Multivariate and geostatistical analyses of the spatial distribution and origin of heavy metals in the agricultural soils in Shunyi, Beijing, China

Anxiang Lu ^{a,b}, Jihua Wang ^b, Xiangyang Qin ^c, Kaiyi Wang ^c, Ping Han ^b, Shuzhen Zhang ^{a,*}

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China

^b Beijing Research Center for Agri-food Testing and Farmland Monitoring, Beijing 100097, China

^c National Engineering Research Center for Information Technology in Agriculture, Beijing 100097, China

ARTICLE INFO

Article history:

Received 19 August 2011

Received in revised form 2 March 2012

Accepted 2 March 2012

Available online 28 March 2012

Keywords:

Multivariate analysis

Geostatistical analysis

Heavy metal

Agricultural soil

ABSTRACT

An extensive survey was conducted in this study to determine the spatial distribution and possible sources of heavy metals in the agricultural soils in Shunyi, a representative agricultural suburb in Beijing, China. A total of 412 surface soil samples were collected at a density of one sample per km², and concentrations of As, Cd, Cu, Hg, Pb and Zn were analyzed. The mean values of the heavy metals were 7.85 ± 2.13 , 0.136 ± 0.061 , 22.4 ± 6.31 , 0.073 ± 0.049 , 20.4 ± 5.2 , and 69.8 ± 16.5 mg kg⁻¹ for As, Cd, Cu, Hg, Pb, and Zn, respectively, slightly higher than their background values of Beijing topsoil with the exception of Pb, but lower than the guideline values of Chinese Environmental Quality Standard for Soils. Multivariate and geostatistical analyses suggested that soil contamination of Cd, Cu and Zn was mainly derived from agricultural practices. Whereas, As and Pb were due mainly to soil parent materials, and Hg was caused by the atmospheric deposits from Beijing City. The identification of heavy metal sources in agricultural soils is a basis for undertaking appropriate action to protect soil quality.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Soil contamination with heavy metals draws great attention because of its potential threat to food safety and detrimental effects on the ecosystem. Heavy metals may come from natural or anthropogenic sources. Natural contents of heavy metals in soils depend primarily on composition of geological parent materials. Human activities such as urban-industrial expansion, fossil fuel combustion and agricultural practices also influence heavy metal contents in soils. Heavy metals in agricultural soils have increased mainly because of the excessive use of fertilizers and pesticides, wastewater irrigation, sewage sludge application and elevated atmospheric deposition (Cai et al., 2009; Chary et al., 2008).

Spatial distribution of heavy metals in agricultural soils is correlated with their natural sources and anthropogenic inputs. Geostatistical methods are useful tools for quantification of the spatial features of soil parameters and performance of spatial interpolation (Xu and Tao, 2004; Lee et al., 2006). A combination of multivariate statistics and geostatistical analysis is an advanced method for identifying pollution characteristics of heavy metals in soils and distinguishing their natural sources and anthropogenic inputs. This approach generally consists in performing principal component analysis (PCA) and mapping the scores with geostatistical tools (Rodríguez et al., 2006;

López et al., 2008; Lado et al., 2008). Furthermore, spatially constrained multivariate analysis methods (MULTISPATI-PCA) were developed to consider the relationship among variables and their spatial structure together (Dray et al., 2008; Saby et al., 2009). Multivariate and geostatistical analyses have also been applied in the studies of spatial uncertainty and hazard assessment (Liu et al., 2006; Hang et al., 2009; Chen et al., 2009).

Beijing, the capital of China, is one of the largest cities in the world. Over the last decades, soil contamination problems in Beijing have emerged gradually as the rapid economic growth (Khan et al., 2008; Luo et al., 2008). There have been concerns about the quality of the agricultural soils around the megalopolis, considering the potential negative environmental influences from the city. Another threat to the agricultural soils is possibly the intensive agricultural practice such as excessive use of chemical fertilizers and pesticides encouraged by economic interest. A few researches have been conducted so far to determine the concentration and spatial distribution of heavy metals in the soils around cities (Saby et al., 2006; Ip et al., 2007; Shi et al., 2008; Hang et al., 2009). However, studies on the characteristics and sources of heavy metals in agricultural soils nearby big cities are still in need (Liu et al., 2006; Chen et al., 2009).

Therefore, an intensive survey was conducted in the present study to profile the heavy metal concentrations in the agricultural soils in the Shunyi District, selected as a representative agricultural area in the Beijing suburb. A total of 412 soil samples were collected and analyzed for As, Cd, Cu, Hg, Pb and Zn. Multivariate and geostatistical analyses were combined to investigate the current state of soil heavy metal contamination in this area and to identify the spatial

* Corresponding author. Tel.: +86 1062849683; fax: +86 1062923563.

E-mail address: sszhang@rcees.ac.cn (S. Zhang).

Fig. 1. Location of the sampling sites.

patterns and the possible sources of the heavy metals. Such research will provide a basis for effectively targeting policies to protect soils from long-term accumulation of heavy metals.

2. Material and methods

2.1. Study area

The Shunyi District is located in the northeast of Beijing and covers about 1021 km². This district has been traditionally associated with agricultural activities, and the approximately 5.0×10^5 ha of the agricultural lands mainly consist of croplands, vegetable farms, fruit farms and grasslands. Shunyi has a typical monsoon-influenced climate, characterized by hot and humid summer and generally cold and dry winter. The annual temperature is approximately 11.5 °C, and the annual precipitation is approximately 600 mm.

2.2. Soil sampling and chemical analysis

A total of 412 topsoil samples (0–20 cm depth) were collected from the agricultural areas in Shunyi District in the period of August to November, 2009 (Fig. 1). The sampling design was based on the distribution of local agricultural land use. Sampling sites were randomly chosen with the density of about one every 1 km² and at least 200 m away from industry, traffic and residential areas. Around

the center of each site, five individual sub-samples were collected from a 10 m × 10 m grid using a wood spade. Sub-samples were bulked to obtain a composite sample for each site. Coordinates of the sampling points were recorded using global positioning system. Information on vegetation and soil type was also recorded. According to the USDA Soil Taxonomy, the soils belong to Ustalfs and Ustochrepts.

Approximately 1.0 kg of each soil sample was taken and mixed thoroughly. The soil samples were air-dried and passed through a 2.0 mm-sieve. Portions (approximately 50 g) of the soil samples were ground in an agate grinder, sieved through a 0.15 mm-sieve, and stored in brown bottles at 4 °C for chemical analysis.

The soil samples were digested in triplicate with the mixture of HNO₃, HCl and H₂O₂ using Method 3050B (USEPA, 1996). Concentrations of Cd, Cu, Pb and Zn in the digestion solution were determined by inductively coupled plasma optical emission spectroscopy (Thermo iCAP 6300, USA). Concentrations of As and Hg in the soils were determined by atomic fluorescence spectrometry (Titan AFS 830, China) after digestion of the soil samples with

Table 1
Descriptive statistics of heavy metal concentrations in the agricultural soils of the Shunyi District.

	Concentration (mg kg ⁻¹)			Std. deviation	C.V. (%)	Skewness	Kurtosis	K-S
	Mean	Min	Max					
As	7.85	3.37	17.3	2.13	27.1	1.11	2.31	1.28*
Cd	0.136	0.015	0.469	0.061	44.9	2.00	6.36	3.00
Cu	22.4	11.8	72.5	6.31	28.2	2.47	12.3	2.80
Hg	0.073	0.004	0.490	0.049	67.1	3.03	19.1	2.19
Pb	20.4	10.3	37.5	5.20	25.5	0.180	−0.480	1.12*
Zn	69.8	20.0	137	16.5	23.6	0.640	2.31	1.76

* Asymptotic significance > 0.05 (2-tailed).

Table 2
Average heavy metal concentrations in the soils from different areas.

Location	Concentration (mg kg ⁻¹)						Reference
	As	Cd	Cu	Hg	Pb	Zn	
Beijing (background)	7.09	0.119	18.7	–	24.6	59.6	Chen et al. (2004)
Beijing (topsoil)	8.35	0.148	23.7	–	28.6	65.6	Zheng et al. (2008)
Beijing (wastewater-irrigated)	–	0.84	32.8	–	49.4	157	Khan et al. (2008)
Beijing (Guanting reservoir)	7.84	0.81	61.5	–	161	86.3	Luo et al. (2007)
Nanjing (agricultural soil)	9.59	0.17	31.2	0.12	30.3	78.9	Liao et al. (2007)
Hanzhou (rural soil)	6.25	0.26	36.6	0.69	46.2	116	Chen et al. (2008)
Hong Kong (suburban soil)	–	0.37	9.72	–	57.8	67.9	Lee et al. (2006)
Shunyi (agricultural soil)	7.85	0.136	22.4	0.073	20.4	69.8	Present study

Table 3
Results of ANOVA and Kruskal–Wallis test for the soil samples among different defined group.

	Land uses (df=3)		Soil types (df=1)	
	F	Sig.	F	Sig.
As	1.998	0.114	19.79	0.001*
Cd ^a	7.377	0.061	0.870	0.351
Cu ^a	17.56	0.001*	3.624	0.057
Hg ^a	7.445	0.059	3.603	0.058
Pb	0.276	0.843	3.642	0.057
Zn ^a	15.06	0.002*	0.532	0.466

^a Chi-square of Kruskal–Wallis test.

* Significance level of 0.05.

HNO₃:HCl (10 ml, 1:1 v/v) at 100 °C for 2 h and hydride generation with NaBH₄ in HCl medium (Lacerda et al., 2004). All the chemicals used were of guaranteed reagent grade. Standard reference materials, GSS-1 and GSS-4 obtained from the Center of National Standard Reference Material of China, were analyzed as part of quality assurance and quality control (QA/QC) procedures. Good agreement was achieved between the data obtained from the present work and the certified values with the recoveries between 93 and 109%. Analysis of the samples including soil digests and blanks was set up in triplicate, and the standard deviation was within 5%.

2.3. Data statistical analysis

Statistical analysis was conducted using SPSS 16.0 (SPSS Inc., USA). Analysis of variance (ANOVA) was used to compare data from the different groups of soil samples (i.e., different land uses and soil types). If the data is non-normally distributed, non-parametric test (Kruskal–Wallis test) was applied. Principal component analysis (PCA) was carried out to cluster metals that behaved similarly to identify potential sources.

2.4. Geostatistical analysis

The main application of geostatistics to soil science has been the estimation, prediction and mapping of soil attributes in un-sampled areas. The semivariogram, $\gamma(\mathbf{h})$, measures the mean variability between two points $\mathbf{x}$ and $\mathbf{x} + \mathbf{h}$, as a function of their distance $\mathbf{h}$.

The experimental semivariances were calculated with Matheron's classical estimator (Matheron, 1965) by the following equation:

$$\gamma(\mathbf{h}) = \frac{1}{2N(\mathbf{h})} \sum_{i=1}^n [Z(\mathbf{x}_i) - Z(\mathbf{x}_i + \mathbf{h})]^2 \quad (1)$$

where $Z(\mathbf{x}_i)$ is the value of Z at location $\mathbf{x}_i$, and $Z(\mathbf{x}_i + \mathbf{h})$ is the value of Z at a location separated from $\mathbf{x}_i$ by distance $\mathbf{h}$. N is the number of pairs of points which are $\mathbf{h}$ distance apart.

Fig. 2. Box-and-whisker plots for As, Cd, Cu, Hg, Pb and Zn in the agricultural soils under different patterns of land use.

Fig. 3. Box-and-whisker plots for As, Cd, Cu, Hg, Pb and Zn in the soils of Ustalfs and Ustochrepts.

Table 4
Total variance explained and component matrix for heavy metals in the soils.

Total variance explained						
Component	Initial eigenvalues			Extraction sums of squared loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	1.83	30.5	30.5	1.83	30.5	30.5
2	1.08	18.1	48.6	1.08	18.1	48.6
3	1.00	16.7	65.3	1.00	16.7	65.3
4	0.947	15.8	81.1			
5	0.649	10.8	91.9			
6	0.488	8.13	100			
Metal	Component matrix					
	Component					
	1	2	3			
As	0.502	0.612	−0.184			
Cd	0.593	0.183	0.358			
Cu	0.787	−0.313	−0.073			
Hg	0.319	0.048	0.781			
Pb	0.363	0.482	−0.377			
Zn	0.613	−0.586	−0.286			

Extraction method: principal component analysis.

In the case that concentrations of heavy metals in soil samples display a skewed distribution, the outliers have a large effect on estimates of the variogram calculated (Lark, 2002). Robust estimators may be used to obtain the experimental variogram with minimum effect of the outliers and then robust kriging are used for estimation (Cressie and Hawkins, 1980):

$$\gamma(\mathbf{h}) = \frac{1}{2} \left\{ \frac{1}{N(\mathbf{h})} \sum_{i=1}^n [Z(\mathbf{x}_i) - Z(\mathbf{x}_i + \mathbf{h})]^{1/2} \right\}^4 \times \frac{1}{0.457 + \frac{0.494}{N(\mathbf{h})}} \quad (2)$$

where $Z(\mathbf{x}_i)$ is the value of Z at location $\mathbf{x}_i$, and $Z(\mathbf{x}_i + \mathbf{h})$ is the value of Z at a location separated from $\mathbf{x}_i$ by distance $\mathbf{h}$. N is the number of pairs of points which are $\mathbf{h}$ distance apart.

The experimental variogram is calculated for several lag distances. It is then fitted with theoretical models such as spherical, exponential and linear models. These models provide information about the structure of the spatial variation and the input parameters for spatial prediction by kriging interpolation (Goovaerts, 1999). Selection of the best-fit variogram model was made on the basis of cross-validation. The procedure of leave-one-out cross-validation is to delete one data and use the remaining data to predict the

deleted observation. Lark (2000) proposed to calculate the statistic $\theta(\mathbf{x}_i)$

$$\theta(\mathbf{x}_i) = \frac{\{Z(\mathbf{x}_i) - \hat{Z}(\mathbf{x}_i)\}^2}{\sigma^2(\mathbf{x}_i)} \quad (3)$$

where $Z(\mathbf{x}_i)$ is the observed value at location $\mathbf{x}_i$, $\hat{Z}(\mathbf{x}_i)$ is the kriging estimated value and $\sigma^2(\mathbf{x}_i)$ is the kriging variance.

If the fitted variogram is a valid representation of the spatial variation, $\sigma(\mathbf{x}_i)$ should be distributed as χ^2 with one degree of freedom with $E[\theta(\mathbf{x}_i)] = 1.0$. Lark (2000) has demonstrated that it is preferable to use the median of $\theta(\mathbf{x})$ instead of the mean value to assess the variogram. The median value of $\theta(\mathbf{x})$ enables comparison of results of cross validation for kriging with different variogram models, the criterion for the decision is to select the model with the median value of $\theta(\mathbf{x})$ closest to 0.455.

The experimental variogram model was obtained using GeoR 1.7-1 package (Ribiero and Diggle, 2001) under R 2.14 software (R Development Core Team, 2011). Kriging interpolation and mapping were conducted using ArcGis 9.0 (ESRI Inc., USA).

3. Results and discussion

3.1. Heavy metal concentrations in the soils

The descriptive statistics of the heavy metal concentrations in the agricultural soils are presented in Table 1. The mean values were 7.85 ± 2.13 , 0.136 ± 0.061 , 22.4 ± 6.31 , 0.073 ± 0.049 , 20.4 ± 5.2 , and $69.8 \pm 16.5 \text{ mg kg}^{-1}$ for As, Cd, Cu, Hg, Pb and Zn, respectively. Application of the K-S test confirmed that the concentrations of Cd, Cu, Hg and Zn in the soils were non-normally distributed; whereas As and Pb concentrations were normally distributed. After log-transformation, the distributions of Cd, Cu, Hg and Zn were still non-normal. For comparison purpose, data gathered from the recent investigations on heavy metal concentrations in the soils in Beijing and in several other cities of China are summarized in Table 2. Heavy metal concentrations in Shunyi were slightly higher than the background values of Beijing topsoils with the exception of Pb, suggesting a slight contamination of heavy metals in this area. Lower Pb concentration can be adequately explained by the fact that the sampling sites were located in an agricultural region where Pb contamination from traffic and industry was less serious than the other areas in the city. The concentrations of these metals were also generally lower than those in the other areas in Beijing and several other cities in China. According to the Chinese Environmental Quality Standard for Soils (State Environmental Protection Administration of China, 1995), the guideline values of heavy metal concentrations in soil for agricultural products and human health are 20, 0.6, 100, 1.0, 350 and 300 mg kg^{-1} for As, Cd, Cu, Hg, Pb and Zn, respectively. Obviously, heavy metal concentrations in these 412 soil samples collected in Shunyi are all below the guideline values.

3.2. Comparison of heavy metal concentrations in the soils among different agricultural land uses and between soil types

Land use and soil type are supposed to influence heavy metal accumulation in agricultural soils. Prior to analyzing their influences on soil metal concentrations, an assumption was made that heavy metal concentrations in the soils differ among the defined groups of agricultural land uses (i.e., crop, fruit, grass and vegetable) and between the two soil types (i.e., Ustalfs and Ustochrepts). ANOVA was applied to the data set to determine whether the mean values of the concentrations of As and Pb differ among the defined groups, and Kruskal–Wallis test was used for the non-normal distributed metals (Cu, Cd, Hg and Zn). The results are listed in Table 3. Significant

Fig. 4. Graphical display of the first three factors of the PCA.

differences were found in Cu and Zn concentrations among different agricultural land uses and As concentration between the two soil types. Figs. 2 and 3 present the box-and-whisker plots of the results. The concentrations of Cu and Zn were higher in the vegetable farm soils than in the other soils (Fig. 2), reflecting heavy metal contamination derived from agricultural practices. Generally, vegetable farms are more intensively managed than the others based on agronomic practices such as excessive fertilization and pesticide application. Higher As concentration in the Ustalfs than in the Ustochrepts (Fig. 3) should attribute to the higher As content in the soil parent materials of Ustalfs (Chen et al., 2002).

3.3. PCA for heavy metals in the soils

PCA was used to identify the origin of the heavy metals in the agricultural soils, and the results are presented in Table 4. The eigenvalues of the third extracted components were all greater than 1.0. Therefore, the heavy metals could be grouped into a three-component model that accounts for 65% of all the data variation. The component matrix showed that Cd, Cu and Zn were strongly associated with the first component (factor 1). The second component (factor 2) included As and Pb. Hg was the only element in the third component (factor 3). Fig. 4 shows a graphical display of the first three factors. Based on the above comparison of heavy metal concentrations in the soils among different agricultural

Fig. 5. Experimental variogram and fitted variogram models with Matheron's classical estimator (a) and Cressie and Hawkins' robust estimator (b). Solid lines: exponential model; dash line: spherical model; dot line: linear model.

land uses and between soil types and as well as the grouping of the metals suggested with PCA results (Table 4), Cd, Cu and Zn (factor 1) were controlled by the anthropogenic input from agricultural production,

whereas As and Pb (factor 2) appeared to be associated with soil parent materials. Atmospheric deposition is as a possible source of Hg (factor 3) in the soils (Jin et al., 2008).

Table 5

The parameters and the cross-validation results of the fitted variogram models with different estimators for the three factors.

	Estimator	Model	C_0	$C + C_0$	$C_0 / C + C_0$	Range (km)	RSS ^a	Mean of $\theta(\mathbf{x})$	Median of $\theta(\mathbf{x})$
Factor 1	Matheron	Exponential*	0.632	1.07	0.591	1.87	0.0339	1.02	0.452*
		Spherical	0.732	1.07	0.684	6.09	0.0348	1.07	0.481
		Linear	0.985	0.999	0.986	22.6	0.0970	1.02	0.404
	Cressie–Hawkins	Exponential	0.571	0.996	0.573	2.46	0.0194	1.33	0.573
		Spherical	0.655	0.989	0.662	7.55	0.0202	1.38	0.606
		Linear	0.861	0.869	0.991	22.6	0.0761	1.32	0.525
Factor 2	Matheron	Exponential	0.608	1.04	0.585	3.35	0.0176	1.12	0.358
		Spherical*	0.667	1.04	0.641	9.47	0.0104	1.14	0.476*
		Linear	0.856	0.867	0.987	22.6	0.0733	1.32	0.382
	Cressie–Hawkins	Exponential	0.448	0.995	0.450	3.72	0.0137	1.68	0.518
		Spherical	0.509	0.981	0.519	9.55	0.00779	1.72	0.522
		Linear	0.732	0.747	0.980	22.6	0.0892	1.78	0.604
Factor 3	Matheron	Exponential	0.567	0.831	0.682	3.63	0.00333	1.46	0.540
		Spherical*	0.610	0.825	0.739	10.2	0.00462	1.44	0.538*
		Linear	0.700	0.708	0.989	22.6	0.0164	1.57	0.581
	Cressie–Hawkins	Exponential	0.528	0.836	0.632	5.95	0.00308	1.75	0.653
		Spherical	0.561	0.816	0.688	14.0	0.00506	1.74	0.638
		Linear	0.638	0.649	0.983	22.6	0.0151	1.91	0.705

^a Residual sum of squares.

* The closest to 0.455.

3.4. Multivariate geostatistical analysis and spatial distribution map

A variogram analysis was conducted to further substantiate the above results of the PCA. Fig. 5 shows the experimental variograms and fitted variogram models with Matheron's classical estimator and Cressie and Hawkins' robust estimator for the scores of the first three factors. The parameters and cross-validation results for these models are presented in Table 5. The model with the median value of $\theta(\mathbf{x})$ closest to 0.455 was selected as inputs for kriging maps. The median values of $\theta(\mathbf{x})$ of selected model were all within the 95% confidence limits. This indicates that the Matheron's classical estimator can adequately model the spatial variation.

The filled contour maps are shown in Figs. 6 to 8. The ranges of the three factors were classified into five quantiles taking the lowest and the highest values into consideration. As shown in Fig. 6a, the spatial distribution of factor 1 demonstrated several localized hotspots. The hotspot with the highest value of factor 1 (Cd, Cu and Zn) was distributed in the south of Shunyi, which coincided with the evidence of vegetable farming in this area in Fig. 6b (see the cycles to highlight), suggesting that vegetable farming may contribute to the contamination of Cd, Cu and Zn. Chemical fertilizers and manures are intensively used to increase agricultural products. In particular, phosphate fertilizers contain high levels of Cd due to its presence in phosphate rocks (Luo et al., 2007; Nan et al., 2002). Cu and Zn are present in almost all agricultural inputs, especially in animal manure because of their use as feed additives to promote animal growth and to control diseases (McBride and Spiers, 2001). Liu et al. (2006) contributed the high

Cu concentration in soils to the extensive manure application in paddy fields. Livestock manures are also important sources of soil Zn and Cu pollution. These sources were found to be responsible for an estimated 37% of Zn and 8% of Cu inputs in the agricultural soils in England and Wales (Nicholson et al., 2003). The application of Cu containing pesticides or fungicides such as Bordeaux mixture in agriculture especially in vegetable and fruit production may also be a source of Cu contamination.

The kriging contour map of factor 2 (Fig. 7a) illustrates the distribution of As and Pb. It is difficult to find any link between the factor distribution and the agricultural land use (Fig. 6b). In comparison we can find several consistent locations of high values of factor 2 and the sites of soils predominantly Ustalfs (Fig. 7b), and factor 2 is therefore likely due to the local variation in parent material. As shown in Fig. 3, there was a significant difference in As concentration between the Ustalfs and the Ustochrepts. Elements of As and Pb may be derived from the soil parent matrix. The background concentration of As in Florida surface soils was evidenced to vary greatly among soil types (Chen et al., 2002). Navas and Machín (2002) also found that soil type determined to some extent the variation of As concentration in the soils of Aragón Spain. The natural level of Pb concentration in the studied region was contributed by the sampling sites away from industry and traffic pollution.

Contaminants released from the central city may migrate to the surrounding suburb areas. Nevertheless, no evidence was found that factors 1 and 2 decreased along with the distance from the center of the city (Figs. 6a and 7a), suggesting insignificant transport of As,

Fig. 6. Filled contour map of factor 1 (a) and agricultural land use map (b).

Fig. 7. Filled contour map of factor 2 (a) and soil type map (b).

Cu, Cd, Pb and Zn from the city to the rural areas. However, the highest value of factor 3 was observed in the south part (cycled in Fig. 8), the closest to the central city. Biasioli et al. (2006) compared a set of soils collected from the city of Torino and its surrounding rural areas. They reported that the transport of heavy metals (Cu, Cr, Pb and Zn) from the city to the surrounding areas was limited to approximately

a 1-km circumferential strip. Hg can accumulate in soils through atmospheric deposition and shows distinguished spatial distribution, because airborne pollutants are supposed to be deposited to soil in a declining trend with distance away from the source. A survey showed that Hg concentrations in the soils of Beijing were 1.0, 0.30 and 0.18 mg kg⁻¹ in the area inside 2nd ring road (in the inner

Fig. 8. Filled contour map of factor 3.

city), between 2nd and 4th ring road (outside the city center), and outside 4th ring road, respectively (Chen et al., 2010). In the present study, the average Hg concentration in the soils was 0.073 mg kg^{-1} . There is a distinct decreasing trend in Hg concentration from the city center to the suburban areas, which suggests that atmospheric Hg contamination in the city plays an important role in Hg accumulation in the agricultural soils in Shunyi.

4. Conclusions

The results of this study showed that although a slightly higher than their background values of Beijing topsoil, the concentrations of As, Cd, Cu, Hg, Pb and Zn in the agricultural soils in the Shunyi District were lower than the guideline values of Chinese Environmental Quality Standard for Soils, indicating an insignificant contamination of these metals in this area. Among the metals investigated in this study, soil As and Pb mainly come from the parent materials. Local contamination from agricultural practices, particularly with the application of fertilizer and manure, is the main source of Cd, Cu and Zn entering the agricultural soils, and atmospheric deposition plays an important role in Hg accumulation in the soils. This case study demonstrates that a combination of multivariate statistics and geostatistical analysis can be an appropriate tool to characterize heavy metal spatial distribution and to determine their sources. In addition, this study will provide a basis for effectively targeting policies to protect soils from long-term heavy metal accumulation.

Acknowledgments

This work was funded by the Agro-scientific Research in the Public Interest, the Ministry of Agriculture of the People's Republic of China (Project 201003008) and National Key Technology R&D Program (Project 2009BADB9B07).

References

- Biasioli M, Barberis R, Ajmone-Marsan F. The influence of a large city on some soil properties and metals content. *Sci Total Environ* 2006;356:154–64.
- Cai Q, Long ML, Zhu M, Zhou QZ, Zhang L, Liu J. Food chain transfer of cadmium and lead to cattle in a lead–zinc smelter in Guizhou, China. *Environ Pollut* 2009;157:3078–82.
- Chary NS, Kamala CT, Raj DSS. Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer. *Ecotoxicol Environ Saf* 2008;69:513–24.
- Chen M, Ma LQ, Harris WG. Arsenic concentration in Florida surface soils: influence of soil type and properties. *Soil Sci Soc Am J* 2002;66:632–40.
- Chen T, Zheng Y, Chen H, Zheng GD. Background concentration of soil heavy metals in Beijing. *Environ Sci (Chinese)* 2004;25:117–22.
- Chen T, Liu X, Zhu M, Zhao K, Wu J, Xu J, et al. Identification of trace elements sources and associated risk assessment in vegetable soils of the urban–rural transitional area of Hangzhou, China. *Environ Pollut* 2008;151:67–78.
- Chen T, Liu X, Li X, Zhao K, Zhang J, Xu J, et al. Heavy metal sources identification and sampling uncertainty analysis in a field-scale vegetable soil of Hangzhou, China. *Environ Pollut* 2009;157:1003–10.
- Chen X, Xia X, Wu S, Wang F, Guo X. Mercury in urban soils with various types of land use in Beijing, China. *Environ Pollut* 2010;158:48–54.
- Cressie N, Hawkins DM. Robust estimation of the variogram. *J Int Assoc Math Geol* 1980;7(12):115–25.
- Dray S, Said S, Debias F. Spatial ordination of vegetation data using a generalization of Wartenberg's multivariate spatial correlation. *J Veg Sci* 2008;19:45–56.
- Goovaerts P. Geostatistics in soil science: state-of-the-art and perspectives. *Geoderma* 1999;89:1–45.
- Hang X, Wang H, Zhou J, Ma C, Du C, Chen X. Risk assessment of potentially toxic element pollution in soils and rice (*Oryza sativa*) in a typical area of the Yangtze River Delta. *Environ Pollut* 2009;157:2542–9.
- Ip CCM, Li X, Zhang G, Wai OWH, Li Y. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ Pollut* 2007;147:311–23.
- Jin YQ, Wang XJ, Lu JL, Zhang CX, Duan QB. Effects of modern and ancient human activities on mercury in the environment in Xi'an area, Shannxi Province, PR China. *Environ Pollut* 2008;153:342–50.
- Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG. Health risks of heavy metals in contaminated soil and food crops irrigated with waste water in Beijing, China. *Environ Pollut* 2008;152:686–92.
- Lacerda LD, de Souza M, Ribeiro MG. The effects of land use change on mercury distribution in soils of Alta Floresta, Southern Amazon. *Environ Pollut* 2004;129:247–55.
- Lado LR, Hengl T, Reuter H. Heavy metals in European soils: a geostatistical analysis of the FOREGS Geochemical database. *Geoderma* 2008;148:189–99.
- Lark RM. A comparison of some robust estimators of the variogram for use in soil survey. *Eur J Soil Sci* 2000;51:137–57.
- Lark RM. Modelling complex soil properties as contaminated regionalized variables. *Geoderma* 2002;106:171–88.
- Lee CS, Li X, Shi W, Cheung SC, Thornton I. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. *Sci Total Environ* 2006;356:45–61.
- Liao Q, Evans LJ, Gu X, Fan D, Jin Y, Wang H. A regional geochemical survey of soils in Jiangsu Province, China: preliminary assessment of soil fertility and soil contamination. *Geoderma* 2007;142:18–28.
- Liu X, Wu J, Xu J. Characterizing the risk assessment of heavy metals and sampling uncertainty analysis in paddy field by geostatistics and GIS. *Environ Pollut* 2006;141:257–64.
- López JM, Borrajo JL, García EDM, Arrans JR, Estévez MCH, Castillo AJS. Multivariate analysis of contamination in the mining district of Linares (Jaén, Spain). *Appl Geochem* 2008;23:2324–36.
- Luo W, Wang T, Lu Y, Giesy JP, Shi Y, Zheng Y, et al. Landscape ecology of the Guanting Reservoir, Beijing, China: multivariate and geostatistical analyses of metals in soils. *Environ Pollut* 2007;146:567–76.
- Luo W, Lu Y, Wang G, Shi Y, Wang T, Giesy JP. Distribution and availability of arsenic in soils from the industrialized urban area of Beijing, China. *Chemosphere* 2008;72:797–802.
- Matheron G. Les variables régionalisées et leur estimation: une application de la théorie des fonctions aléatoires aux sciences de la nature. Paris, France: Masson; 1965. 305pp.
- McBride MB, Spiers G. Trace element content of selected fertilizers and dairy manures as determined by ICP-MS. *Commun Soil Sci Plan* 2001;32:139–56.
- Nan ZR, Li JJ, Zhang JM, Cheng GD. Cadmium and zinc interactions and their transfer in soil crop system under actual field conditions. *Sci Total Environ* 2002;285:187–95.
- Navas A, Machín J. Spatial distribution of heavy metals and arsenic in soils of Aragón (northeast Spain): controlling factors and environmental implications. *Appl Geochem* 2002;17:961–73.
- Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers BJ. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci Total Environ* 2003;311:205–19.
- R Development Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. 2011. Available from: <http://www.R-project.org>.
- Ribiero PJ, Diggle PJ. geoR: a package for geostatistical analysis. *R News* 2001;1:15–8.
- Rodríguez MJA, López AM, Grau CJM. Heavy metal contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geostatistical methods to study spatial variations. *Environ Pollut* 2006;144:1001–12.
- Saby NPA, Arrouays D, Boulonne L, Jolivet C, Pochot A. Geostatistical assessment of Pb in soil around Paris, France. *Sci Total Environ* 2006;367:212–21.
- Saby NPA, Thioulouse J, Jolivet CC, Ratte C, Boulonne L, Bispo A, et al. Multivariate analysis of the spatial patterns of 8 trace elements using the French soil monitoring network data. *Sci Total Environ* 2009;407:5644–52.
- Shi G, Chen Z, Xu S, Zhang J, Wang L, Bi C, et al. Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environ Pollut* 2008;156:251–60.
- State Environmental Protection Administration of China. Chinese environmental quality standard for soil GB; 1995. 15618–1995.
- USEPA. Method 3050B: acid digestion of sediments, sludges and soils. United States Environmental Protection Agency; 1996.
- Xu S, Tao S. Coregionalization analysis of heavy metals in the surface soil of Inner Mongolia. *Sci Total Environ* 2004;320:73–87.
- Zheng YM, Chen TB, He JZ. Multivariate geostatistical analysis of heavy metals in topsoils from Beijing, China. *J Soils Sediments* 2008;8:51–8.