

Distinguishing anthropogenic and natural sources of trace elements in soils undergoing recent 10-year rapid urbanization: a case of Donggang, Eastern China

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Abstract A total of 59 samples consisting of 45 topsoils samples and 14 subsoils samples were collected from urban soils of Donggang and were analyzed for soil properties and 12 trace elements. The mean contents of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn in topsoils were 5.76, 0.20, 9.88, 44.82, 17.69, 0.05, 578.96, 19.98, 28.38, 0.21, 58.88, and 58.32 mg kg⁻¹, respectively. The mean enrichment factor results suggested that Hg, Cd, Pb, Cu, Se, and Zn were enriched in topsoils compared with subsoils. Spatial distribution maps of trace elements indicated that Hg, Cd, Pb, Cu, Se, and Zn had similar patterns, with the highest values in the industrial region. There were no significant associations displayed between spatial distributions of As, Co, Cr, Mn, Ni, and V and the industrial region. Through correlation analysis, stepwise regression analysis, and redundancy analysis, three main sources of 12 trace elements were identified. Cd, Hg, and Se originated from industrial emissions and coal combustion, and As, Co, Cr, Mn, Ni, and V had a lithogenic origin.

The combination of human activities and natural sources contributed to the contents of Cu, Pb, and Zn, and the human activities included industrial and traffic emissions.

Keywords Trace elements · Sources · Redundancy analysis · Stepwise regression analysis · Geostatistics · Urban soils

Introduction

Soil is the most important reservoir of trace elements in the terrestrial ecosystem, and trace elements (especially heavy metals) in soils have been shown as an important indicator of environmental quality (Franco-Uria et al. 2009; Li et al. 2013). Toxic elements (i.e., Hg, Cd) can inherently threaten the plant growth and human health. Some elements (i.e., Se, Cu) play essential roles in maintaining the biological activities, but these elements exceeding some thresholds are also harmful to biological activities. Urban soil is an important part of the urban environment with dense population, traffic, and industry, and it is commonly characterized by unpredictable layering, poor structure, and high concentrations of several heavy metals (Manta et al. 2002). If people are exposed to soils with high heavy metal levels, their health might be affected, especially for the children and elderly (Alloway 1995). There are substantial evidences that a high Pb level in soils could affect blood Pb level, intelligence, and behavior (McDermott et al. 2011). Currently, urban soil contamination has become a serious problem in many countries, which has drawn the surge of attention from governments and people, because majority of people now live in cities (Alloway 1995; Davis et al. 2009).

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In urban soil environment, trace elements may originate from vehicle emissions, industrial discharge, and fossil fuel burning (Alloway 1995; Cachada et al. 2012; Chen et al. 2005). China is the largest developing country, where the rapid economic development occurs in the last 3 decades. Definitely, urbanization and industrialization are the most typical features of economic development in China. There are more than 1000 coal-fired plants for electricity generation and residential heating in China, most of which are located around urban regions. Jiang et al. (2005) reported that the mercury emissions from coal combustion in China have reached 219.5 t. The amount of vehicles in China has reached 137 million, which is an important factor to raise the trace elements in the cities. Some studies on trace elements have been conducted in some large cities of China (e.g., Beijing, Shanghai, Hong Kong, Guangzhou, Xi'an, and Changchun) with high degree of the industrialization and urbanization (Chen et al. 1997, 2005, 2012; Lu et al. 2007b; Shi et al. 2008; Yang et al. 2011), and significant heavy metals pollution was found significant in urban soils (Chen et al. 1999; Wei and Yang 2010). The medium and small cities, accounting for 56 % of the total amount of cities, with high percentage of the total population in China, are experiencing the rapid industrialization and urbanization in the recent decade. However, the works on the small cities are commonly ignored, and there is little information available on the source characteristics of soil trace elements in these cities in eastern China, where urban soil environment is also interfered by the intensive human activities. Therefore, the knowledge about sources and spatial patterns of trace element under the circumstance of rapid urbanization and industrialization is essential, because this would serve as a reference for city planning and urban environment quality assessment.

Several authors have used correlation analysis and principle component analysis to identify the sources of elements from natural background and human activities (Acosta et al. 2010; Facchinelli et al. 2001; Franco-Uria et al. 2009; Zhang 2006). However, these methods mentioned above are semiquantitative methods and difficult to determine the contribution of environmental factors to the contents of trace elements. Stepwise regression analysis and redundancy analysis, as the classical multivariate methods, can quantitatively link the trace elements with the environmental variables and discriminate the contribution of natural and human factors. In addition, many geostatistical techniques including ordinary kriging and indicator kriging have been used to map spatial distribution and possible hot spots of elevated concentrations of trace element contamination in urban soils (Davis et al. 2009; Lu et al. 2012; Lv et al. 2014a; McGrath et al. 2004). The combination of stepwise regression analysis, redundancy analysis, and geostatistical analysis can corroborate each other and could be an appropriate tool for sources appointment of trace elements in the complex soil environment (Lu et al. 2012; Zheng et al. 2008).

Donggang, as a new city built in 1989, is experiencing the rapid industrialization and urbanization in the last 10 years. This study presented the survey of spatial distribution delineation and pollution sources identification of 12 trace elements in urban soils of Donggang. The specific objectives of this paper were (1) to explore average concentrations and enrichment factors of trace elements, (2) to map the spatial distribution of trace elements contents, and (3) to identify the relative origins resulting from natural background or human activities.

Materials and methods

Study area

The study was conducted in the urban area of Donggang (119° 22' 50" E–119° 35' 47" E, 35° 23' 26" N–35° 28' 48" N), located in northeastern Shandong Province of Eastern China (Fig. 1). Donggang extends about 1636 km², in which the elevation ranges from 0 to 411 m above sea level. The study area is a typical continental monsoon climate. The average annual temperature is 13 °C, and the mean annual precipitation is 870 mm, most of precipitation falls between May and September (Rizhao Municipal Bureau of Statistics 2012). The rapid industrialization and urbanization occur during the last 10 years. The study area has an urban population of approximately 600,000 in 2012, growing from approximately 300,000 in 2000; currently, the urban area has increased to 80 km² from 34 km² in 2000 (Rizhao Municipal Bureau of Statistics 2012). The motorized vehicle density has grown from 0.06 million in 2000 to 0.25 million in 2012. The investigation area consists of various types of urban land use, including traffic, residential, commercial, and industrial regions, and urban green land. The major industries are metallurgical industry, metal-processing industry, coal-fired power plant, building material manufacturing, dye and texture industry, as well as plastic manufacturing, and the locations of main industrial sites are shown in Fig. 1, most of which are located within the industrial region in the northwestern part of study area. Traffic, residential, and commercial areas are mainly concentrated in the eastern and southern areas.

Soil sampling and chemical analysis

In this study, 59 samples were collected from urban soils of Donggang, including 45 topsoil samples (0–20 cm) and 14 subsoil samples (150–200 cm). All the samples were analyzed for soil pH, organic matter (OM), four minerals (Fe₂O₃, CaO, MgO, and Al₂O₃), and 12 trace elements (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn).

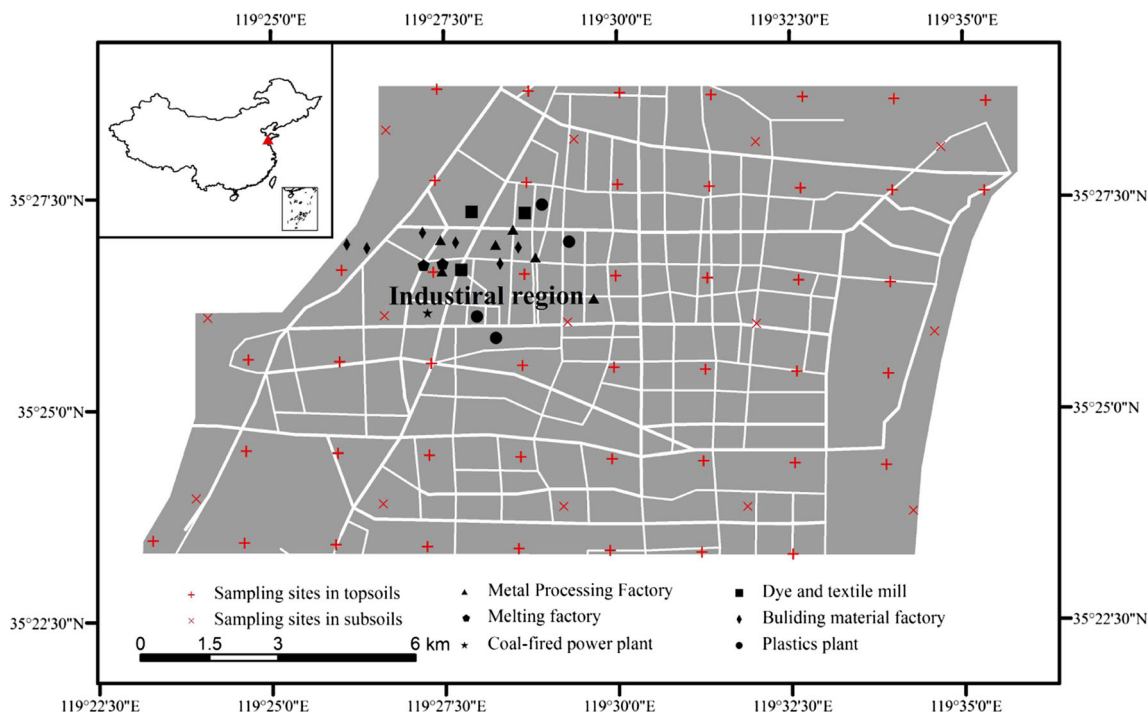


Fig. 1 The location of study area with sampling sites

The sampling sites were placed in the study area using the grid design. The samples in topsoils were obtained at a density of 2×2-km grids, and at every sampling site, four to six subsamples from upper 20-cm soils were taken and mixed thoroughly to obtain a composite sample. Sampling sites of subsoils were placed at a density of one sample for every 16 km². Samples were collected between depths of 150 and 200 cm, representing the lithogenic level that was free from anthropogenic influence. All the collected soil samples were stored in polyethylene bags for transportation and storage. Geographic coordinates of all sample sites were recorded using a global position system (GPS) with 10-m precision. Locations of sampling sites are shown in Fig. 1.

Soil pH values were measured by a pH meter in a 1:2.5 soil-water suspension. OM contents were determined using oil bath-K₂CrO₇ titration (Lu 2000). Fe₂O₃, MgO, CaO, and Al₂O₃ were investigated by X-ray fluorescence spectrometry (XRF). The samples for analyzing Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn were digested using H₂SO₄-HNO₃-HF, and the levels of Cr, Co, Cu, Mn, Ni, V, and Zn concentrations in the samples were determined by flame atomic absorption spectrophotometer, while Cd and Pb were determined by graphite furnace atomic absorption spectrophotometer (Lu 2000). The samples for As, Se, and Hg determination were digested by H₂SO₄-HNO₃-HMnO₄ and were determined with atomic fluorescence spectrometer (Lu 2000). A standard reference material, GSS-1 soil, obtained from Center for National Standard Reference Material of China, was included in chemical analysis. Recoveries of all elements varied 10±100 %.

Statistical and geostatistical analysis

Pearson correlation coefficients were performed to determine the relationships among trace elements in the urban soils. Analysis of variance (ANOVA) was used to compare the mean contents of samples between topsoils and subsoils. Pearson correlation coefficients and ANOVA were conducted using SPSS 19.0 (IBM, USA). Redundancy analysis (RDA) was applied to evaluate the data to acquire the sources of trace elements and was carried out using CANOCO 4.5 (Microcomputer Power, Inc., Ithaca, NY, USA). Before the RDA, detrended correspondence analysis (DCA) for trace elements with lengths of gradient lower than 3 confirmed that RDA was appropriate to examine the environmental factors influencing the contents of trace elements. Manual forward selection was conducted in the RDA to determine the significance of environmental factors ($P < 0.05$) using Monte Carlo tests (999 permutations). pH, OM, Al₂O₃, Fe₂O₃, MgO, and CaO were the soil properties affecting the contents of trace elements in soils, while density of traffic lines, density of industrial sites, population density, and land use types (industrial zone, urban green land, and residential and commercial zone) represented the human factors. In particular, land use types were categorical variables and were included in regression and RDA with the classical approach of “dummy variables,” which assigned the number 1 for presence and 0 for absence (Liu et al. 2013). Ordinary kriging was used to map the spatial distribution of trace elements contents and was conducted using ArcGIS 9.3 (Esri Inc. USA).

Results

Descriptive statistics of soil properties and trace elements contents

The mean value of soil pH in topsoils was 7.09, varying from 5.09 to 9.14, indicating that the soil totally was close to neutral property. The pH value in subsoils had a mean value of 7.43 and was significantly higher than that in topsoils. These may be attributed to the eluviation process of base cations (Alloway 1995; Jenny 1941). The average content of organic matter (OM) in topsoils was 1.35 %, significantly higher than the content in subsoils (0.50 %). Al_2O_3 , Fe_2O_3 , MgO, and CaO had a mean value of 13.14, 3.42, 0.90, and 1.62 % in topsoils, with the ranges of 6.86–14.99, 1.01–4.84, 0.16–2.89, and 0.64–2.91 %, respectively. The mean contents of Al_2O_3 , Fe_2O_3 , and MgO in topsoils were significantly lower than those in subsoils due to the eluviation process (Jenny 1941), while the mean content of CaO in topsoils was close to subsoils.

Through analysis of variance (ANOVA), the mean contents of Cd, Cu, Hg, Pb, Se, and Zn in topsoils were significantly higher than those in subsoils (Table 1), suggesting possible human inputs, while the mean contents of As, Cr, Co, Mn, Ni, and V in topsoils were significantly lower than those in subsoils. The mean contents of Cd, Hg, Mn, Pb, Se, and Zn in topsoils were higher than the background values (BV) of eastern Shandong province (Dai et al. 2011), while those of As, Cr, Co, Cu, Ni and V in topsoils were lower than the BV of eastern Shandong Province. The coefficient of variation (CV), as independent measure of relative dispersion, is a useful tool to compare distributions where units may be different (Weinberg and Abramowitz 2008). The elements dominated by a natural source may have low CVs, while the CVs of the elements affected by anthropogenic sources should be quite high. Coefficients of variation in topsoils varied from 0.20 to 3.50, which followed the decreasing order of $\text{Cd} > \text{Hg} > \text{Cr} > \text{Se} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Mn} > \text{As} > \text{Pb} > \text{V}$. It should be noted that the CVs of Hg and Cd were significantly higher than other elements; the two elements may be dominated by anthropogenic sources. The skewness is a measure for the degree of symmetry in the data distribution (Weinberg and Abramowitz 2008). All the raw data of the trace elements in topsoils except for V and Pb were positively skewed with skewness higher than 0. This is common in urban soils due to point pollution inputs (Manta et al. 2002; Yang et al. 2011). The Kolmogorov-Smirnov test (K-S test) can identify if the data follows a normal distribution, in order to facilitate the following ordinary kriging interpolation. The K-S test confirmed that the concentrations of Cd, Cr, Cu, Hg, Pb, Se, and Zn in the topsoils were non-normally distributed, whereas As, Co, Mn, Ni, and V concentrations were normally distributed. After log-transformation, the contents of Cd, Cr, Cu, and Zn followed a lognormal distribution, while the distributions of Pb, Se, and Hg were still non-normal.

Spatial distribution of trace elements in topsoils

Ordinary kriging was used to delineate spatial distribution maps of trace elements contents. Table 2 showed the results of variograms fitting, with Gaussian model for As, Cr, Ni, and Zn, spherical model for Cd, Co, Hg, Mn, Pb, Se, and V, as well as exponential model for Cu. The R^2 values ranged from 0.771 to 0.999, and the residuals values were close to 0, which showed that the variograms models gave good descriptions of spatial variations. The nugget/sill ratio varied between 2.0 and 34.8 %, and thus the trace elements had relatively strong spatial dependence.

Spatial patterns of 12 trace elements in soils are shown in Fig. 2. Spatial distributions of Cr and Ni were similar, and the hot spots with high values were located in the northern and southwestern parts of the study area. Co, Mn, and V also followed similar patterns with higher concentrations trending NE-SW across the total study area. The hot spot with the highest values of As was associated with the southwestern part of study area. The spatial distribution of Cd, Cu, Hg, Pb, Se, and Zn showed similar trends with high values in northwestern part of study area.

The hot spots with highest values can be identified through overlapping the kriged map and industrial pattern (Figs. 1 and 2). The high values of Cd, Cu, Hg, Pb, Se, and Zn were associated with industrial region, where smelting factories, metal-processing factories, coal-fired power plant, building materials factories, petroleum refining plant, dye and texture mills, and plastic factory were concentrated. The enrichment of these elements close to industrial region was easily linked to human activities arising from industrial production processes, whereas there were no significant associations displayed between spatial distribution of As, Co, Cr, Mn, Ni, and V and industrial sites, indicating that the hot spots may be derived from the high geologic background.

Enrichment factor results of trace elements

Enrichment factor (EF), evidenced by the concentration ratio between upper and underlying layers, is an effective method to identify the anthropogenic or natural sources of trace elements in soils (Lv et al. 2014b). Commonly, topsoil layers were affected by human inputs, while the subsoils represent the lithogenic content due to slight anthropic effect. In the present study, one sample in subsoils could be linked to four samples or less in topsoils (Fig. 1). Commonly, a natural enrichment has the EF value less than 2 (Facchinelli et al. 2001). The mean EFs of As, Co, Cr, Mn, Ni, and V were less than or close to 1, with the average contents of 1.03, 0.90, 1.16, 0.88, 1.00, and 1.05 (Fig. 3), indicating that those elements in topsoils were not enriched and may come from parent rock. The mean EFs of Cu, Pb, and Zn in the range 1–2, while those of Cd, Hg, and Se were higher than 2, indicating that those

Table 1 Descriptive statistics of 12 trace elements in urban soils per milligram per kilogram

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn	
Topsoils	Minimum	3.50	0.02	2.10	7.40	3.00	162.00	2.60	11.70	0.04	15.50	9.10	
	Maximum	9.50	4.81	17.90	207.20	49.60	1166.00	72.00	40.50	0.82	81.00	117.40	
	Mean	5.76	0.20a	9.88	44.82	17.69	578.96	19.98	28.38	0.21	58.88	58.32	
	Median	5.50	0.09	10.10	40.10	16.10	568.00	19.60	28.00	0.19	58.70	56.00	
	SD	1.46	0.70	2.64	26.68	8.96	150.61	9.16	5.89	0.11	11.93	20.05	
	CV	0.25	3.50	0.27	0.60	0.51	0.26	0.46	0.21	0.53	0.20	0.34	
	Skewness	0.81	6.68	0.15	5.26	2.16	0.92	4.15	-0.11	3.87	-1.05	0.75	
	Kurtosis	0.37	44.77	2.62	32.68	5.86	3.15	24.36	0.45	20.25	3.10	2.33	
	Minimum	2.72	0.04	5.10	23.20	6.90	0.01	261.00	11.00	13.00	0.08	37.80	20.07
	Maximum	12.48	0.34	16.90	211.20	62.20	0.04	1148.00	91.00	26.64	0.22	96.00	59.47
Subsoils	Mean	6.48	0.08b	11.33	50.64	16.39	700.75	24.71	18.41	0.13	66.06	40.62	
	Median	5.68	0.06	11.40	38.10	13.30	619.00	20.95	17.79	0.12	63.25	40.23	
	SD	2.76	0.07	3.18	44.69	12.80	222.75	18.45	3.56	0.04	16.18	9.91	
	CV	0.43	0.88	0.28	0.88	0.78	0.32	0.75	0.19	0.34	0.24	0.24	
	Skewness	1.07	3.74	-0.28	3.47	3.41	0.28	3.45	0.58	0.77	-0.05	-0.25	
	Kurtosis	0.37	14.53	-0.02	12.94	12.72	-1.23	0.07	0.52	-0.60	-0.74	0.46	
	F	2.282*	3.863**	2.463*	2.549*	2.379*	7.092**	3.770**	2.511*	2.461*	5.003**	2.229*	
	BV (Dai et al. 2011)	6.30	0.108	11.00	56.20	19.60	0.029	552.00	23.50	25.40	0.16	68.50	56.10

BV background values of eastern Shandong province

*Significant at the 0.05 level

**Significant at the 0.01 level

Table 2 The results of variogram modeling for trace elements

	Model	Nugget	Sill	Nugget/sill (%)	Range/m	R ²	Residuals
As	Gaussian	0.032	0.122	26.4	22326	0.728	3.49E-06
Cd	Spherical	0.010	0.510	2.0	3540	0.981	2.43E-03
Co	Spherical	0.008	0.029	27.6	10350	0.999	1.18E-07
Cr	Gaussian	0.080	0.252	31.7	16887	0.981	1.46E-04
Cu	Exponential	0.085	0.623	13.6	93300	0.771	2.48E-03
Hg	Spherical	0.079	0.452	17.5	7090	0.993	1.88E-04
Mn	Spherical	0.029	0.103	28.0	21140	0.971	2.66E-05
Ni	Gaussian	0.067	0.254	26.6	16870	0.983	1.56E-04
Pb	Spherical	0.004	0.080	4.7	17940	0.995	6.30E-06
Se	Spherical	0.006	0.171	3.3	7020	0.869	3.07E-04
V	Spherical	0.017	0.081	20.6	15330	0.997	3.07E-06
Zn	Gaussian	0.076	0.217	34.8	15000	0.998	1.29E-05

elements were enriched in topsoils. The highest *EF* values of Cd, Cu, Hg, Pb, Se, and Zn were located in the industrial region in the northwestern part, which coincided with the hot spots of those elements. It can be clearly demonstrated that the human activities gave rise to the significant accumulation of Cd, Cu, Hg, Pb, Se, and Zn in the industrial region.

Correlation analysis results

As indicated in Table 3, soil pH and CaO showed significantly negative correlation with As, while they had low correlation with other elements. Co, Cr, Mn, Ni, and V showed high positive correlation with soil minerals, and Pb, Cu, and Zn were moderately correlated to soil minerals. For Cd, Hg, and Se, there were very low correlations between these elements and soil properties.

The strong correlations between trace elements in soils may suggest that these trace elements had common sources (Chen et al. 2012; Lv et al. 2014a; Manta et al. 2002). There were strongly positive correlations between the pairs Cd-Hg, Cd-Cu, Cd-Pb, Cd-Se, Cd-Zn, Cu-Hg, Cu-Pb, Cu-Se, Cu-Zn, Hg-Pb, Hg-Se, Hg-Zn, Pb-Se, and Pb-Zn, which indicated their probably common origin. There were also highly positive correlations between Co, Mn, and V, and among Co, Cr, and Ni, suggesting the similar source of these elements. As seemed an isolated element and had low correlation with all elements except for Mn.

Stepwise regression analysis

The results of stepwise regression analysis on trace elements are shown in Table 4. All regression models were significant at 0.01 levels. The goodness of regression equations varied from 0.548 to 0.904, indicating the good accuracy of regression equation modeling.

As, Co, Cr, Mn, Ni, and V were exclusively predicted by soil properties, totally explaining 56.3, 86.2, 90.4, 68.9, 86.4, and 87.9 % of the variance of these elements. It can be suggested that As, Co, Cr, Mn, Ni, and V were dominated by soil parent materials and came from natural sources. For Cd and Hg, merely the variables representing various human activities were included in their regression equations, suggesting that these elements originated from human inputs. The contents of Cu, Se, Pb, and Zn were predicted by both human factors and soil basic properties. The soil basic properties solely explained 38.1, 31.2, 57.2, and 57.7 % variance of Cu, Se, Pb, and Zn, and 21.6, 57.1, 51.6, and 38.1 % variance of these elements were determined by human variables.

Redundancy analysis

The RDA model indicated that pH, OM, Al₂O₃, Fe₂O₃, MgO, CaO, density of traffic lines, industrial zone, and density of industrial sites were the nine significant predictors ($P < 0.05$) for the 12 trace elements (Fig. 4). Environmental factors totally explained 56.3 % of the variance of trace elements. Axis 1 explained 35.6 % of the total variance, while axis 2 determined 20.7 % of the total variance. Cd, Hg, Cu, Pb, Se, and Zn were highly correlated with density of industrial sites, industrial zone, and density of traffic lines, which could be the main sources of these elements. Meanwhile, Cu, Pb, and Zn exhibited some association with the soil basic properties including Fe₂O₃, Al₂O₃, and CaO, indicating that parent materials also contributed to the contents of Cu, Pb, and Zn in soils. There were strong associations between soil properties and Cr, Co, Ni, V, and Mn, suggesting that parent materials dominated the contents of these elements. In accordance with correlation analysis, As was also an isolated element and showed some correlations with CaO, pH, and Al₂O₃. It can be seen that the results of RDA were consistent with stepwise regression analysis.

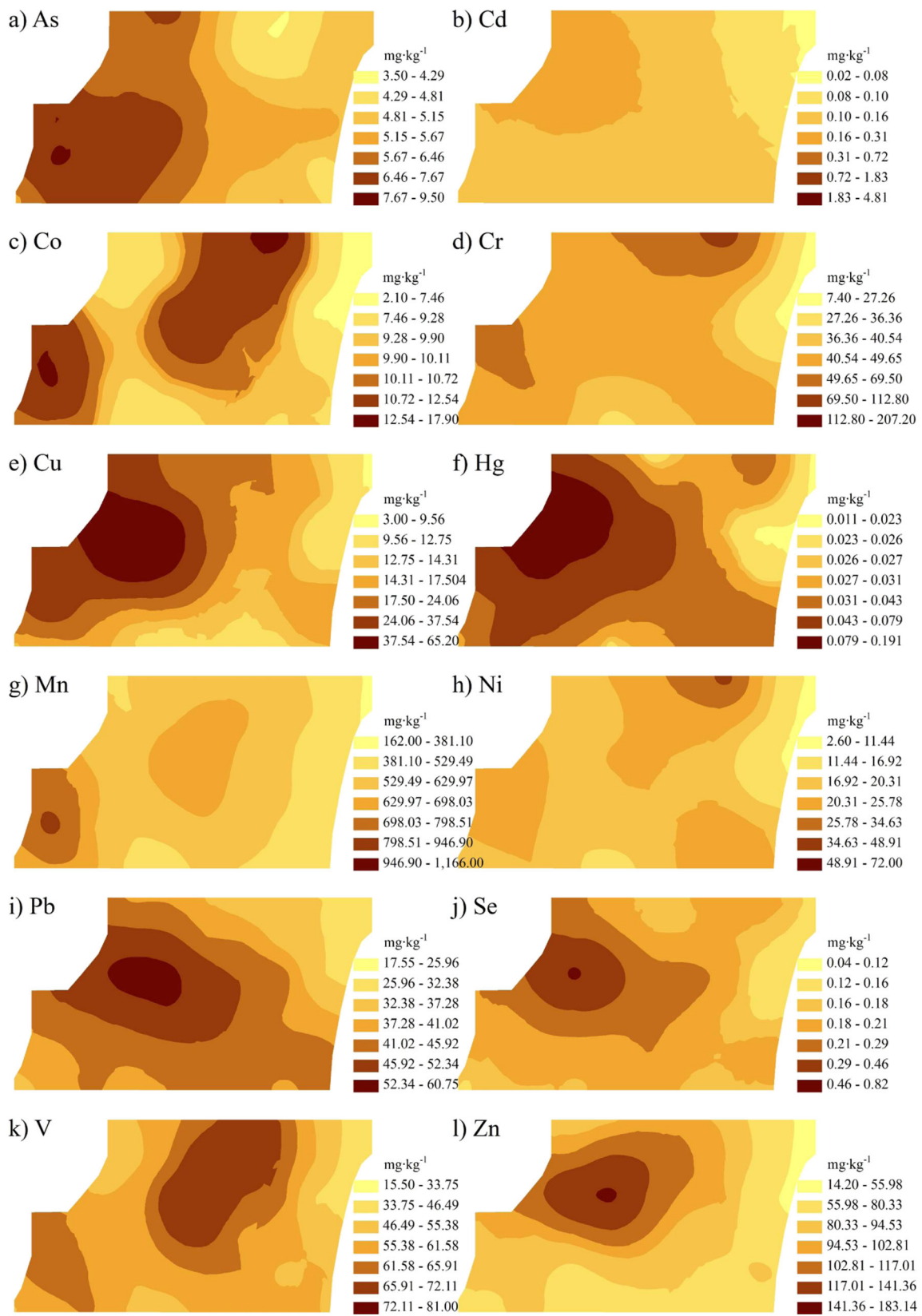
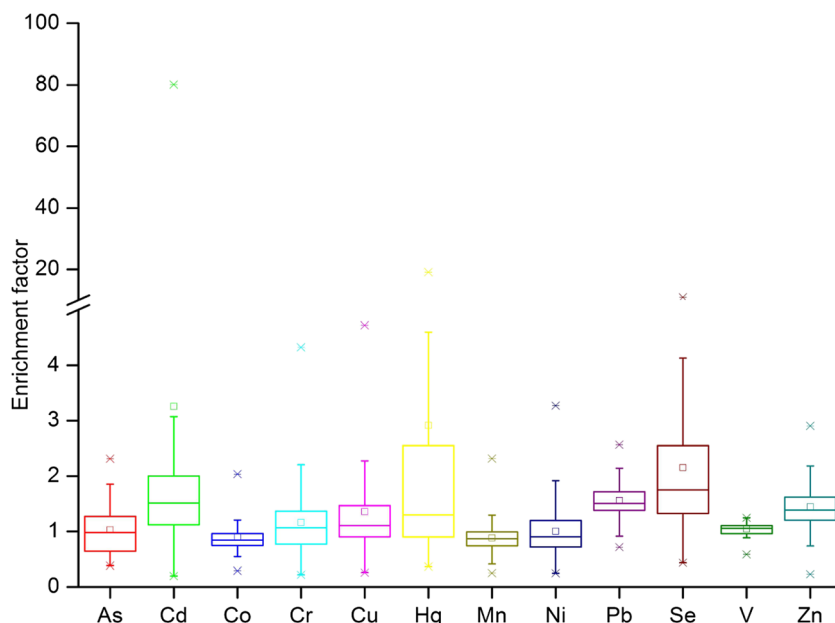


Fig. 2 Spatial distribution of 12 trace elements in topsoils

Fig. 3 Box plot of enrichment factors (EFs) for trace elements in urban soils



Discussion

According to the results of three multivariate methods, 12 elements could be divided into three sources. Cd, Hg, and Se originated from human activities, and the combination of human inputs and natural sources contributed to the contents of Cu, Pb, and Zn, while As, Co, Cr, Mn, Ni, and V were dominated by parent materials and came from natural sources.

Cd, Hg, Se, and partially Cu, Pb, and Zn, with high correlation in correlation analysis and RDA, could be regarded as anthropogenic elements. Commonly, the association of Cd, Hg, Cu, Pb, and Zn indicated the human influences (Lv et al. 2014a; Rodríguez Martín et al. 2013). Pearson correlation results indicated that there were high correlations among these six elements, which may commonly reflect anthropogenic affects of urban soils (Cai et al. 2012; Chen et al.

Table 3 The results of Pearson correlation coefficients

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	V	Zn
As	1	0.095	0.115	-0.114	0.269	0.096	0.470**	-0.130	0.179	0.104	0.123	-0.023
Cd	0.095	1	-0.068	-0.036	0.571**	0.510**	0.001	-0.023	0.544**	0.852**	-0.035	0.474**
Co	0.115	-0.068	1	0.676**	0.261	-0.043	0.811**	0.753**	0.256	0.131	0.872**	0.443**
Cr	-0.114	-0.036	0.676**	1	0.048	0.011	0.264	0.975**	-0.026	0.092	0.389**	0.215
Cu	0.269	0.571**	0.261	0.048	1	0.529**	0.413**	0.089	0.576**	0.620**	0.306*	0.667**
Hg	0.096	0.510**	-0.043	0.011	0.529**	1	0.044	0.034	0.577**	0.618**	-0.038	0.531**
Mn	0.470**	0.001	0.811**	0.264	0.413**	0.044	1	0.353*	0.362*	0.176	0.822**	0.356*
Ni	-0.130	-0.023	0.753**	0.975**	0.089	0.034	0.353*	1	0.056	0.129	0.484**	0.297*
Pb	0.179	0.544**	0.256	-0.026	0.576**	0.577**	0.362*	0.056	1	0.667**	0.391**	0.732**
Se	0.104	0.852**	0.131	0.092	0.620**	0.618**	0.176	0.129	0.667**	1	0.180	0.752**
V	0.123	-0.035	0.872**	0.389**	0.306*	-0.038	0.822**	0.484**	0.391**	0.180	1	0.575**
Zn	-0.023	0.474**	0.443**	0.215	0.667**	0.531**	0.356*	0.297*	0.732**	0.752**	0.575**	1
pH	-0.485**	0.115	-0.312*	-0.239	0.044	0.179	-0.372*	-0.224	0.141	0.159	-0.219	0.122
OM	-0.104	0.205	0.165	0.152	0.399**	0.574**	0.132	0.218	0.133	0.572**	0.205	0.165
Al ₂ O ₃	0.058	0.043	0.599**	0.167	0.269	0.029	0.556**	0.265	0.296*	0.247	0.815**	0.344*
Fe ₂ O ₃	-0.029	-0.011	0.812**	0.480**	0.318*	0.111	0.682**	0.600**	0.342*	0.204	0.856**	0.302*
CaO	-0.518**	0.133	0.250	0.360*	0.130	0.089	-0.040	0.378*	0.021	0.221	0.164	0.206
MgO	-0.259	-0.050	0.793**	0.864**	0.102	-0.119	0.403**	0.870**	0.015	0.081	0.647**	0.324*

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

Table 4 The regression models for 12 trace elements

Dependent variables	Included variables	Regression equation	R ²	Adjusted R ²	Significance
As	X ₁ , X ₆	-0.413X ₁ -0.323X ₆	0.581	0.563	0.01
Cd	X ₇ , X ₁₀	0.225+0.851X ₇ +0.595X ₁₀	0.718	0.711	0.01
Co	X ₄ , X ₅ , X ₆	-0.105+0.542X ₄ +0.675X ₅ -0.411X ₆	0.877	0.862	0.01
Cr	X ₂ , X ₃ , X ₅ , X ₆	-0.068+0.213 X ₂ -0.456X ₄ +1.308X ₅ -0.477X ₆	0.915	0.904	0.01
Cu	X ₄ , X ₇ , X ₈ , X ₁₀	0.464X ₄ +0.851X ₇ +0.265X ₈ +0.595X ₁₀	0.564	0.548	0.01
Hg	X ₂ , X ₇ , X ₁₀	-0.227+0.350X ₂ +0.427X ₇ +0.478X ₁₀	0.607	0.568	0.01
Mn	X ₄ , X ₅ , X ₆	-0.242+0.791X ₄ +0.242X ₅ -0.609X ₆	0.725	0.689	0.01
Ni	X ₂ , X ₄ , X ₅ , X ₆	-0.092+0.236X ₂ -0.327X ₄ +1.223X ₅ -0.415X ₆	0.880	0.864	0.01
Se	X ₂ , X ₃ , X ₇ , X ₁₀	0.195+0.341X ₂ +0.180X ₃ +0.772X ₇ +0.517X ₁₀	0.739	0.713	0.01
Pb	X ₂ , X ₃ , X ₈ , X ₉ , X ₁₀	0.375X ₂ +0.356X ₃ +0.358X ₈ +0.308X ₉ +0.316X ₁₀	0.774	0.751	0.01
V	X ₁ , X ₂ , X ₃ , X ₄	-0.099X ₁ -0.251X ₂ +0.328X ₃ +0.741X ₄	0.890	0.879	0.01
Zn	X ₂ , X ₃ , X ₄ , X ₇ , X ₈	0.188X ₂ +0.297X ₃ +0.281X ₄ +0.489X ₇ +0.188X ₈	0.858	0.840	0.01

X₁ pH, X₂ organic Matter, X₃ Al₂O₃, X₄ Fe₂O₃, X₅ MgO, X₆ CaO, X₇ density of industrial sites, X₈ density of traffic lines, X₉ population density(X₉), X₁₀ industrial zone, X₁₁ urban green land, X₁₂ residential and commercial zone

2012; Franco-Uria et al. 2009; Zhang et al. 2009). As mentioned previously, the mean values of Cd, Cu, Hg, Pb, Se, and Zn in soils were higher than the natural background values of eastern Shandong Province (Dai et al. 2011); in particular, the mean EFs of Cd, Hg, and Se were higher than 2. The contents of Cd, Cu, Hg, Pb, Se, and Zn showed a low relationship with soil properties; in general, the elements from anthropic sources do not present any correlation with soil properties, and the lithogenic elements tend to be associated with soil properties (Lv et al. 2014a). Stepwise regression analysis and RDA suggested that Cd, Cu, Hg, Pb, Se, and Zn had strong correlation with the human factors (Table 4, Fig. 4),

which confirmed the results of enrichment factors and correlation analysis. It can be concluded that Cd, Hg, Se, and partially Cu, Pb, and Zn in urban soils of Donggang mainly originated from anthropogenic activities.

The areas with high concentration of Cd, Cu, Hg, Pb, Se, and Zn were found closely in industrial region, including most of industrial sites (Figs. 1 and 2), where there are metallurgical industry, metal-processing industry, coal-fired power plant, building materials manufacturing, dye and texture industry, and plastic manufacturing in study area. It can be clearly demonstrated that industrial product processes could be important sources of these elements. Commonly, the Cd, Pb, Zn, Cu, and Hg pollution could be associated with smelting industry and metal-processing factories, because the fume and waste from those product processes often contain abundant metals (Alloway 1995; Zhang 2006). Fossil fuel combustion should play an important role in the Pb, Hg, and Se pollution (Alloway 1995; Llorens et al. 2001; Shpirt and Punanova 2011; Yang et al. 2011). The coal-fired power plant of 700 MW in study area consumes 8000 t of coal per day and produces about 700,000 t of wastes per year (Rizhao Municipal Bureau of Statistics 2012). Coal contains several naturally occurring elements, and it is very familiar that Cd and Hg are enriched in the raw coal (Alloway 1995; Nriagu and Pacyna 1988; Swaine 1990), but Se was commonly known as an essential element for maintaining plant and human health (Kabata-Pendias and Pendias 2001; Xu et al. 2005). Se content in coal is 10–100 times of igneous rock, because decayed organism resulted in the Se accumulation in the coalification process (Xu et al. 2005). In China, the average contents of Hg, Pb, and Se in the raw coal are 0.154, 16.64, and 2.82 mg kg⁻¹, and their enrichment factors compared with crustal abundance are 7.09, 5.68, and 144.10, respectively (Bai et al. 2007). Because of the substantial consumption of coal-fired power

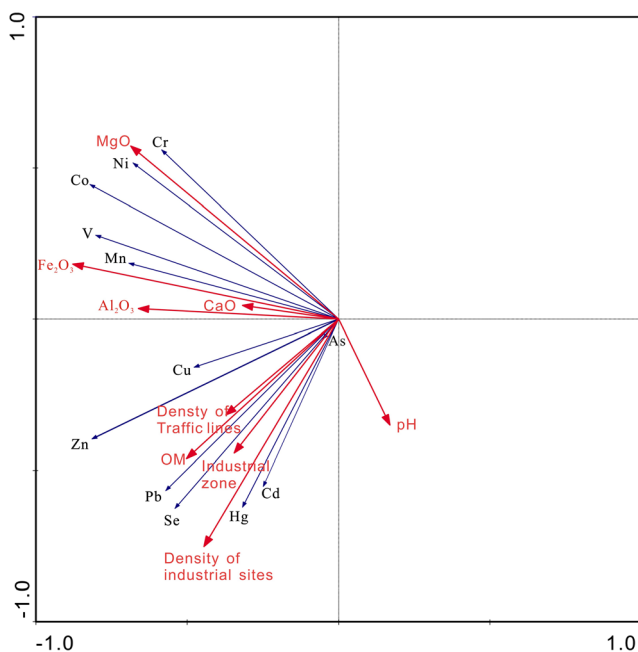


Fig. 4 RDA plot showing the relationships between trace elements and environmental factors

plants, a significant quantity and variety of trace elements are transferred after the combustion to the surrounding environment. Fly ash and bottom ash have been identified as the main outputting waste in the combustion process. Despite the high efficiency of particulate retention devices, a small proportion of fly ash can escape the particulate retention devices and emit to atmosphere (Querol et al. 1995; Tian et al. 2010). Fly ash could inter into the urban soils through atmosphere deposition. Trace elements tend to enrich several times in fly ash than raw coal during the combustion process. Pb and Se are mainly condensed in fly ash during the coal combustion, and Otero-Rey et al. (2003) reported that the content ratios of Pb and Se between fly ash and raw coal reach 4.14 and 6.67, while Hg is more volatile and mainly is in the flue phase. In addition, bottom ash from combustion process is an important construction material, and there are some building material factories in study area. Bottom ash stored outdoor can be easily blown off site by wind into surrounding environment, while leaching of coal ash also resulted in the pollution of trace elements (Llorens et al. 2001). Cd and Pb compounds are commonly used as stabilizers and pigments for plastics production (Alloway 1995; Lin et al. 2002; Lu et al. 2007a), and thus the production process of plastics can be an important source of Cd and Pb in the study area. Fume and effluents from textile dyeing facilities contain Cd and Cu used in dye production technologies or in the molecule of textile dyes (Lin et al. 2002), which can result in the raised contamination of these elements.

On the other hand, traffic emissions have been considered as another source of Pb, Cu, and Zn. The stepwise regression analysis and RDA indicated that density of traffic line was identified as an important predictor of Pb, Cu, and Zn contents (Table 4, Fig. 4). High Pb concentrations in soils could be naturally linked to the utilization of leaded petrol (Chen et al. 2010; Zhang 2006), due to the application of tetraethyl lead as antiknock additive in petrol. Although the usage of leaded petrol in China has been banned since 2000, the historical Pb contamination can be still exhibited in urban soils. Zn can be derived from the wear of vulcanized vehicle tires and corrosion of galvanized automobile parts (Adachi and Tainosho 2004; Smolders and Degryse 2002). The deterioration of the mechanical parts in vehicles also can result in Cu being emitted to urban soils, because Cu is a common material used in mechanical parts (Chen et al. 2012; Yang et al. 2011). Cu is also used in car lubricants, and oil leak due to wear of the automobile's oil sump could result in the raised Cu contents (Al-Khashman 2004; Jiries et al. 2001). Consequently, it seemed reasonable to conclude that Cd, Hg, Se, and partially Cu, Pb, and Zn may originate mainly from industry and traffic sources.

Apart from the human influence, the contents of Cu, Pb, and Zn pointed to the lithogenic influence, and most of *EF*s of those elements were in the range 1–2 (Fig. 3). Cu, Pb, and Zn

were related to soil basic properties in RDA and correlation analysis. The contents of Cu, Pb, and Zn in igneous rocks commonly present higher contents status than sedimentary rock and metamorphic rock. The works of Rodriguez et al. (2008) in Ebro River Basin, Nanos and Rodríguez Martín (2012) in Duero River Basin, and Lv et al. (2015) in Ju County found that parent materials influenced the contents of Cu, Pb, and Zn. It can be seen that natural sources also contributed to the contents of Cu, Pb, and Zn apart from human inputs.

Cr, Co, and Ni, with high correlations, were dominated by the lithogenic nature. The mean contents of Cr, Co, and Ni were lower than background values of eastern Shandong Province, and most of the *EF* values of these elements in soils were close to or less than 1. MgO, Fe₂O₃, and CaO represent major rock-forming elements (Chen et al. 2008; Yang et al. 2011) and were also identified as the main factors affecting the contents of Cr, Co, and Ni. There were no significant associations displayed between spatial patterns of these elements and industrial sites. It is well known that the contents of Co, Cr, and Ni are dependent on the contents in bedrocks, and soils originating from basic rocks present much higher contents of Cr, Ni, and Co than soils from other basic rocks (Alloway 1995; Facchinelli et al. 2001; Lv et al. 2014a). Wei and Yang (2010) found that Cr and Ni were the least polluted elements in the urban soils in China. Therefore, Co, Cr, and Ni were associated with parent rocks and come from natural source.

Mn, V, and As could also be considered as lithogenic elements. Stepwise regression analysis and RDA suggested that soil properties were the dominating factors of Mn, V, and As contents. Mn is generally considered as the major element in soils (Lee et al. 2006; Norra et al. 2006), slightly affected by human activities. Some studies have reported that As comes from human sources, especially coal combustion (Li et al. 2013; Yang et al. 2011). In the present study, As was positively correlated with Mn but negatively correlated with human elements (Table 3). Moreover, As contents of topsoils in most of samples were lower than subsoils, indicating the natural source of As. Based on these, we confirmed that As, Mn, and V were controlled by bedrocks and came from natural source.

Conclusions

A total of 59 samples including 45 topsoils samples and 14 subsoils samples were collected in the urban soils of Donggang and were analyzed for soil pH, OM, four soil minerals, and 12 trace elements. The mean concentrations of Hg, Cd, Pb, Cu, Se, and Zn in topsoils were generally higher than those in subsoils, and *EF* results indicated that these elements were enriched in the study areas. Ordinary kriging results suggested that spatial distributions of Cd, Cu, Hg, Pb, Se,

and Zn showed similar patterns, and the hot spots with high values coincided with the industrial region in northwestern part. There were also similar spatial distributions observed among Co, Mn, and V and between Cr and Ni, while As itself showed high values in southwestern part. No significant associations were displayed between spatial distribution of As, Co, Cr, Mn, Ni, and V and industrial sites. Three sources of 12 elements could be determined. Cd, Se, and Hg came from human activities, including industrial emission and coal combustion. As, Co, Cr, Mn, Ni, and V had lithogenic sources. Cu, Pb, and Zn originated from the combination of anthropogenic and natural sources, where industrial and traffic emissions contributed to the raised contents of these elements.

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