30]
Linares (Jaen), Spain	126	20.59	4077.00	145.40	123.90	49.94	67.89	26.11		[31]
The background contents of heavy metals in soil, China		29.30	26.00	24.00	74.20	61.00	37.40	11.20	0.37	[23,24]

Soil location	Soil sample (sample amount)	Br	Sb	Sn	Co	Cs	Sr	V	Reference
Xi'an, China	XS001 (11)	3.50	4.80	11.00	16.40	10.60	241.90	81.10	In this study
	XS002 (11)	4.90	6.60	10.30	14.70	7.90	241.40	89.30	
	XS003 (11)	4.20	6.80	11.80	17.10	7.90	250.90	84.60	
	XS004 (11)	2.50	11.70	21.40	13.90	7.50	251.80	84.30	
Aegean region nearby Mugla City, Turkey	9		<5	<10	8.56		53.78	23.89	[4]
Pforzheim, Germany	6		1.60	6.00			75.20		[26]
Aragon, Spain	133			8.50	7.00				[27]
Halsall Moss and Downholland Moss, Lancashire, UK	28			79.00	20.00			103.00	[28]
Avileĩs, Spain	33		8.00		5.70		20.33	29.50	[29]
Ireland	1310		0.53	1.68	6.20		49.70	52.20	[30]
Linares (Jaen), Spain	126		11.49	5.60	12.30		149.85	72.19	[31]
The background value of heavy metals in soil, China		5.40	1.21	2.60	12.70	4.76	167.00	82.40	[23,24]

Soil location	Soil sample (sample amount)	Zr	Rb	Ce	Cl	S	Reference
Xi'an, China	XS001 (11)	209.00	95.40	91.20	113.90	339.20	In this study
	XS002 (11)	218.40	105.70	86.70	525.10	510.20	
	XS003 (11)	213.20	104.40	91.90	210.30	339.50	
	XS004 (11)	224.80	100.60	75.10	108.60	242.70	
Aegean region nearby Mugla City, Turkey	9	6.89					[4]
Pforzheim, Germany	6	331.00	90.10				[26]
Aragon, Spain	133						[27]
Halsall Moss and Downholland Moss, Lancashire, UK	28						[28]
Avileĩs, Spain	33						[29]
Ireland	1310		53.30	34.80		0.073	[30]
Linares (Jaen), Spain	126	103.83					[31]
The background value of heavy metals in soil, China		256.00	113.00	68.40			[23,24]

respectively. All values of the elements showed spatial distribution variance in different locations and cities (Table 2). However, it seemed that the observed similarities as well as variations may not reflect the reality of the natural and anthropogenic diversities among the different cities. Therefore, a further analysis procedure would be urgently needed to establish.

3.3. *Correlation analyses*

Elements in soil are affected by multiple processes. It is found that the elements seldom followed a normal distribution [32,33]. The lognormal distribution was once widely recognized, and was even regarded as a "fundamental law of geochemistry" [34]. In recent years, the lognormal distribution positively skewed distributions in environmental chemistry. Correlation analyses have been widely applied in environmental studies [30,35]. They provided an effective way to reveal the relationships between multiple variables and thus they were helpful for the understanding of the influencing factors as well as sources of chemical components.

A log-transformation was carried out to treat these elements statistically using multivariate techniques. Results of Pearson's correlation coefficients and their significance levels ($P < 0.05$) of correlation analysis were shown in Table 3. The relationship among the elements were varied and exhibited very complicated. The TOC values showed high negative correlation scores with As (−0.813), Br (−0.869), Ce (−0.847), Co (−0.753), and Cr (−0.915) respectively. But some elements showed positive correlation with TOC (Pb: 0.799, Sn: 0.792, Sb: 0.578, and Zr: 0.584), which would suggest the organic matters potentially originated from agricultural uses and industrial emissions. They had a relatively high capacity to preferentially scavenge released heavy metals during weathering such as Pb, Sb; the pH values indicated fairly negative relationship with As (−0.811), Cl (−0.855), P (−0.848), S (−0.961), Zn (−0.906) and N (−0.983) respectively. Comparing with the Baoji urban soil from industrial areas [18], soils of the developed areas in Xi'an urban city showed the higher mean pH values around 8, which reflected the chemical reactions in soil caused by anthropogenic additives. While the significantly positive correlation coefficients were observed between the hazardous elements which meant the accumulation concentrations of elements came from the same sources (Table 3). For example, As significantly related with Cr (0.979), Cu with V (0.983), N with S (0.956), Pb with Zr (0.943), Cl with Zn (0.973), Sb with Sn (0.899), Co with Ce (0.899), Br with Cr (0.975). Although the good correlations between metals were measured, the corre-

Table 3
Correlation coefficients among elements in soil.

	As	Bi	Br	Ce	Cl	Co	Cr	Cs	Cu	La	Ni	P
As	1	−0.057	0.963	0.839	0.732	0.527	0.979	0.312	0.231	0.537	−0.087	0.865
Bi	−0.057	1	−0.184	0.495	−0.645	0.797	0.032	0.559	−0.933	0.730	−0.816	−0.122
Br	0.963	−0.184	1	0.745	0.857	0.446	0.975	0.047	0.415	0.333	0.156	0.724
Ce	0.839	0.495	0.745	1	0.295	0.899	0.874	0.552	−0.298	0.853	−0.502	0.670
Cl	0.732	−0.645	0.857	0.295	1	−0.056	0.722	−0.358	0.824	−0.182	0.610	0.521
Co	0.527	0.797	0.446	0.899	−0.056	1	0.624	0.501	−0.582	0.845	−0.621	0.303
Cr	0.979	0.032	0.975	0.874	0.722	0.624	1	0.216	0.203	0.524	−0.052	0.747
Cs	0.312	0.559	0.047	0.552	−0.358	0.501	0.216	1	−0.697	0.882	−0.926	0.603
Cu	0.231	−0.933	0.415	−0.298	0.824	−0.582	0.203	−0.697	1	−0.692	0.914	0.110
La	0.537	0.730	0.333	0.853	−0.182	0.845	0.524	0.882	−0.692	1	−0.877	0.590
Ni	−0.087	−0.816	0.156	−0.502	0.610	−0.621	−0.052	−0.926	0.914	−0.877	1	−0.295
P	0.865	−0.122	0.724	0.670	0.521	0.303	0.747	0.603	0.110	0.590	−0.295	1
Pb	−0.690	−0.679	−0.591	−0.973	−0.095	−0.975	−0.753	−0.572	0.478	−0.889	0.607	−0.506
Rb	0.303	−0.561	0.547	−0.018	0.797	−0.145	0.394	−0.810	0.817	−0.537	0.862	−0.087
S	0.926	−0.428	0.935	0.571	0.898	0.172	0.869	0.090	0.552	0.219	0.216	0.840
Sb	−0.804	−0.404	−0.623	−0.907	−0.194	−0.724	−0.754	−0.804	0.352	−0.916	0.659	−0.855
Sn	−0.983	−0.101	−0.902	−0.906	−0.593	−0.630	−0.957	−0.472	−0.051	−0.683	0.270	−0.887
Sr	−0.712	0.242	−0.552	−0.467	−0.432	−0.082	−0.554	−0.612	−0.139	−0.473	0.273	−0.965
V	0.361	−0.857	0.553	−0.140	0.900	−0.426	0.356	−0.680	0.983	−0.593	0.888	0.169
Zn	0.868	−0.502	0.942	0.488	0.973	0.121	0.848	−0.144	0.681	0.047	0.412	0.682
Zr	−0.629	−0.698	−0.451	−0.920	0.063	−0.893	−0.633	−0.812	0.611	−0.989	0.801	−0.616
N	0.864	−0.442	0.808	0.501	0.772	0.071	0.753	0.279	0.463	0.278	0.073	0.932
TOC	−0.813	−0.228	−0.869	−0.847	−0.590	−0.753	−0.915	−0.026	−0.096	−0.459	0.008	−0.428
pH	−0.811	0.589	−0.800	−0.378	−0.855	0.063	−0.706	−0.102	−0.620	−0.100	−0.256	−0.848

	Pb	Rb	S	Sb	Sn	Sr	V	Zn	Zr	N	TOC	pH
As	−0.690	0.303	0.926	−0.804	−0.983	−0.712	0.361	0.868	−0.629	0.864	−0.813	−0.811
Bi	−0.679	−0.561	−0.428	−0.404	−0.101	0.242	−0.857	−0.502	−0.698	−0.442	−0.228	0.589
Br	−0.591	0.547	0.935	−0.623	−0.902	−0.552	0.553	0.942	−0.451	0.808	−0.869	−0.800
Ce	−0.973	−0.018	0.571	−0.907	−0.906	−0.467	−0.140	0.488	−0.920	0.501	−0.847	−0.378
Cl	−0.095	0.797	0.898	−0.194	−0.593	−0.432	0.900	0.973	0.063	0.772	−0.590	−0.855
Co	−0.975	−0.145	0.172	−0.724	−0.630	−0.082	−0.426	0.121	−0.893	0.071	−0.753	0.063
Cr	−0.753	0.394	0.869	−0.754	−0.957	−0.554	0.356	0.848	−0.633	0.753	−0.915	−0.706
Cs	−0.572	−0.810	0.090	−0.804	−0.472	−0.612	−0.680	−0.144	−0.812	0.279	−0.026	−0.102
Cu	0.478	0.817	0.552	0.352	−0.051	−0.139	0.983	0.681	0.611	0.463	−0.096	−0.620
La	−0.889	−0.537	0.219	−0.916	−0.683	−0.473	−0.593	0.047	−0.989	0.278	−0.459	−0.100
Ni	0.607	0.862	0.216	0.659	0.270	0.273	0.888	0.412	0.801	0.073	0.008	−0.256
P	−0.506	−0.087	0.840	−0.855	−0.887	−0.965	0.169	0.682	−0.616	0.932	−0.428	−0.848
Pb	1	0.121	−0.367	0.848	0.784	0.294	0.321	−0.290	0.943	−0.289	0.799	0.152
Rb	0.121	1	0.467	0.306	−0.134	0.200	0.886	0.669	0.407	0.231	−0.497	−0.373
S	−0.367	0.467	1	−0.584	−0.853	−0.752	0.640	0.969	−0.312	0.956	−0.638	−0.961
Sb	0.848	0.306	−0.584	1	0.899	0.743	0.247	−0.414	0.935	−0.639	0.578	0.490
Sn	0.784	−0.134	−0.853	0.899	1	0.735	−0.183	−0.762	0.759	−0.818	0.792	0.733
Sr	0.294	0.200	−0.752	0.743	0.735	1	−0.151	−0.573	0.470	−0.906	0.179	0.833
V	0.321	0.886	0.640	0.247	−0.183	−0.151	1	0.776	0.492	0.513	−0.274	−0.660
Zn	−0.290	0.669	0.969	−0.414	−0.762	−0.573	0.776	1	−0.162	0.864	−0.686	−0.906
Zr	0.943	0.407	−0.312	0.935	0.759	0.470	0.492	−0.162	1	−0.334	0.584	0.165
N	−0.289	0.231	0.956	−0.639	−0.818	−0.906	0.513	0.864	−0.334	1	−0.434	−0.983
TOC	0.799	−0.497	−0.638	0.578	0.792	0.179	−0.274	−0.686	0.584	−0.434	1	0.399
pH	0.152	−0.373	−0.961	0.490	0.733	0.833	−0.660	−0.906	0.165	−0.983	0.399	1

lation coefficient matrix could become larger and the results could be more complex with the increasing of kinds of elements.

3.4. Multivariate analysis

Due to the increase in kinds of elements in current studies, results from correlation analyses appeared more complicated. Therefore, the relationships among all the element variables could be better analyzed and visualized by a multivariate analysis method. Although it was difficult to classify these elements into specific pollution sources, natural phenomena and possible contributions from major human activities might be significant. Therefore, the cluster analysis and factor analysis would be performed.

In cluster analysis (CA), the cluster tree of all the element variables in soil was produced by the Pearson's correlation coefficient and the Ward method [36], and the factor scores were extracted using varimax rotation scheme. The results presented that three principal components (PCs) were identified and considered (Fig. 2 and Table 4). From a statistical point of view, the factor analysis data showed good agreement with clustering analysis results, thus three factors were classified as described below.

The first factor, accounted for 36.40% of the total variables observed, was highly correlated with the logarithms of the variables Ce, Cr, V, Rb, Cu, Ni, La and Pb. This factor represented the contribution of these metal particulates emitted from different industries and other anthropogenic sources, which was duly supported by the CA. The elements, Ni, Cr, Cu, Pb and V, were normally associated with organic matter, and high concentration of those elements were found in the immediate vicinity of oil refineries, power plants and other industrial installations [29,37–39]. So, the heavy metals in this group appeared closely related to oil industrial activities as well as exhaust emissions from both gasoline and diesel fuelled traffic activities.

The second factor, responsible for 32.09% of the total element variables, indicated great correlation with the logarithms of the variables N, P, Cl, Zn, Zr, S and Sr. Those elements were mainly

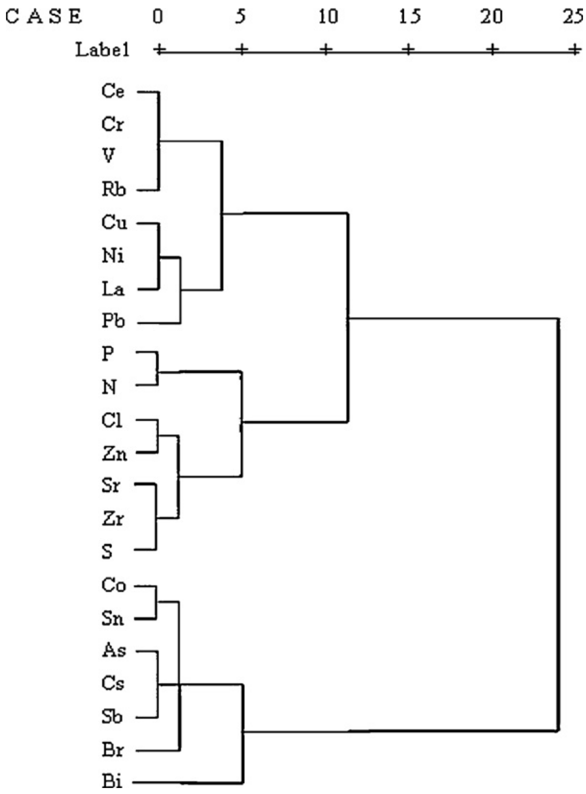

Fig. 2. Hierarchical clustering analysis of the hazardous elements in urban soil from Xi'an western industrial areas, China.

conceived of coming from agricultural activities, for example, the elements of N and P were usually functioned as fertilizer, and the elements Cl correlated with insecticides and pesticides. Also, the organic sulfide, phosphate and carbonate-bound elements were generally more easily volatilized and formed gas stream when suffering high temperature process [40–43]. Therefore, this factor was related to agricultural activities as well as the precipitant of gas stream.

Table 4
Varimax rotated factor matrix.

Variable	Factor 1	Factor 2	Factor 3
Log As	0.27	0.57	0.77
Log Bi	−0.60	−0.39	0.70
Log Br	0.51	0.54	0.66
Log Ce	0.89	0.45	−0.07
Log Cl	0.61	0.79	0.09
Log Co	−0.20	0.02	0.98
Log Cr	0.69	0.63	0.35
Log Cs	−0.83	0.45	0.33
Log Cu	0.84	0.33	−0.43
Log La	0.73	0.35	−0.58
Log Ni	0.89	−0.08	−0.45
Log P	−0.11	0.96	0.26
Log Pb	−0.95	−0.25	0.18
Log Rb	1.00	0.00	0.06
Log S	0.45	0.86	0.25
Log Sb	0.35	−0.65	−0.67
Log Sn	−0.09	−0.64	−0.76
Log Sr	0.21	−0.98	−0.02
Log V	0.90	0.35	−0.26
Log Zn	0.65	0.72	0.24
Log Zr	0.46	−0.37	−0.81
Log N	0.22	0.97	0.09
Eigen values	8.01	7.06	6.93
% of variance	36.40	32.09	31.51
Cumulative %	36.40	68.49	100.00

Table 5
Abundances of trace elements in coals and coal fly-ash (mg kg^{-1}).

Element	Coal		Coal fly-ash
	China [46–48]	World average [45]	Clarke [50,51]
As	3.80	1.5–15	60
Bi	0.10	0.1–0.2	<7.60 [45]
Br	9.00	0.5–90	
Ce	49.82	2–70	
Cl	264.00	50–2000	
Co	7.05	4–8	20
Cr	15.35	0.5–60	70
Cs	2.00	0.3–5	8.4 [45]
Cu	18.35	15–35	48
La	17.79	1–40	92 [45]
Ni	13.71	0.5–50	51
Pb	15.55	20–30	53
Rb	8.00	2–50	46
S	0.2–8% [49]	–	13.7% [45]
Sb	0.83	0.05–10	8
Sn	1.00	1–10	4.1
Sr	149.00	50–200	1100
V	35.05	2–100	120
Zn	42.18	10–60	100
Zr	67.00	20–40	160

The third factor, accounted for 31.51% of the total variables, also presented high correlation with the logarithms of the variables Co, Sn, As, Cs, Sb, Br and Bi. This was believed to originate from coal fly ash and metallurgy [44–54] (see Table 5), which was also supported by the CA results. Particularly, we noted that the dominant industrial sources presented in the following areas, such as power plants, metallurgical and mechanical industries, where the industrial activities mainly depended on the chemical energy from the coal. Thus, it was evidenced that anthropogenic metals such as Co, Sn, As, Cs, Sb, Br and Bi were mainly associated with "coal combustion" factor.

Therefore, the three different factors with high level of rescaled distance (see Fig. 2), were identified and well distinguished.

3.5. Environment risk assessment

To evaluate the elements risk and identify their environmental impact, the Nemero Synthesis Index evaluation method was used to groups named XS001, XS002, XS003, and XS004. Based on the Chinese background value of heavy metals in soil [23,24], the evaluation results were calculated according to Eqs. (1) and (2). The Single Factor Index evaluations were shown in Fig. 3A. The results revealed the Single Factor Index (*PI*) of hazardous metals was higher than 1, which indicated the hazardous metals had significantly polluted the urban soil. For example, the PI value ranged from 1.35 to 4.59 for Bi among the samples, 1.34–4.22 for Pb, 3.97 to 9.67 for Sb, 3.96–8.23 for Sn, 1.11–2.92 for Zn and so on. Although the original average contents of Sb and Sn were relatively lower in nature crust and parent soil [49,55], they had significant Single Factor Index across all areas in Xi'an due to correlate closely with metallurgy industrial activities. Additionally, the Nemero Synthesis Index (*PN*) could elucidate and differentiate effectively the contamination level of whole hazardous metals at the different locations. Fig. 3A indicated that the XS004 location was polluted seriously than others because of Sn, Pb and Sb. The PN values decreased in the order of PN_{XS004} (7.00) > PN_{XS003} (4.18) > PN_{XS002} (4.05) > PN_{XS001} (3.47). From the sample collecting locations, the mapping XS001 site situated closely to the river, thus the contaminants from industrial areas emissions were dramatically diluted because of the presence of flowing water. However, the XS004 site, occupied at the corner of southeast (SE) of the mapping areas, would be strongly polluted according to the calculated data and classification ($PN_j > 3$). The interpolated trend of elevated contamination level would occur

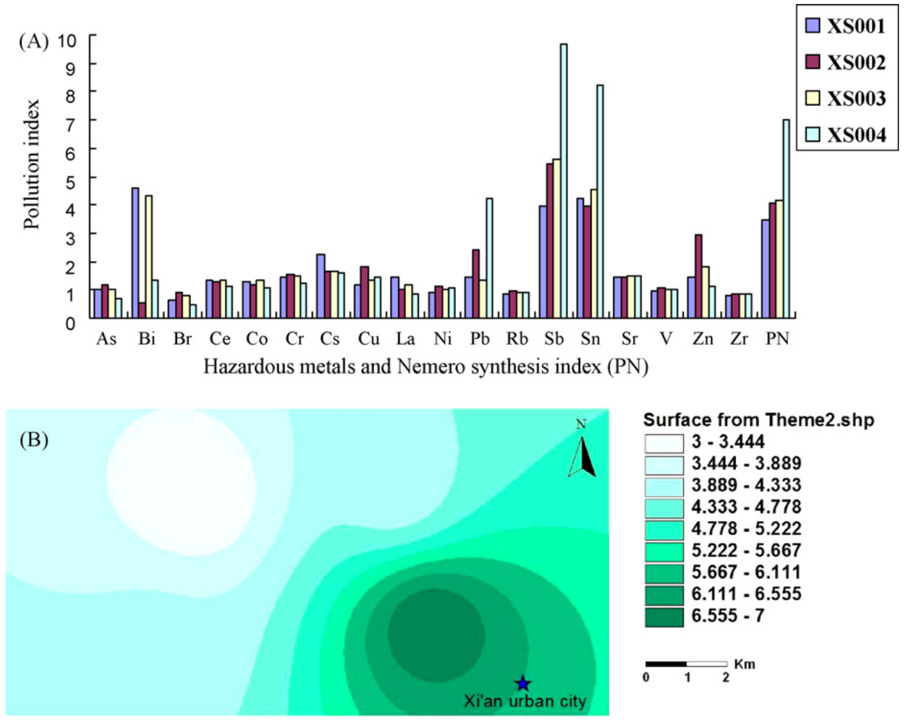

Fig. 3. Single Factor Index (*PI*) values of hazardous metal in urban soil from Xi'an western industrial areas, China (A) and the interpolated gradient of contaminant level occur along a stripe running from the northwest towards the southeast (NW–SE) through the Xi'an urban city (B).

along a stripe running from the northwest towards the southeast (NW–SE) through the Xi'an urban city (Fig. 3B), which attributed to prevailing wind effect in Xi'an city, northwest of China. The gradient of contamination distribution from northwest to southeast (Fig. 3B) was linked to industrial activities' discharges. The investigated area of contamination could not be explained by one specific anthropogenic pollution source on the basis of available data. However, this area was obviously industrialized. So, it was suggested the complex mixtures of dominant industrial pollution sources and anthropogenic emission would cause the contaminations in soil collection. The results were in agreement with and confirmed by the report from the Chinese Business View in 2007, demonstrating that the dust emissions from Xi'an western industrial areas amounted to 1000 kg in 2006. The distribution of those hazardous dust pollutants discharged from industrial activities would be consistent with local prevailing northwest wind and the contaminants would be diffused to the center of Xi'an urban city. Consequently, the environment quality and health of whole Xi'an urban city would be potentially threatened and influenced in the future.

4. Conclusions

Hazardous elements in soil around the industrial areas in Xi'an city were mainly influenced by industrial and anthropogenic activities, such as using of fossil fuels, agricultural activities, atmospheric deposition, and coal combustion. They were distinguished by means of classic multivariate analyses methods (factor analysis and cluster analysis). The findings indicated that more attention should be paid to heavy metal contamination and emission abatement techniques in Xi'an industrial areas, especially Bi, Pb, Zn, Sb, and Sn. Moreover, the contamination distribution trends were mainly NW–SE corresponding with the predominant wind direction as well as along the location of industries. As a result, the environment of the center of Xi'an urban city would be unavoidably affected. This study suggested that much more importance should be not only given to institute a systematic monitoring of the hazardous pollutants in Xi'an industrial areas, but also to the industrial emission abatement techniques and urban setting and plan.

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