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Landscape ecology of the Guanting Reservoir, Beijing, China: Multivariate and geostatistical analyses of metals in soils

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Concentrations of metals, sources and spatial distributions in soils around Guanting Reservoir were determined.

Abstract

Surface soil samples were collected from 52 sites around Guanting Reservoir in Beijing, China, and contents of 'total' metals (Cu, Zn, Pb, Cd, As, Ni and Cr) were determined. The results indicate that the degree of heavy metal pollution in the soils declines in the order of Cd > Cr > Zn > As > Cu > Ni > Pb. Based on the results of a combination of multivariate statistics and geostatiscal analyses, it was concluded that land application of phosphate fertilizer, wastewater and sludge were the primary sources of Cd and Zn in soils. Whereas As, Cu, Cr and Ni in some soils were due to natural rock weathering. The sources of Pb in soils only partially originated from land application of phosphate fertilizer, but mainly from vehicle exhaust. The greatest concentrations of all metals, except for Pb, were found in Huailai County and the towns of Yanghedaqiao and Guanting.

Keywords: Heavy metals; Soil pollution; Principal component analysis; Geographic information system

1. Introduction

Due to their non-biodegradable nature and long-biological half-lives for elimination from the body (Radha et al., 1997), heavy metal contamination of the environment has attracted a great deal of attention world-wide (Li et al., 2004). Some heavy metals are toxic to plants and grazing animals by restricting proper function of soil microorganisms, and ultimately affecting the health of the people. Soils are the critical interface environments where rock, air and water interact. Soils can also be a source of pollution to surface and ground waters, living organisms, sediments, and oceans (Facchinelli et al., 2001). The content of heavy metals in soil and their impact upon ecosystems can be influenced by many factors, such as parent material, climate and anthropogenic activities such as industry, agriculture and transportation. Each of these factors has been investigated to prevent further environmental deterioration and to examine possible methods of remediation (Dijkstra, 1998; Sheppard et al., 2000).

Due to the heterogeneity of the soil and the often accidental nature of contaminating processes, concentrations of heavy metals can vary remarkably over very short distances. Since natural variability and anthropogenic input vary over space, the relationships of soil heavy metal concentrations are scale-dependent (Xu and Tao, 2004). Because of the need to quantify and reduce the uncertainties and minimize the investigation costs geostatistical and multivariate statistical

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methods have been developed and applied to soil systems (Ferguson et al., 1998).

Kriging and principal component analysis (PCA) are common tools in geostatistical and multivariate statistical methods. They have been widely used to identify pollution sources, to apportion natural- vs. human-caused contribution, and to describe spatial distribution of pollutants (Atteia et al., 1994; Tao, 1995; Carlon et al., 2001; Facchinelli et al., 2001). Applications of these methods to soils at a regional scale have been well documented (Ratha and Sahu, 1993; Carcia et al., 1996; Ruiz et al., 1998). Historically, the Guanting Reservoir area has been used as one of the two important water sources for agriculture, industry and municipalities in Beijing. Since the 1970s, the Guanting Reservoir area has undergone significant agricultural and industrial development and consequently much water pollution has occurred. The sources of contamination include local industrial or domestic wastewater discharge as well as non-point contamination (such as farming). Two well-known pollution events took place in 1972 and 1989. Polluted water containing high concentrations of As, Cr and Hg caused fish in the reservoir to die while residents who drank the water became sick (Jiang and Wang, 2003; Du and Wu, 2004). Thus, since 1997, the Guanting Reservoir has no longer been used as a source of drinking water for Beijing. This is a serious issue since Beijing currently has a severe shortage of water. According to a preliminary environmental investigation of the reservoir in 2003, there were more than 300 industrial and mining enterprises, producing about 7844.76×10^4 t of wastewater per year. Most of this wastewater was directly discharged into the reservoir without any treatment (Du et al., 2004). With regard to potential toxic impacts, the concentrations of these heavy metals continued to increase slowly in recent years, though limited metal analyses of the reservoir water showed As, Cd, Cr, Cu, Ni, Zn and Pb to be at concentrations that were not exceeding the criteria for the protection of aquatic life (Liang et al., 2003). Also, there were apparent effects of heavy metals in the sediments of the reservoir on benthic invertebrates (Chen et al., 2001; Zhou et al., 2002). Since irrigation accounted for approximately 80% of total water usage in the area, it was hypothesized that this might have resulted in increased accumulation of heavy metals in soils (Chen et al., 2001). This is due to the fact that the irrigation water is predominantly wastewater. Thus, investigations of heavy metal contamination of soils around the reservoir, natural and anthropogenic sources of soil and water contamination, and regional variations in heavy metal concentrations in soils were conducted. Results from these studies will provide critical data for policy makers in deciding which actions they will need to undertake in order to resume drawing drinking water for Beijing from this reservoir. However, only recently there have been studies investigating heavy metal distribution in the soils around the reservoir. The present study was conducted as a preliminary survey of soils contaminated by heavy metals around the polluted reservoir, and the contributory relationships. The approach was to survey concentrations of metals on a regional scale with multivariate and geostatistical methods. The goals of the study were to (1) investigate average regional concentrations of several heavy metals (As, Cd, Cr, Cu, Ni, Pb, Zn) in soils around the reservoir; (2) determine their spatial variation; (3) identify possible sources; and (4) estimate the relative proportions arising from natural processes and those arising from human activities.

2. Materials and methods

2.1. Study area

Guanting Reservoir is located approximately 100 km northwest of Beijing. It has a surface area of 46,768 km^2, and the total arable land in the watershed is 2×10^6 hm^2 (Huang et al., 2003). The climate in the region is cool temperature, continental monsoon with an annual precipitation between 370 and 480 mm. The drainage area in the Guanting basin is approximately 25,000 km^2, with an average soil erosion of 110 million t/a (Chen et al., 2001). The primary rock types are intermediate and acidic igneous; and the soil types are fluvo-aquic (FAS), calcareous-cinnamon (CCS), fluvo-cinnamon (FCS) and meadow-wind sandy (MWSS) (Gong et al., 2002). Land uses in the region include farms and orchards as well as fallow lands. Most areas are dedicated to agricultural cultivation, focusing mainly on corn and a variety of vegetables for cash crops.

2.2. Sampling

A total of 52 sampling blocks (100×100 m) were selected, based on the distribution of industrial and agricultural productions around Guanting Reservoir. A nested sampling scheme was applied to the industrial and agricultural areas. The more intensified the industrial and agricultural areas, the denser the sampling blocks. Throughout the survey a global positioning system (GPS) was used to locate the sampling locations (Fig. 1). A composite surface soil sample (0–10 cm) was collected from each sampling block. The sampling scheme took into account sites representing the most relevant characteristics of the environment and each soil type. The sampling procedure was intended to obtain a representative composite sample consisting of five sub-samples collected at each site. Therefore, the 52 soil samples were composed from a total of 260 soil sub-samples collected. Samples were extracted using an automatic core drill.

2.3. Analytical methods

Soil samples were air-dried, crushed in an agate mortar, passed through a nylon sieve of 100 mesh, and digested with HNO_3 and H_2O_2 using Method 3050B (USEPA, 1996). Careful handling was performed to avoid input or loss of trace elements during preparation and analysis of the samples. All materials used during analytical determinations were kept in Teflon or other metal free containers. Concentrations of heavy metals (Cd, As, Cu, Ni, Pb and Zn) in the digestion solution were determined using inductively coupled argon plasma emission spectroscopy (ICAPES). The method detection limit (MDL), which is defined as the minimum concentration of substance that can be measured and reported with 99% confidence, was determined using EPA 40CFR Part 136, Appendix B. Standard reference materials, GSS-1 soils, obtained from the Center of National Standard Reference Material of China were analyzed as part of the quality assurance and quality control (QA/QC) procedures. Satisfactory recoveries were obtained for Cu (92–95%), Ni (101–108%), Pb (94–106%), Cd (96–99%), As (97–101%) and Zn (94–103%).

2.4. Multivariate and geostatistical methods

The frequency distributions of heavy metal concentrations were investigated by calculating the skewness and kurtosis coefficients. For kriging estimation, the semivariogram $r(h)$ was used to quantify the spatial dependence of soil heavy metal concentrations. Then, based on the spatial structure of $r(h)$, the kriging estimator for heavy metal concentrations at unsampled locations were calculated (Isaaks and Srivastava, 1989). In this study, the

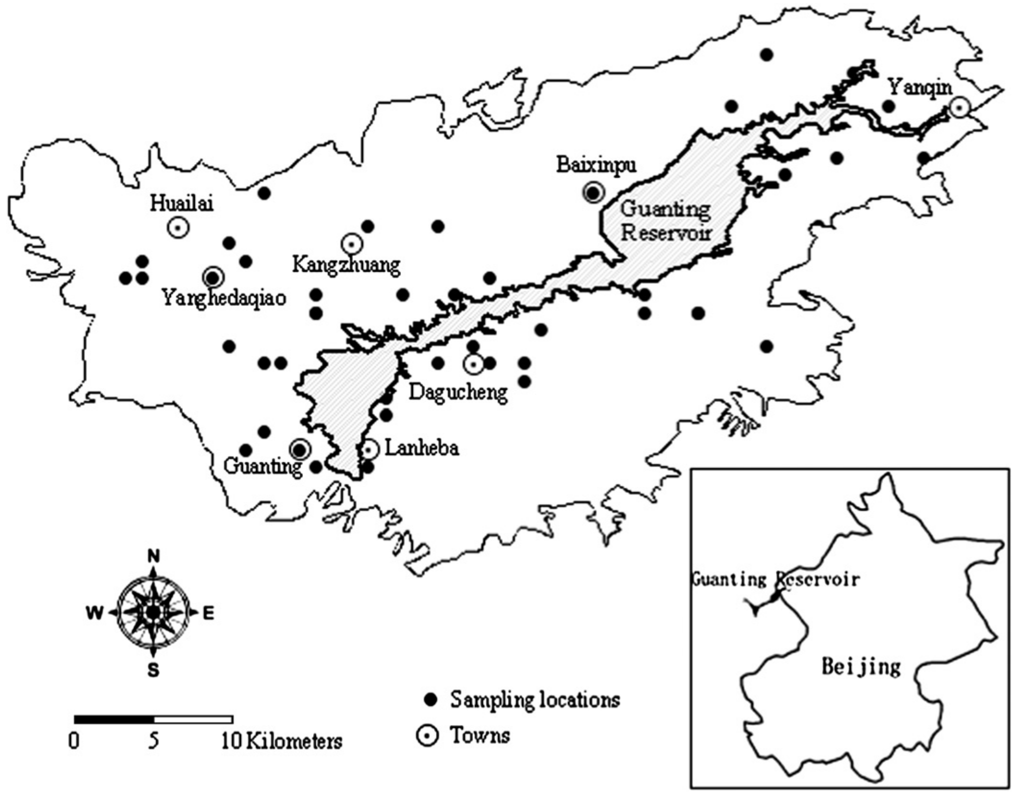

Fig. 1. Map of soil sampling sites around Guanting Reservoir.

experimental semivariogram models were obtained using the software package GS+ (Gamma Design, 1994), while kriging estimation was conducted using the software of ArcGIS 8.2 for Windows.

Principal components analysis (PCA) was used to investigate the variation of heavy metal concentrations among soil samples. PCA is a multivariate statistical analysis converting the variables (analytic concentrations) into factors or principal components. These are linear combinations of the variables that are themselves not correlated but together explain the total variance of the data. The first factor explains the most variance, the second factor the next greatest amount of variance and so on. It follows that the dimensionality of the original data space can be reduced to a few factors, commonly two or three, retaining most of the overall variance. Furthermore, the factors can be rotated, in a way that each factor explains a different subset of correlated variables (i.e. analyzes). This makes the factors more comprehensive and potentially explicable. The PCA allows a factor score for each sample to be calculated. When plotted by factor scores, samples with similar analytic compositions (i.e. scores) are aggregated closer than those with more dissimilar compositions. The similarities among samples can then be used to elucidate potential sources. Details of this method are provided by Einax et al. (1997).

3. Results and discussion

3.1. Preliminary data description

The descriptive statistics of metal concentrations in soils in the vicinity of Guanting Reservoir are presented in Table 1. Concentrations of Cd, Cr, Cu, Ni, Pb and Zn were transformed by taking the natural logarithm (ln) to more closely approximate the normal distribution, since natural logarithm transformation significantly reduced both the skewness and the kurtosis coefficients for these metals. According to the skewness and kurtosis parameters (Table 1), as well as one-sample Kolmogorov–Smirnov test, the concentration of As approached a normal distribution while those of Cd, Cr, Cu, Ni, Pb and Zn approached a ln–normal distribution. Considering the concentrations of metals in the dominant soil and rock types around Guanting Reservoir and its geography, geology, landscape and climate, which are close to Beijing's, the heavy metal background levels in soils of Beijing (Chen et al., 2004) were used as reference values for unpolluted soils around Guanting Reservoir.

The results of the summary statistics (Table 1) indicate that mean concentrations of most heavy metals, except Cr, were significantly different from their corresponding reference values using a one-sample *t*-test ($P < 0.05$). The mean concentration of Cd (0.68 mg/kg dry wt) was much greater than its background value (0.15 mg/kg dry wt) and also significantly greater than its alerting value (0.5 mg/kg dry wt) (Wei et al., 1992) which would be predicted to have potential ecological effects. All 52 composite soil samples exceeded the reference value for Cd and concentrations of Cd in some samples even exceeded the critical value (1.0 mg/kg dry wt) (Wei et al., 1992) with serious ecological effects. It can thus be concluded that the Cd contamination in surface soils around Guanting Reservoir has been very heavy.

Pb had the least mean concentration (8.21 mg/kg dry wt), while concentrations of only two soil samples exceeded the reference value of Pb. Thus, it can be concluded that Pb contamination in soils around Guanting Reservoir is very minimal.

The mean concentration of Cr was 32.35 mg/kg dry wt, which was not significantly greater than its reference value

Table 1
Descriptive basic statistics of the heavy metal concentration in the studied soils

Heavy metal	Range (mg/kg)	Min. (mg/kg)	Max. (mg/kg)	Mean ± S.D. (mg/kg)	Skewness (mg/kg)	Kurtosis (mg/kg)	Coefficient of variation (%)	Reference values ± S.D.[b] (mg/kg)	Number exceeding reference values[c]
As	7.84	3.06	10.9	6.88 ± 2.11*	−0.03	−0.83	30.66	7.81 ± 3.22	13
Cd	0.81	0.39	1.2	0.68 ± 0.17*	0.01[a]	0.17[a]	24.67	0.15 ± 0.11	52
Cr	42.58	16.78	59.4	32.35 ± 8.65NS	0.12[a]	0.23[a]	26.73	31.3 ± 9.29	21
Cu	61.51	2.86	64.4	13.54 ± 9.95*	0.19[a]	0.54[a]	73.44	19.7 ± 6.33	7
Ni	27.38	5.95	33.3	15.81 ± 6.04*	−0.09[a]	0.25[a]	38.17	27.9 ± 7.90	2
Pb	163.14	1.74	165	8.21 ± 22.5*	2.50[a]	11.03[a]	274.04	25.1 ± 5.08	2
Zn	86.34	22.99	109	54.28 ± 17.6*	−0.09[a]	0.41[a]	32.36	59.6 ± 16.29	10

Significant at the 0.05 (*) level of probability when compared with reference value.
NS, not significant, comparing with reference value.
[a] ln-transformed data.
[b] Chen et al. (2004).
[c] The number whose value is significantly greater than the corresponding reference value ($P < 0.05$).

(31.30 mg/kg dry wt). However, concentrations of Cr in 21 soil samples did significantly exceed the reference value. Thus, Cr contamination in soils around Guanting Reservoir should also be given attention. The mean concentrations of As, Zn, Cu and Ni were 6.88, 54.28, 13.54 and 15.81 mg/kg dry wt, respectively. The number of samples significantly exceeding the corresponding reference value for As, Zn, Cu and Ni were 13, 10, 7 and 2, respectively. Ratios of the mean concentrations in soils around Guanting Reservoir divided by the corresponding reference value decreased in the order of Cd > Cr > Zn > As > Cu > Ni > Pb. Multiplying the ratios by the number of values significantly exceeding the respective reference provides a combined estimate of both the magnitude and the extent of contamination around the reservoir. This weighted result suggests that the magnitude of heavy metal pollution in soils around Guanting Reservoir decline in the order of Cd > Cr > As > Zn > Cu > Ni > Pb.

Coefficients of variation for most heavy metals, except Pb, were small. It is expected that those elements having smaller coefficients of variation may be dominated by natural sources, while those with greater coefficients of variation are more likely to be affected by anthropogenic sources.

3.2. Correlation coefficients between heavy metal contents

Relationships between concentrations of metals were investigated using Pearson correlation coefficients of either ln-transformed or non-ln-transformed concentrations (Table 2). According to the values of Pearson correlation coefficients (R), As, Cd, Cr, Cu, Ni and Zn were closely related ($P \leq 0.01$), which might suggest a common origin. Pb showed strong positive correlations ($P \leq 0.01$) with Cd and Zn, but poorer correlations with As, Cr, Cu and Ni.

3.3. Principal component analysis (PCA)

Relationships among metals were investigated using PCA. The components were ranked by their eigenvalues. The cumulative percentages of the variations explained by the first two components, and the corresponding eigenvectors are given (Table 3). The values of the first two principal components (PCs) after rotation for the maximum variance are also given. The first two PCs were chosen based on their eigenvalues which were both greater than 1.0. The total variance explained by the first two PCs was greater than 85.57%. The initial component matrix for the metals indicates that Cr, Ni, As, Cd, Zn and Cu are associated, because they display relatively great values for the first component (F1), while Pb is isolated with the second factor (F2). The rotation of the matrix also supports these results. Cd and Zn contribute some proportions to the second PC, showing their associations with Pb, although the second factor (F2) includes only Pb.

The relationships among the seven heavy metals can be seen when scores of factor 2 are plotted as a scatter plot versus scores of factor 1 (Fig. 2). The small distances in the factor plots indicate a significant correlation between Zn–Cd, Ni–Cr and As–Cu, which may suggest that the corresponding pairs of elements have the same sources. Pb is separated from the other heavy metals by a large distance (Fig. 2). This result may suggest that Pb is poorly related with other heavy metals and has different sources. However, the correlation coefficients and PCA provide little information about the scale-dependent relationships among metal concentrations. A poor correlation between individual metals could be the result of the counteractions of different correlation behaviors at various spatial scales. From this perspective, geostatistical analysis takes advantage of providing insights into scale-dependent relationships of regionalized variables.

Table 2
Correlation coefficients of heavy metal contents (lower triangle)

	As	Cd	Cr	Cu	Ni	Pb	Zn
As	1						
Cd	0.74**	1					
Cr	0.82**	0.87**	1				
Cu	0.60**	0.54**	0.72**	1			
Ni	0.79**	0.82**	0.93**	0.71**	1		
Pb	0.18NS	0.42**	0.17NS	0.08NS	0.17NS	1	
Zn	0.65**	0.90**	0.76**	0.60**	0.72**	0.56**	1

NS, not significant.
**$P \leq 0.01$.

Table 3
Total variance explained and component matrixes (two factors selected)[a]

Total variance explained

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of Variance	Cumulative (%)
1	4.85	69.31	69.31	4.85	69.31	69.31	4.35	62.20	62.20
2	1.14	16.26	85.57	1.14	16.26	85.57	1.64	23.38	85.57
3	0.45	6.43	91.99						
4	0.28	4.01	96.00						
5	0.17	2.45	98.45						
6	0.07	0.96	99.41						
7	0.04	0.59	100.00						

Component matrixes

Element	Component matrix		Rotated component matrix	
	F1	F2	F1	F2
Cr	0.95	−0.20	0.96	0.16
Cd	0.93	0.16	0.94	0.15
Ni	0.92	−0.21	0.86	0.15
Zn	0.89	0.32	0.82	−0.02
As	0.86	−0.17	0.81	0.49
Cu	0.76	−0.32	0.71	0.63
Pb	0.37	0.89	0.02	0.97

[a] Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in three iterations.

3.4. Spatial structure and distribution analysis of heavy metal concentrations in soils around Guanting Reservoir

The best-of-fit models were retained for kriging. For As, Cd, Cu, Pb and Zn, these were the isotropic spherical variograms, with nugget (see Eq. (1)):

$$r(h) = \begin{cases} C_0 + C\left[1.5(h/a) - 0.5(h/a)^3\right] & \text{for } h \le a \\ C_0 + C \quad h > a \end{cases} \qquad (1)$$

where h is the lag distance; C_0, the nugget variance; C, the sill; and a, the range. However, the fit of the geostatistical model for Cd was not significant. For Cr and Ni, the best model was isotropic exponential variogram (see Eq. (2)):

$$r(h) = C_0 + C[1 - \exp(-h/a)] \qquad (2)$$

The fit of the geostatistical model for Pb was not significant. The types of model and their coefficients are given in Table 4. The models are also represented as solid lines, with the experimental values plotted as points (Fig. 3). Apart from Cd and Pb, the fit of geostatistical model for the other heavy metal concentrations was significant ($P < 0.05$), indicating that most models best described spatial dependence of the metal concentrations.

The spatial structures of metals are dominated by geological effects (with relatively long range) and human activities (with relatively short range) (Webster et al., 1994). For the study area, semivariograms of Cd, Pb and Zn are dominated by the short-range structure, while those of As, Cr, Cu and Ni are

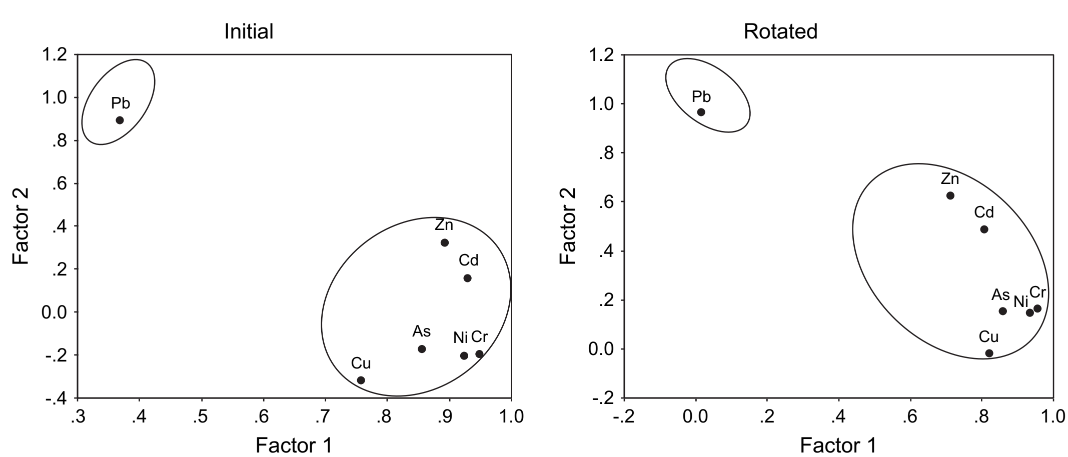

Fig. 2. Factor score distributions for heavy metal concentration in soils around Guanting Reservoir.

Table 4
Geostatistical models describing the concentrations of heavy metal in surface soils around Guanting Reservoir

Variable	Transformation	Model	C_0	C_0+C	$C_0/(C_0+C)$	a (m)	r^2
As	None	Spherical	2.30	4.45	0.52	9420	0.72**
Cd	ln(Cd)	Spherical	0.01	0.06	0.17	2140	0.01NS
Cr	ln(Cr)	Exponential	0.03	0.06	0.50	17,080	0.49*
Cu	ln(Cu)	Spherical	0.21	0.41	0.51	68,710	0.79**
Ni	ln(Ni)	Exponential	0.10	0.20	0.50	34,300	0.49*
Pb	ln(Pb)	Spherical	0.04	0.61	0.07	2140	0.05NS
Zn	ln(Zn)	Spherical	0.00	0.11	0.00	2140	0.38*

Significant at the 0.05(*) or 0.01(**) level of probability.
NS, not significant.

dominated by the long-range structure (Table 4). The ratio of nugget effects (C_0) (nugget effect is used to quantify the sampling and assaying errors and the short scale variability) to sill (C_0+C) (sill is the total vertical scale of the variogram) is a very important indicator for reflecting the spatial variation on a regional scale (Robertson et al., 1997). The value of the ratio shows which factor is predominant between regional factors (natural factors) and non-regional factors (anthropogenic factors). If the value is less than 0.5, it means that the heavy metal in soil has a strong spatial autocorrelation on the studied scale. Therefore, the contents of As, Cr, Cu and Ni in soils around Guanting Reservoir are mainly affected and controlled by natural factors, while Cd, Pb and Zn are dominated by human activities.

Based on data description, analysis of correlation coefficients, PCA, and geostatistical analysis, it can be concluded that the primary input of Pb has been due to human activities, while the input of Cd and Zn is from both natural and human activities. Only natural processes account for As, Cu, Cr and Ni concentrations.

The variogram models were used as input to ordinary kriging and the resulting contour maps are shown in Fig. 4. The contour maps illustrate several relatively great concentrations 'hotspots' exist for each of the metals studied. The greatest concentrations of As, Cd, Cr, Ni, Zn and Cu are near Huailai County, Yanghedaqiao and the entrance of the reservoir (approaching Guanting town). This is downstream of the Yanghe and Sanggan Rivers – the two most polluted sub-water systems flowing to Guanting Reservoir (Ma et al., 2003). The greatest concentration of As and larger concentrations of Cd, Cr, Cu and Ni were observed near Yanqing County where the Weishui River flows through. In general, pollution is greatest in the east, less in the west, and least in the center of Guanting Reservoir areas.

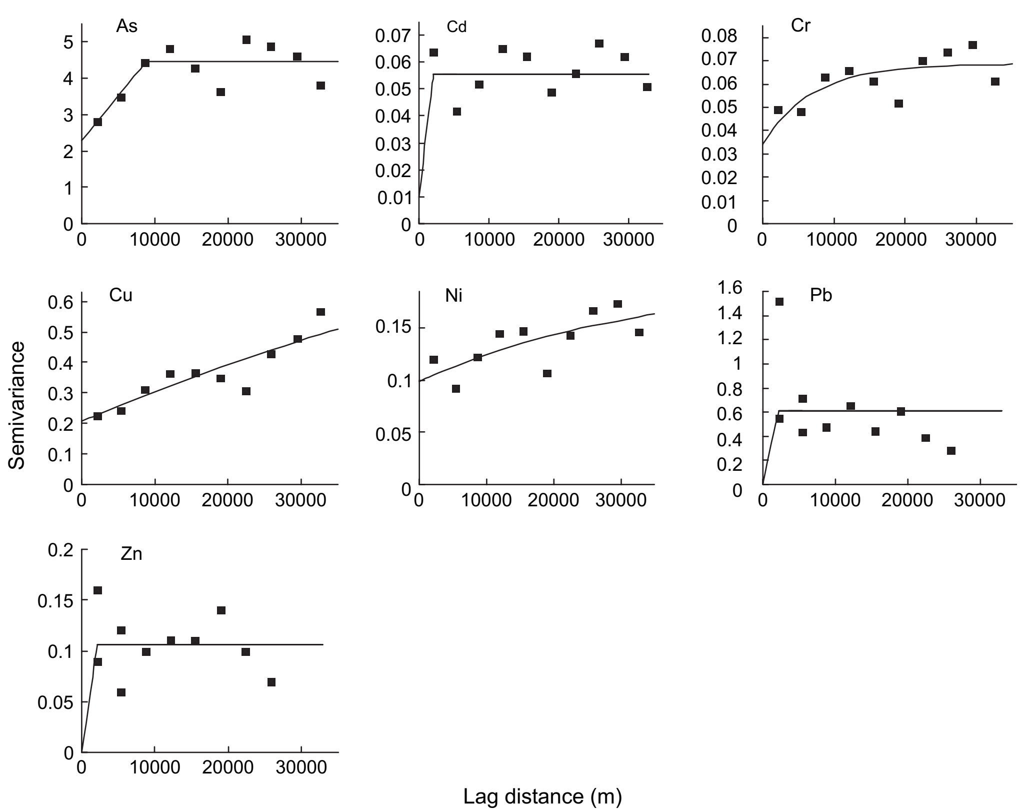

Fig. 3. Semivariograms of In-transformed heavy metal concentrations (except As) plotted as points and fitted models shown as solid lines.

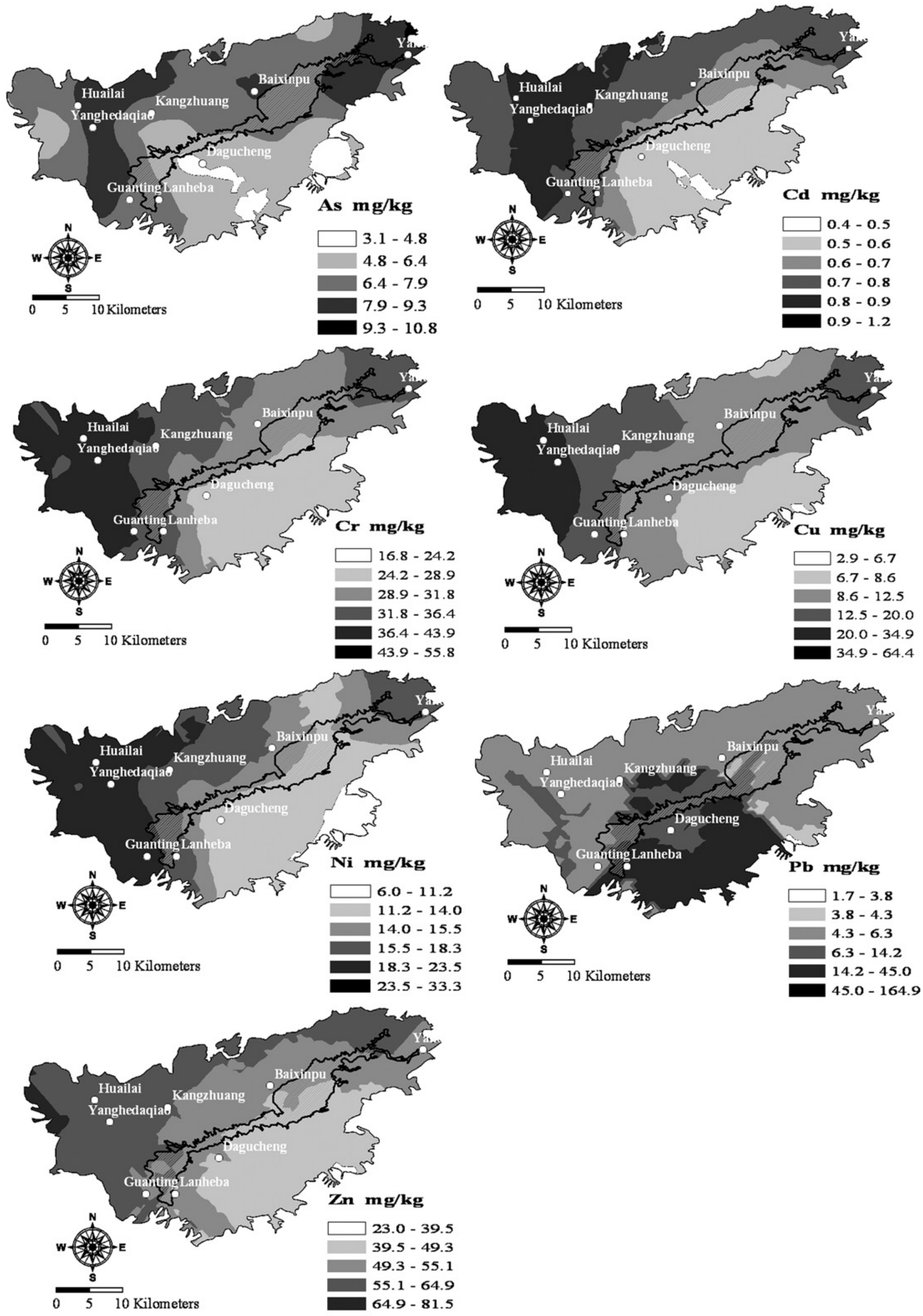

Fig. 4. Contour maps for all heavy metal concentrations in surface soils (0–10 m) around Guanting Reservoir.

4. Source identification and discussion

The soils of Huailai County are deficient in phosphate. Thus, phosphate fertilizer has been applied in large quantities to increase agricultural production after the first phosphate fertilizer plant was established in Huailai (Yang et al., 2004). The local pyrite and phosphate rocks used by the phosphate fertilizer plant contained large concentrations of Cd (1.94 and 0.258 mg/kg dry wt for pyrite and phosphate rocks, respectively). According to the monitoring conducted in 1973, the concentrations of Cd in sludge and wastewater generated by the phosphate fertilizer plant were as great as 6.53 mg/kg dry wt and 87.5 mg/L, respectively (OLGGWP, 1977). Since inputs of Cd in fertilizers, concentrations of Cd in sludge and wastewater are greater than that already present in the soil, application of phosphate fertilizer, wastewater and sludge are the predominant sources of Cd in soils of Huailai County and subsequent runoff to both Cd and PO_4^{-3} to Guanting Reservoir (Sun and Hao, 2004).

According to contour maps the Cd and Zn distributions in soils around Guanting Reservoir are similar. This is due to the fact that they likely have similar sources, regardless whether it is man-made or geochemical. Zn concentrations are correlated with those of Cd (Table 2). Thus, zinc in the soils around Guanting Reservoir may be due to the application of phosphate fertilizer. It is well known that there are high concentrations of Zn and Cd in phosphate deposits (Adriano, 1986; Eriksson et al., 1995; Nan et al., 2002). Alternatively, the predominant rocks (intermediate igneous rock and acidic igneous rock) around Guanting Reservoir have levels of Zn (86.6 and 73.8 mg/kg dry wt, respectively) (NEPA, 1990) greater than the reference value of Zn in soils. This, in combination with the results of statistical analyses, suggests that both the natural factors and the anthropogenic factors (such as fertilizing soils with Zn-containing phosphate fertilizers) have affected concentrations of Zn in soils around Guanting Reservoir.

It was reported in 1973 there were 30 enterprises that released wastewater containing As into the Yanghe River, but only three of these enterprises drained wastewater containing As that exceeded National Discharge Standards of Wastewater (OLGGWP, 1977). Furthermore, the As in wastewater can be rapidly self-purified around the mouth of the drainage. Therefore, wastewater irrigation is not likely to be responsible for As pollution in soils around Guanting Reservoir. Compared with As concentrations (2–8 mg/kg dry wt) in soils in Huailai County that were measured in 1973 (OLGGWP, 1977), present As concentrations (3.06–10.90 mg/kg dry wt) are slightly greater (Table 1). Also, the concentrations of As in two major rock types around Guanting Reservoir were 8.1 and 7.7 mg/kg dry wt (NEPA, 1990), approaching or exceeding its reference value (7.81 mg/kg dry wt) (Table 1). This result suggests that As pollution in some soils around Guanting Reservoir is due to natural causes.

Wastewater drainage of Cr into Guanting Reservoir was relatively small compared to other metals. Although there were 27 enterprises discharging wastewater containing Cr, nine of which released Cr with concentrations that exceeded the National Discharge Standards of Wastewater (OLGGWP, 1977). The two predominant rock types in the watershed of Guanting Reservoir had Cr concentrations of 58.3 and 46.8 mg/kg dry wt (NEPA, 1990), greater than the reference of Cr (31.3 mg/kg dry wt). It is thus certain that the greater Cr concentrations in some soils around Guanting Reservoir are due to natural weathering of rocks.

No enterprises had been reported to discharge wastewater containing Ni (OLGGWP, 1977). The small concentrations of Ni in soils were similar to that of the predominant minerals around Guanting Reservoir, which had Ni concentrations of 22.6 and 19.9 mg/kg dry wt, respectively (NEPA, 1990).

Huailai County has a history of grape cultivation for more than 1200 year. In recent years, the grape cultivation area in the County has been expanded to 7333.3 ha (BSZ, 2004). Cu pollution in some soils around Guanting Reservoir might be the result of application of Cu-based fungicide in former vineyards or orchards. However, Cu concentrations in the predominant rocks of the Guanting Reservoir watershed were great (NEPA, 1990). Combining results from our statistical analyses with the information about sources, although there were possibilities of Cu pollution in soils, natural factors would be the main reasons for the low-level Cu pollution in soils around Guanting Reservoir.

Common sources of Pb in soils are manure, sewage sludge, lead–arsenate pesticides, vehicle exhausts and industrial fumes (Kober et al., 1999). Because concentrations of Pb were correlated with those of Cd ($P < 0.01$) and As ($P < 0.5$) (Table 2), land application of phosphate fertilizer containing Cd and lead–arsenate pesticides is likely to be one of the primary reasons for Pb pollution in the soils. But the most important reason, as in other areas of the world, is vehicle exhaust. The patterns of the greatest concentrations of Pb correspond to the major regional traffic axes on the south of the reservoir, approaching Beijing.

Huailai County has a high density of population and industrial enterprises (such as iron-making plant, sulfuric acid plant, plating plant, spinning mill, Zn and Pb mining, paper mill, leather industry, nitrogen fertilizer plant, coking plant, pesticide plant and brewery) that discharge great amounts of wastewater and solid wastes (Du et al., 2004). This has caused heavy metal pollution in soils around Guanting Reservoir. On the other hand, Yanghedaqiao is located downstream of the Yanghe River, which is a tributary of Guanting Reservoir that is polluted by domestic sewage and industrial wastewater (Ma et al., 2003). This may be a reason that Huailai County, Yanghedaqiao and Guanting towns have the greatest concentrations for all metals studied except Pb.

Water quality of the Weishui River is relatively good because there are few small-sized industrial enterprises aside from the Yanqing Paper Mill and Fertilizer Factory (Zhang et al., 2001). This may explain the observation that pollution is less in the western portion of the reservoir than in the east (Fig. 3). Agricultural land in the east and west of the watershed, where Huailai and Yanqin are located, is more heavily used than that in the center of Guanting Reservoir area (Du et al., 2004). Therefore, the heavy metal pollution of soils in the east and west of Guanting Reservoir is more serious than that in the center.

Since the concentration of Cd in the soils around Guanting Reservoir exceeds the national guideline value, the national government should take appropriate action to protect the water source of Guanting Reservoir. Clearly, it should not allow any activities that would add any additional Cd. The metals of greatest concern in soils around Guanting Reservoir seem to be Cd, Cr and Zn. Control is needed to prevent further pollution in the sites with the greatest concentrations observed.

And, the maps of heavy metals in soils around Guanting Reservoir are provided with the information for the purpose.

5. Conclusions

The average concentrations of Cd, Cr, Zn, As, Cu, Ni and Pb in soils around Guanting Reservoir were found to be 0.68, 32.35, 54.28, 6.88, 13.54, 15.81 and 8.21 mg/kg dry wt, respectively. The magnitude or enrichment in soil of metals investigated declines in the order of Cd > Cr > Zn > As > Cu > Ni > Pb. When weighted for the extent of soil contamination the order becomes Cd > Cr > As > Zn > Cu > Ni > Pb.

Semivariograms of Cd, Pb and Zn were dominated by a short-range structure, while those of As, Cr, Cu and Ni were dominated by a long-range structure. Spatial variations on a regional scale for Cd, Pb and Zn are greater than those of other metals. Therefore, the contents of As, Cr, Cu and Ni in soils around Guanting Reservoir are mainly influenced by natural factors, while Cd, Zn and Pb are affected by either human activities or both human and natural factors.

Based on data description, correlation coefficients analysis and PCA and geostatistical analysis, the primary input of Pb is due to human activities. Both human and natural activities influence concentrations of Cd and Zn.

Land application of phosphate fertilizer, wastewater and sludge has been the primary process responsible for the relatively severe Cd pollution in soils around Huailai County. Zinc pollution in some soils around Guanting Reservoir may have resulted from land application of phosphate fertilizer containing relatively great concentrations of Cd, as well as from rocks. Pollution from As, Cr and Ni is likely due to natural sources (rock origin). Partial Cu pollution may have resulted from the application of copper-based fungicide in former vineyards or orchards, but it is primarily due to natural weathering of rocks. The sources of Pb in soils around Guanting Reservoir may have arisen from land application of phosphate fertilizer, but more likely are accounted for by vehicle exhaust. Huailai County, Yanghedaqiao and Guanting towns are relatively large concentration hotspots for all heavy metals, except Pb.

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References

Adriano, D.C., 1986. Trace Elements in the Terrestrial Environment. Springer-Verlag, New York.

Atteia, O., Dubois, J.P., Webster, R., 1994. Geostatistical analysis of soil contamination in the Swiss Jura. Environmental Pollution 86, 315–327.

BSZ (Bureau of Statistics of Zhangjiakou), 2004. Statistical Yearbook of Zhangjiakou (2003). China Statistics Press, Beijing (in Chinese).

Carcia, R., Maiz, I., Millan, E., 1996. Heavy metal contamination analysis of roadsoils and grasses from Gipuzkoa (Spain). Environmental Technology 17, 763–770.

Carlon, C., Critto, A., Marcomini, A., Nathanail, P., 2001. Risk based characterisation of contaminated industrial site using multivariate and geostatistical tools. Environmental Pollution 111, 417–427.

Chen, M., Liu, X.D., Wei, L.W., Chen, H.H., Zhang, L.J., Wang, Y.H., Lin, J., 2001. Distribution of pollutants in water and silt along the upper Yongdinghe River. Rock and Mineral Analysis 20, 131–141 (in Chinese).

Chen, T.B., Zheng, Y.M., Chen, H., Zheng, G.D., 2004. Background concentrations of soil heavy metals in Beijing. Environmental Science 25, 117–122 (in Chinese).

Dijkstra, E., 1998. A micromorphological study on the development of humus profiles in heavy metal polluted and non-polluted forest soils under Scots pine. Geoderma 82, 341–358.

Du, G.S., Wang, J.T., Zhang, W.H., Feng, L.Q., Liu, J., 2004. On the nutrient status of Guanting Reservoir, 2001–2002. Journal of Lake Sciences 16, 277–281 (in Chinese).

Du, X., Wu, D.W., 2004. The reflection on the water environmental prevention for Guanting Reservoir. Beijing Irrigation Works 1, pp. 30–32 (in Chinese).

Einax, J.W., Zwanzinger, H.W., Geib, S., 1997. Chemometrics in Environmental Analysis. VCH A Wiley Company, Weinheim.

Eriksson, J., SöderstrSom, M., Andersson, A., 1995. Cadmium contents in the plough layer of Swedish agricultural soils. Report 4450. Swedish Environmental Protection Agency, Stockholm (in Swedish with English summary).

Facchinelli, A., Sacchi, E., Mallen, L., 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environmental Pollution 114, 245–276.

Better methods for risk assessment. In: Ferguson, C.C., Darmendrail, D., Freier, K., Jensen, B.K., Jensen, J., Kasamas, H., Urzelai, A., Vegter, J. (Eds.), Risk Assessment for Contaminated Sites in Europe. Scientific Basis, vol. 1. LQM Press, Nottingham.

Gamma Design, 1994. Geostatistics for the Environmental Sciences (Version 2.3). Gamma Design, Plainwell, MI.

Gong, Z.M., Cao, J., Zhu, X.M., Cui, Y.H., Guo, L.Q., Tao, S., Shen, W.R., Zhao, X.M., Han, L.X., 2002. Organochlorine pesticide residues in agricultural soils from Tianjin. Agro-Environmental Protection 21, 459–461 (in Chinese).

Huang, M.X., Zhou, C.H., Zhang, S., Zhang, X.M., 2003. Bioavailable phosphorus export by surface runoff from agricultural field plots in Guanting watershed, Beijing. Journal of Lake Sciences 15, 118–124 (in Chinese).

Isaaks, E.H., Srivastava, R.M., 1989. An Introduction to Applied Geostatistics. Oxford University Press, New York.

Jiang, S.J., Wang, J., 2003. The analysis of water pollution and its trend in Guanting Reservoir. Beijing Irrigation Works 2, pp. 31–32 (in Chinese).

Kober, B., Wessels, M., Bollhofer, A., Mangini, A., 1999. Pb isotopes in sediments of Lake Constance, Central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and regional atmosphere - Constrains on the origin(s) and flux(es) of metals. Geochimica et Cosmochimica Acta 63, 1293–1303.

Li, X.D., Lee, S.L., Wong, S.C., Shi, W.Z., Thorntonc, I., 2004. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. Environmental Pollution 129, 113–124.

Liang, T., Wang, H., Ding, S.M., Xue, J.F., Cai, C.X., Zhang, X.M., 2003. An evolution of water quality in Guanting Reservoir during the past three decades. Progress in Geography 22, 38–44 (in Chinese).

Ma, D.J., Zhang, F.G., Gao, Y.X., Zhang, Y.M., Chen, H., 2003. The water quality analysis and evaluation of Guanting Reservoir. Journal of Heibei Institute of Architectural Engineering 21, 70–72 (in Chinese).

Nan, Z.R., Li, J.J., Zhang, J.M., Cheng, G.D., 2002. Cadmium and zinc interactions and their transfer in soil–crop system under actual field conditions. The Science of the Total Environment 285, 187–195.

National Environmental Protection Agency (NEPA), 1990. The Background Values of Soil Elements of China. Chinese Environmental Science Press, Beijing (in Chinese).

OLGGWP (Office of Leading Group for Guanting Water Protection), 1977. The Study of Guanting Water Protection (A Summary of Research Results in 1973–1975). China Water Resources and Hydropower Press, Beijing (in Chinese).

Radha, R., Tripathi, R.M., Vinod, K.A., Sathe, A.P., Khandekar, R.N., Nambi, K.S.V., 1997. Assessment of Pb, Cd, Cu, and Zn exposures of 6- to 10-year-old children in Mumbai. Environmental Research A80, 215–221.

Ratha, D.S., Sahu, B.K., 1993. Source and distribution of metals in urban soils of Bombay, India, using multivariate statistical techniques. Environmental Geology 22, 276–285.

Robertson, G.P., Klingensmith, K.M., Klug, M.J., Paul, E.A., Crum, J.C., Ellis, B.G., 1997. Soil resources, microbial activity, and primary production across an agricultural ecosystem. Ecological Applications 7, 158–170.

Ruiz, F., Gonzalesregalado, M.L., Borrego, J., Morales, J.A., Pendon, J.G., Munoz, J.M., 1998. Stratigraphic sequence, elemental concentrations and heavy metal pollution in Holocene sediments from the Tinto–Odiel Estuary, Southwestern Spain. Environmental Geology 34, 270–278.

Sheppard, D.S., Claridge, G.G.C., Campbell, I.B., 2000. Metal contamination of soils at Scott base, Antarctica. Applied Geochemistry 15, 513–530.

Sun, F., Hao, F.F., 2004. The study of non-point pollution loadings around Guanting Reservoir based on GIS. Beijing Water Conservancy 1, pp. 16–18 (in Chinese).

Tao, S., 1995. Kriging and mapping of copper, lead and mercury contents in surface soil in Shenzhen area. Water, Air and Soil Pollution 83, 161–172.

USEPA (United States Environmental Protection Agency), 1996. Method 3050B: acid digestion of sediments, sludges and soils (revision 2).

Webster, R., Atteia, O., Dubois, J., 1994. Coregionalization of trace metals in the soil of Swiss Jura. European Journal of Soil Science 45, 205–218.

Wei, F.S., Chen, J.S., Wu, Y.Y., Zheng, C.J., 1992. The study of environmental background values of soil in China. Environmental Science 12, 12–19 (in Chinese).

Xu, S., Tao, S., 2004. Coregionalization analysis of heavy metals in the surface soil of Inner Mongolia. The Science of the Total Environment 320, 73–87.

Yang, L.L., Mao, R.Z., Li, H.J., 2004. Discussion on patterns and techniques of optimum utilization of water and land in Huailai County. Research of Soil and Water Conservation 11, 27–30 (in Chinese).

Zhang, F.E., Ma, D.J., Gao, Y.X., Chen, H., Zhang, Y.M., 2001. The situation of the Guanting Reservoir. Journal of Heibei Institute of Architectural Engineering 19, 1–5 (in Chinese).

Zhou, X.F., Tang, W.H., Jin, X.C., 2002. The analysis, evaluation and control of sediment pollution in Guanting Reservoir. Water Supply and Drainage 28, 88 (in Chinese).