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Spatial distribution of metals in urban topsoils of Xuzhou (China): controlling factors and environmental implications

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Abstract The contamination of soils by metals from various sources is a subject of increasing concern in recent times. Twenty-eight elements (Fe, Ti, Cr, Al, Ga, Pb, Sc, Ba, Li, Cd, Be, Co, Cu, Mn, Ni, V, Zn, Mo, Pt, Pd, Au, As, Sb, Se, Hg, Bi, Ag and Sn) have been analyzed from urban topsoil from the city of Xuzhou. The concentrations of these analyzed elements have been correlated to some soil parameters such as organic matter, pH, cation exchange capacity, carbonate content, and granulometric fractions (clay, silt and sand). Results of the statistical analysis show a large variety and complexity in these relationships. The spatial distributions of these metal concentrations were also constructed using geographical information system. The spatial distribution patterns of the elements analyzed show that traffic and industrial activities are the principal anthropogenic pollutant sources.

Keywords Urban topsoils · Heavy metal · GIS · Spatial distribution · Soil contamination · China

Introduction

Metal usages and associated heavy metal contamination to the environment have increased since the industrial revolution. This is particularly a problem in soil because of long residence times for heavy metals and the largely irreversible nature of their contamination (Markus and Mabratney 1996). The centralization of industry and the presence of intensive human activities in urban areas have exacerbated the problem of heavy metal contamination in urban soils. The awareness of the adverse effect urbanization is having on the environment has led to more detailed environmental geochemical investigations and mapping in different countries over the past decade. With the rapid growth of computer technology and statistical methods of analysis, (Geographical Information System) GIS is becoming one of the most important tools for studying environmental geochemistry problems (Zhang and Selinus 1998) and has been found to be very useful. Soil is a heterogeneous conglomeration of weathered material (be it rock material or other soil constituents such as dead plants or animals), a variety of organic and mineral solids, and aqueous and gaseous components. Heavy metal behaviors (bioavailability, toxicity, mobility and transport in the environment) in soils are mainly determined and constrained by soil properties: soil texture, content of organic matter, type of clay minerals and Al, Fe and Mn oxides, and prevailing physicochemical conditions in the soil: soil saturation, soil aeration, pH and redox potential (Leštan et al. 2002). The principal aims of this study are to compile spatial distribution maps using GIS and to examine the relationships between heavy metals and some soil physical and chemical parameters.

Materials and methods

Study area

Xuzhou is in the northwestern part of Jiangsu, one of the provinces of China, the geographical position being 33°43′–34°58′N and 116°22′–118°40′E. Xuzhou (China) is an important centre of historic and modern day industrial activities where coal provided the fuel for manufacturing. The prevailing wind direction is from the northwest, although in general, wind velocities are low, even approaching zero at times. This enhances the deposition of particulates within the city.

Sampling and analysis

A total of 21 topsoil samples (depth = 0–10 cm) were collected within the city of Xuzhou (Fig. 1).

Sampling sites were selected where chemicals (such as fertilizers, pesticides) and sewage sludge were not known to have been used. To avoid effects due to the differential uptake of metals by vegetation, sampling was carried out where plants with superficial roots are not present. At each sampling point, three sub-samples, each with a 20×20 cm surface, were taken and then mixed to obtain a bulk sample. Such a sampling strategy was adopted to reduce the possibility of random influence of urban waste. All samples were collected with a stainless steel spatula and kept in PVC packages.

The soil samples were air-dried and sieved through a 2-mm sieve. All bulk (< 2 mm) topsoil samples were analyzed for: sand (50–2,000 μm), silt (2–50 μm) and clay (< 2 μm) using Coulter Laser equipment. Samples were stirred and ultrasound used to facilitate particle dispersion (Navas and Machin 2002);

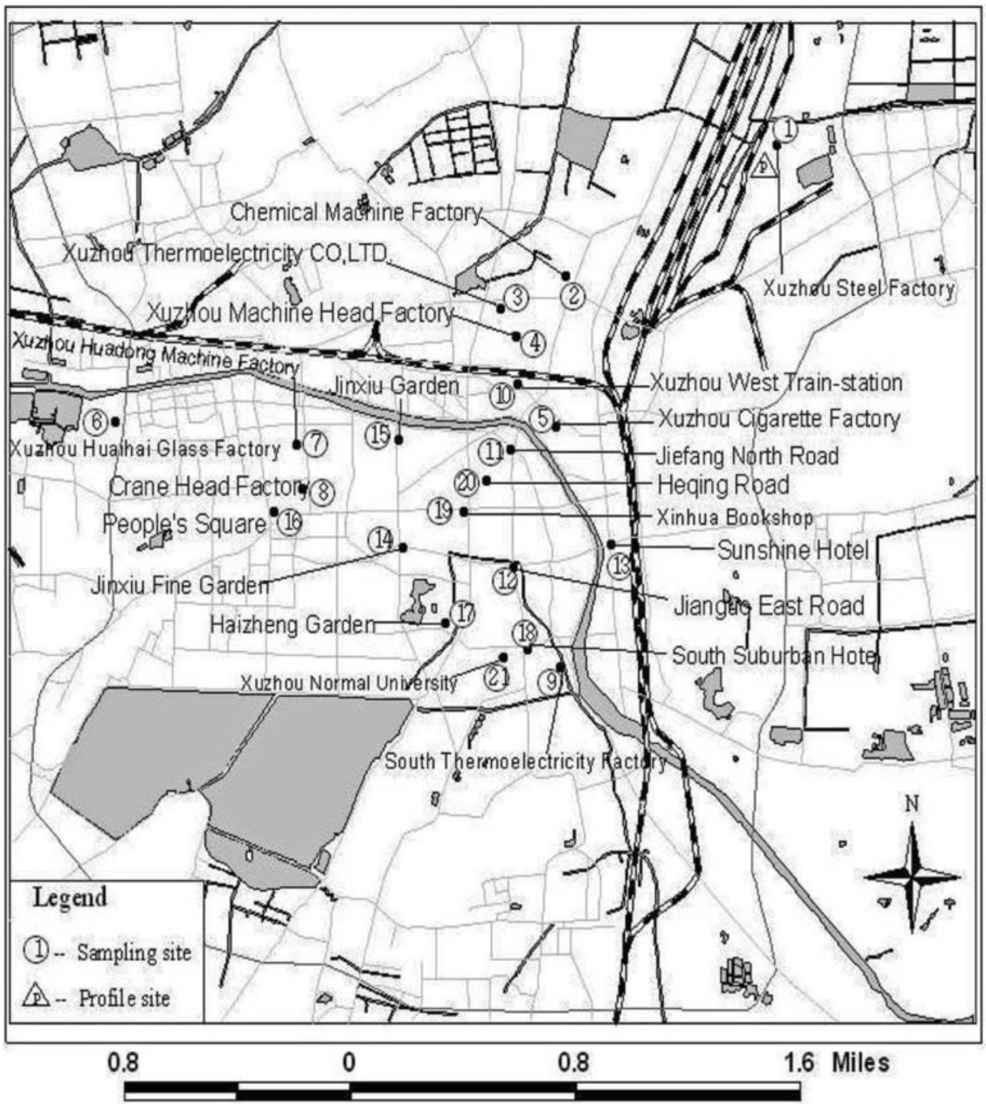

Fig. 1 Map of the Xuzhou city (Jiangsu) with location of sampling sites of topsoils

Table 1 Concentrations (mg kg^{-1}) of metals in topsoils from the urban area of Xuzhou (Fe and Al: %; Pt, Au, Pd: ng g^{-1})

Sample	Al	Fe	Ti	Ag	Se	Sc	Ga	Ba	Li	Bi	V	Pb	Cu	Zn	Cd
1	5.13	3.89	3410	0.13	0.38	18	13	433	26	0.34	65	22	28	79	0.15
2	5.86	4.03	3502	0.44	0.84	19	15	486	35	2.1	75	92	55	180	0.63
3	6.67	3.77	3922	0.40	0.23	15	17	488	40	0.3	11	42	31	92	0.13
4	5.87	2.97	3540	0.16	0.28	17	13	437	32	0.29	68	33	32	73	0.13
5	5.84	3.50	3516	0.25	0.68	20	17	487	42	0.40	5	51	61	290	0.54
6	5.63	3.29	3407	0.14	1.0	19	14	460	36	0.36	69	58	36	145	0.42
7	6.23	3.45	3749	0.19	0.24	13	16	459	38	0.30	82	29	28	98	0.15
8	5.93	4.15	3677	0.18	0.81	20	15	628	37	0.44	82	120	59	358	0.74
9	5.92	2.90	3658	0.17	0.20	16	13	464	33	0.30	72	28	27	82	1.00
10	5.41	3.66	3241	1.10	0.93	25	7	567	37	0.49	62	87	‘64	297	0.93
11	6.07	3.22	3484	0.40	0.26	17	18	425	36	0.30	77	41	39	196	0.23
12	5.39	2.69	3344	0.23	0.25	17	13	460	27	0.27	64	26	24	80	0.53
13	5.80	2.90	3527	0.11	0.32	17	12	470	34	0.30	70	36	31	118	0.60
14	5.67	2.78	3570	0.11	0.20	17	16	445	33	0.28	73	25	24	76	0.20
15	5.78	3.05	3502	0.72	0.32	20	15	485	33	0.32	69	45	44	142	0.58
16	5.67	2.66	3453	0.058	0.13	17	13	454	25	0.23	66	16	17	53	0.11
17	6.61	3.17	3970	0.20	0.49	13	16	47	39	0.38	81	32	35	117	0.32
18	6.95	3.93	4069	0.32	0.56	18	17	501	47	0.44	89	54	80	380	2.90
19	5.98	3.03	3624	0.18	0.20	16	15	462	33	0.27	74	26	26	102	0.71
20	6.73	3.66	3889	0.12	0.19	15	16	499	42	0.32	91	27	29	83	0.16
21	8.04	4.15	4349	0.30	0.31	17	18	614	44	0.34	101	41	33	86	0.24

Sample	Ni	Co	Cr	As	Hg	Sb	Mn	Mo	Be	Sn	Pt	Au	Pd
1	25	12	66	9.2	0.0312	0.82	450	1.0	1.6	3.7	3.0	3.5	3.0
2	33	14	162	577	1.30	53	527	1.6	1.8	4.0	4.0	1.5	1.4
3	38	17	70	13	0.83	0.93	760	1.2	2.1	11	3.1	4.2	2.9
4	23	9.3	68	13	0.52	0.94	505	0.90	1.6	4.2	3.3	4.4	2.8
5	104	11	67	12	0.22	1.00	522	2.30	1.9	4.1	4.7	24	2.7
6	24	9.8	63	12	0.15	0.93	430	1.60	1.7	3.9	1.6	0.89	2.3
7	30	12	70	15	0.056	1.0	636	1.2	1.9	4.0	1.7	3.0	2.9
8	33	13	102	16	0.12	1.1	606	2.5	1.9	4.3	1.6	2.3	2.5
9	27	10	65	13	0.11	0.91	506	0.97	1.7	4.0	1.8	7.9	3.1
10	42	10	92	15	0.21	1.60	508	4.9	1.7	8.2	3.9	5.6	3.2
11	23	11	72	16	0.63	1.0	508	1.5	1.8	10	1.4	3.1	2.6
12	28	8.9	82	8.7	0.058	0.92	434	0.87	1.5	4.5	4.1	5.7	3.0
13	25	9.8	87	9.9	0.12	0.95	441	0.97	1.7	3.4	2.7	3.8	2.7
14	27	11	66	13	0.18	0.89	476	1.2	1.7	4.2	2.9	3.7	2.2
15	30	10	65	13	0.59	1.00	489	1.5	1.6	7.5	3.1	5.4	3.3
16	24	9.8	67	8.7	0.024	0.79	451	0.71	1.5	2.2	3.2	0.8	3.0
17	31	11	74	14	0.21	1.00	513	1.2	1.9	4.7	1.0	1.3	1.1
18	54	14	84	17	0.32	1.10	602	1.8	2.1	6.8	1.1	2.8	2.8
19	28	11	73	12	0.10	0.96	500	1.2	1.7	3.2	3.3	3.5	3.5
20	34	14	73	15	0.082	0.96	641	0.92	2.0	3.6	1.31	3.6	3.7
21	39	19	79	15	0.26	0.94	902	1.7	2.2	6.4	1.0	2.3	2.0

Table 2 Descriptive basic statistics of some soil parameters in the studied soils

	pH	TOC (%)	TIC (%)	CEC (cmol/kg)	Clay (%)	Silt (%)	Sand (%)
					< 2μm	2–50 μm	50–1,000 μm
Mean	8.02	7.45	9.84	18.35	7.0	69.3	23.5
SD	0.26	2.85	0.35	5.29	3.09	21.2	24
Range	0.98	8.68	1.29	20.23	10.36	60.1	65.9
Min.	7.51	2.51	9.15	7.47	2.34	30.8	0
Max.	8.49	11.19	10.44	27.7	12.7	90.95	65.9

Note: *TOC* total organic content, *TIC* carbonate content, *CEC* cation exchange capacity

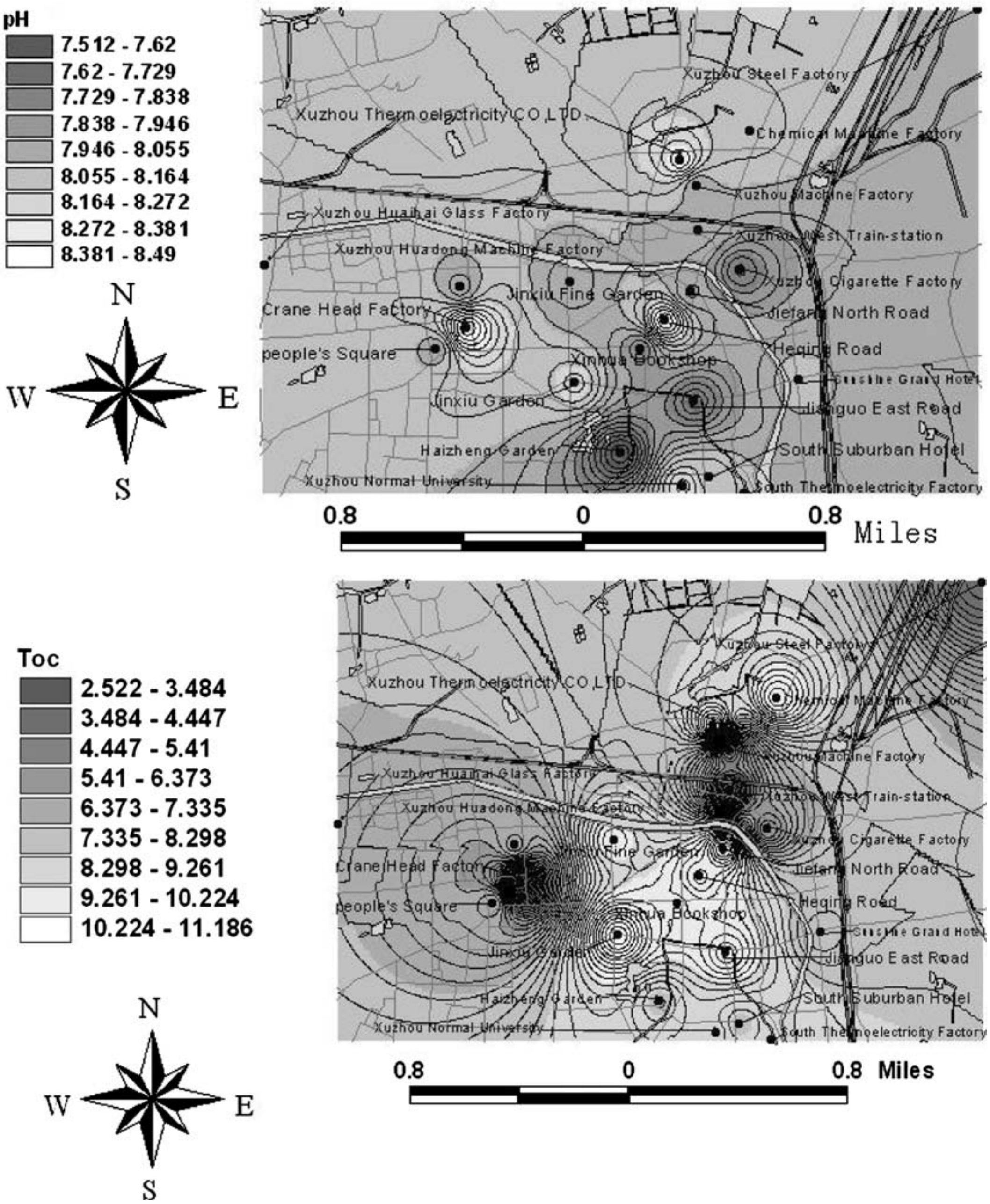

Fig. 2 Spatial distribution of pH, organic matter, clay contents in the studied soils using GIS ARCVIEW 3.0. (*Different colors* in each figure are shown because of much more iso-lines)

total organic carbon (TOC) by chromic acid digestion; pH_{water} on a 5 g to 25 ml slurry using an PHS-3C pH-meter; cation exchange capacity (CEC) by the ammonium acetate (NH_4OAc) sodium acetate (NaOAc) method (Navas and Machin 2002); and carbonate content (TIC) by back titrating an excess of 0.5 M HCl added to 1 g of sample with 0.5 M NaOH (Sutherland 2003).

The element concentrations for Ti, Fe, Cr, Al, Ga and Pb were determined by X-ray fluorescence spectrometry (XRF, Philips PW1400 apparatus), on bulk-sample pressed, boric-acid backed pellets. The accuracy of determinations was checked by using certified reference materials. Analytical errors were below 1% for Al, below 3% for Ti, Fe and below 10% for Pb, Ga and Cr.

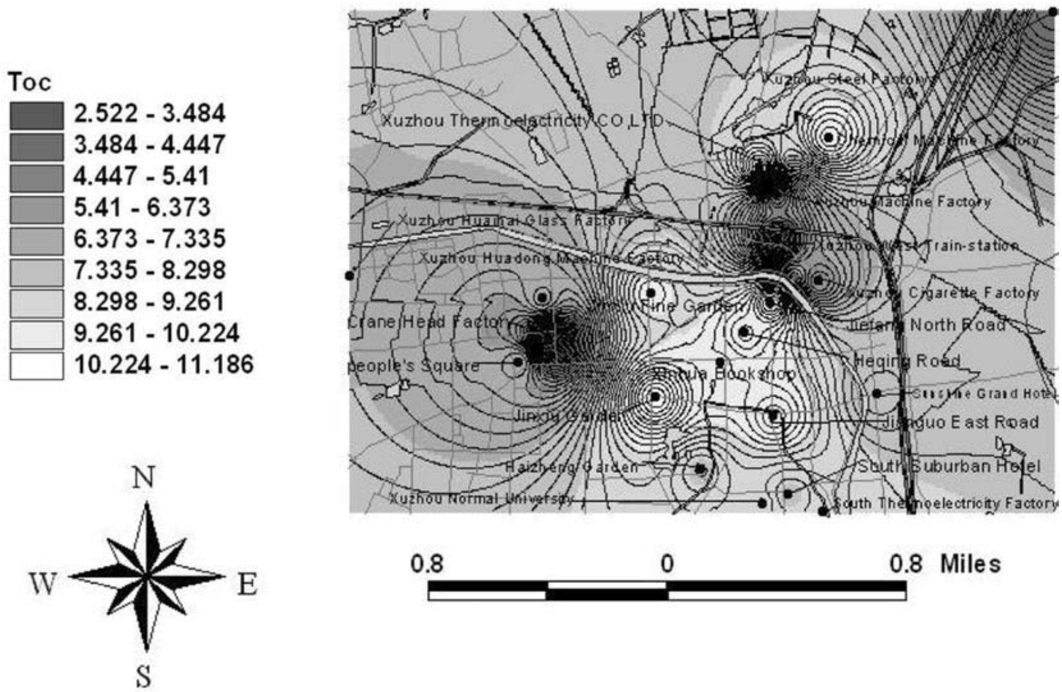

Fig. 2 (Contd.)

Samples (approximately 0.2 g) were dissolved in a hot HF–HNO_3–HCl acid mixture (approximetely 15 mL), and refluxed with the acid mixture if the sample was only partly dissolved. Sc, Ba, Li, Cd, Be, Co, Cu, Mn, Ni, V, Zn, Mo, Pt, Pd and Au concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). The elements As, Sb, Se, Hg, Bi, Ag and Sn were determined by inductively coupled plasma atom emission spectrometry (ICP-AES). All calibration standards were prepared in the acid matrix used for the soil samples. Caution was used in preparing and analyzing samples to minimize contamination from air, glassware and reagents, which were all of good quality. Replicated measures of standard reference materials (ESS-1 and ESS-2 were provided by China Environmental Monitoring General Station), reagent blanks and duplicated soil samples (approximately 21 of the total number of soil samples was used for this purpose) randomly selected from the set of available samples were used to assess contamination and precision. The analytical precision, measured as relative standard deviation, was routinely between 5 and 6%, and never higher than 10%.

The analyzed element concentrations are listed in Table 1. Metal accumulation and sources in topsoils are discussed elsewhere (Wang and Qin 2005). Only the results of GIS treatment and relations between some soil parameters and the studied metals are reported here.

Data processing

The relationships between some soil parameters and the metal elements were assessed using Pearson Correlation analysis. The maps of isolevels of metals have been produced to document spatial distribution in the studied soils using GIS ARCVIEW 3.0 for Windows. The use of GIS-based maps was selected for their capability to visualize spatial relationships between environmental data and other land features (Walsh 1988). In particular, GIS is a valuable tool for interpreting spatial variability and evidencing different contamination sources.

Results and discussion

Relationships with some soil parameters and controlling factors

As is widely recognized in the literature there are a number of physical and chemical properties of soils

Table 3 Pearson correlation coefficients between some soil parameters and metals in the studied soils

	Al	Fe	Ti	Ag	Se	Sc	Ga
CEC	−0.465*	−0.018	−0.545*	0.294	0.389	0.520*	−0.033
pH	0.283	0.388	0.245	−0.023	0.201	0.162	0.125
TOC	0.319	−0.184	0.264	−0.011	−0.484*	−0.402	0.310
TIC	−0.482*	−0.223	−0.449*	−0.060	0.099	0.254	−0.335
Clay	0.635**	0.469*	0.631**	0.009	−0.059	−0.105	0.452*
Silt	0.524*	0.318	0.558**	0.038	−0.082	−0.145	0.449*
Sand	−0.544*	−0.339	−0.574**	−0.033	0.084	0.141	−0.454*

	Ba	Li	Bi	Co	Cr	As	Hg
CEC	0.096	0.026	0.137	−0.412	0.222	0.093	−0.043
pH	0.522*	0.303	0.105	0.472*	0.242	0.091	0.105
TOC	−0.240	0.113	0.136	0.269	0.114	0.216	0.363
TIC	−0.269	−0.473*	0.243	−0.337	0.261	0.257	0.173
Clay	0.563**	0.616**	−0.051	0.589**	0.004	−0.072	0.177
Silt	0.300	0.639**	−0.057	0.430	−0.106	−0.077	0.218
Sand	−0.336	−0.642**	0.059	−0.455*	0.095	0.079	−0.213

	V	Pb	Cu	Zn	Cd	Ni	Pd
CEC	−0.347	0.471*	0.380	0.436*	0.165	0.156	0.354
pH	0.407	0.410	0.125	0.061	0.029	−0.095	0.078
TOC	0.323	−0.347	−0.232	−0.242	−0.094	−0.086	−0.079
TIC	−0.507*	0.119	0.044	0.07	0.156	−0.205	−0.133
Clay	0.714**	0.284	0.247	0.142	0.047	0.289	0.038
Silt	0.599**	0.156	0.296	0.204	0.193	0.384	0.052
Sand	−0.62**	−0.172	−0.290	−0.196	−0.178	−0.375	0.056

	Sb	Mn	Mo	Be	Sn	Pt	Au
CEC	0.096	−0.329	0.479*	−0.223	−0.076	0.245	0.272
pH	0.087	0.443*	0.122	0.360	0.063	−0.153	−0.311
TOC	0.213	0.188	−0.387	0.181	0.254	0.043	−0.146
TIC	0.262	−0.455*	0.050	−0.464*	−0.130	0.383	−0.129
Clay	−0.084	0.756**	0.075	0.063	0.230	−0.332	0.142
Silt	−0.089	0.586**	0.04	0.602**	0.255	−0.260	0.294
Sand	0.091	−0.614**	−0.043	−0.615**	−0.251	0.270	−0.277

Note: *Correlation is significant at the 0.05 level. **Correlation is significant at the 0.01 level

affecting metal mobilization–immobilization processes (Jones and Jarvis 1981; Reiuwerts et al. 1998; Navas and Machin 2002). Summary statistics for the analyzed soil parameters in all studied samples are presented in Table 2. The main physico-chemical parameters determined for studied topsoils from the city of Xuzhou include: values of pH ranging in a narrow interval (7.51–8.49), which suggests neutral to sub-alkaline conditions for all the topsoils; CEC showing a very broad interval of variation, from 7.47 to 27.7 cmol/kg, with a mean value of 20.23 cmol/kg; organic matter contents ranging from 2.51 to 11.19%, with most values approximately 7.45%; TIC of the analyzed soils vary from 9.15 to 10.44, with an average value of 9.84%. The mean clay content is 7.0% and varies between 2.34 and 12.7% and the mean silt is 69.3% and varies between 30.8 and 90.95%. The spatial distributions of these soil properties can be seen in Fig. 2.

To analyze the relationships between these soil parameters and the metal concentrations, a Pearson *R* correlation analysis has been applied to the sample set of the studied soils (Table 3). pH is generally acknowledged to be the principal factor governing concentrations of soluble metals (Brallier et al. 1996). Metal solubility tends to increase at lower pH and decrease at higher pH values. As can be seen in Table 3, between pH and the metal concentrations there are: (1) significant and positive correlations with Ba, Co, Mn, Pb, Fe, Li, V, Al, Ti, Cr and Be; (2) no significant correlations with Sb, Sn, Pt, Pd, As, Hg, Cd, Zn, Cu, Ag, Sc, Se, Mo, Ni and Bi.

Between the CEC and the element contents there are: (1) positive correlations with Mo, Pb, Zn, Cu, Se and Sc;

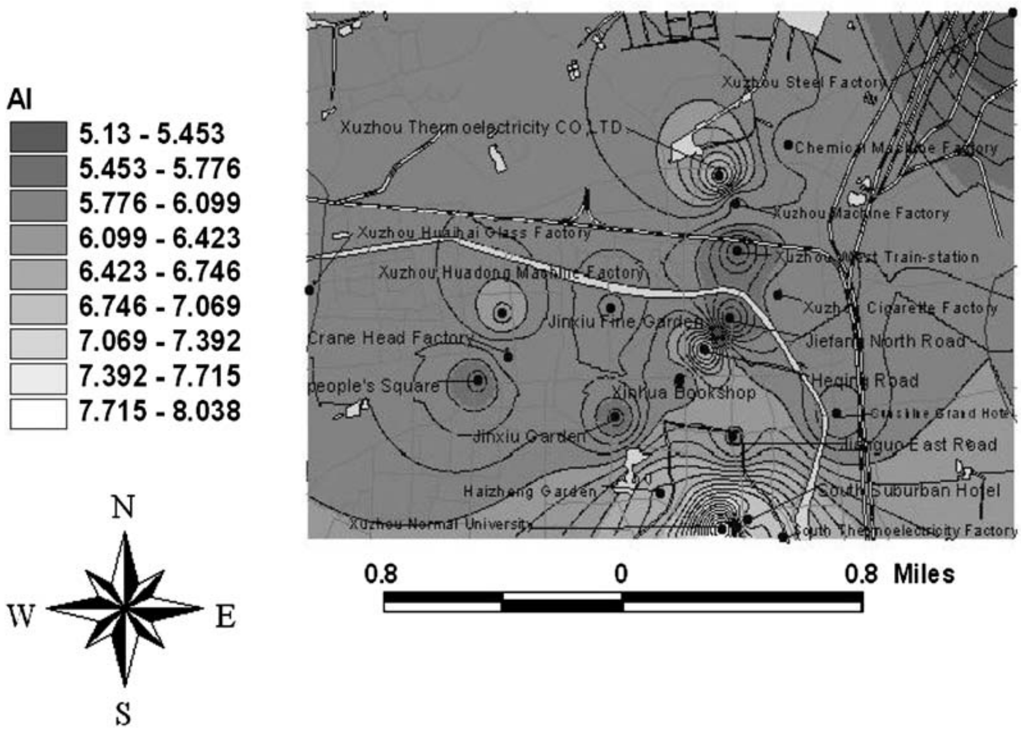

Fig. 3 Spatial distributions of Al, V, Cu, Zn and As in the studied soils of Xuzhou mapped using GIS ARCVIEW 3.0. (*Different colors* in each figure are shown because of much more iso-lines)

(2) negative correlations with Al, Ti and Co; no correlations with Sb, Mn, Be, Sn, Pt, Pd, Au, Cd, Ni, Cr, As, Hg, Ba, Li, Bi, Ga and Ag.

Concentrations (mg kg^{-1}) of metals in topsoils from the urban area of Xuzhou (Fe and Al: %; Pt, Au, Pd: ng g^{-1}).

Organic matter accumulates at the soil surface and has a significant influence on metal binding. Of particular importance is the potential for the retention of atmospherically derived metal inputs in the surface humic layer of soils: this has important implications for metal mobility down the soil profile and bioavailability of metals to surface dwelling organisms (Reiuwerts et al. 1998). Between TOC percentages and element concentrations there are: (1) positive correlations with Al, Ti, V, Co, As, Hg, Sb and Sn; (2) negative correlations with Fe, Se, Sc, Ba, Pb, Cu, Zn and Mo and no correlations with Ag, Li, Bi, Cd, Ni, Cr, Mn, Be, Pt, Au and Pd. Between TIC percentages and the element concentrations there are significantly negative correlations with Mn, Al, Be, V, Ti and Li.

The influence of soil texture on metal solubility in soils is best expressed in terms of the division of soils into clay, silt and sand fractions. These terms are in turn defined by particle size fractions of the soil with respective classifications of <2 μm, 2–50 μm and 50–2,000 μm (Qian et al. 1996). Between the clay percentage and the element concentrations there are: (1) significant and positive correlations with Mn, V, Co, Al, Fe, Ti, Ga, Ba and Li; (2) no significant correlations with the other elements such as Sb, Mo, Be, Sn, Ag, Se, Sc and Bi. Between silt percentages and the element concentrations there are significantly positive correlations with Al, Ti, Ga, Li, V, Mn and Be. Between sand percentages and the elements there are significant negative correlations with Al, Ti, Ga, Li, V, Co, Mn and Be.

Results of the statistical analysis have shown a large variety and complexity in these relationships. These results are also in agreement with the results reported by Manta et al. (2003).

Spatial distribution of metals

Distribution patterns of the studied elements in the whole urban area of Xuzhou are visualized by a set of concentration maps obtained by processing data in Table 1 with the GIS ARCVIEW 3.0 program. To economize the space, distributions of representative metals such as Al, V, Cu, Zn, As are shown in Fig. 3.

As, Hg, Bi, Cr and Sb show similar spatial distributions, highlighting a significantly polluted zone corresponding to the industrial centre of the city (upper-right side of the maps). The spatial distribution of these

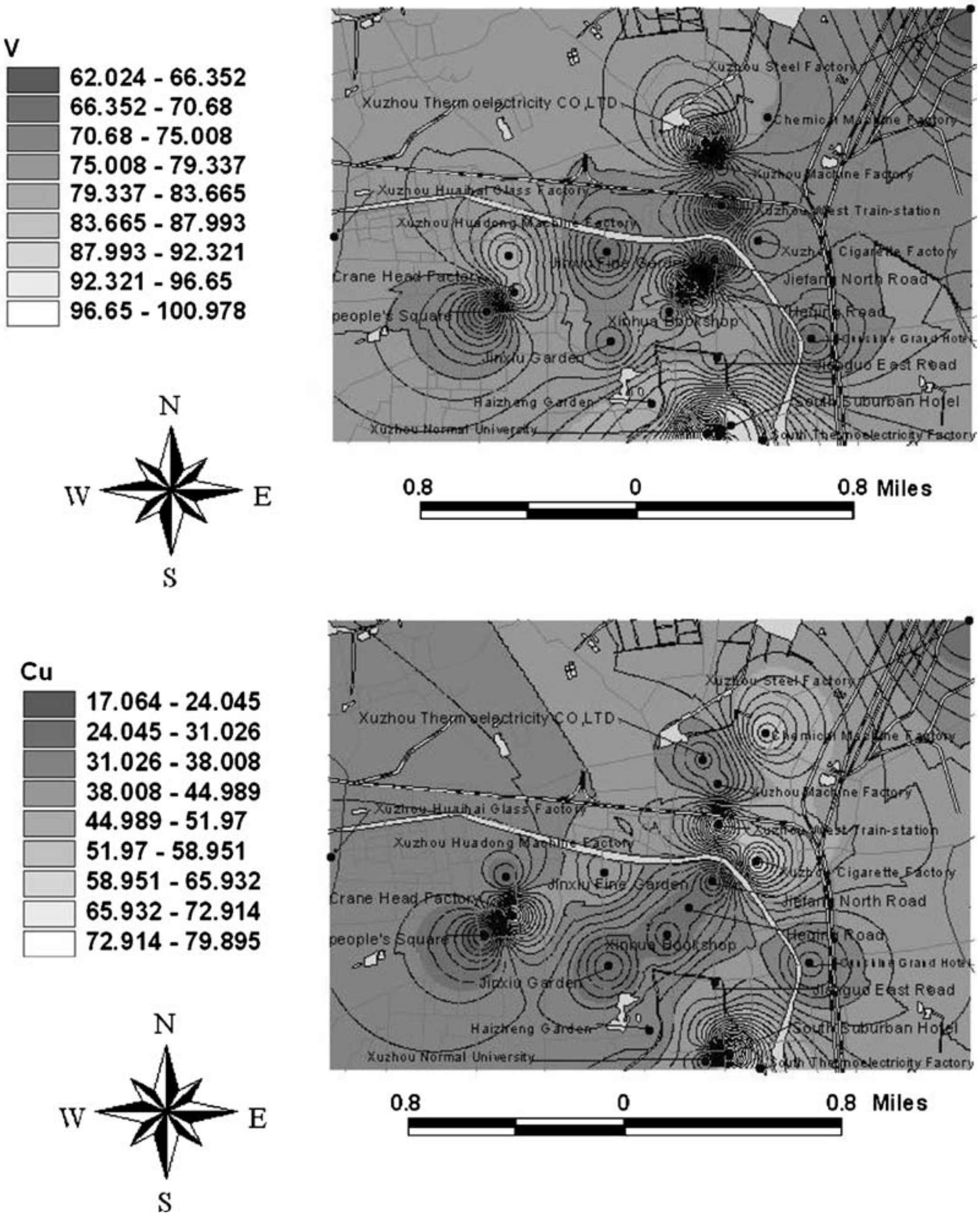

Fig. 3 (Contd.)

elements suggests the dominant role of industrial activities as the pollutant source. Inter-element relationships provide interesting information on metal sources (Manta et al. 2003). Significant correlations exist among these five metals (Table 4), which may indicate common contamination source for these metals.

Zn, Cu and Pb also show similar spatial distributions coinciding with the main roads, which suggest these three metals are probably due to vehicular emissions. The influence of traffic is characterized by Zn and to a lesser extent by Cu and Pb (Miguel et al. 1997).

The spatial distribution patterns of Ti, Al, Ga, V, Co and Mn are relatively even. These six metals concentrations are in normal ranges of unpolluted soils (Wang and Qin 2005) and also correlate with the clay percentage in the studied soils (Table 5), which show these metals are due to input of soil parent material (Wilcke et al. 1998).

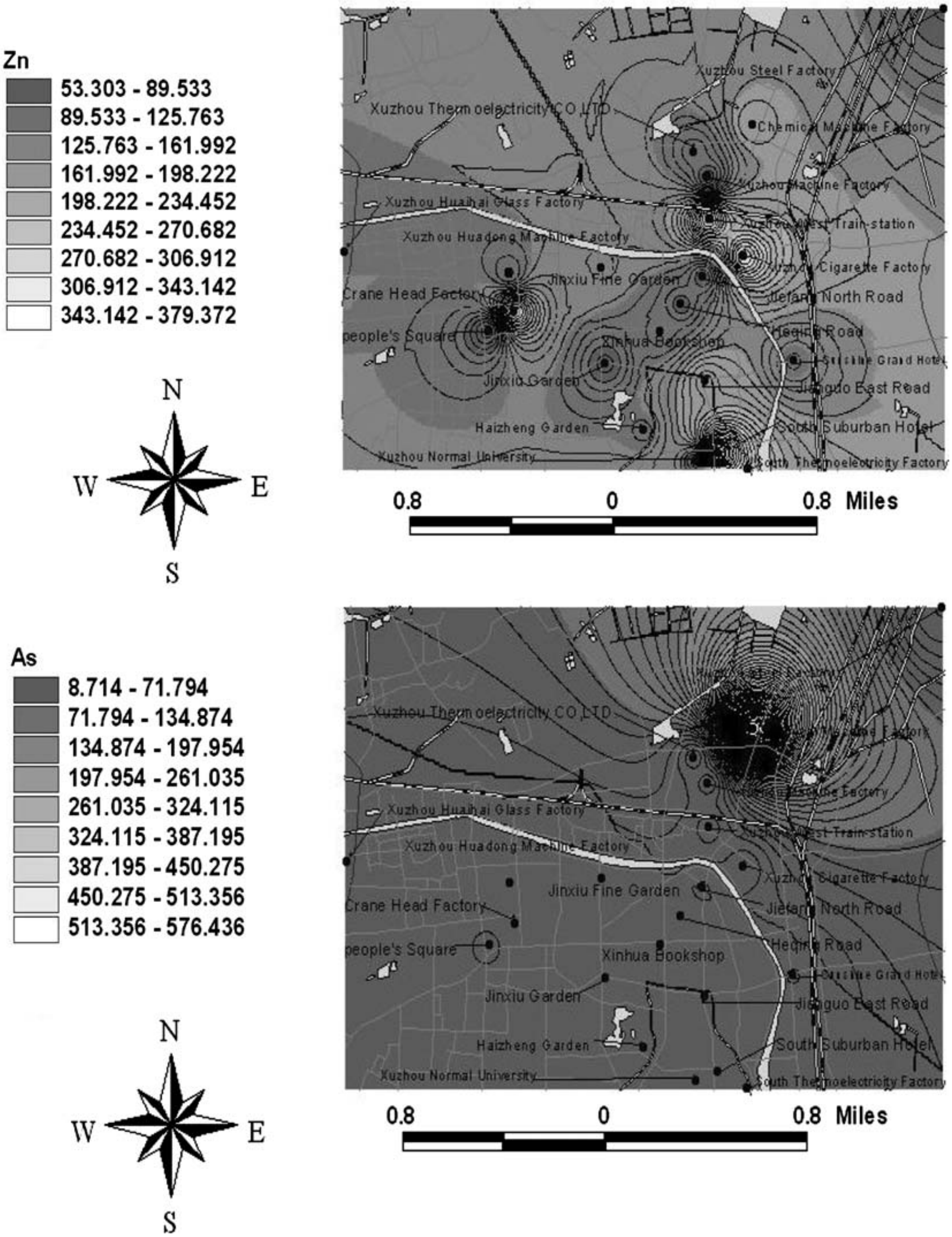

Fig. 3 (Contd.)

Conclusions

This study has highlighted the need for further research, by increasing sampling density to better characterize the metal and As contents of the topsoils of Xuzhou as a function of their physical and chemical characteristics. The results obtained serve to increase knowledge on the distributions of As and metals. The data will be of use for further detailed studies in this city as well as to complement other geochemical databases. This work will be the basis to define the requirements for further

Table 4 Correlations between metal concentrations in the studied soils

	As	Cr	Sb	Hg	Bi
As	1				
Cr	0.887**	1			
Sb	1.00**	0.888**	1		
Hg	0.728**	0.590**	0.725**	1	
Bi	0.988**	0.915**	0.988**	0.715**	1

Note: **Correlation is significant at the 0.01 level (two-tailed). *Correlation is significant at the 0.05 level (one-tailed)

Table 5 Correlations between metal concentrations in the studied soils

	Al	Ti	Ga	V	Mn	Co
Clay	0.635**	0.631**	0.452*	0.714**	0.756**	0.589**

Note: **Correlation is significant at the 0.01 level (two-tailed). *Correlation is significant at the 0.05 level (one-tailed)

research to better establish permitted levels of metals for soil conservation, as well as to identify areas of potential toxicity due to heavy metal participation in biogeochemical cycles. The use of the GIS software has proved to be cost-effective and a powerful technique for processing data on the studied soils that has been compiled for producing geochemical maps of the analyzed elements in the soils of Xuzhou.

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