

Multivariate statistical and lead isotopic analyses approach to identify heavy metal sources in topsoil from the industrial zone of Beijing Capital Iron and Steel Factory

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Received: 5 December 2016 / Accepted: 18 April 2017 / Published online: 6 May 2017
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Abstract Heavy metals are considered toxic to humans and ecosystems. In the present study, heavy metal concentration in soil was investigated using the single pollution index (PI_i), the integrated Nemerow pollution index (PIN), and the geoaccumulation index (I_{geo}) to determine metal accumulation and its pollution status at the abandoned site of the Capital Iron and Steel Factory in Beijing and its surrounding area. Multivariate statistical (principal component analysis and correlation analysis), geostatistical analysis (ArcGIS tool), combined with stable Pb isotopic ratios, were applied to explore the characteristics of heavy metal pollution and the possible sources of pollutants. The results indicated that heavy metal elements show different degrees of accumulation in the study area, the observed trend of the enrichment factors, and the geoaccumulation index was Hg > Cd > Zn > Cr > Pb > Cu ≈ As > Ni. Hg, Cd, Zn, and Cr were the dominant elements that influenced soil quality in the study area. The Nemerow index method indicated that all of the heavy metals caused serious pollution except Ni. Multivariate statistical analysis indicated that Cd, Zn, Cu, and Pb show obvious correlation and have higher loads on the same principal component, suggesting that they had the same sources, which

are related to industrial activities and vehicle emissions. The spatial distribution maps based on ordinary kriging showed that high concentrations of heavy metals were located in the local factory area and in the southeast-northwest part of the study region, corresponding with the predominant wind directions. Analyses of lead isotopes confirmed that Pb in the study soils is predominantly derived from three Pb sources: dust generated during steel production, coal combustion, and the natural background. Moreover, the ternary mixture model based on lead isotope analysis indicates that lead in the study soils originates mainly from anthropogenic sources, which contribute much more than the natural sources. Our study could not only reveal the overall situation of heavy metal contamination, but also identify the specific pollution sources.

Keywords Soil · Heavy metal · Pollution assessment · Sources identification · Multivariate statistical analysis · Pb isotopes

With the development of urbanization and urban planning, more and more industrial enterprises would continuously be closed down or relocated from the city center. Soils at former industrial sites are particularly prone to having relatively high concentrations of heavy metals derived from the discharge of a variety of industrial pollutants in the form of gasses, liquids, and solids (Fakoyade and Onianwa 2002). If not properly managed, the remaining sites which would be redeveloped for business or construction may have a long-term potential impact on the surrounding environment and pose a serious health risk to the public (Wong et al. 2006; Luo et al. 2012; Osipova et al. 2015). Therefore, it is necessary to investigate, classify, and analyze the nature and degree of the hazards on the environmental, identify the potential sources of the

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pollutants, and carry out remediation of the contaminated land according to the evaluation results.

The concentration of heavy metals in soil depends primarily on the geological parent material composition, but it can also originate from anthropogenic sources like mining, smelting, electroplating, fuel production, power transmission, intensive agriculture, waste water irrigation, sludge dumping, and dust (Rattan et al. 2005). The approaches of source analysis of heavy metal include profile analysis, spatial distribution analysis, multivariate statistical analysis, isotope tracer method, etc. (Davis et al. 2009; Lv et al. 2014; Li et al. 2016; Jiang et al. 2017). Among which, geospatial methods are the most cost effective tools in understanding the location of the contaminants which also provide us with a comprehensive picture about their spatial distribution over a larger area (Nobi et al. 2010). The spatial distribution of metal concentrations is helpful to assess the possible sources of enrichment and to identify hotspots with high metal concentrations (Li et al. 2013). Multivariate statistical analysis is a useful technique for identifying common patterns in data distribution, leading to a reduction of the initial dimensions of the data sets and facilitating its interpretation (Castellano et al. 2007; Franco-Uria et al. 2009). As one of the most effective multivariate analysis methods, principal component analysis (PCA) is widely used to reduce data and to extract a smaller number of independent factors (principal components) for analyzing relationships among observed variables. The results of the PCA are easy to interpret in resulting scores and loading plots for visual inspection (Chabukdhara and Nema 2012; Shan et al. 2013). Correlation analysis is often used to identify the relationships between multiple variables and thus can provide an effective way to reveal the relationships between multiple variables and thus have been helpful for understanding the influencing factors as well as sources of chemical components (Zhang et al. 2008; Tiwari and Singh 2014).

The isotope tracer method has unparalleled advantages that it requires little databases of samples to identify the sources and pathways of heavy metal contamination (Geagea et al. 2008). Furthermore, the stable isotope composition is characteristic for the pollution source. And it was relatively fixed in the process of pollutant transference and transformation (Cheng and Hu 2010). At present, precise analysis results of stable isotope ratios can be easily obtained. So, stable isotope analyses can be applied to the pollution affair arbitration, source apportioning, and trail pollutants. The isotopic composition of Pb has been extensively applied to identify the sources and transport pathways of Pb in studies of Pb contamination in different environmental media including soils (Huang et al. 2012; Li et al. 2012; Walraven et al. 2014; Cuvier et al. 2016; Nikolaj et al. 2016), sediments (Sun et al. 2011; Wijaya et al. 2013; Hosono et al. 2016), plants (Huang et al. 2012; Deng et al. 2016), and atmospheric aerosols (Ewing et al. 2010; Zhu et al. 2010). Lead isotopic characterization appears to be applicable as a “fingerprinting” tool for tracing the sources of Pb pollution.

Beijing Capital Iron and Steel Factory was formally located in the Shijingshan industrial area, downtown Beijing, China. It was one of the largest steel makers in the area but relocated its factory in 2011. The entire industrial area (approximately 8.5 km²) was converted into a comprehensive service center for business administrative offices and tourism. However, the area might have been polluted by industrial activities, such as coking, steel refining, sintering, iron making, casting and coating, and effluent discharge.

Therefore, the primary objectives of this study are the following: (1) determine the concentration of heavy metals (As, Hg, Cr, Cd, Cu, Zn, Pb, Ni, Mn, and Fe) in surface soil collected from the Beijing Capital Iron and Steel Factory area and the surrounding area; (2) evaluate the present condition of the soil quality; (3) map the distributions of each metal with geostatistical analysis; and (4) identify the pollution source of these heavy metals using multivariate analysis and Pb isotope analyses.

Materials and methods

Study site description

This study was carried out in the original Beijing Capital Iron and Steel Factory Zone and its surrounding area (E 122°6.5′~122°12.8′, N 39°52.2′~39°56.7′), which is located in the Shijingshan District in the west of Beijing. The area is characterized by a temperate monsoon climate (hot rainy summers and cold dry winters) with an annual average regional temperature of 13.4 °C and annual rainfall of 500–700 mm. The prevailing wind directions in winter and spring are NW and N, respectively, with SE winds prevailing during the summer. The investigated area comprised of two parts: the former plant area and its surrounding area.

Sampling and pretreatment

A total of 136 samples, consisting of 130 samples of surface soil, 2 background soils, 2 coal fly ash samples, and 2 core samples, were collected in the study area (Fig. 1). The sampling points of topsoils (0~10 cm) were randomly distributed in the study area based on a regular grid of 200 × 200 m in the former plant area, and each grid had at least one sampling point. Approximately, a 800 × 800-m sampling area was chosen in the surrounding area. To ensure the representativeness of the samples, three subsamples were gathered with 10 m away from each other and mixed properly to obtain a composite sample mixture from each sampling point. Global positioning systems (GPS) were used to locate the sampling locations throughout the sampling process. The location of the background soil was chosen far from industry, traffic, and residential area. Soil

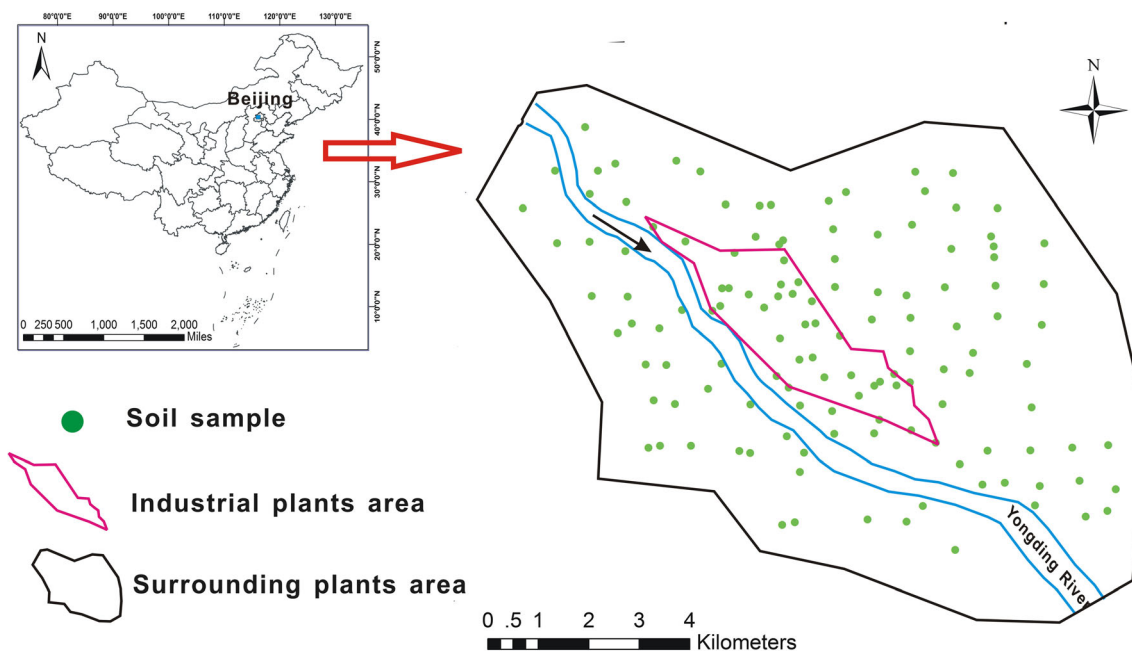


Fig. 1 Study area and sampling sites

samples comprising of five individual cores collected at 0–20 cm depth were collected from the background sites. Coal and coal fly ash samples were collected from the coking plant of the factory.

After well mixed, the samples were placed in polythene plastic bags for transport to the laboratory. Samples were naturally air-dried at room temperature and sieved through a 2.0-mm sieve to remove plants, stones, coarse materials, and other debris. Portions of the samples were pulverized using an agate mortar and passed through a 100-mesh nylon sieve for subsequent analysis. All procedures of handling were carried out without contacting any metals to avoid potential cross-contamination of the samples.

Physical and chemical analysis

Soil pH was measured in a 1:5 soil-to-water suspension after stirring for 2 h (Liang et al. 2013). For the analysis of heavy metals, the soil samples were digested using a tri-acid mixture. Briefly, 0.1 g of dry sample was placed in a Teflon crucible with 9 mL HNO₃, 3 mL HF, and 1 mL HClO₄. The solution was then heated successively to 190 °C in a heating block until it was nearly dry. The procedure was repeated with 1 mL HF and 1 mL HClO₄ in order to totally remove silica from the sample. After evaporating the digestion liquids to near dryness to remove HF and HClO₄, the residuals were re-dissolved by HNO₃ (2%) and diluted with distilled water. Water used for dilution and dissolution was purified using a Millipore deionizing system at 18.2 MΩ. HF, HNO₃, and HClO₄ were Suprapur reagents. The solutions from the digested samples were stored at 4 °C until analysis. The total Hg and As were measured

by atomic fluorescence spectrophotometer (AFS9800, HaiGuang, CHN); the other metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer, USA). Standard reference materials (GSS- and GSD-) obtained from the Center of National Standard Reference Materials of China, as well as blank samples, were included in each batch of analyses for quality assurance and quality control (QA/QC) procedures. All samples were analyzed in duplicate and the analytical precision was accepted when the relative standard deviation was within 5%.

The lead isotope ratio determinations were carried out by inductively coupled plasma mass spectrometry (ICP-MS, X Series 2, Thermo Fisher, USA). Precision and accuracy were verified frequently after every six analyses using the certified standard reference material SRM 981 (National Institute of Standards and Technology, Gaithersburg, USA). Each solution was repeatedly measured for six times. Repeated measurements of the SRM 981 Pb reference material and samples over different analytical sessions showed uncertainties of 0.3% for ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb.

Methods of heavy metal pollution assessment

To quantify the contamination risk and obtain the potential contaminated region, the single pollution index (PI_i), the integrated Nemerow pollution index (PI_N), and the geoaccumulation index (I_{geo}) evaluation method were applied for this study.

The PI_i of each metal was defined as the ratio of its concentration to the reference value of the corresponding metal using the following equation (Wei and Yang 2010):

$$PI_i = C_i / S_i \quad (1)$$

where PI_i is the pollution index corresponding to each sample, C_i is the detected concentration of each heavy metal (i), and S_i is the background values. The PI_i of each metal was calculated, and classified as either low ($PI_i \leq 1$), moderate ($1 < PI_i \leq 3$), or high contamination ($PI_i > 3$).

The integrated Nemerow pollution index (PI_N) was used to evaluate the overall level of soil heavy metal pollution by integrating the PI_i values of the test metals (Chen et al. 2012). This method emphasizes the influence of the major pollutants, and reflects the average pollutant concentration relative to their objective levels (Liang et al. 2013). The integrated Nemerow pollution index is expressed as follows:

$$PI_N = \sqrt{\frac{\text{Max}PI_i^2 + \text{Ave}PI_i^2}{2}} \quad (2)$$

where $\text{Max}PI_i$ and $\text{Ave}PI_i$ are the maximum and average value of the pollution indices for individual heavy metals, respectively. According to the PI_N value, the soil quality concerning heavy metal safety was classified as safety ($PI_N \leq 0.7$), warning ($0.7 < PI_N \leq 1$), light pollution ($1 < PI_N \leq 2$), moderate pollution ($2 < PI_N \leq 3$), and heavy pollution ($PI_N > 3$).

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and preindustrial concentrations originally used with bottom sediments (Muller 1969); It is calculated by the equation:

$$I_{geo} = \log_2 \left(C_n / 1.5B_n \right) \quad (3)$$

where C_n is the measured concentration of the heavy metal and B_n is the background value of the corresponding element in the earth's crust. The factor 1.5 is introduced to minimize the effect of possible variations which might be attributed to lithological variations. Generally, the I_{geo} for each metal is calculated and consists of seven grades: uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$), and extremely contaminated ($I_{geo} \geq 5$).

Statistical analysis

Mathematical and statistical analyses were performed using Microsoft Excel (Ver. 2010) and the SPSS 22.0 software in

this study. The correlations between the original variables are presented in the form of nonparametric Pearson correlation coefficients. In addition, the Bartlett sphericity test and Kaiser-Meyer-Olkin test indicated that the normalized data were suitable for PCA. Varimax with Kaiser Normalization rotation was applied to maximize the variances of the factor loadings across variances for each factor. The spatial distribution of heavy metals in topsoils was analyzed using ArcGIS (Ver. 10.1, ESRI). Kriging interpolations were conducted to visually examine the spatial distribution of the topsoil heavy metal concentrations.

Results and discussion

Descriptive statistics

The statistical characteristics of soil heavy metals are listed in Table 2. Soil pH values were in a narrow range from 7.22 to 9.84, with an average of 8.35, suggesting weak alkaline. The concentrations of several elements from the soil samples are listed in Table 1. The mean concentrations of As, Hg, Cr, Cd, Cu, Zn, Pb, Ni, Mn, and Fe in the soil samples were 12.21, 0.481, 112.54, 0.69, 33.80, 236.3, 56.64, 20.71, 1078.8, and 62,600 mg/kg, respectively. The mean concentrations of As, Hg, Cr, Cd, Cu, Zn, and Pb were all higher than their respective background values (Chen et al. 2004). In particular, Cr most often exceeded the standard, with the measurements at all 130 sampling sites surpassing the background value. Approximately, 98% of samples for Cd, 98% for Hg, 97% for Zn, 94% for Cu, 84% for Pb, and 83% for As exceeded their corresponding background values. Therefore, there was significant pollution of heavy metals in soils of study area. Concentrations of Ni were comparable to the background value, while the surface soil samples showed very high levels of Hg, Zn, and Cd, indicating serious pollution by these heavy metals. When compared with the criteria listed in the second grade environmental quality standard for soils in China (GB15618–1995), approximately 43, 11.5, 10.8, and 8.5% of the soil samples were moderately or heavily polluted by Cd, As, Zn, and Hg, respectively. The concentrations of Pb, Zn, Cd, and Hg in the soils showed greater spatial heterogeneity than the concentrations of the other heavy metals across the study area. In comparison, Ni concentrations were quite homogeneous, with coefficients of variation (CV) of 0.29. It has been reported that the coefficient of variation values of heavy metals dominated by natural sources are relatively low, while CV values of heavy metals affected by anthropogenic sources are quite high (Han et al. 2006). Accordingly, Pb, Zn, Cd, and Hg concentrations in surface soils tend to be affected by anthropogenic activities, while Ni may be more often associated with natural sources.

Table 1 Statistics of the determined elements in soil samples

Metal	Concentrations (mg/kg)			SD	CV	BV (mg/kg)	BV-contamination rate (%)	GV (mg/kg)	GV-exceeding rate (%)
	Minimum	Maximum	Mean						
As	3.26	41.55	12.21	7.64	0.63	7.09	83.08	20	11.54
Hg	0.024	7.469	0.481	0.89	1.85	0.044	98.46	1	8.46
Cr	41.86	750.28	112.54	83.82	0.75	29.8	100	250	4.62
Cd	0.08	4.28	0.69	0.60	0.87	0.119	98.46	0.6	43.08
Cu	10.46	136.42	33.80	17.67	0.52	18.7	93.85	100	2.31
Zn	40.1	3484	236.3	376.7	1.59	57.5	96.92	300	10.77
Pb	18.40	693	56.64	73.45	1.30	24.6	83.85	350	0.77
Ni	5.53	37.77	20.71	6.10	0.29	26.8	14.62	60	0
Mn	487.4	2794	1078.8	637.6	0.59	nd	nd	nd	nd
Fe	30,300	207,300	62,600	37,500	0.60	nd	nd	nd	nd

SD standard deviation, CV coefficient of variation, BV background values, GV guideline values, nd no data is available

Assessment of heavy metal pollution

The levels of heavy metal pollution in the surface soils from the study area based on the single pollution index, the integrated Nemerow pollution index, and the geoaccumulation index evaluation methods are shown in Table 2 and varied greatly across the different metals. The mean values of PI_i decrease in the order of $Hg > Cd > Zn > Cr > Pb > Cu \approx As > Ni$. The mean PI_i for Hg (10.94), Cd (5.80), Zn (4.11), and Cr (3.78) were higher than 3, which indicated high pollution by these metals, while the mean PI_i for Ni (0.77) was less than 1, which indicated low pollution by Ni in the study area. According to the integrated Nemerow pollution index, all analyzed metals except Ni cause heavy pollution ($PI_N > 3$) due to the fact that the PI_N calculation considered the elements with extremely high loadings, which is represented by a maximum value of PI_i . The high PI_N value of this area is dominated by extremely high concentrations of heavy metals at some sites. The I_{geo} value of each test metal is distributed in following decreasing order: $Hg > Cd > Zn > Cr > Pb > Cu > As > Ni$.

Hg had a relatively high I_{geo} value (2.87), and was classified as being responsible for moderate to heavy pollution. The I_{geo} of Cd, Cr, and Zn was 1.95, 1.33, and 1.45, respectively, and categorized as moderate pollution. Overall, the pollution levels caused by Hg, Cd, Zn, and Cr were relatively high, resulting in a high potential risk to environmental quality, ecology, and residents' health, which should be paid great attention on. The conclusions drawn in this work are in accordance with previous studies carried out in a small urban area of the Capital Iron and Steel Factory (Chen and Cui 2010), as well as in a steel industrial city Anshan of China (Xiao et al. 2015).

Multivariate statistical analysis results

Correlation coefficient analysis

The Pearson correlation analysis results for heavy metals in the soils of the study area are summarized in Table 3. Inter-element relationships provided interesting information on the sources and pathways of the heavy metals. The results

Table 2 Pollution indices of test metals in the surface soils from the study area

Metal	Single pollution index			Nemerow pollution index	Geoaccumulation index
	Minimum	Maximum	Mean		
As	0.46	5.86	1.72	4.32	0.20
Hg	0.54	169.74	10.94	120.27	2.87
Cr	1.40	25.18	3.78	18.00	1.33
Cd	0.67	35.97	5.80	25.76	1.95
Cu	0.56	7.30	1.81	5.31	0.27
Zn	0.70	60.59	4.11	42.94	1.45
Pb	0.75	28.17	2.30	19.99	0.62
Ni	0.21	1.41	0.77	1.14	-0.96

Table 3 Pearson correlation coefficients between the test metals

Metal	Hg	Cd	Cr	Cu	Pb	Zn	As	Ni	Mn	Fe
Hg	1									
Cd	0.175*	1								
Cr	-0.029	0.116	1							
Cu	0.179*	0.343**	0.074	1						
Pb	0.190*	0.634**	0.111	0.366**	1					
Zn	0.225*	0.530**	0.157	0.242**	0.882**	1				
As	0.169	0.476**	0.001	0.074	0.332**	0.310**	1			
Ni	0.083	0.158	0.032	0.111	0.098	0.093	-0.110	1		
Mn	0.039	0.202*	0.674**	0.026	0.186*	0.223*	0.048	0.012	1	
Fe	0.038	0.216*	0.583**	0.083	0.222*	0.300**	-0.002	0.079	0.491**	1

Correlation significant at * $p < 0.05$ level; ** $p < 0.01$ level

revealed significantly positive correlations ($p < 0.01$) between Cd, Cu, Pb, and Zn, indicating significant homology. In addition, the elevated concentrations of Cu, Cd, Pb, and Zn, which further indicated that the degree of pollution with these metals were affected not only by the intrinsic properties of soils but also, more importantly, by the long-term industrial activities. These results were consistent with the works of Li et al. (2009) and Lv et al. (2014) in other industrial areas of China. Other positive correlations were found among Cr, Fe, and Mn, as well as As, Cd, Pb, and Zn. Hg also revealed relatively strong correlation with Cd, Pb, and Zn, demonstrating that the concentrations of Hg partly came from the same sources as Cd, Pb, and Zn. There was no significant correlation between the concentrations of Ni with any of the other elements, indicating a degree of uniqueness, which might further support the conclusion that Ni was primarily originated from local natural sources.

Principal component analysis

Principal component analysis (PCA) has been proved to be an effective tool to infer the hypothetical source of heavy metals (Chabukdhara and Nema 2012; Liu et al. 2014). In the present study, PCA identified four components for all sites, and the percent of variance explained by each of them were calculated and presented in Table 4. The results of the factor loaded with a quartimax rotation, as well as the eigenvalues and communalities, which indicated that there were four eigenvalues higher than 1.0. Therefore, the heavy metals could be grouped into a four-component model that accounts for 73.5% of the total variance. The 31.4% variance was explained by the first principal component (F1), showing elevated loadings of Cd, Cu, Pb, and Zn, and moderate loading of As. The second principal component (F2), which accounted for 19.1% of the total variance, was predominantly by Cr, Mn, and Fe. The third principal component (F3) showed highly positive factor loading on Ni and negative loading on As, representing 12.4%

of the variance. The fourth principal component (F4) with a variance loading of 10.6% was dominated by Hg.

Principal component analysis shows that metals with higher loads on the same principal component may have the same source (Han et al. 2006; Singh et al. 2015). In general, principal component analysis data showed good agreement with correlation analysis results. Compared with the background values of Beijing soils, Cu, Pb, Cd, and Zn from the studied soils show elevated concentrations. Pb and Cu are representative elements for pollution by traffic (Zhang 2010), and Zn and Cd are commonly used as identification factors for pollution of industrial origin (Friedlander 1973). Therefore, it seemed reasonable to infer that Cd, Cu, Pb, and Zn in the surface soil of the study area can be concluded from the sources of traffic pollution (automobile exhaust emissions, and wear of automobile tires, etc.) and industrial activities. Romić and Romić (2003) studied the distribution of heavy metals in the surface soil of farmland, and found that Fe and Mn belong to the same factor, which is mainly controlled by natural factors. However, this study is not in agreement with the previous result. Chromium, used as an additive compound for the production of steel, can increase the wear resistance, hardness, and corrosion resistance of the steel product (Huang et al. 2009). The content of Cr, Fe, and Mn in the surface soil of the study area varies greatly. In addition, Cr was also present in high concentrations in the analyzed soils. Hence, these three elements were mainly controlled by particle deposition from the steel production as well as emissions from stockpile and transport of raw materials. The concentrations of Ni were close to or lower than the background value of Beijing, and the coefficients of variation was small. Therefore, Ni was associated with the crustal material source. In this study, Hg is an isolated anthropogenic element in multivariate analysis, which also has been demonstrated in the works of Cai et al. (2012) and Liu et al. (2016). Chen et al. (2010) reported that Hg contamination in the urban area of Beijing is marked by features of

Table 4 Total variance explained and component matrixes for heavy metals in soil

Component	Initial eigenvalues		Extraction sums of squared loadings		Rotation sums of squared loadings		Element	Component matrix				Rotated component matrix					
	Total	% of variance	Total	% of variance	Total	% of variance		F1	F2	F3	F4	F1	F2	F3	F4		
	Cumulative	%	Cumulative	%	Cumulative	%	Cumulative	%	Cumulative	%	Cumulative	%	Cumulative	%	Cumulative	%	
1	3.139	31.391	31.391	31.391	31.391	31.391	25.965	25.965	Cd	0.640	0.442	-0.346	0.318	0.859	-0.019	-0.245	-0.166
2	1.915	19.148	50.539	19.148	50.539	23.024	48.989	Cr	0.571	-0.707	-0.043	0.026	0.080	0.902	-0.081	-0.024	-0.024
3	1.243	12.425	62.964	12.425	62.964	12.281	61.270	Cu	0.612	0.390	0.296	0.064	0.689	0.040	0.274	0.258	0.258
4	1.056	10.564	73.529	10.564	73.529	12.258	73.529	Pb	0.858	0.271	0.031	0.119	0.854	0.263	0.026	0.160	0.160
5	0.763	7.634	81.162	7.634	81.162			Zn	0.781	0.163	0.120	-0.255	0.619	0.310	-0.013	0.487	0.487
6	0.609	6.086	87.248	6.086	87.248			As	0.253	0.285	-0.730	0.010	0.496	-0.130	-0.601	-0.138	-0.138
7	0.527	5.268	92.516	5.268	92.516			Ni	0.027	0.247	0.628	0.466	0.246	-0.151	0.750	-0.160	-0.160
8	0.388	3.884	96.399	3.884	96.399			Hg	0.261	0.296	0.246	-0.791	0.115	-0.091	-0.042	0.905	0.905
9	0.194	1.938	98.338	1.938	98.338			Mn	0.547	-0.692	-0.063	-0.078	0.041	0.875	-0.132	0.059	0.059
10	0.166	1.662	100.000	1.662	100.000			Fe	0.502	-0.509	0.163	0.148	0.153	0.713	0.162	-0.048	-0.048

non-point sources associated with human activities. Unlike other elements, the accumulated Hg in the surface of soil can be released into the air and widely exchanged between the soil and the air, thus can be transported over long distances (Jin et al. 2008). Hence, the sources of Hg in the topsoil were distinguished from other elements in the study area. However, not all heavy metals could be distributed on one component; for example, As had moderate loading on F1 and negative loading on F3. This suggested that As might be controlled by more factors.

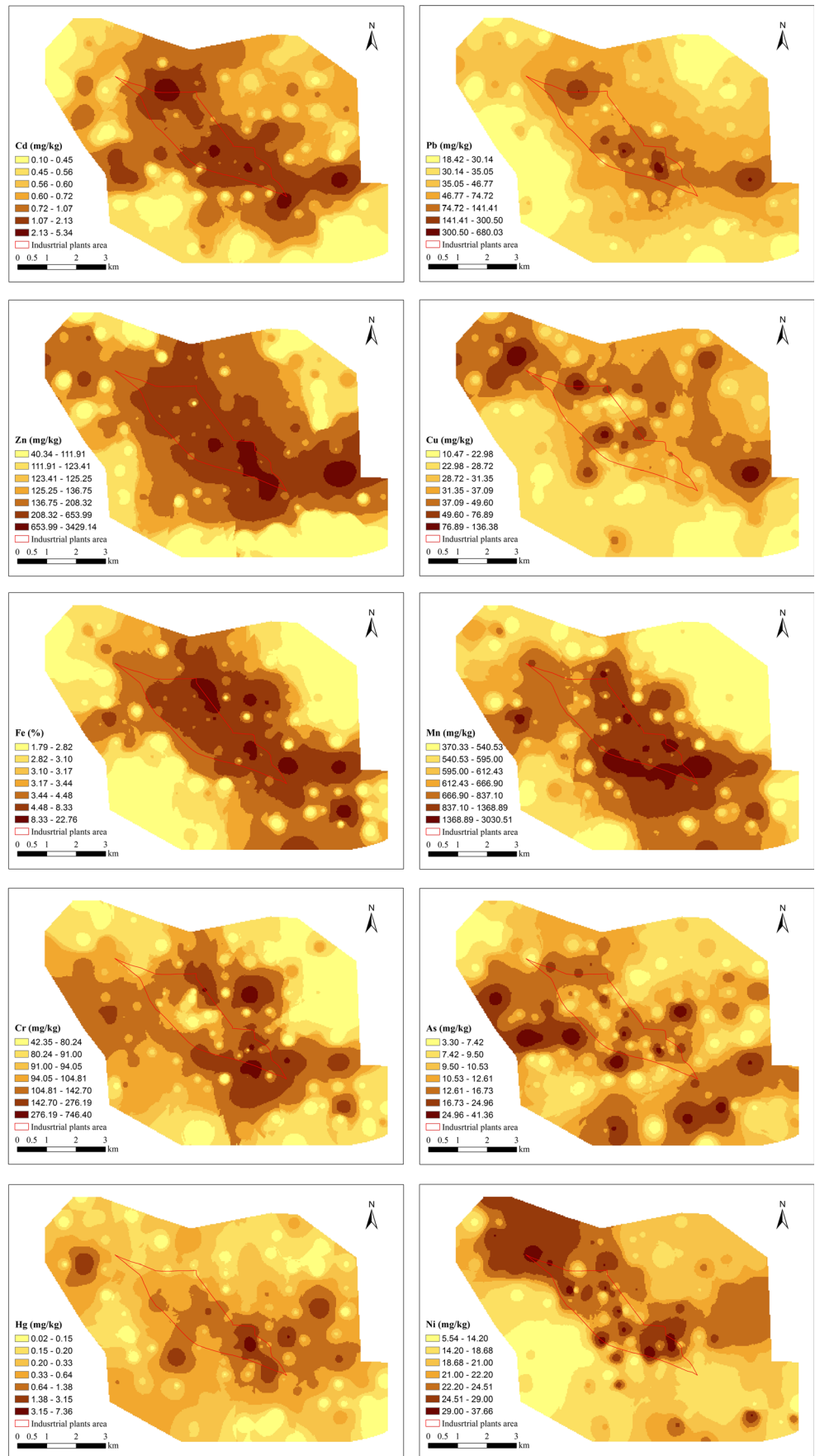
Spatial distribution of heavy metals

The spatial distributions of heavy metal concentrations in topsoils from the study area obtained by ordinary kriging and quantile classification method are presented in Fig. 2. In general, darker colors indicate overlap of higher metal concentrations; lighter colors suggest both low concentrations and little overlap of areas with high metal concentrations. The spatial distribution maps indicate high variation of the heavy metal concentrations in soil. It may be concluded from Fig. 2 that spatial distributions of Pb, Cd, and Zn have similar spatial variations, coinciding with their close correlation obtained by statistical analysis; likewise, similar features were found between Fe and Mn. Analysis on the spatial distribution pattern provided a refinement and reconfirmation of the results in the statistical analysis, in which strong associations were found among these metals. The spatial distribution pattern also revealed that high concentration of heavy metals was recorded near the local factory area and in the southeast-northwest part of the study region. Considering the local weather, northwest wind prevailed in dry winter and spring, southeast wind prevailed in summer. Therefore, it can be preliminarily concluded that the concentrations of heavy metals were closely associated with the long-term industrial activities from the factory.

Pb isotopic compositions

Although the above results provide preliminary conclusions regarding the source of metals, further studies are necessary to obtain a better understanding of pollution sources based on isotope techniques. Twenty-three surface soil samples with relatively high Pb concentrations (10 and 13 samples were from the original factory area and surrounding area, respectively), 2 background soils, 2 coal fly ash samples, and 2 coal samples were selected for Pb isotope analysis. Owing to the lack of data concerning Pb isotope ratios of steel-making dust and vehicle exhaust particles, the Pb isotopic signatures of these two potential end-members are cited from other studies to evaluate the analytical results (Chen et al. 2008; Cao et al. 2014; Yao et al. 2015).

Fig. 2 Spatial distribution of total metals in the study area



Three-isotope plot

The relationship between the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the soil samples as well as potential end-members is shown in Fig. 3. The soil samples obtained from different sampling locations show differences in the lead isotopic composition. Lead isotope ratios in soil samples ranged from 2.0192 to 2.1446 and from 1.1468 to 1.2093 for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$, respectively. The potential end-members showed distinct isotopic compositions, which might be attributed to the broad range of isotopic compositions in soils. The Pb isotope ratios of the test soils from the surrounding area remained in a relatively narrow range, compared with those from the original factory area.

The isotopic compositions of the soil samples scatter among a triangle composed of the background soil, coal, and steel-making dust, which indicates that the soils have simultaneously suffered from the influence of industrial atmospheric deposition and natural background. In the original factory area, the Pb isotope ratios of some soils located near the steel-making dust, on the upper left portion of the diagram, are characterized by relatively low $^{208}\text{Pb}/^{206}\text{Pb}$ and high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, indicating that Pb in these soils has been influenced by the settlement of iron and steel smelting dust. For the most soils, their Pb isotopic composition fall close to those for the background soil and coal, which are clearly different from the Pb isotopic composition of the dust generated by steel production. Therefore, it is likely that Pb in these soils is mainly influenced by coal combustion and the natural background. In the process of iron ore smelting and steel making, a large amount of coal is used as fuel. The combustion of coal distributes the heavy metals in solid and gaseous products, with most of them accumulated in the ash. Some of these metals become part of the fly ash, part of them is released into the atmosphere by the stack, and finally most of them accumulate in the soil surface through wet and dry deposition.

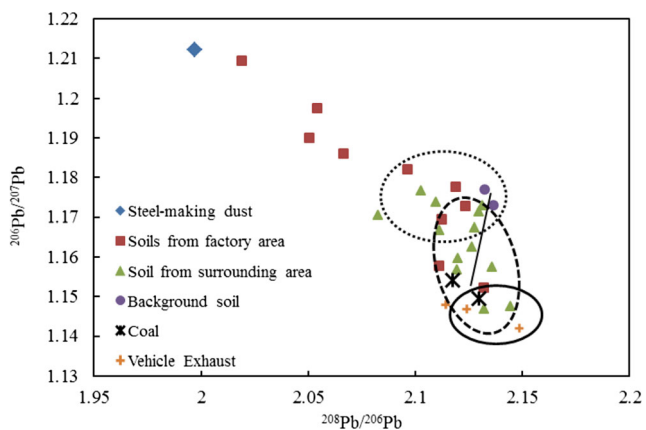


Fig. 3 Comparison between the Pb isotope composition of soil samples and various sources

Note that the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of some samples collected from the surrounding area are higher than the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of known sources, which reflect the possible existence of other sources of Pb. Former studies stated that vehicle exhaust, coal combustion, and industry emissions are considered to be three major sources of urban lead in China (Zhu et al. 2010; Zhu et al. 2013; Deng et al. 2016). The samples with high $^{208}\text{Pb}/^{206}\text{Pb}$ values plot close to the composition of vehicle exhaust particles from China as reported in previous studies suggesting that traffic discharge contributes to the surface soil in the study area.

Relative contributions

Direct measurement of three different radiogenic lead isotope ratios provides three independent equations, which potentially allow the quantification of the fractional contribution (F) from three sources to the Pb burden of a sample. The following ternary mixture model was employed to calculate the contribution of Pb from various end-members (Gobeil et al. 1995):

$$\begin{aligned} \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{sample}} &= \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_A F_A \\ &+ \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_B F_B \\ &+ \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_C F_C \end{aligned} \tag{4}$$

$$\begin{aligned} \left(\frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_{\text{sample}} &= \left(\frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_A F_A \\ &+ \left(\frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_B F_B \\ &+ \left(\frac{^{208}\text{Pb}}{^{206}\text{Pb}} \right)_C F_C \end{aligned} \tag{5}$$

$$F_A + F_B + F_C = 1 \tag{6}$$

where A, B, and C stand for the three end-members of Pb.

The relative contributions of the three end-members are shown in Table 5. For the soils from the original factory area, the average fractional contribution from the three end-members decrease in the order of background soil (38%) > steel production dust (31%) = coal combustion (31%), indicating that lead pollution in the original factory area was mainly derived by the emission of industrial activities, accounting for 62%. The contribution of the end-members differs greatly between the samples. For some soils, the contribution from steel production dust and coal combustion were as high as 85 and 91%, while in some low pollution soils, about 84% of Pb was attributed to the natural background. In the surrounding area, the Pb contribution from dust generated by steel production was relatively low with only 5%; the fractional contribution from coal combustion ranged from 17~95%, with an average of 57%, followed by the

Table 5 Relative contributions percentage of three end-members for study soils

Samples		Pb (mg/kg)	F_A	F_B	F_C
Original factory area	f1	335	0.59	0.11	0.30
	f2	693	0.85	0.23	-0.08
	f3	114	0.47	0.25	0.28
	f4	65	0.26	0.61	0.12
	f5	74	0.58	0.46	-0.04
	f6	170	-0.05	0.14	0.91
	f7	80	0.10	-0.02	0.91
	f8	48	0.06	0.74	0.20
	f9	76	0.12	0.43	0.44
	f10	53	0.10	0.84	0.06
	Mean	171	0.31	0.38	0.31
	SD	203	0.29	0.28	0.36
	CV	1.19	0.95	0.73	1.18
Surrounding area	S1	98	0.32	-0.04	0.71
	S2	139	0.04	0.09	0.86
	S3	97	0.13	0.31	0.56
	S4	60	0.21	0.53	0.26
	S5	59	0.05	0.21	0.74
	S6	308	-0.08	0.16	0.92
	S7	303	0.10	-0.05	0.95
	S8	67	0.02	0.62	0.36
	S9	91	0.02	0.79	0.19
	S10	77	0.16	0.54	0.30
	S11	94	0.01	0.82	0.17
	S12	75	0.01	0.42	0.57
	S13	78	-0.06	0.40	0.66
Mean	119	0.05	0.38	0.57	
SD	85	0.12	0.29	0.31	
CV	0.72	2.35	0.78	0.55	

SD standard deviation; CV coefficient of variation; A, B, and C steel-making dust, background soil, and coal consumption, respectively.

natural background (38%). Note that some soil samples showed negative fractional contribution, which may be due to other sources of Pb.

Conclusions

- (1) The surface soils at the abandoned site of the Capital Iron and Steel Factory in Beijing and its surrounding area were suffering heavy metal pollution in different degrees. Compared with the national standard for soil quality, 43% of the Cd concentrations were higher than the reference value in this region. Viewed from the background value of soil heavy metals, the concentrations of Cr in all samples exceeded the background levels, the observed trend of the enrichment factors, and the geoaccumulation

index was $Hg > Cd > Zn > Cr > Pb > Cu \approx As > Ni$. Hg, Cd, Zn, and Cr showed rather heavy pollution. The Nemerow index method indicated that all of the heavy metals caused serious pollution except Ni.

- (2) Correlation coefficient analysis and principal component analysis were conducted to identify the sources of heavy metals. The concentration of Ni appeared to be controlled by the parent material (natural sources), while Cd, Cu, Pb, and Zn were mainly derived from vehicle emissions and industrial activities, while Cr, Fe, and Mn were mainly associated with industrial emissions. Spatial distribution maps of heavy metal contents based on geostatistical analysis indicated similar patterns of spatial distribution for Cd, Pb, and Zn as well as for Fe and Mn. The distribution pattern also revealed that the high concentrations matched the predominant wind directions.
- (3) The Pb isotopic compositions of dust from steel production, subsoil from profile, and fire coal from Capital Iron and Steel Factory differed significantly and can be used to identify the specific sources of Pb in soil. The Pb isotopic composition of the soil collected in the vicinity of the steel plant was close to that of dust from steel production; the soil collected near the coking plant was mainly influenced by coal combustion. The major contributors of the lead in the soil of the surrounding area were coal combustion dust and background soil. This soil was also affected by dust from steel production and vehicle exhaust particles. Thus, stable isotope analyses can be applied to identify and apportion the contribution of distinct Pb sources to soil.

Acknowledgements This research was financially supported by the National High Technology Research and Development Program of China (973 Program: No. 2014CB238906), the National Natural Science Foundation of China (No. 41425014; 41625006), China Postdoctoral Science Foundation Funded Project (No. 2015 M582578), and the Feature Institute Program of the Chinese Academy of Sciences (Comprehensive Technical Scheme and Integrated Demonstration for Remediation of Soil and Groundwater in Typical Area).

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