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ORIGINAL PAPER

Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China

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Abstract It is accepted that the historical routine use of agrochemicals may have resulted in undesirable concentrations of metals in the environment. To investigate and assess the effects of land use on concentrations of heavy metals around the Guanting Reservoir in China, 52 surface soil samples (depth of 2–10 cm) were taken from areas where four types of land use were practiced (including arable land, woodland, bare land, orchard land). The metals and metalloids (As, Cr, Ni, Cu, Zn, Cd, and Pb) were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Significant accumulation of As, Cd, and Cr was found in soils of arable land. Based on correlation and cluster analysis, it can be concluded that Cd and Zn originate mainly from phosphate fertilizer, Pb from the use of insecticides, fertilizers, and sewage sludge as well as air deposition, and Cu from copper-based fungicides, while As, Ni and Cr might come from parent soil material. According to an ecological risk analysis of metals based on the ecological index suggested by Hakanson, the four types of land can be ranked by severity of ecological risk as follows: arable land > woodland > bare land > orchard land, with a high ecological risk of Cd for all four types. Management measures for land use planners for avoiding water, soil, and sediment pollution caused by metals around the Guanting Reservoir are presented.

Keywords Metals · Land use · Ecological risk

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Introduction

Soils are of central significance in ecosystem research because they are the site of many kinds of interactions between minerals, air, water, and the living environment (Bloemena et al. 1995). Soil generally reacts more slowly to outside influences than do water and air, as it is able to bind substances or incorporate them into soil complexes. In this way, soil accumulates both organic and inorganic substances. However, a side effect of this function is that

soil collects not only nutrients but also pollutants (Adriano 1992). Since surface layers of soil, where pollutants can accumulate and reach relatively high concentrations, are the main rooting zone for vegetation and also the area with the greatest exposure to animal and human life, they are the focus of our research.

It is now accepted that the historical routine use of agrochemicals (such as pesticides and fertilizers) may have resulted in undesirable concentrations of trace elements, such as arsenic, cadmium, copper, mercury, lead, and zinc accumulating in some soils (Van Gaans et al. 1995; Merwin et al. 1994; Webber and Wang 1995; Harris et al. 2000). The contamination of soil with elevated concentrations of trace elements can have adverse effects on soil biology (microbiological communities and invertebrates) and hence soil ecosystem function (Merrington et al. 2002; Giller et al. 1998). Elevated concentrations of trace elements in soils can also have phytotoxic effects and result in trace element contamination of edible crops (Merry et al. 1986; Cobb et al. 2000). Humans can be exposed to toxic trace elements through direct soil ingestion as well as through the consumption of food produced on contaminated land (Nicholson et al. 2003).

Land use change can simultaneously cause both beneficial and harmful effects, because any change in land use has important consequences for many biological, chemical, and physical processes in soils and so, indirectly, the environment (Goulding et al. 1995; Goulding and Blake 1998, 1993; Sverdrup et al. 1995). Soil pollution (especially metal pollution) has become an important environmental issue in developed countries (e.g., the Netherlands, the United Kingdom, and Spain) due to changes in the land use pattern over the last few decades (Adriano 2001). Knowledge of metal concentrations for different land use types, which has scarcely been investigated, is of critical importance in assessing human impact on metal concentrations in soils (Chen et al. 2005a). There have been several studies on the accumulation of metals in soils under different land use in China, with different accumulation effects being found in soils under different land use (Zheng et al. 2005a, b, c, d; Chen et al. 2005b, c; Bloemena et al. 1995; Gaw et al. 2006). However, past studies focused mainly on the metal contaminations of soils affected by farming, industry, or urban development. There have been few studies on the metal contamination of soils in ecologically sensitive areas such reservoir areas, which are the source sites of drinking water.

The Guanting Reservoir is one of the five major water systems in Beijing. Prior to 1997, water from the reservoir was used as a source of drinking water for Beijing. Since then, however, industrial pollution and farming contamination have substantially degraded the quality of water in the reservoir (Ma et al. 2001; Wang et al. 2003). Soil can be polluted by wastewater irrigation. The metals in soils can also reach aquatic ecosystems by erosion and runoff from agricultural land (Pinay et al. 1992). Soils contaminated in these ways may have an impact on water quality. Protection of the soil around the Guanting Reservoir is of great importance for safeguarding the water quality in the reservoir.

Currently there is limited information available to regulatory authorities with a mandate to manage metals in soils under different land uses around the Guanting Reservoir. Analysis of the effects of land use on metal concentrations in soils is, therefore, critical for the making of policies aimed at reducing metal inputs to soil and guaranteeing the maintenance or even improvement of soil functions and water quality of the reservoir. The data provided in this study are considered important for reservoir remediation, especially since the Guanting Reservoir will serve as one of the main drinking water sources for Beijing in the foreseeable future. In this work, the potential ecological risk of soil contamination was assessed using the contamination factors and degrees of contamination suggested by Hakanson (1980). The ecological risk index was used as a diagnostic tool for determining the degree of pollution in sediment or soil.

The aims of the study were (1) to determine contents of As, Cd, Cr, Cu, Ni, Pb and Zn in soils of different land use; (2) to determine their natural or anthropogenic source using multivariate analysis; and (3) to assess the ecological risk from different land uses and provide land planners with some management policies to reduce the input of metals into the environment.

Materials and methods

Site description

The Guanting Reservoir is located northwest of Beijing city (Latitude 40.19°$\sim$ 40.50°, Longitude

115.43° ~ 115.97°). The study area covers about 920 km^2, including the 98 km^2 reservoir and 820 km^2 of surrounding land. The land use types around the Guanting Reservoir are woodland, orchard land, arable land, and bare land, which together account for about 90% of the total area. Agriculture is the major land-use in the area around the Guanting Reservoir. From the 1960s to the 1980s, large amounts of agrochemicals were applied to the agricultural areas of the Guanting Reservoir. In the past several years, the average chemical fertilizer application was about 107 kg/ha and pesticide usage was about 4.5 kg/ha. However, the efficiency of their usage was only 30–60%. Most chemical fertilizers and pesticides used entered the water environment by several means such as surface water run-off and soil erosion. The major soil type in this area is calcareous cinnamon soil. The main parent materials are lithogenic rocks. The characteristics of soils are as follows: pH = 7.6 ± 0.2, total P = 666 ± 37 mg/kg, total N = 1203 ± 174 mg/kg, total C = 1.8 ± 1.3%.

Sampling

Sampling sites around Guanting Reservoir (Fig. 1) were selected according to land use. Results are reported for 52 composite soil samples. At each sampling site, five surface samples (0–10 cm in depth) were collected from a 100×100 m^2 plot (located on crossing diagonals: four in the corners and one at the crossing point). A composite surface soil sample was collected from each sampling plot. The sampling scheme takes into account sites representing the most relevant characteristics of the environment and each soil type.

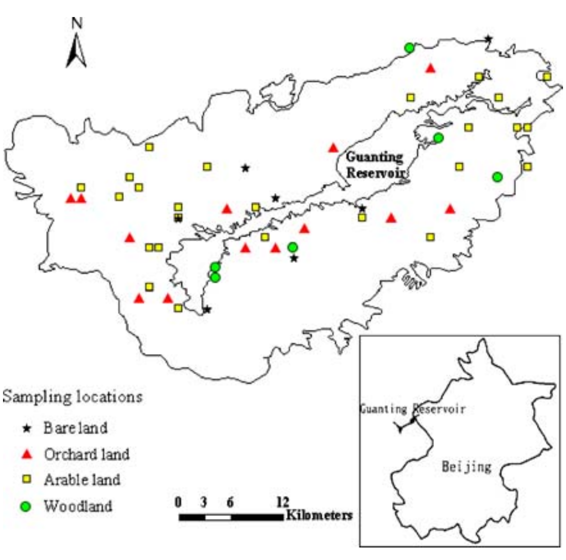

Fig. 1 Sampling locations around the Guanting Reservoir

Metal analysis

Soil samples were air-dried, crushed in an agate mortar, passed through a nylon sieve of 0.149 mm, and digested with HNO_3 and H_2O_2 using Method 3050B (USEPA 1996). Concentrations of metals (Cd, As, Cu, Ni, Pb and Zn) in the digestion solution were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). 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. Rigorous QA/QC protocols were followed, including insertion of "blind" standard reference materials for determination of the accuracy of the methods, and analytical duplicates to allow estimation of the precision of the method. Satisfactory recoveries were obtained for Cu (92–95%), Ni (101–108%), Pb (94–106%), Cd (96–99%), As (97–101%) and Zn (94–103%).

Statistical analyses

Statistical analyses were conducted using Microsoft Excel and SPSS 10.01 software (SPSS, Chicago, IL). The distribution of data was tested with the Kolmogorov-Smirnov method. Statistical evaluation was performed by analysis of variance (ANOVA), and Pearson's rank correlation (data with normal distribution). Post-hoc tests were employed with LSD (the data were normally distributed and passed the test of homogeneity of variances). The level of significance was set at $P < 0.05$ (two-tailed).

To evaluate the analytical data, correlation analysis and cluster analysis (CA) were used. The Pearson correlation coefficient (data with normal

distribution), r, was used to measure the strength of a linear relationship between two metals. CA was used to elucidate the latent relationships between heavy metals in soils of the same kind of land use around the Guanting Reservoir, and for investigating heavy metal sources. Hierarchical CA was performed using the following settings: the linkage type used was furthest neighbor and the distance method was the Pearson correlation.

Results and discussion

Descriptive parameters and probability distribution of the concentrations of metals around the Guanting Reservoir

Since the probability distributions of the raw data sets of Cu and Pb were heavily skewed, it was necessary to transform data prior to further statistical analyses. Descriptive parameters and probability distributed are shown in Table 1. The Kolmogorov-Smirnov test indicated that the concentrations of As, Cd, Cr, Ni and Zn followed normal distributions and that those of Cu and Pb were ln-normal distributed (K-S $P > 0.05$). Combining all data yielded a normal distribution and allowed a confident comparison of mean values for different types of land use.

The range of Pb (164.88 mg/kg dry wt) (between the minimum and maximum values) was largest, and its variation (coefficient of variation = 274.04%) and skewness (skew = 6.89) were also the highest of all the studied samples. This suggests that there are several locations having great Pb concentrations, which means the soil in some areas is more contaminated.

The coefficients of variation for most metals, except Cu and Pb, were between 20 and 40%. This means that human activities have moderate effects on the concentrations of most metal pollution in soils around the Guanting Reservoir.

Based on the range of background concentration shown in Table 1, most of the As, Cr, and Ni values measured in soils are within their corresponding range of background concentrations. However, some values of Cd, Pb, Cu, and Zn exceed the range of the corresponding background concentrations. This result suggests that, in some locations, pollution Cd, Pb, Cu, and Zn in soils has taken place. The concentrations of Cu and Pb in some locations have values in the range considered toxic to plants (Table 1). Although the Cd concentrations in all samples exceeded the mean background concentration, they do not exceed the range considered toxic for plant growth (3–8 mg/kg dry wt).

Effects of land use on concentrations of metals in top soils around the Guanting Reservoir

Four types of land uses (arable land, orchard land, bare land, and woodland) were identified for the Guanting Reservoir area. Concentrations of metals in soils from different land uses are presented in Table 2. Based on the results of an ANOVA of metal concentrations in soils of different land use (Table 3), there were significant differences between different land uses for As, Cd and Cr, and no significant differences for Cu, Ni, Pb and Zn. Using post-hoc tests with LSD, it was found that significantly greater concentrations of As, Cd, and Cr values existed in soils of arable land around the Guanting Reservoir. However, mean concentrations of Cu and Pb that occurred in soils of orchard land were not significantly greater than those in other types of land (Table 2).

Correlation analysis was conducted to determine the extent of the relationships among metals in soils of different land use. The correlation matrix in Table 4 shows that Pb does not correlate with any metal in soils of arable land ($P > 0.05$), suggesting perhaps different soil sources from other metals. Cd, Cr, Ni, and Zn are closely related to each other ($r > 0.92$, $P < 0.01$). This suggests that Cd, Cr, Ni, and Zn may have another common origin.

In soils of orchard land, Ni, As, Cd, and Cr are closely related to each other ($r > 0.8$, $P < 0.01$) (Table 4), suggesting they have a common source. Pb and Zn form another group based on their significantly positive correlation ($r = 0.81$, $P < 0.01$). This suggests that Pb and Zn might have another source. Cu is poorly correlated with other metals, which means that it has a source different from the two sources above.

The correlation matrix in Table 5 shows that Pb is weakly correlated with other metals (except Ni) in soils of bare land ($P > 0.05$), while concentrations of As,

Table 1 Summary statistics of heavy metals in soils around the Guanting Reservoir (mg/kg dry wt)

	As	Cd	Cr	Cu	Ni	Pb	Zn
Minimum	3.06	0.39	16.78	2.86	5.95	1.74	22.99
Maximum	10.9	1.2	59.36	64.37	33.33	164.88	109.33
Mean	6.88	0.68	32.35	13.54	15.81	8.21	54.28
Skew	–0.03	0.8	0.97	2.93	1.04	6.89	0.96
Kurt.	–0.83	1.23	1.52	12.63	1.17	48.63	1.36
Coefficient of variation, %	30.66	24.67	26.73	73.44	38.17	274.04	32.36
K-S *P*	0.89	0.34	0.43	0.91[a]	0.24	0.12[a]	0.29
Mean of background concentration[b]	7.81 ± 3.22	0.15 ± 0.11	31.3 ± 9.29	19.7 ± 6.33	27.9 ± 7.90	25.1 ± 5.08	59.6 ± 16.29
Value considered toxic range for plant growth[c,d]	20	3–8	75–100	60–125	100	100–400	70–400

[a] Data set is ln-transformed

[b] Chen et al. (2004)

[c] Ross (1994)

[d] Singh and Steinnes (1994)

Cd, Cr, Cu, Ni, and Zn were correlated ($P < 0.05$). However, there were correlations between concentrations of As and Cu, Cr and Cu, and Ni, between Pb and Zn in soils of woodland ($P < 0.05$), while Cd was significantly related to Zn ($P < 0.01$).

The correlation analysis provides little information about the sources of metals. Thus, cluster analysis was performed on elemental concentrations in the arable land, orchard land, bare land, and woodland soils, using the furthest neighbor linkage method based on correlation coefficients (the Pearson coefficient). The results are illustrated in the dendrograms in Figs. 2–4. The distance cluster represents the degree of association between elements. The smaller the value on the distance cluster, the more significant the association. A criterion for distance clusters requiring that they be between 10 and 15 was adopted.

In arable soils, three distinct clusters were identified (Fig. 2). Cluster I contains Cr, Ni, Cd, Zn, As, and Cu. Since the concentrations of Cr and Ni in soils of arable land are less than their corresponding background concentrations, it can be deduced that they originated from natural sources. However, the mean concentration of Cd is greatest in soils of all kinds of land use. This might be caused to a great extent by the large-scale land application of phosphate fertilizers that contained Zn, As, and Cr (Yang et al. 2004; Ma and Liu 1998; Wang 2000; Tayler 1997). In addition, wastewater irrigation and land application of sludge are likely important sources of Cd and Cr in soils around Guanting Reservoir (Sun and Hao 2004). In addition, the elevated concentrations of arsenic on arable land have resulted from the use of arsenic-based insecticides to control chewing insects (Merry et al. 1983; NSWEPA 1995). In summary, these metals probably came from natural parent materials of soils, application of pesticide and fertilizer, and wastewater irrigation.

Cluster II contains Pb, which have originated from the natural parent materials of the soils because the range of Pb on arable land is 1.95–11.17 mg/kg dry wt (Table 2), which is less than the limited range of its background concentration (11.5–38.2 mg/kg dry wt, shown in Table 1).

In orchard soils, three distinct clusters can be identified (Fig. 3). Cluster I contains Cr, Ni, As, and Cd. Although there is no significant difference for each of these metals in soils among orchard land, bare land, and woodland (Table 2), it should be emphasized that the concentrations of these metals in orchard land still represent a considerable absolute quantity. It can be deduced that Cr, Ni, As, and Cd probably came from natural materials.

Cluster II contains Cu. The mean concentration of Cu on orchard land around Guanting Reservoir represents a considerable absolute quantity greater than those in the other types of land. There is a long history of grape cultivation (more than 1,200 years) around Guanting Reservoir. More than ten large

Table 2 The concentrations of heavy metals in soils from different land use around the Guanting Reservoir (mg/kg dry wt)

Heavy metal	Land use	Mean*	SD	Minimum	Maximum
As	Arable land (n = 25)	7.80[a]	2.00	3.31	10.90
	Orchard land (n = 14)	5.57[b]	2.02	3.06	8.79
	Bare land (n = 7)	6.70[ab]	1.72	3.68	8.65
	Woodland (n = 6)	6.30[ab]	1.56	4.58	8.44
Cd	Arable land (n = 25)	0.75[a]	0.17	0.53	1.20
	Orchard land (n = 14)	0.60[b]	0.14	0.39	0.79
	Bare land (n = 7)	0.63[ab]	0.13	0.39	0.75
	Woodland (n = 6)	0.66[ab]	0.16	0.50	0.92
Cr	Arable land (n = 25)	35.98[a]	9.62	20.76	59.36
	Orchard land (n = 14)	27.87[b]	6.05	20.05	38.57
	Bare land	30.41[ab]	6.99	16.78	38.00
	Woodland (n = 6)	29.96[ab]	5.52	25.70	38.13
Cu	Arable land (n = 25)	14.68[a]	6.94	4.99	28.61
	Orchard land (n = 14)	15.81[a]	16.07	3.94	64.37
	Bare land (n = 7)	9.50[a]	3.70	3.07	13.53
	Woodland (n = 6)	8.24[a]	3.61	2.86	12.76
Ni	Arable land (n = 25)	17.76[a]	6.51	8.08	33.33
	Orchard land (n = 14)	13.72[a]	5.93	5.95	30.04
	Bare land (n = 7)	14.70[a]	4.25	6.25	18.39
	Woodland (n = 6)	13.87a	4.21	10.22	21.63
Pb	Arable land (n = 25)	5.31[a]	2.09	1.95	11.17
	Orchard land (n = 14)	17.16[a]	43.10	1.77	164.88
	Bare land (n = 7)	3.86[a]	1.11	2.00	5.80
	Woodland (n = 6)	4.51[a]	2.00	1.74	7.82
Zn	Arable land (n = 25)	58.84[a]	14.56	37.82	92.70
	Orchard land (n = 14)	50.11[a]	21.66	24.93	109.33
	Bare land (n = 7)	46.08[a]	12.43	22.99	58.05
	Woodland (n = 6)	54.53[a]	21.82	34.90	95.99

[*] Land uses followed by different letters are significantly different at the $P < 0.05$ level

Table 3 ANOVA of heavy metals for different land uses around the Guanting Reservoir

	As	Cd	Cr	Ni	Zn	Cu[a]	Pb[a]
F	4.227	3.125	3.417	1.797	1.362	2.008	0.427
Significance	0.010	0.034	0.025	0.160	0.265	0.125	0.734

[a] ln transformation

grape vine plantations (including the famous Great Wall Grape Vine Plantation) are located in the area. A wide range of relatively high copper concentrations in orchard soils, especially in vineyard soils, has been reported in the international literature (Merry et al. 1983; Deluisa et al. 1996; Besnard et al. 2001). Holland and Solomona (1999) proposed that elevated soil copper concentrations in orchard soils arise from the long-term use of copper-based fungicides. The application of Cu-based fungicide in former vineyards or orchards could be mainly responsible for the great concentration of Cu in orchard land around the Guanting Reservoir. Therefore, Cu in the orchards came from pesticides.

Table 4 Correlations between heavy metal contents in the studied soils of arable land and orchard land[a]

	As	Cd	Cr	Cu	Ni	Pb	Zn
As		0.69**	0.72**	0.63**	0.64**	0.21	0.75**
Cd	0.80**		0.96**	0.78**	0.94**	0.21	0.94**
Cr	0.82**	0.78**		0.79**	0.97**	0.18	0.92**
Cu	0.39	0.31	0.60*		0.80**	0.10	0.85**
Ni	0.81**	0.7**	0.85**	0.30		0.20	0.92**
Pb	0.00	0.41	0.08	–0.04	0.01		0.32
Zn	0.48	0.78**	0.54*	0.33	0.43	0.81**	

[a] Pearson coefficients for arable land and orchard land are shown above and below the diagonal line, respectively

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Table 5 Correlations between heavy metal contents in the soils of bare land and woodland[a]

	As	Cd	Cr	Cu	Ni	Pb	Zn
As		0.86*	0.86*	0.89**	0.92**	0.75	0.86*
Cd	–0.09		0.96**	0.96**	0.94**	0.75	0.99**
Cr	0.76	0.22		0.89**	0.88**	0.67	0.94**
Cu	0.90*	–0.25	0.82*		0.96**	0.75	0.98**
Ni	0.74	0.17	0.87*	0.87*		0.80*	0.95**
Pb	–0.09	0.84*	0.04	–0.41	–0.15		0.77*
Zn	–0.30	0.96**	0.03	–0.48	–0.10	0.89*	

[a] Pearson coefficients for bare land and woodland are shown above and below the diagonal line, respectively

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

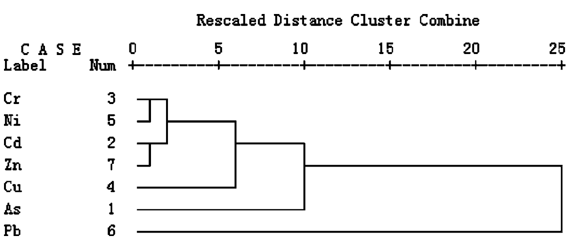

Fig. 2 Dendrogram of the cluster analysis of arable soils based on heavy metal concentrations

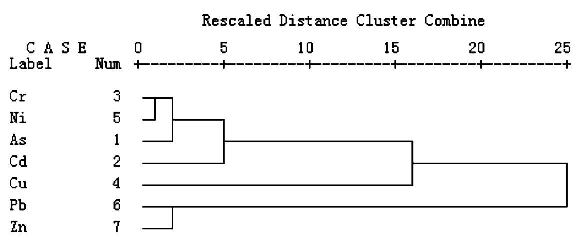

Fig. 3 Dendrogram of the cluster analysis of orchard soils based on heavy metal concentrations

Cluster III contains Pb and Zn. In our study, the mean concentration of Pb in orchard land was significantly great, which is consistent with other studies (Merry et al. 1983; Merwin et al. 1994; Gaw et al. 2003). The elevated lead concentrations in orchard samples has been shown to be most likely due to the use of insecticides that contained lead (Gaw et al. 2003). Zinc is an ingredient in pesticides, especially fungicides (Long 1983), and fertilizer use has been implicated in elevated zinc concentrations in soils (Taylor and Percival 2001). It was revealed by another study that the Zn content in soils came from long-term anthropogenic activity connected with grape-growing (Facchinelli et al. 2001). Thus, it can be concluded that Zn in soils of orchard land comes mainly from impurities

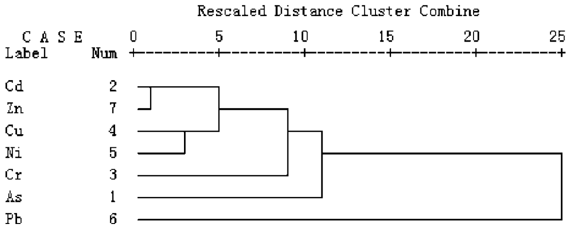

Fig. 4 Dendrogram of the cluster analysis of bare land soils based on heavy metal concentrations

in fertilizer and pesticides used in vineyards around Guanting Reservoir.

In the bare land soils, two distinct clusters were identified (Fig. 4). Cluster I contains As, Cd, Cr, Zn, Ni, and Cu. Mean concentrations of As, Cr, and Ni in soils of bare land were greater than those in orchard and woodlands. It was estimated that about 1.6361×10^8 tons of industrial waste and domestic rubbish per year were dumped on bare land upstream of Guanting Reservoir (OLGGWP 1977; Du et al. 2004). (For example, concentrations of Cd in some sludge, pyrite, and phosphate rocks were 6.5, 1.9, and 0.2 mg/kg around Guanting Reservoir, respectively.) Thus, this cluster of metals might originate from land application of fertilizers and solid wastes.

Cluster II contains Pb. The group of Pb is remarkably different from the other metals in terms of distance in CA, which implies a different origin from the other metals. The range of Pb in soils of bare land (Table 2) is less than the range of background concentrations of Pb (Table 1). It can be deduced that Pb came from natural parent materials of soils.

In woodland soils, two distinct clusters can be identified (Fig. 5). Cluster I contains Cd, Zn, and Pb. Atmospheric pollutants might have affected forests and soils. In particular, the long-range atmospheric transport of metals could lead to pollutant deposition even in more remote areas (De Vries et al. 2002). In Sweden, for example, with increasing industrial activity, Pb and Cd contents have increased by 50% in upper soil organic layers (EEA 1998). An investigation showed that the Guanting Reservoir area was rich in coal mines, pyrite, and phosphate rocks, which contain large concentrations of Cd and Zn (OLGGWP 1977). This means that air deposition may be responsible for the high concentrations of Cd, Zn, and Pb in some woodland soils.

Cluster II contains Cr, Ni, Cu, and As. Concentrations of these metals in woodland are significantly less than those in arable land (Table 2). Woodland soil contained less Cr, Ni, Cu, and As because it had received less fertilizer and pesticide than arable and orchard soils. This means that these metals may originate from the natural parent materials of the soils.

Assessment of ecological risks of metals in soils of different land use around the Guanting Reservoir

The assessment of soil contamination was conducted using the contamination factor and degree. In the version suggested by Hakanson (1980), an assessment of soil contamination was conducted through reference of the concentrations in the surface layer of bottom sediments to pre-industrial concentrations:

$$C_r^i = \frac{C_i}{C_n^i}.$$

Here C_i is mean concentration of an individual metal examined and C_n^i is the pre-industrial concentration of the individual metal. In our work, we applied the background concentration of a metal in the soil of Beijing (Table 1) as the pre-industrial concentration of each individual metal. C_r^i is the single-element index. The sum of contamination factors for all metals examined represents the contamination degree (C_d) of the environment:

$$C_d = \sum_{i=1}^{n} C_r^i$$

E_r^i is the potential ecological risk index of an individual metal. It can be calculated by

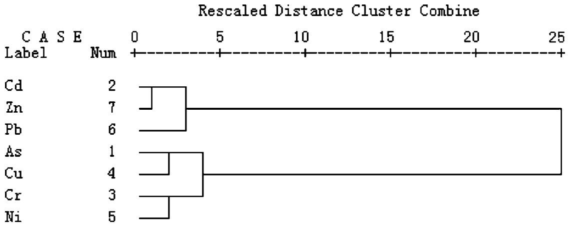

Fig. 5 Dendrogram of the cluster analysis of woodland soils based on heavy metal concentrations

$$E_r^i = T_r^i \times C_r^i,$$

where T_r^i is the toxic response factor provided by Hakanson (Zn = 1, Cr = 2, Cu = Ni = Pb = 5, As = 10, Cd = 30). RI is the potential ecological risk index, which is the sum of E_r^i.

$$RI = \sum_{i=1}^{n} E_r^i = \sum^{n} T_r^i \times C_r^i$$

Hakanson (1980) defines four categories of C_r^i, four categories of C_d, five categories of E_r^i, and four categories of RI, as shown in Table 6.

Based on the single-element index (C_r^i) (Table 7) and its grades (Table 6), the soil of arable land was classified as moderately contaminated with As and Cr, considerably contaminated with Cd, and slightly contaminated with Cu, Ni, Pb, and Zn. The soils of orchard land, bare land, and woodland were classified as considerably contaminated with Cd and slightly contaminated with As, Cr, Cu, Ni, Pb, and Zn.

The assessment of the overall contamination of soil was based on the degree of contamination (C_d). The degree of contamination was of the following order: arable land > orchard land > woodland > bare land (Table 7). However, by ANOVA of C_d, it was found there was no significant difference ($P > 0.05$) for C_d between land use. The range of C_d for all kinds of land use is 7.99–9.75, which indicates moderate contamination of the environment around Guanting Reservoir. The maximum value of C_d (16.33 in soils of orchard land, shown in Table 7) indicates considerable contamination in soils of orchard land.

Combining the potential ecological risk index of individual metals (E_r^i) and the potential ecological risk index of the environment (RI) (Table 8) with their grade classifications (Table 6), soils in all kinds of land use were classified as posing considerable potential ecological risk with Cd and little potential ecological risk with As, Cr, Cu, Ni, Pb, and Zn. The potential ecological risk indices of the environment for the different types of land use can be ranked in the following order: arable land > woodland > bare land > orchard land. Also, the potential ecological risk index of the environment of arable land was found to be significantly greater than that of orchard land by ANOVA of RI. However, further study is needed to

Table 6 Indices and grades of potential ecological risk of heavy metal pollution

C_r^i	Contamination degree of individual metal	C_d	Contamination degree of the environment	E_r^i	Grades of ecological risk of individual metal	RI	Grades of potential ecological risk of the environment
$C_r^i < 1$	Low contamination	$C_d < 5$	Low contamination	$E_r^i < 40$	Low risk	$RI < 65$	Low risk
$1 \le C_r^i < 3$	Moderate contamination	$5 \le C_d < 10$	Moderate contamination	$40 \le E_r^i < 80$	Moderate risk	$65 \le RI < 130$	Moderate risk
$3 \le C_r^i < 6$	Considerable contamination	$10 \le C_d < 20$	Considerable contamination	$80 \le E_r^i < 160$	Considerable risk	$130 \le RI < 260$	Considerable risk
$C_r^i \ge 6$	Very high contamination	$C_d \ge 20$	Very high contamination	$160 \le E_r^i < 320$	Great risk	$RI \ge 260$	Very high risk
				$E_r^i \ge 320$	Very great risk		

Table 7 Single-element index and degree of contamination in soils of different land use around the Guanting Reservoir

		C_r^i							C_d
		As	Cd	Cr	Cu	Ni	Pb	Zn	
Arable land (*n* = 25)	Mean	1.00	5.02	1.15	0.75	0.64	0.21	0.99	9.75
	SD	0.26	1.16	0.31	0.35	0.23	0.08	0.24	2.42
	Min.	0.42	3.53	0.66	0.25	0.29	0.08	0.63	6.21
	Max.	1.40	8.00	1.90	1.45	1.19	0.45	1.56	15.5
Orchard land (*n* = 13)	Mean	0.71	4.00	0.89	0.80	0.49	0.68	0.84	8.43
	SD	0.26	0.95	0.19	0.82	0.21	1.72	0.36	3.19
	Min.	0.39	2.60	0.64	0.20	0.21	0.07	0.42	4.79
	Max.	1.13	5.27	1.23	3.27	1.08	6.57	1.83	16.33
Bare land (*n* = 7)	Mean	0.86	4.22	0.97	0.48	0.53	0.15	0.77	7.99
	SD	0.22	0.85	0.22	0.19	0.15	0.04	0.21	1.83
	Min.	0.47	2.60	0.54	0.16	0.22	0.08	0.39	4.45
	Max.	1.11	5.00	1.21	0.69	0.66	0.23	0.97	9.64
Woodland (*n* = 6)	Mean	0.81	4.37	0.96	0.42	0.50	0.18	0.92	8.14
	SD	0.20	1.06	0.18	0.18	0.15	0.08	0.37	1.58
	Min.	0.59	3.33	0.82	0.15	0.37	0.07	0.59	6.32
	Max.	1.08	6.13	1.22	0.65	0.78	0.31	1.61	10.00

Table 8 Potential ecological risk assessment results of heavy metals in soils of different land use

		E_r^i							RI^*
		As	Cd	Cr	Cu	Ni	Pb	Zn	
Arable land (*n* = 25)	Mean	9.99	150.48	2.30[a]	3.73	3.18	1.06	0.99	171.72[a]
	SD	2.57	34.89	0.61	1.76	1.17	0.42	0.24	40.12
	Min.	4.24	106.00	1.33	1.27	1.45	0.39	0.63	117.66
	Max.	13.96	240.00	3.79	7.26	5.97	2.23	1.56	272.43
Orchard land (*n* = 13)	Mean	7.14	120.14	1.78[b]	4.01	2.46	3.42	0.84	139.79[b]
	SD	2.59	28.38	0.39	4.08	1.06	8.59	0.36	37.35
	Min.	3.92	78.00	1.28	1.00	1.07	0.35	0.42	87.31
	Max.	11.25	150.00	2.46	16.34	5.38	32.84	1.83	203.25
Bare land (*n* = 7)	Mean	8.58	126.57	1.94	2.41	2.63	0.77	0.77	143.69[ab]
	SD	2.20	25.53	0.45	0.94	0.76	0.22	0.21	29.87
	Min.	4.71	78.00	1.07	0.78	1.12	0.40	0.39	86.47
	Max.	11.08	150.00	2.43	3.43	3.30	1.16	0.97	170.59
Woodland (*n* = 6)	Mean	8.06	131.00	1.91	2.09	2.48	0.90	0.91	147.37[ab]
	SD	2.00	31.72	0.35	0.92	0.75	0.40	0.37	32.41
	Min.	5.86	100.00	1.64	0.73	1.83	0.35	0.59	113.64
	Max.	10.81	184.00	2.44	3.24	3.88	1.56	1.61	197.28

* Land uses followed bydifferent letters are significantly different at the $P < 0.05$ level

explain the reasons for the greater potential ecological risk caused mainly by Cd in woodland soils. On the whole, the range of *RI* for all kinds of land use is 139.79–171.72, indicating considerable potential ecological risk around Guanting Reservoir. The maximum value of *RI* (272.43 in soils of arable land,

shown in Table 8) denotes very high potential ecological risk for arable land.

The results presented here also have implications for managing land. Of the contaminants detected in this work, the concentrations of Cd were most problematic in terms of their potential ecological risk. Although most metal concentrations in soils sampled around Guanting Reservoir did not exceed values considered toxic for plant growth (Table 1), concentrations of Cu and Pb in soils of orchard land are within the range of values considered toxic for plants (Tables 1, 2). Therefore, some remediation measures will be needed for soils of orchard land in terms of food safety. Moreover, the continued input of Cd, Cr, and As into arable land, and of Cd, Cr, Cu, As, and Pb into orchard land will also need to be managed in order to protect the soil resources. Cd, As, and Ni have great mobility in soil and are likely to pollute the groundwater, and even underground water nearby (Li and Pu 1992; Conner 1994; Babich et al. 1998). To avoid water and sediment pollution caused by metals in soils around Guanting Reservoir, most farming activities along the Guanting Reservoir should be banned in future.

Conclusion

A significant degree of metal pollution, particularly Cd, Cr, and As. Cd and Zn, exists in some soils of arable land around Guanting Reservoir. Such pollution probably originates mainly from phosphate fertilizer, Pb from the use of insecticides, fertilizers, and sludge as well as air deposition, and Cu from copper-based fungicides, while As, Ni, and Cr might come from soil parent material. Moderate contamination of the environment was found around the Guanting Reservoir with the following order of degree of contamination: arable land > orchard land > woodland > bare land. However, the potential ecological risk index to the environment was of the following order: arable land > woodland > bare land > orchard land, with considerable potential ecological risk from Cd for all kinds of land use. This means that the inputs of Cd, Cr, and As for arable land, and of Cd, Cr, Cu, As, and Pb for orchard land will need to be managed in order to protect the environment around the Guanting Reservoir. Some remediation measures will be needed for soils of orchard land in the interests of food safety.

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