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Distributions, sources and pollution status of 17 trace metal/metalloids in the street dust of a heavily industrialized city of central China

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ABSTRACT

A series of representative street dust samples were collected from a heavily industrialized city, Zhuzhou, in central China, with the aim to investigate the spatial distribution and pollution status of 17 trace metal/metalloid elements. Concentrations of twelve elements (Pb, Zn, Cu, Cd, Hg, As, Sb, In, Bi, Tl, Ag and Ga) were distinctly amplified by atmospheric deposition resulting from a large scale Pb/Zn smelter located in the northwest fringe of the city, and followed a declining trend towards the city center. Three metals (W, Mo and Co) were enriched in samples very close to a hard alloy manufacturing plant, while Ni and Cr appeared to derive predominantly from natural sources. Other industries and traffic had neglectable effects on the accumulation of observed elements. Cd, In, Zn, Ag and Pb were the five metal/metalloids with highest pollution levels and the northwestern part of city is especially affected by heavy metal pollution.

1. Introduction

Over half of the global populations live in urbanized areas (United Nations, 2012). The quality of life in such settings is largely influenced by environmental and human health related issues (Wong et al., 2006). Street dust, which consists of soil, deposited airborne particulates, construction material, soot and fume discharged from the industry and vehicles, etc, is one of the most important host media of environmental pollutants. To certain degree, street dust is a more pertinent indicator to urban environmental quality than single compartmental monitoring of air, water and soil, because it reflects pollutants from the multi-media (Wong et al., 2006). Hence, pollutants in street dust originate from a wide variety of sources, e.g., industries (Zheng et al., 2010; Ordóñez et al., 2003), transportations (Liu and Cen, 2007; Li et al., 2001), consumer products like lead paint (Farfel et al., 2005), aerosols and soils (Ferreira-Baptisa and De Miguel, 2005), and the pollutant's sources, compositions and distributions were differed from one city to another, mainly depended on the city's peculiarity (De Miguel et al., 1997; Wei and Yang, 2010).

Upon being combined with the street dust, contaminants could be remobilized and enter the ambient environment at certain circumstances, such as being lifted into the air through re-suspension process or being leached out into the water system (Martuzevicius et al., 2011; Joshi et al., 2009). As a consequence, contaminants in street dust can deteriorate the human's health through several pathways: re-suspension-inhalation, hand-mouth ingestion and dermal contact (Roels et al., 1980; Ferreura-Baptisa and De Miguel, 2005; Zheng et al., 2010).

Pollutants in street dust that have received much attentions fall into several categories, including organic pollutants such as polycyclic aromatic hydrocarbons (PAH) and phthalate esters (Saeedi et al., 2012; Martuzevicius et al., 2011; Chen et al., 2005), bacteria or pathogens (di Giorgio et al., 1996; Furumai et al., 2011), trace metals and metalloid (De Miguel et al., 1997; Ferreura-Baptisa and De Miguel, 2005; Zheng et al., 2010), etc. Due to the property of concealment, persistence and high toxicity, some trace metals and metalloids have been paid extensively endeavors for their pollution

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status and associated health problems in street dust during the past several decades (Day et al., 1975; Duggan, 1980; Li et al., 2001; Lu et al., 2010; Shi et al., 2011). While, most studies, especially that conducted in China, focused only on a limited numbers of heavy metal/metalloids that with high toxic (such as Pb, Zn, Cd, Cr, As), and the studied areas are usually simple and not complicated in terms of industrial categories.

In this paper, we investigated as many as trace metal/metalloids (totally 17 elements) in the street dust of a heavily industrialized city, Zhuzhou in central China, which has more complicated industries. The aims of this study are to explore the spatial distribution patterns and pollution status of these elements, and to reveal their respectively sources. Although pollution of some elements (Hg, Pb, Zn, Cd, Cu, As) in the agricultural soil and the river sediments around this city has been reported (Li et al., 2011; Wang, 2002; Wang and Arne, 2003), systematical studies of trace metal/metalloids in the street dust of this city have not been carried out. The 17 trace metal/metalloids (Ag, As, Bi, Cd, Co, Cr, Cu, Ga, Hg, In, Mo, Ni, Pb, Sb, Tl, W and Zn) chosen in this study are mainly based either on the possibility of emissions from the industries, or on the concern of their health risks to human beings and the environment. The results of this research will provide an important insight into these trace metal/metalloids in the urban environment, and is conducive to the scientific society, the local enterprises and the policy makers of the municipality.

2. Materials and methods

2.1. Study area

Zhuzhou, the second largest city of Hunan province is located in the middle of Xiangjiang (a tributary of Yangtze river) watershed (Fig. 1) and is 50 km from the provincial capital Changsha. The city has developed rapidly from being a small town in the early 1950s to becoming an industrialized hub. The population of Zhuzhou city was around one million by the end of 2009, and distributed over an area of 105 km^2. The climate is of a typical north subtropical monsoon type, with wind direction predominantly from the northwest, and the annual average temperature, precipitation and weed speed is 17.6 °C, 1409 mm, and 2.1 m s^{-1}, respectively.

A range of heavy industries has been established here since early 1950s, such as Zhuzhou Electrical Railway Engine Corp., Zhuzhou Hard Alloy Metal Corp., South China Power Equipment Corp. and Zhuzhou Smelting Corp., and all of them are backbone enterprises and are established during the China's first and second "Five-year plan"(1953–1962). Beside these, several important chemical and construction material manufactories were also founded here. The basic information and locations of these major industries (MI) in Zhuzhou city are presented in Table 1 and Fig. 1, respectively. Of the major industires, Zhuzhou smelter group (MI 1 in Fig. 1 and Table 1) produce Pb and Zn as its main products and reclaim more than tens of associated metals and metalloids at the same time; the Hard alloy group (MI 6) synthesize tungsten and molybdenum products (carbide), tantalum, niobium and cobalt products; the Electrical Engine Plant (MI 5) and Vehicle Manufacturing Plant (MI 7) produce the railway locomotives and freight carriages, respectively; MI 4 and MI 8 are coal-fired power plant and airplane engine producer, respectively; while, MI 2 and MI 3 are basically the non-metal related chemical reagent producers.

The city comprises of four administrative districts with roughly equal land areas (Fig. 1). Shifeng in the northwest is a typical industrial zone, where the Pb–Zn smelter, two chemical manufactories, the coal-fired power plant and the railway locomotives producer are located; Hetang is a business area including the city downtown, where the hard alloy plant and the railway freight carriages producer are located; Lusong comprises a mix of commercial and residential, where the airplane engine producer is located; while Tianyuan is a new district that has only been significantly urbanized since the last decade, with the municipal government and some new industrial such pharmacy and electronic industry.

2.2. Sampling and chemical analysis

A total of 55 samples of street dust were collected in January 2010, when it was cold and dry season. During the sampling, the weather was sunny and windless. The sampling campaign was chosen in winter mainly because the weather was in favor of accumulating street dust on the ground compared to summer season when plenty of rainfalls occur. The sampling sites were roughly distributed all over the urban areas (Fig. 1), with 16 from Shifeng district, 15 from Tianyuan district, 13 from Hetang district and 11 from Lusong district, respectively. At each site, about 300 g of dust present on impervious surfaces (road, pavement) within an area of 2–10 m^2 was collected using plastic utensils (brush and dustpan) and transferred into air-tight polyethylene bags for storage. The amount of street dusts taken within the same area at different locations were not the same, and even varied remarkably at some places, that depend on the sweeping frequency, wind speed of a specific location, the material that the pavement used, etc. After air-drying, the coarse impurities of the samples, such as stone, cigarette butt, plastic and leaves, were firstly removed, and then all the rest were grounded with an agate mortar and pestle to passed through a 100 mesh nylon sieve (0.149 mm).

Concerning chemical analysis of Hg and As, 0.1–0.3 g of each sample was digested at 95 °C in a water bath for 1 h using 5 ml aqua regia (a mixture of HCl and HNO_3 at 3:1 v/v). An appropriate aliquot of the digest was analyzed using cold vapor atomic fluorescence spectrophotometry (CVAFS; for Hg, Tekran Model 2500, Tekran Instruments Corp.; for As, AFS-920, Beijing Jitian Instrument Corp.). For the analysis of remaining 15 metal/metalloids, a wet digestion procedure coupled with inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC-e, PerkinElmer Inc., Canada) detection was adopted from Qi and Grégoire (2000). Briefly, 50 mg of sample were digested using 1 ml of HF and 1 ml of HNO_3 in the PTFE-lined stainless steel bombs heated to 190 °C for 24 h. Insoluble residues were dissolved using 6 ml of 40% v/v HNO_3 heated to 140 °C for 5 h. After cooling down, about 0.4 ml of the digest was transferred to a centrifuge tube, and added with 500 ng rhodium in liquid solution, then make up to approximate 10 ml with Milli-Q water (18.2 MΩ cm, Millipore Inc.). Rhodium was used as an internal standard to correct for matrix effects and instrumental drift. All the reagents used were trace metal grade.

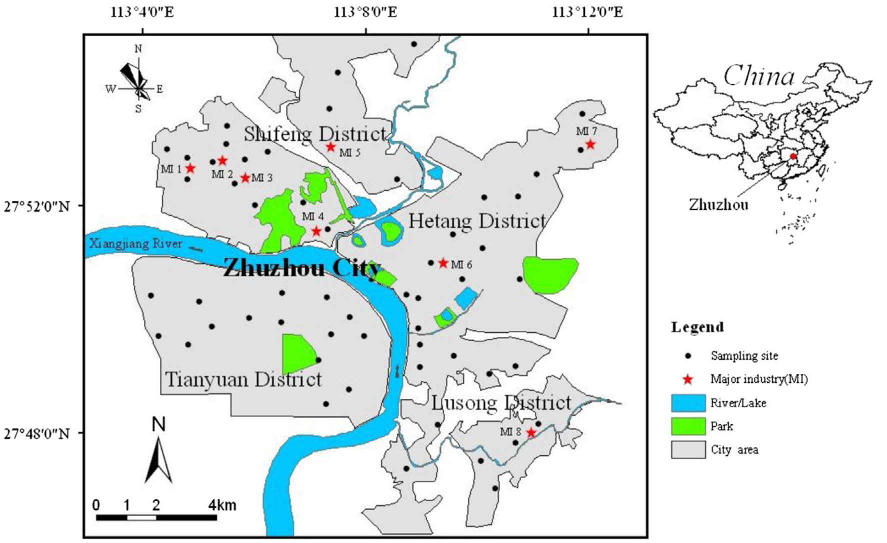

Fig. 1. Map showing the locations of major industries (MI) and street dust sampling sites of Zhuzhou city, China.

Table 1
Basic information regarding the major industries (MI) in Zhuzhou city.

Major industries (MI) ID	Industrial enterprises	Products	Possible elements emitted
MI 1	Zhuzhou Smelter Group	Main products: Zn and Pb; By-products: Cu, Au, Ag, Bi, Cd, In, Te, Sb, As, Sn, Ga, Hg, Co, Se and sulfuric acid.	Zn, Pb, Cu, Au, Ag, Bi, Cd, In, Te, Sb, As, Sn, Ga, Hg, Co, Se
MI 2	Hunan Zhuzhou Chemical Industrial Group	Rutile-based pigment, sulfuric acid, superphosphate fertilizers, caustic soda, polyvinyl chloride resins, chloral, hydrazine hydrate.	Ti, Na and other non-metal elements
MI 3	Hunan Zhicheng Chemicals Co. Ltd	Hydrogen peroxide, sodium carbonate, ammonium chloride, urea, methanol preparation, production of concrete construction blocks.	Non-metal elements
MI 4	Zhuzhou Huayin Coal-fired Power Plant	2 units with a capacity of 310 MW.	Trace metal/metalliods in the coal
MI 5	Zhuzhou Electrical Engine Plant	Electric locomotives, mass transit vehicles.	Fe and possible alloys
MI 6	Zhuzhou Hard Alloy Group	Tungsten and molybdenum products (carbide), tantalum, niobium and cobalt products.	W, Mo, Ta, Nb, Co
MI 7	Vehicle Manufacturing Plant	Railway freight carriages.	Fe and possible alloys
MI 8	South Power Equipment Company	Airplane-engine, motorcycle.	Fe and possible alloys

For quality assurance and quality control (QA/QC), the duplicates, method blanks and standard reference materials (soil and sediment SRM: GBW07305, GBW07405, GBW(E)070009 and NIST 2710) were analyzed. Mean recoveries for studied elements (C(element, measured)/C(element, certified) × 100) in the four SRMs were between 85% and 113% (as see in Table S1 provided in the supporting information). The duplicate samples showed the bias was less than 5%, indicating the samples are thoroughly homogenized.

In addition, pH in samples was determined in a 2.5:1 (w/w) water/dust suspension using a pH meter (NY/T 1377-2007), and organic matter (OM) content was determined by potassium dichromate method (NY/T 1121.6-2006).

2.3. Data process techniques

The descriptive statistics of the dataset and the principal component analysis (PCA) were carried out using SPSS 11.0 for Windows (SPSS Inc. USA). Also, the same software were deployed to test the statistical significances of differences by using one-way analysis variance (ANOVA) and independent-samples *T* test. The spatial interpolation and mapping techniques were conducted using ArcGIS v.9.2 (ESRI Co, USA). The spatial interpolation method applied in this study was Inverse Distance Weighting (IDW) which based on the relations between the locations of sampling sites and the major industries in Zhuzhou city.

Pollution status for single element was assessed by geoaccumulation index (I_{geo}) approach (Müller, 1969). This method assigns the metal/metalloid pollution to seven (0–6 grade) enrichment classes, ranging from background concentration to very heavily polluted, as follows:

$$I_{geo} = \log_2\left[\frac{C_{Sample}}{\left(1.5 \times C_{Background}\right)}\right] \quad (1)$$

The factor 1.5 is introduced in this equation to minimize the effect of possible variations in the background values, $C_{Background}$, which may be attributed to lithogenic variations in dust. The description of I_{geo} classes is supplied in Table 2.

3. Results and discussion

3.1. Trace metal/metalloids concentration in street dust

Descriptive statistics of studied metal/metalloid content, as well as pH and OM of street dust of Zhuzhou city are presented in Table 3 in relation to the provincial background value of each element in the soil. Seven of the metal/metalloids analyzed (Pb, Zn, Cd, Hg, In, Bi and W) showed variations of 2–3 orders of magnitude in concentration among samples. The corresponding variability for Cu, Tl, Sb, As, Ag and Mo was on the scale of 1–2 orders of magnitude. The distribution of the aforementioned 13 metal/metalloids were positively skewed with skewness more than 3.8 as shown in Table 3, indicating most samples have lower content and few featured with relatively high content. For Co, Ni, Cr and Ga, their contents only extended over a comparatively narrow range (within one order of magnitude): Co (8–84 mg kg^{-1}), Ni (20–105 mg kg^{-1}), Cr (60–302 mg kg^{-1}) and Ga (6.6–13.0 mg kg^{-1}). On the contrary, pH and OM level in the street dusts were fairly variable (7.0–12.4 and 1.2%–10.74%, respectively). Since most elements were not normally or log-normally distributed, except for Cr, Ga, pH and OM, we report the median values to represent their averages in this study, and conduct comparison using these values with other studies.

Table 2
The I_{geo} classes with respect to the street dust quality.

I_{geo} value	I_{geo} class	Designation of street dust quality
$I_{geo} \le 0$	0	Uncontaminated
$0 < I_{geo} \le 1$	1	Uncontaminated to moderately contaminated
$1 < I_{geo} \le 2$	2	Moderately contaminated
$2 < I_{geo} \le 3$	3	Moderately to heavily contaminated
$3 < I_{geo} \le 4$	4	Heavily contaminated
$4 < I_{geo} \le 5$	5	Heavily to extremely contaminated
$I_{geo} > 5$	6	Extremely contaminated

In a specific comparison, street dusts collected within 4 km to the smelter in this research contained significantly higher ($p < 0.01$) concentrations of Hg, Pb, Zn, Cd, Cu and As than the agricultural soils close to the same smelter (<4 km) (Li et al., 2011, Table 4). The reasons maybe comprise of two aspects. First of all, the lower deposition rate of heavy metals in the countryside (Wang and Arne, 2003); and secondly, the rotary cultivation of agricultural soils that dilute the pollutant content in the buck soil plough layer. Furthermore, urban street dust displays significantly higher alkalinity than the agricualtural soil that can be ascribed to inclusion of a high proportion of particulate deriving from construction materials (such as concrete, limestone). The tendency of higher OM content in the street dust possibly reflect practises within urban area concerning handling of organic refuse and waste (e.g. garbage, offal and litter).

In a global perspective (Table 5), trace metal/metalloids concentrations in street dusts of Zhuzhou were comparable to those of two Zn-smelting related industrial cities: Huludao in northeastern China (Zheng et al., 2010) and Avilés in northern Spain (Ordóñez et al., 2003), but in-turn exceptionally higher compared to most other investigations, with exception of a few elements such as Zn, Pb, Cu and Cr in cities like Hong Kong, Shanghai and Madrid, and that could be significantly elevated due to vehicle emissions (Li et al., 2001; Tanner et al., 2008; Shi et al., 2011; De Miguel et al., 1997).

3.2. Spatial distribution patterns and possible sources

The spatial distribution of Pb, Zn, W, Mo, Ni, Cr in street dust in Zhuzhou city is illustrated in Fig. 2, and these six elements represent

Table 3
Statistical summary of trace metal/metalloids content (mg kg^{-1}) and pH, presence of organic matter (OM, %) in the street dust of Zhuzhou city ($N = 55$).

Elements	Min	Max	AM	SD	Median	Skewness	Reporting limit	Reference value[a]
Pb	96	17,578	956	2815	254	5.03	1	29.7
Zn	317	35,400	2379	5145	1140	5.46	1	94.4
Cd	2.2	691	41.4	117.3	10.3	4.71	0.1	0.126
Cu	39	1020	139	148	98	4.44	1	27.3
Hg	0.08	14.60	0.92	2.70	0.21	4.69	0.01	0.116
As	15	1194	89	183	42	5.05	1	15.7
Sb	3.7	115	15.8	21.7	9.8	3.81	0.1	1.87
Tl	0.45	13.60	1.08	1.86	0.64	6.03	0.01	0.61
Ag	0.46	28.70	2.49	4.56	1.17	4.49	0.01	0.108
In	0.28	86.60	4.06	12.68	1.03	5.72	0.01	0.033
Bi	1.0	295	12.3	40.8	3.2	6.50	0.1	1.05
Ga	6.6	13.0	9.4	1.7	9.2	0.43	0.1	20.8
W	2.3	809	34.5	115.7	9.5	6.09	0.1	3.31
Mo	1.3	90.1	6.4	12.4	3.2	6.02	0.1	1.4
Co	8	84	13	11	15	4.85	1	14.6
Ni	20	105	40	16	35	1.95	1	31.9
Cr	59	302	125	54	115	1.78	1	71.4
pH	6.96	12.44	9.41	1.24	9.49	0.18	0.01	5.6
OM	1.18	10.74	4.58	2.10	4.25	0.84	0.01	2.14

Min, minimum; Max, Maximum; AM, arithmetical mean; SD, arithmetical standard deviation.

[a] Reference value of Hunan soils, EMSC (1990).

Table 4
Comparison of selected metal/metalloids, pH and organic matter (OM) in street dusts with upper layer (0–20 cm) agricultural soils (Li et al., 2011) both collected within 4 km from the Pb/Zn smelter.

Environmental media		Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Hg (mg kg^{-1})	As (mg kg^{-1})	pH	OM (%)
Street dust ($N = 13$)	Min–Max	235–17578	979–35400	16–691	46–1020	0.28–14.6	29–1194	6.96–10.23	1.59–8.39
	AM	3224	6442	141	270	3.23	237	8.42	4.96
	Median	1227	2340	45	207	1.27	99	8.36	4.90
Agricultural soil ($N = 60$)	Min–Max	143–1197	168–3349	3–41	34–157	0.38–2.89	15–93	4.75–7.72	2.04–8.82
	AM	466	970	13	74	1.20	43	5.86	4.21
	Median	432	791	12	69	1.12	37	5.81	4.09

for three distinct sources as explained below. Maps of remaining elements, as well as pH and OM are showed in Fig. S1 (Supporting Information). From Fig. 2 and Fig. S1, as well as comparison results among the four administrative districts (Table S2), it was found that a metal/metalloid is associated with one of following sequential categories: 1, Shifeng >> Tianyuan >> Hetang ≈ Lusong (Pb, Zn, Cd, Hg, Bi and In); 2, Shifeng >> Tianyuan ≈ Hetang ≈ Lusong (Cu, As, Tl, Sb, Ag and Ga); 3, Hetang >> Shifeng ≈ Tianyuan ≈ Lusong (Mo, W); and 4, Shifeng ≈ Tianyuan ≈ Hetang ≈ Lusong (Ni, Cr and Co). The difference is tested by the ANOVA method, and ">>" represented $p < 0.05$, while "≈" means the difference is not significant. Elements associated with patterns 1 and 2 exhibit the highest

Table 5
Comparison of trace metal/metalloids content in the street dust of various cities worldwide (unit in mg kg^{-1}).

City	Pb	Zn	Cd	Cu	Hg	As	Sb	Cr	Co	Ni	Reference
Industrial cities/communities											
Zhuzhou,China (Median)	254	1140	10.3	98	0.21	42	9.8	115	13	35	This study
Huludao,China (Median)	235	1374	19.7	162	0.61	–*	–	–	–	–	Zheng et al., 2010
Avilés, Spain (GM**)	514	4892	22.3	183	2.56	17	8.0	42	7	28	Ordóñez et al., 2003
Miscellaneous cities											
Beijing, China (Mean)	54	219	1.1	46	0.34	6	2.1	87	9	34	Liu and Cen, 2007; Tanner et al., 2008
Shanghai, China (Mean)	237	753	1.0	258	0.14	8	–	264	–	66	Shi et al., 2011
Nanjing, China (Mean)	103	394	1.1	123	0.12	13		126	11	56	Hu et al., 2011
Guangzhou, China (Median)	185	492	1.3	79	–	–	–	50	6	16	Duzgoren-Aydin et al., 2006
Xi'an, China (Median)	131	295	–	72	0.43	10	3.7	65	–	–	Han et al., 2006
Urumchi, China (Mean)	54	294	1.2	95	–	–	–	54	11	43	Wei et al., 2009
Baoji, China (Median)	383	612	–	113	1.00	18		123	16	42	Lu et al., 2010
Hongkong, China (Mean)	240	4024	1.8	534	0.6	–	–	324	10.2	–	Tanner et al., 2008
Luanda, Angola (Mean)	351	317	1.2	42	0.13	5	3.4	26	3	10	Ferreira-Baptisa and De Miguel, 2005
Kavala, Greece (Mean)	301	272	0.2	124	0.10	17	–	196	–	58	Christoforidis and Stamatis, 2009
London, U.K. (GM)	370	372	2.7	80	–	–	–	–	–	–	Schwar et al, 1988
Oslo, Norway (Mean)	180	412	1.4	123	–	–	6.0	–	19	41	De Miguel et al., 1997
Madrid, Spain (Mean)	1927	476	–	188	–	–	–	61	3	44	De Miguel et al., 1997
Ottawa, Canada (GM)	33	101	0.3	38	0.02	1	0.4	42	8	15	Rasmussen et al., 2001
Bursa, Turkey (Mean)	210	57	3.1	–	–	–	–	–	–	67	Arslan, 2001
Amman, Jordan (Mean)	271	351	1.9	139	–	–	–	29	32	66	Al-Momani, 2009
Seoul, Korea(Mean)	245	296	3.0	101	–	–	–	–	–	–	Chon et al., 1995

Note:* "–", Not available; ** GM: geometric mean.

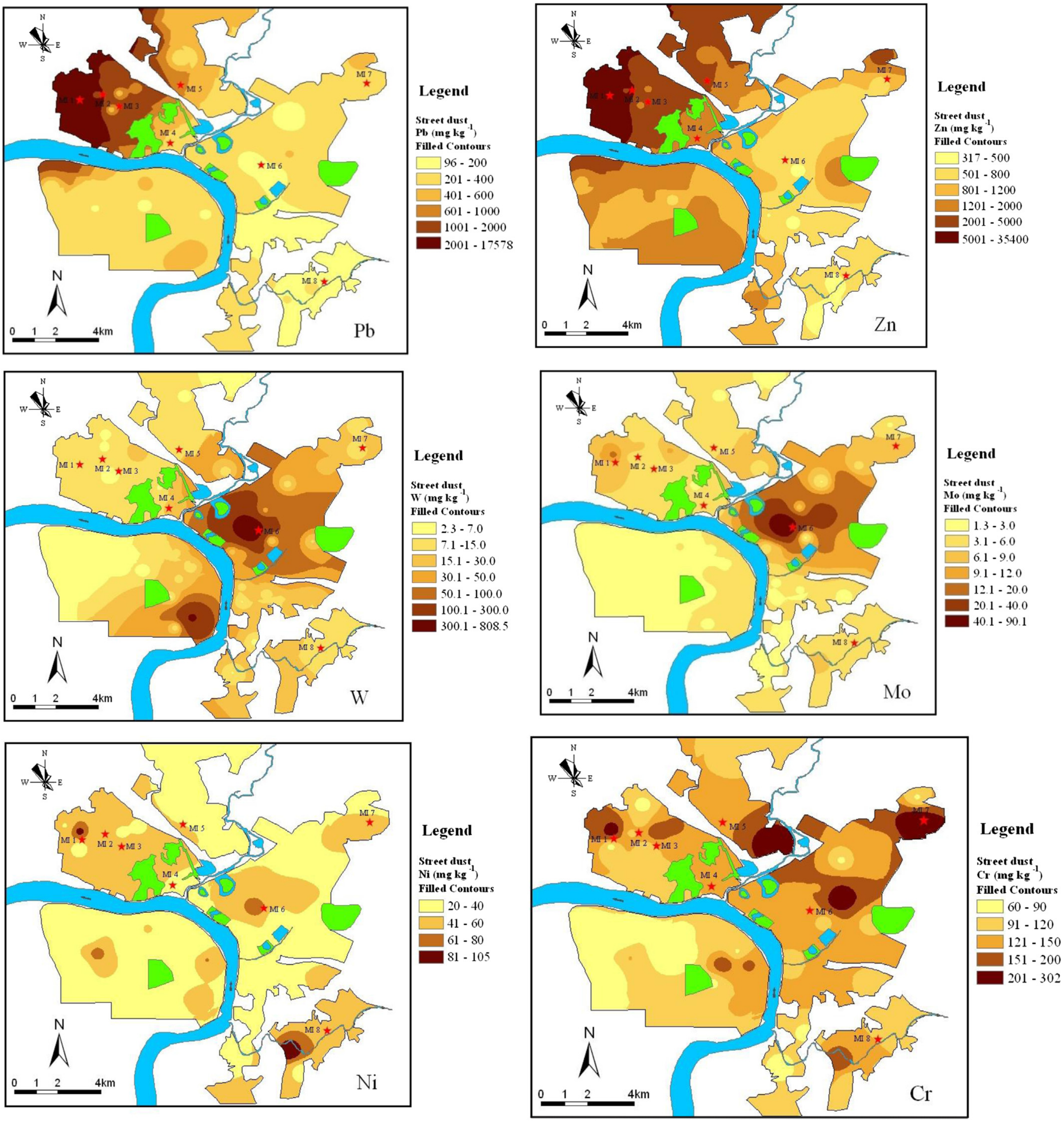

Fig. 2. Spatial distribution of selected metals (Pb, Zn, W, Mo, Ni, Cr) in street dust of Zhuzhou city.

concentrations in the northwest with declining levels in downwind direction towards the city center. Elements Mo and W form a cluster of their own, with peaking concentrations in Hetang district; while the signal of Ni, Cr and Co in street dust exhibit a relatively smooth distribution throughout the city.

The principal component analysis (PCA, Fig. 3 and Table S3 in supporting information) was conducted to disclose the pollution sources, which was responsible for the patterns of investigated metal/metalloids. Results showed the first principal component includes significant loadings for Pb, Zn, Cd, Cu, Hg, As, Bi, In, Tl, Sb, Ag and Ga; the second one for Mo, W and Co; and the third one relates to Ni and Cr. These three principal components totally explained 86.6% variance of the data, with each component of 61.0%, 17.6% and 8.0%, respectively. Considering the locations of major industries in Zhuzhou (Fig. 1) and the spatial distributions of trace metal/metalloids in street dust (Fig. 2 and Fig. S1), it can be confirmed that the first principal component essentially represent emissions related to the Pb/Zn smelter while the second principal component represent the hard alloy metallurgy plant.

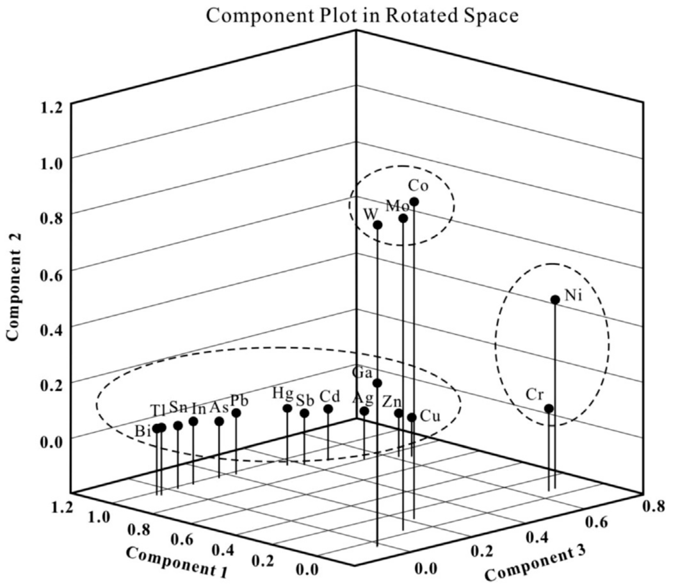

Fig. 3. 3D-plot of scores for investigated elements obtained from principal component analysis (PCA) results in the space generated by the first three components.

The Zhuzhou smelter (MI 1) in Fig. 1 started operation since in late 1950s and is one of the largest Pb/Zn producers in China (approximate annual production of 450 000 tonnes Zn and 100 000 tonnes Pb, respectively). In addition, large quantities of metal/metalloids associated with the Pb/Zn ore, such as Cd, Cu, As, Hg, have been emitted into the surrounding environment during the smelter's operation (Wang and Arne, 2003; Liu et al., 2003; Li, 2007; Li et al., 2011). An overview of the environmental quality of 9 mining and smelting areas in Hunan province indicated that over 30 tonnes of trace metals were discharged from this smelter annually during the early 2000s, constituting over 90% of the total emissions of trace metals in Zhuzhou city (Lei et al., 2008). Unfortunately, however, the authors didn't disclose the compositions of trace elements. Liu et al. (2003) reported 7–24 tonnes of Cd was emitted from three stacks of the smelter in the period of 1999–2001. Measurements of dry deposition of Pb, Zn, Cd and Cu conducted at various sites in Zhuzhou city showed the peak deposition flux was close to the smelter stack constructions, with the highest Cu, Pb, Zn, Cd deposition rate of 35, 90, 200 and 6 kg km^{-2} per month, respectively (Wang and Arne, 2003). Our previously research revealed that the surface soil (0–20 cm) within 4 km to the smelter has accumulated 6.5 tonnes Hg, 2750 tonnes Pb, 3920 tonnes Zn, 64 tonnes Cd, 296 tonnes Cu and 114 tonnes As, respectively (Li et al., 2011). The composition of elements identified predominantly released by Zhuzhou Pb/Zn smelter (Ag, As, Bi, Cd, Cu, Ga, Hg, In, Pb, Sb, Tl, Zn) in this study is primarily identical to a Pb and a Zn smelter in Northern France (Sterckeman et al., 2002; Douay et al., 2008a) except for Ni, which was emitted in significantly larger quantities from the French smelters. In the present study, results indicate that the smelter source of Ni together with Co are less significant.

The hard alloy plant is also a huge enterprise, producing tungsten molybdenum alloy, as well as tantalum, niobium and cobalt

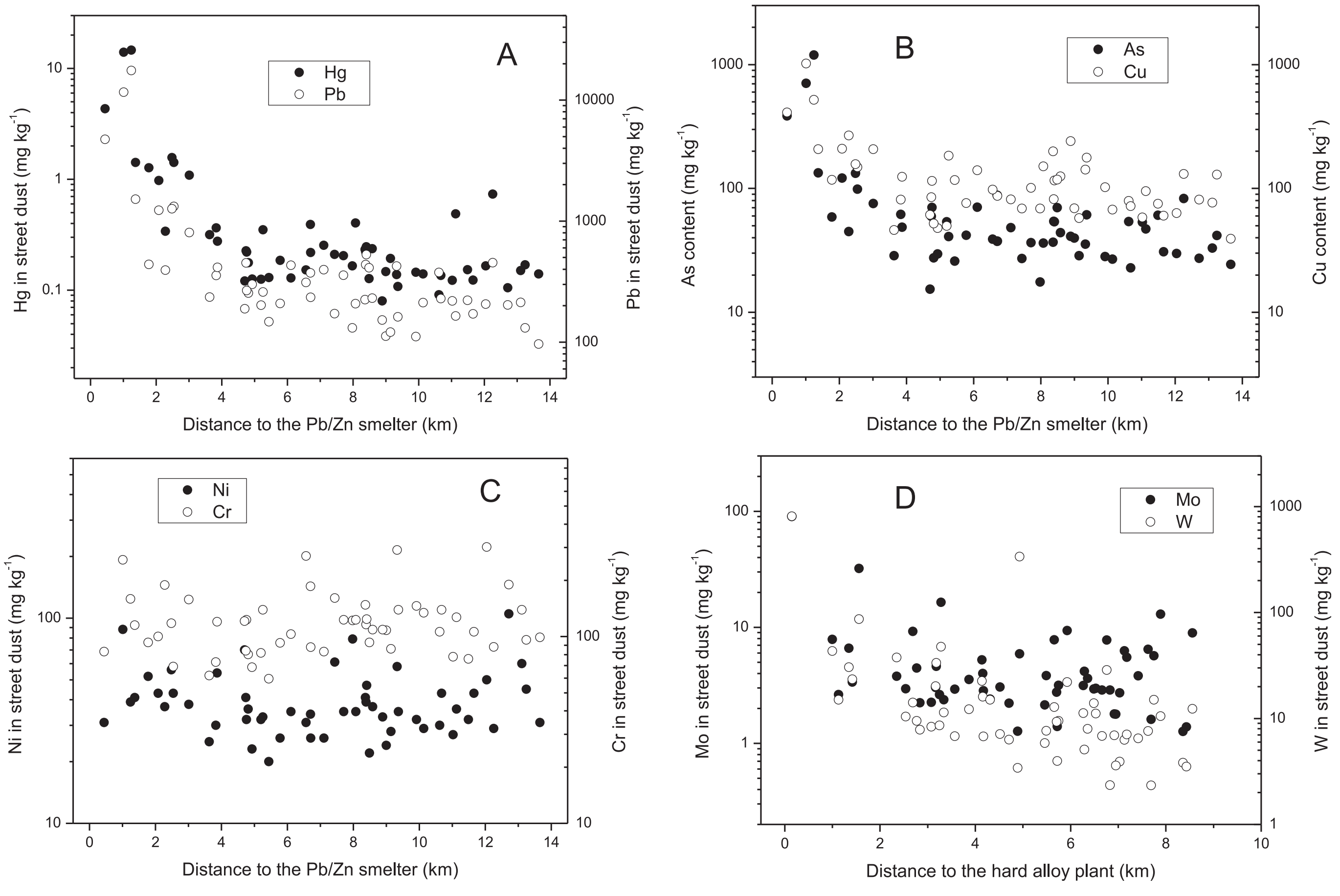

Fig. 4. Selected trace metal/metalloids concentrations in street dust as a function of the distance to the Pb/Zn smelter(A, B, C) and to the hard alloy plant (D).

alloy, and hence Mo, W and Co are released to the environment as reflected in Figs. 2 and 1S.

To further unravel the influence of Pb/Zn smelting and hard alloy producing on the trace metal/metalloids distributions, plots of selected element contents vs. distance to the Pb/Zn smelter and the hard alloy plant were constructed (Fig. 4). As can be seen from Fig. 4, concentrations of elements associated with both patterns 1 and 2 decreased exponentially in the first several kilometers from the smelter, and dropped slowly after that. The mobility of pattern 1 elements (Pb, Zn, Cd, Hg, Bi, and In, Fig. 4A) were obviously higher than that of pattern 2 elements (Cu, As, Tl, Sb, Ag and Ga, Fig. 4B), with exponential decrease distance of ~5 km and ~3 km to the smelter, respectively. The hard alloy plant caused pollution of Mo, W, Co only in a relatively narrow distance (e.g. within 1–2 km, Figs. 2 and 4D and 1S). The larger area impacted by the smelter than the hard alloy plant maybe was the result of higher stacks (up to 133 m) emissions with the smelter which is in favor of air pollution dispersion.

OM content in street dust was comparatively high in the commercial area of Hetang district, which may be related to intensive catering trade and resulting emissions of VOC and generation of organic garbage. Concerning dust pH, it appears a slightly reverse trend in the spatial distribution compared to that of elements of patterns 1 and 2, with higher alkalinity towards southeast zone, with LS district significantly ($p < 0.05$) higher than other three districts. This suggests that the Pb/Zn smelting process not only discharges trace metal/metalloids, but also releases a significant amount of acidic compounds, such as SO_2 that impact the surrounding environment. This statement is supported by the monitoring of atmospheric pollutants (SO_2, NO_x, CO, TSP) undertaken at different locations in Zhuzhou city (Wang, 2002), and higher acid gas concentrations was found close to the smelter.

Unlike the industrial city of Avilés in Spain (Ordóñez et al., 2003) and other cities such as Madrid (De Miguel et al., 1997) and Hong Kong (Tanner et al., 2008; Li et al., 2001), the contribution of the transportation sector to local Pb pollution in Zhuzhou was undistinguishable. This may be a result of the leaded gasoline in China has been phased out for more than 10 years (Li et al., 2012). But for Madrid and Hong Kong, the results may reflect the influence of leaded gasoline on the urban Pb pollution a few decades ago. Other potential sources to metals in street dust of Zhuzhou, e.g. coal-fired power plant (MI 4 in Fig. 1), could not be easily distinguished, and this probably was due to the exceptionally high levels of metal/metalloids present in particulates derived from the Pb/Zn smelter (cf. previous reports dealing with analysis of particulate from the Pb/Zn smelters (Guo and Zhao, 2008; Sterckeman et al., 2002), that dimmed the impact of power plant (fly ash from coal-fired power plants typically contain metals in the concentration range up to hundreds of mg kg^{-1} (Iwashita et al., 2007)).

3.3. Pollution assessment

Compared with the elemental reference values of Hunan soils (Table 3), the enrichment factors (median/reference value) ranged from 1.1 (Tl) to 82 (Cd), demonstrating accumulation of all elements in the street dust of Zhuzhou. The pollution status of the analyzed 17 trace metal/metalloids in street dust of Zhuzhou city was evaluated by using the concept of geoaccumulation index. Fig. 5 indicates that the severity of pollution gauged by the median of geoaccumulation index value decreased in the following order for the elements: Cd > In > Zn > Ag > Pb > Sb > Cu > Bi > W > As > Mo > Hg > Cr > Ni > Tl > Co > Ga, and the difference is checked and marked with the same or different letters (Fig. 5). The filled contours of I_{geo} value of Cd and W were showed in Fig. 6, and maps of rest elements are demonstrated in Fig. S2. The pollution status of Cd, In, Zn, Ag and Pb were severe in Zhuzhou, with overall medians of geoaccumulation index >2, belonging to classes of moderate to extreme contamination (cf. Table 2). In the vicinity of the Pb/Zn smelter, the maximum geoaccumulation indices were as high as 11.84 and 10.77 for Cd and In, respectively. However, some elements (Ni, Tl, Co, and Ga) exhibit median of $I_{geo} < 0$, indicating a largely uncontaminated status (See Figs. 5 and 2S and Table 2). The medians of geoaccumulation index of other trace metal/metalloids (Sb, Cu, Bi, W, As, Mo, Hg, Cr) varied inbetween 0 to 2, with contamination status from uncontaminated to moderate contaminated.

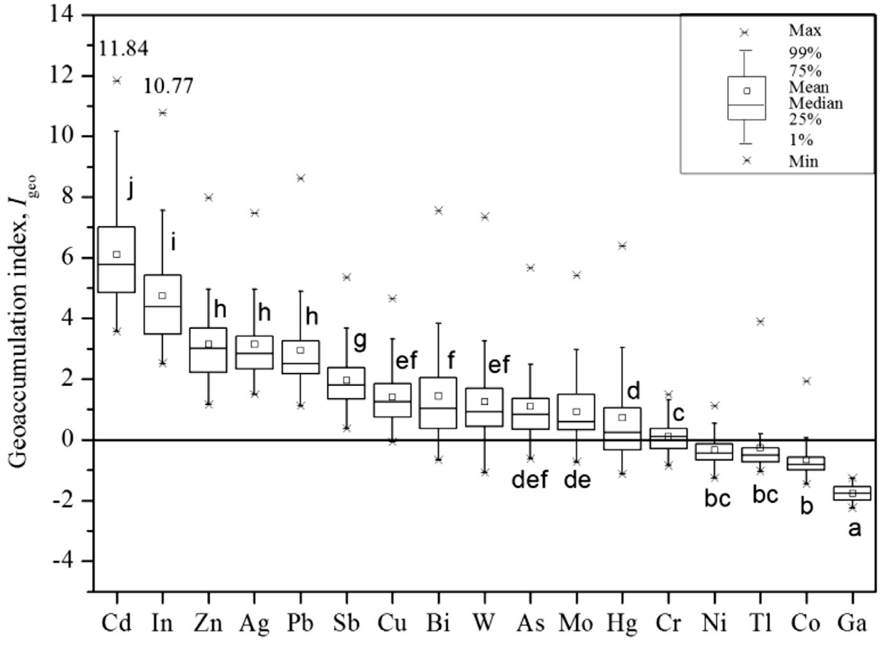

Fig. 5. Box plot of geoaccumulation index value (I_{geo}) of 17 trace metal/metalloids in street dust of Zhuzhou city. Note: different letters aside the box of each elements indicated the difference of the mean is significant ($p < 0.05$).

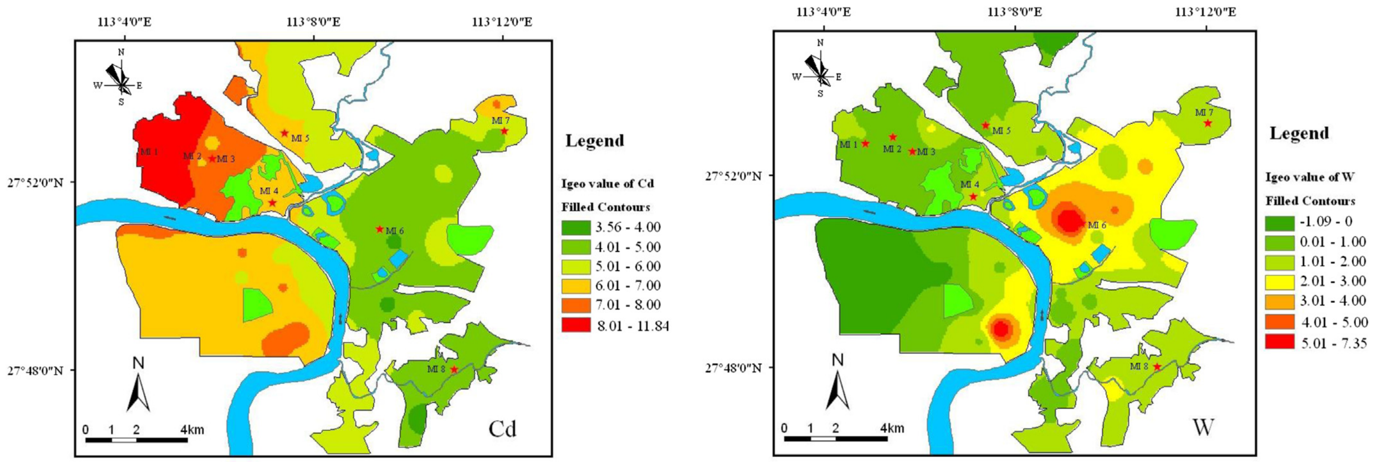

Fig. 6. Filled contours of geoaccumulation index value (I_{geo}) of Cd and W in street dust of Zhuzhou city.

On the whole, the pollution caused by the hard alloy plant (represented by W, Mo and Co) was less severe, and largely confined to a limited zone, while the pollution introduced by the Pb/Zn smelter was overwhelming and influenced a large area downwind of the source, which unfortunately is a densely populated area.

4. Conclusions

In the present study, the spatial distribution, main sources, and pollution status of 17 trace metal/metalloids in the street dusts in Zhuzhou, China have been scrutinized. Decades of Pb/Zn smelting operations in Zhuzhou has caused extensive metal pollution of Pb, Zn, Cd, Cu, As, Hg, Bi, In, Tl, Sb, Ag, Sn and Ga in street dusts, while a hard alloy plant introduced W, Mo, Co pollution. It was found that Cd, In, Zn, Ag and Pb exhibit the most serious pollution status followed by Sb, Cu, Bi, W, As, Mo, Hg and Cr that can be regarded to be moderately enriched. Remaining elements investigated (Ni, Tl, Co and Ga) were at uncontaminated levels. The northwestern part of the city, where the Pb/Zn smelter is located, form a zone of severe metal pollution.

Although control measures for reducing trace metal/metalloid concentrations in street dusts could be implemented through reinforcing the street sweeping, replacement of contaminated urban soil/street dust with clear soil (Amato et al., 2010; Boreland and Lyle, 2006; Douay et al., 2008b), the priority strategy for Zhuzhou must eventually involve restriction of the emissions from the metallurgy/machinery plants, since this is the most cost effective way of pollution control.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.07.041.

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