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Sources and the distribution of heavy metals in the particle size of soil polluted by gold mining upstream of Miyun Reservoir, Beijing: implications for assessing the potential risks

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Abstract Mining has been carried out upstream of Miyun Reservoir, Beijing, for several decades, and has caused metal emissions to the environment, threatening human health. We conducted a soil survey to assess metal contamination in this area and to determine distribution of heavy metals in the particle size. We attempted to determine the possible sources of the metals and the significance of metals in the fine particle fractions to soil risk assessments. Thirty-four soil samples were collected, and eight samples were partitioned into seven size fractions. Most of the metal concentrations in the soils were higher than the background levels in Beijing, and the metal concentrations and total organic matter (TOC) contents generally increased as the particle size decreased. Each metal except Hg significantly positively correlated with the TOC. The metals in the coarse-grained soils were mainly derived from parent materials, but the metals in the fine fractions were mostly anthropogenic. Statistical analyses showed that there were three metal sources: Cd, Cu, Hg, Pb, and Zn had anthropogenic sources; Co, Cr, Ni, and V had mixed anthropogenic and natural sources; and As and Be had natural sources. The trace metals were primarily in the clay and fine silt fractions, and they might pose health risks through the inhalation of resuspended soil particles (PM10 and PM2.5). The elevated accumulation factors, enrichment factors, and ecological risk indices for the metals in the fine fractions suggest that risk assessments should be based on the fine particle size.

Keywords Soil contamination · Heavy metals · Enrichment factor · Source indentification · Environmental risk

Introduction

Soils are essential and important components of urban and non-urban environments, contributing both directly and indirectly to the quality of life experienced by the population (Abrahams 2002; de Hollander and Staatsen 2003). Soils are subject to both natural and anthropogenic deposition of heavy metals, including particles from soil erosion, road construction, industrial emissions, mining activities, and in wet and dry atmospheric deposition (Adachi and Tainosho 2005; Navarro et al. 2008). Heavy metals are a major cause of concern because they are potentially toxic elements that are persistent (Grandjean and Landrigan 2006), and are often found at high concentrations in soil (Manta et al. 2002; Imperato et al. 2003; Davydova 2005; Biasioli

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et al. 2007; Wong et al. 2006). Heavy metals accumulated in soils can affect human health through aquatic and terrestrial food chains, and this has caused widespread concern.

Heavy metal contamination in a soil is commonly assessed by comparing the total metal concentrations in a bulk sample with soil quality standards and regulations (Ljung et al. 2006a, b; Morton-Bermea et al. 2009). However, the migration of heavy metals and their conversion between different forms are closely related to the soil particle characteristics. The distributions of metals in different particle size fractions in soils have been described in the literature. Some metals have been found at higher concentrations in finer particles (such as <2, <10, and <50 μm fractions) than in coarse fractions in urban soils, and metal concentrations have been found to increase with decreasing particle size (Ljung et al. 2006b; Ajmone-Marsan et al. 2008; Madrid et al. 2008; Acosta et al. 2009). A number of researchers have found that fine soil particles generally contain higher heavy metal concentrations than do coarser fractions because the finer particles have a higher surface area per unit weight, higher clay mineral and organic matter contents, and they contain Fe–Mn oxide phases that serve as sorbents for heavy metals (Qian et al. 1996; Rodriguez-Rubio et al. 2003). Fine particles can also be soluble or easily suspended and cross gastric mucosa relatively easily, so can be absorbed into human tissues more efficiently than can coarse fractions (Lin et al. 1998). The finest soil particles (<10 μm; PM10) can be resuspended by air flows generated by wind or traffic, leading to an atmospheric particulate load (Ho et al. 2003), and this is a major environmental problem in large cities (Lee et al. 2005). Ljung et al. (2006a, b) found that children involuntarily ingest considerable amounts of small soil particles, and that these particles must be considered when assessing potential risks associated with urban playgrounds. Information on the distribution of metals in soil particle size fractions is important, therefore, for realistically assessing the health hazards associated with metals in soils.

There have been numerous studies of metal contamination in urban soils in developed countries, but few such studies have been conducted in developing countries, including China (Banerjee 2003; Wong et al. 2006). Furthermore, heavy metal contamination has not been studied in different soil particle size fractions in mining areas. The water quality in Miyun Reservoir, Beijing, has a direct impact on the drinking water safety and the health of a large population because Miyun Reservoir is a major drinking water source for Beijing. However, there has been a great deal of mining activity upstream of Miyun Reservoir over the last few decades, causing metals to be continuously emitted into the soil and aquatic environments in the area, and this contamination now poses serious threats to human health. A detailed study is required to assess the environmental changes caused by, and the potential risks associated with, the mining activities, and to allow policies for protecting drinking water sources for Beijing to be formulated. The concentrations, distributions, sources, and risks associated with heavy metals in different soil particle size fractions around Miyun Reservoir watershed have not yet been systematically assessed. Most previous studies of metal contamination have been focused on Cd, Cr, Cu, Ni, Pb, and Zn (Luo et al. 2011), and little attention has been paid to other trace elements, such as As, Be, Co, Hg, and V. Although the distributions of metals in various soil particle size fractions have been studied, the sources of the metals found in the different particle size fractions have not been investigated.

The primary objectives of this study were (1) to determine the physicochemical and mineral properties of soils from an area upstream of Miyun Reservoir and to determine the concentrations of selected metals in the bulk soil and in different soil particle size fractions, (2) to assess the distributions and the potential sources of the metals in different soil particle size fractions, (3) to assess the potential risks to human health associated with these soils using the ecological risk index (Eir), enrichment factors (EFs), and accumulation factors (AFs), particularly relating to the contribution to risk provided by fine soil particles around drinking water sources.

Materials and methods

Study area description

The study area is located in the north of Miyun County, Beijing, China, upstream of Miyun Reservoir (Fig. 1). Beijing, located in northern China, is the nation's political, cultural, and educational center, and one of the most populous cites in the world. The study area is located approximately 80 km northeast of Beijing. The

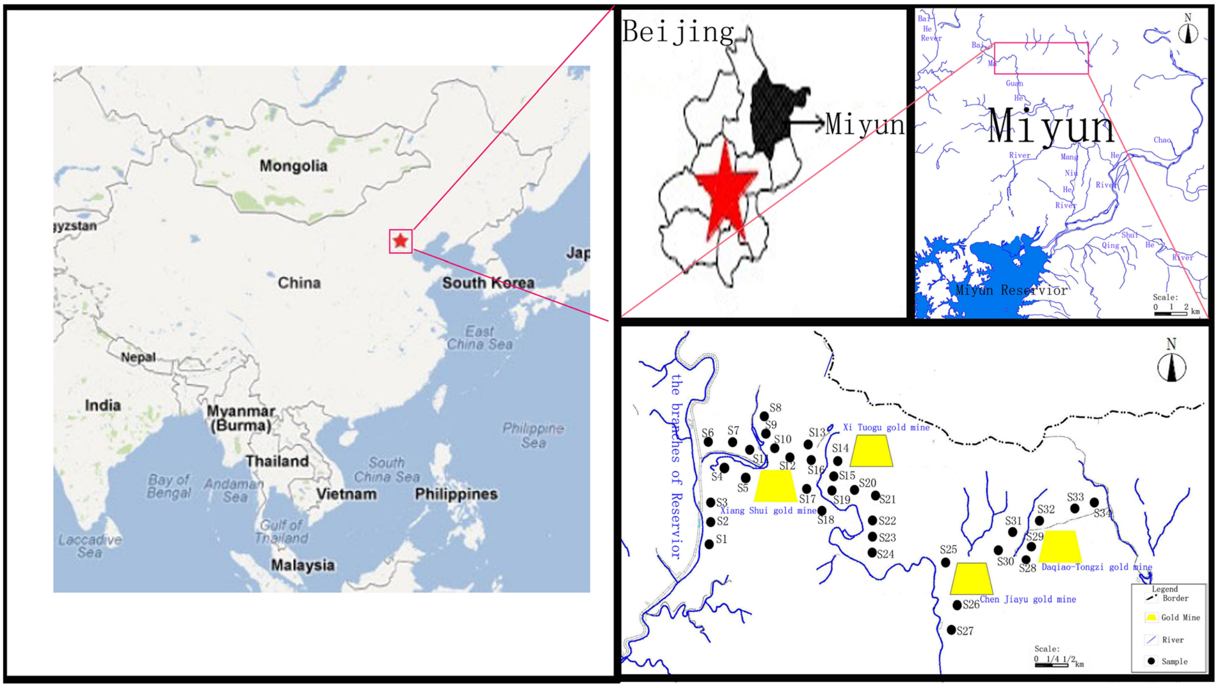


Fig. 1 Schematic map of the studied area and sampling point

climate in the region is cool continental monsoon with an annual precipitation between 370 and 588 mm. The study area is located in a warm temperate zone, and is representative of continental monsoon climate with semihumid or semi-arid climatic characteristics that the evaporation is greater than the rainfall in a year. It is cold and arid in winter and torrid and humid in summer. The annual mean temperature is about 8–10 °C. The mean annual rainfall is 400–600 mm, and rainfall patterns are highly variable, both monthly and annually. The majority of the rainfall occurs between July and September.

Miyun Reservoir is in the northern part of Beijing, between 40° 31′ N and 40° 45′ N and between 115° 56′ E and 117° 10′ E, and has a watershed of about 15,788 km2. The Miyun Reservoir was built in 1960 and is the largest reservoir in Beijing area, and has been used as the only surface drinking water storage facility for Beijing since 1997. More than ten million people who live in the city of Beijing rely on the Miyun Reservoir for drinking water. The major sources of water to Miyun Reservoir are the Chaohe and Baihe rivers, but the Sheyuchuanhe, Baimaguanhe, Mangniuhe, and Qingshuihe rivers also flow into it. The Miyun Reservoir water quality directly affects the health and safety of the residents of Beijing City because it is their only source of drinking water.

There are abundant gold resources upstream of Miyun Reservoir, and mining activities have affected the soil and water in the study area. The areas where gold has been mined (including the Xituogu, Chenjiayu, and Daqiao-tongzi gold mines) were selected for this study, and soil samples were collected from along the tributaries to the Miyun Reservoir in these areas.

Sampling and test methods

Soil and tailing samples were collected from 34 sites in the gold mining and surrounding areas. The schematic map of the studied area and sampling points is shown in Fig. 1. The latitude and longitude of sampling sites and their distance from Miyun Reservior were tabulated (Table 1). Each soil sample was collected from the surface (0–20 cm) using a spade, ensuring that the sample was not affected by equipment containing metals. Three replicate surface soil samples were collected at each site. The sample locations were determined using a global positioning system and detailed environmental conditions were recorded for each sample point. The soil samples were stored in polyethylene bags at 4 °C until they were prepared and analyzed.

Table 1 The specific location of sampling sites in the study area

Sampling site	Pure distance from the reservoir (m)	Latitude	Longitude
S1	13,260	40° 40′ 48.42″	116° 55′ 1.62″
S2	14,122	40° 41′ 6.72″	116° 55′ 2.16″
S3	15,829	40° 41′ 25.14″	116° 55′ 31.62″
S4	15,608	40° 41′ 56.28″	116° 56′ 3″
S5	15,248	40° 41′ 25.92″	116° 56′ 47.1″
S6	15,235	40° 41′ 24.44″	116° 56′ 51.65″
S7	15,228	40° 41′ 19.86″	116° 56′ 57.96″
S8	15,220	40° 41′ 18.70″	116° 56′ 59.55″
S9	14,777	40° 41′ 2.46″	116° 57′ 9.24″
S10	14,865	40° 41′ 0.60″	116° 57′ 13.91″
S11	14,682	40° 40′ 40.56″	116° 57′ 46.92″
S12	14,675	40° 41′ 40.44″	116° 57′ 38.7″
S13	15,539	40° 41′ 18.3″	116° 57′ 34.74″
S14	13,230	40° 40′ 12.9″	116° 56′ 44.34″
S15	13,320	40° 40′ 12.3″	116° 56′ 58.26″
S16	13,280	40° 40′ 9.74″	116° 57′ 3.58″
S17	13,896	40° 39′ 58.2″	116° 58′ 11.46″
S18	13,785	40° 39′ 54.81″	116° 58′ 15.81″
S19	14,246	40° 39′ 55.90″	116° 58′ 50.39″
S20	14,088	40° 39′ 56.1″	116° 58′ 55.26″
S21	13,478	40° 39′ 30.72″	116° 59′ 34.98″
S22	14,885	40° 40′ 1.14″	117° 00′ 20.22″
S23	14,238	40° 39′ 54.48″	117° 00′ 26.52″
S24	14,305	40° 39′ 43.74″	117° 00′ 28.92″
S25	14,025	40° 39′ 38.7″	117° 00′ 31.98″
S26	13,933	40° 39′ 24.78″	117° 00′ 26.7″
S27	13,968	40° 39′ 22.00″	117° 00′ 21.70″
S28	13,505	40° 39′ 12.66″	116° 59′ 45.48″
S29	13,804	40° 39′ 16.22″	117° 02′ 23.58″
S30	13,947	40° 39′ 15.58″	117° 02′ 52.86″
S31	13,568	40° 39′ 6.07″	117° 03′ 1.42″
S32	13,293	40° 38′ 56.49″	117° 02′ 45.48″
S33	13,422	40° 39′ 5.84″	117° 02′ 34.14″
S34	13,822	40° 39′ 25.56″	117° 02′ 47.64″

The bulk soil samples were air-dried, gently crushed, ground, and homogenized using an agate mortar, and sieved through a 200-mesh sieve before being analyzed. Portions of eight of the bulk soils were then partitioned into seven fractions, <2, 2–5, 5–10, 10–50, 50–74, 74–165, and 165–350 μm. The 74–165 and 165–350 μm fractions were separated by sieving the bulk samples, the 2–5, 5–10, 10–50, and 50–74 μm fractions were separated by repeated sedimentation and decanting, and the <2 μm fraction was separated by centrifugation. The separated fractions were then dried.

The mineral compositions of six air-dried bulk soil samples were determined by X-ray diffraction (XRD), and the semiquantitative mineral composition calculation was based on the K value method (Schultz 1964). The XRD instrument used was a Dmax 2200 (Rigaku, Tokyo, Japan), using a standard CuKα target, 40 Kv, 20 mA, a scanning scope of 2–60°, a scanning step length of 0.04°, and a scanning speed of 10° min−1. Samples were placed on glass petrographic slides and then analyzed in the air-dried, ethylene alcohol at 300 and 550 °C treatment states for identification of mineral components present (Ji et al. 2004).

The chemical properties of the soil samples were analyzed. The soil pH was determined using a potentiometric method on a soil–CaCl2 (0.01 M) suspension (with a soil/solution ratio of 1:5, ISO 10390) (Ajmone-Marsan et al. 2008). The total organic carbon (TOC) contents in the soil samples were determined using a TOC analyzer (Elementar, Hanau, Germany).

The concentrations of Be, Cd, Co, Cr, Cu, Ni, Pb, Zn, and V were determined in each soil sample and each soil particle size fraction by inductively coupled plasma mass spectrometry (Element XR; Thermo Fisher Scientific, Waltham, MA, USA). Briefly, 0.1 g of a sample was sealed in a Teflon beaker, 1 mL HF (40 %), 2 mL H2O2 (30 %), and 5 mL HNO3 (65 %) were added (Zhang et al. 2009) and the sample was digested in the microwave. The beaker was placed on a hot plate at 140 °C until the sample was completely dissolved and vaporized to dryness. Then, 1 mL HNO3 was added to the beaker and the sample was heated to completely dissolve all of the salts. Finally, the solution was transferred into a 50-mL volumetric flask and diluted to 50 mL using ultrapure water. The solution was then ready for the quantitative analysis of the elements of interest.

The As and Hg concentrations were determined using atomic fluorescence spectroscopy (AFS-920; Beijing Jitian Instrument Co., Beijing, China). Of the dry sample, 0.3 g was mixed with 5 mL double-distilled water, then 5 mL of a freshly made 3:1 HCl–HNO3 mixture was added to digest the sample. The digestion tube was covered with a glass ball and heated at 95 °C in a water bath for 2 h. Double-distilled water was then added to dilute the solution to 50 mL ready for analysis (Huang et al. 2013).

Quality assurance and quality control (QA/QC) measures were incorporated into the analyses. The precision and accuracy of each of the methods were determined by analyzing two standard reference materials (soils GSS-1 and GSS-3), which were obtained from the Chinese Center of National Standard Reference Material, with each batch of 12 samples. The analytical precision, the relative standard deviation, for the methods was generally below 5 %. Reagent blanks and duplicate samples were included in the analytical program to detect contamination and assess the precision and accuracy of the analysis. The recoveries of the elements from the standard reference materials GSS-1 and GSS-3were 96.3–105 %.

Background values of heavy metals

The background heavy metal concentrations were taken, at the provincial level, from the report "The Background Concentrations of Soil Elements of China" (China National Environmental Monitoring Center 1990). This was the final report for the national research program "Investigations on Background Data for Concentrations of Elements in Soils of Mainland China", which started in 1986. Chen et al. (1991) described the sample collection and chemical analysis used in that program in detail.

Data analyses

Enrichment factor

The EF can be used to differentiate between metals originating from human activities and those from natural processes, and to assess the degree of anthropogenic influence (Han et al. 2006). One such method that has often been used is to normalize a measured element against a reference element to estimate the impact of anthropogenic pollution on the environmental medium of interest. The reference element chosen is usually conservative and stable, such as Al, Fe, Sc, or Ti (Reimann and de Caritat 2000; Bergamaschi et al. 2002). The enrichment factor is calculated using Eq. 1 (Ding and Ji 2010).

$$\mathrm{EF} = \left([X]_{\mathrm{sample}}/[\mathrm{RE}]_{\mathrm{sample}}\right)/\left([X]_{\mathrm{baseline}}/[\mathrm{RE}]_{\mathrm{baseline}}\right) \quad (1)$$

where $[X]_{\mathrm{sample}}$ is the concentration of the element of interest in the study area, $[\mathrm{RE}]_{\mathrm{sample}}$ is the concentration of the reference element in the study area, $[X]_{\mathrm{baseline}}$ is the concentration of the element of interest in the background soils in Beijing, and $[\mathrm{RE}]_{\mathrm{baseline}}$ is the concentration of the reference element in the background soils in Beijing. EFs can help differentiate between anthropogenic and natural sources and help determine the degree to which a sample has been contaminated with a particular metal. Five contamination categories have been defined, based on the EF (Han et al. 2006) (Table 2).

Accumulation factor

Sheppard and Evenden (1992) proposed using a factor that takes the relative accumulation of metals in the fine soil particle fractions into account, and the accumulation factor (AF) has been widely used in studies of metal distributions in different soil particle size fractions (Ajmone-Marsan et al. 2008; Acosta et al. 2009). The AF is usually calculated as a ratio between the metal concentration in a particular particle size fraction and the metal concentration in the bulk soil. In this study, the AF for each metal of interest in each of the particle size fractions was calculated with respect to the bulk soil concentration using Eq. 2.

$$\mathrm{AF} = X_{\mathrm{fraction}}/X_{\mathrm{bulk}} \quad (2)$$

where X_{fraction} and X_{bulk} are the heavy metal concentrations (mg kg−1) in a particular particle size fraction and in the bulk sample, respectively.

Potential ecological risk index

The potential ecological risk index method, suggested by the Swedish scientist Hankinson, can be used to assess the effects of a single metal in a particular environment and also to assess the combined influences of many metals, and it has been widely used in heavy metal

Table 2 Judge standard of contamination degree by enrichment factor

Rank	EF value	Contamination degree
1	<2	Nonpollution-slight pollution
2	2–5	Moderate pollution
3	5–20	Significant pollution
4	20–40	Strong pollution
5	>40	Extremely strong pollution

pollution assessments of soils and sediments. The formulae used to calculate the index are as follows (Håkanson 1980):

- to determine the contamination factor of a single metal: $C_r^i = C_{\mathrm{surface}}^{\mathrm{i}}/C_{\mathrm{n}}^{\mathrm{i}}$
- to determine the potential ecological risk index for a single metal: $E_{\mathrm{r}}^{\mathrm{i}} = T_{\mathrm{n}}^{\mathrm{i}} \times C_{\mathrm{r}}^{\mathrm{i}}$
- to determine the potential ecological risk index of a number of metals: $\mathrm{RI}=\sum E_{\mathrm{r}}^{\mathrm{i}}$

where $C_{\mathrm{surface}}^{\mathrm{i}}$ is the measured heavy metal concentration in the soil, $C_{\mathrm{n}}^{\mathrm{i}}$ is the reference value (the background concentration in the study area), and $T_{\mathrm{n}}^{\mathrm{i}}$ is the toxic response coefficient ($\mathrm{Zn}=\mathrm{Be}=\mathrm{V}=1<\mathrm{Cr}=2<\mathrm{Cu}=\mathrm{Ni}=\mathrm{Co}=\mathrm{Pb}=5<\mathrm{As}=10<\mathrm{Cd}=30<\mathrm{Hg}=40$).

Statistical analysis

The data were statistically analyzed using SPSS version 19.0 for Windows software (SPSS, Inc., Chicago, IL, USA). Pearson's correlation coefficient analysis, principal component analysis (PCA), and cluster analysis (CA) were used to identify relationships between the metals and their possible sources (Han et al. 2006; Astel et al. 2011; Luo et al. 2010; Yalcin et al. 2010).

PCA was used to determine the hypothetical sources of the heavy metals (Li et al. 2009). PCA is widely used to reduce the amount of data in a dataset and to extract a small number of latent factors (principal components; PCs) that can be used to analyze relationships between observed variables (Loska and Wiechuya 2003). The PCs were rotated using a varimax normalized rotation to aid interpretation of the PCA results. When PCA with varimax-normalized rotation was performed, each PC score contains information on all of the metal elements combined into a single number, while the loadings indicate the relative contribution each element makes to that score. PC loading plots were used to assess similarities in the concentrations and potential sources of the metals that were analyzed by identifying clusters of metals. CA was used to further classify the elements by their different sources, based on similarities in their properties. Hierarchical cluster analysis is the most widely used method, and that was used in this study. The CA results were plotted as a dendrogram to assess the cohesiveness of the clusters formed, and this readily shows similarities between the elements. CA is complementary to PCA. Correlation analysis was also used to identify relationships between different metals.

Results and discussion

Chemical and mineral properties

The TOC contents and pH values of the bulk soils from the gold mining areas are presented in Table 3. In general, pH plays an important role in controlling the bioavailability and the potential ecological risks associated with heavy metals. Most of the soils were relatively neutral (pH 6.11–7.56), but a few were acidic or slightly acidic (pH 4.07–5.86). The lowest pH (4.07) was found in a tailing sample (S5). The relatively low pH values found in the soils surrounding the gold mines was probably caused by the presence of gold mine tailings, which acidify water they come into contact with (Jiménez-Rodrguez et al. 2009). The TOC content in the soils ranged from 0.16 to 6.37 %, with a mean of 1.73 %. The highest TOC content was found in sample S20, which was collected from an arable area, and this may have been caused by the use of organic fertilizer. Our results agreed with the results of previous surveys (Huang et al. 2012).

The TOC contents in the different particle size fractions are shown in Fig. 2. Generally, the TOC content clearly increased as the particle size decreased, which agrees with previous reports of organic matter distributions in different soil particle size fractions (Tang et al. 2009).

The minerals in the bulk soil samples were analyzed according to the "Minral X-ray Powder Identification Manual" (Institute of Geochemistry Chinese Academy of Sciences, Gui Yang. 1978), and the results are shown in Fig. 3. Similar soil mineral compositions were found in each of the soil samples, and the minerals found were quartz, feldspar (plagioclase and potassium feldspar), illite, kaolinite, smectite, and calcite. The relative amounts of the major minerals present in the soil samples were determined by semiquantitative component analysis, which was developed by RIR (reference intensity ratio) method, and the results are shown in Fig. 4. The relative amounts of the primary minerals (quartz and feldspar) were 81–94 %, and the relative amounts of the secondary minerals (illite, kaolinite, and smectite) were 6–19 %. The relative amounts of clay minerals (illite, kaolinite, and smectite) were higher at sampling

Table 3 Statistical results of heavy metal total concentrations(mg kg−1), pH and TOC(%) in the bulk soil samples

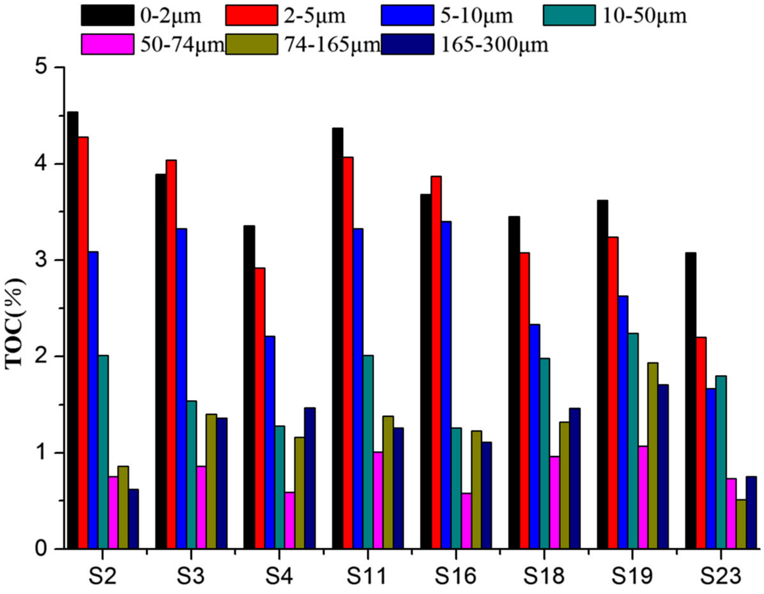
Element	Gold mine soils(n=34)						Background value
	Maximum	Minimum	Mean	Median	SD	Skewness	
Be	2.87	1.01	1.71	1.66	0.41	1.12	1.35
V	172.00	45.20	104.10	108.50	28.30	0.16	77.4
Cr	358.00	55.30	189.89	183.50	73.86	0.45	66.7
Co	34.30	10.70	20.17	20.30	5.60	0.43	15.0
Ni	99.80	24.90	54.20	55.85	15.20	0.66	28.2
Cu	131.00	24.70	58.30	55.85	21.20	1.34	23.1
Zn	342.00	60.70	155.08	138.50	63.70	1.69	97.2
Cd	3.27	0.11	0.65	0.42	0.71	2.11	0.0534
Pb	565.00	12.40	109.00	42.05	145.08	1.68	24.7
As	13.48	1.72	6.90	6.26	3.10	0.54	9.4
Hg	6.74	0.02	1.62	0.34	2.24	1.14	0.0576
pH	7.56	4.07	6.27	6.50	0.87	−0.62	–
TOC	6.37	0.16	1.73	1.47	1.51	1.39	–

points S5 and S28 than at the other sampling points (Fig. 4). Most of the heavy metal concentrations were also higher at sampling points S5 and S28 than at the other sampling points. The large amounts of clay minerals and the heavy metal concentrations found in the samples led us to conclude that the clay minerals might play a significant role in the enrichment of metals in the soils.

The distribution of heavy metals in the bulk soil and the particle size fractions

A statistical summary of the distributions of the selected metals (As, Be, Cd, Cr, Co, Cu, Hg, Ni, Pb, V, and Zn) in the bulk soil samples is shown in Table 3. The heavy metal concentrations, except for the As concentrations, were higher in the soil samples in the gold

Fig. 2 The TOC contents (%) in the different particle size fractions (μm) of the soil (*n*=8)



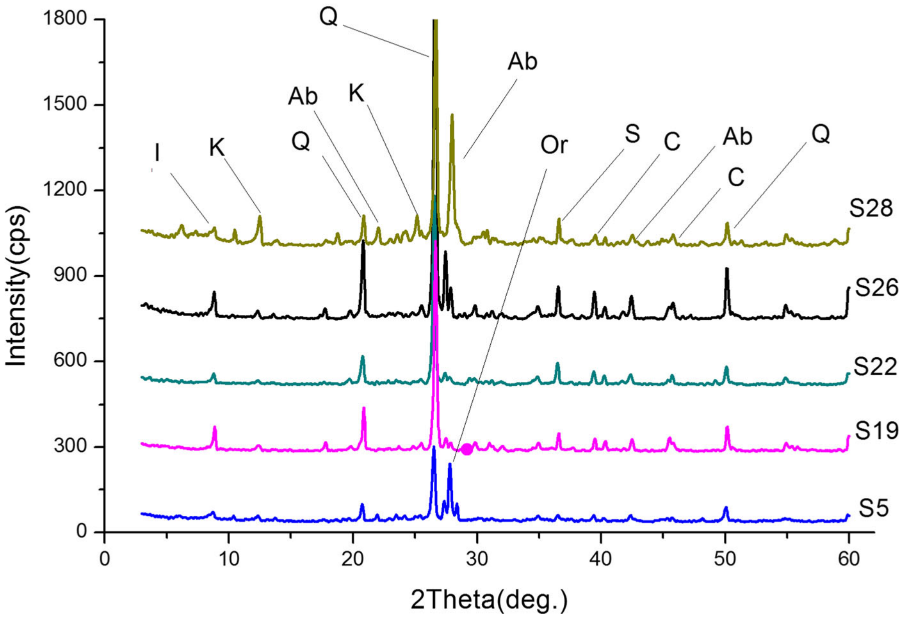
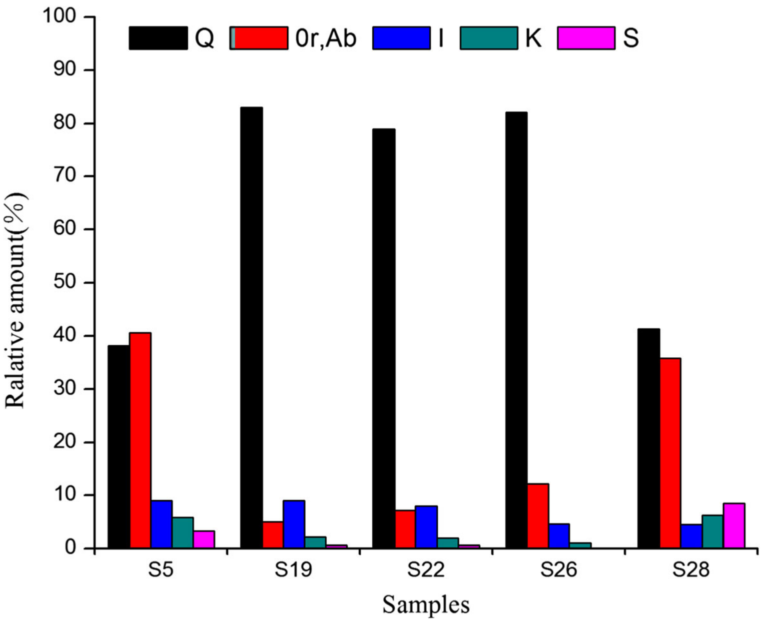


Fig. 3 The X-ray diffraction patterns of the soil, major peaks of respective minerals are labeled (Q quartz, Ab plagioclase, Or potassium feldspar, I illite, K kaolinite, S smectite, C calcite)

mining areas than the background concentrations for Beijing, with considerably higher mean concentrations than background concentrations being observed for Cr (189.89 mg kg−1), Pb (109.00 mg kg−1), Cu (58.30 mg kg−1), Hg (1.62 mg kg−1), and Cd (0.65 mg kg−1). The mean Hg concentration was more than 30 times higher than the background concentration in Beijing soils. These results agreed with the results of previous studies of heavy metals in mining areas (Huang et al. 2012; Liao 2007). Huang et al. (2012) studied the characteristics of heavy metal pollution in soils in the gold mining areas upstream of Miyun Reservoir and found that there was severe Cd (1.30 mg kg−1), Hg (2.67 mg kg−1), and Pb (271.31 mg kg−1) pollution,

Fig. 4 The relative amounts of the major minerals present in the soil samples



and that the mean Hg concentrations was more than 90 times higher than the background concentration in Beijing soils. These levels of heavy metal pollution are likely the results of the gold mining and smelting processes used in the area (Huang et al. 2012). Liao (2007) also found severe Hg contamination in the Mangniu River upstream of Miyun Reservoir.

As can be seen from Table 3, Cd, Hg, and Pb showed median values that were less than their mean concentrations. The remaining metals manifested almost comparable mean and median concentrations, and exhibited the lowest asymmetry. Large standard deviations (SDs) were found for most of the heavy metal concentrations in the soil samples (Table 3), indicating that there were wide variations in the concentrations in the study area soils, which could have been caused by the mining and smelting processes in the study area. The skewness values were higher than zero for all of the heavy metals, meaning that the concentrations were skewed toward low values, which agrees with their median concentrations being lower than their mean concentrations (Lu et al. 2010). The positive values of skewness reflect the accretion in this area and thus the addition of carbonate material to the soil area.

Most gold mining and smelting activities in the study area have now ceased. The gold mining and smelting processes that were used included the amalgamation technique and the cyanide leaching process, and these led to distinctive contamination patterns. The gold mining tailings contain heavy metals, including Cr, Cu, Pb, and Zn from the gold mines. The tailings from the gold extraction and smelting processes also contain highly toxic heavy metal elements, such as Cd, Cr, Cu, Pb, Zn, and Hg. Once deposited, the tailings undergo chemical weathering and release toxic metals to the water (including the groundwater), the soil, and organisms. Most of the heavy metal concentrations were very much higher in the tailing samples in this study than the background concentrations in Beijing, which should be of great concern.

The mean heavy metal concentrations in the different soil particle size fractions are shown in Fig. 5. These values of concentration and standard error were given in Table 4. The mean concentrations generally increased as the particle size decreased. The highest metal concentrations were typically found in the <2 μm size fraction. Our results were compared with the results of other studies, and, for example, Ljung et al. (2006a, b) found higher As concentrations in the <50 μm size fraction than in larger particle size fractions in soils from 25 leisure venues. It has been found that As, Cd, Cu, and other heavy metals readily accumulate in fine soil particle size fractions (Acosta et al. 2009; Tang et al. 2009).

Statistical analyses of potential sources of heavy metals to the soils

Correlation coefficient analysis

Correlation coefficients for the relationships between the heavy metal concentrations in the bulk soils and the different soil particle size fractions were calculated (Table 5) to establish inter-element relationships in the soil samples. Cd, Cu, Hg, and Pb significantly positively correlated with each other, which may suggest a common origin. Co, Cr, Ni, and V also significantly positively correlated with each other, and may have had a common source (Ajmone-Marsan et al. 2008; Luo et al. 2011). As had a positive and very significant correlation with Be, indicating that they were likely to have had the same source.

The correlations between the total metal concentrations and the TOC contents in the soil samples were analyzed, and the correlation coefficients were As/TOC R2=0.6104 (P=0.000), Be/TOC R2=0.60035 (P=0.000), Cd/TOC R2=0.24991 (P=0.000), Co/TOC R2=0.41922 (P=0.000), Cr/TOC R2=0.18493 (P=0.001), Cu/TOC R2=0.3813 (P=0.000), Hg/TOC R2=0.00118 (P=0.307), Ni/TOC R2=0.33189 (P=0.000), Pb/TOC R2=0.13855 (P=0.003), V/TOC R2=0.54991 (P=0.000), and Zn/TOC R2=0.25588 (P=0.000). It was clear that there were significant positive correlations between the concentrations of the metals, except for Hg, and the TOC content, showing that the heavy metal concentrations were related to the TOC contents in the soils. Organic carbon, soil particles, and heavy metals all interact, and, however, smaller soil particle sizes have higher organic carbon contents and stronger abilities to accumulate heavy metals, leading to great potential risks to the environment (Fig. 2). However, the Hg distribution in the study area was mostly influenced by where the amalgamation technique was used to extract gold.

The possible sources of the heavy metals were assessed from the correlations between the metal concentrations and the TOC contents in the seven particle size fractions. The results are presented in Figs. 6 and 7. The As and Be concentrations were similar to the

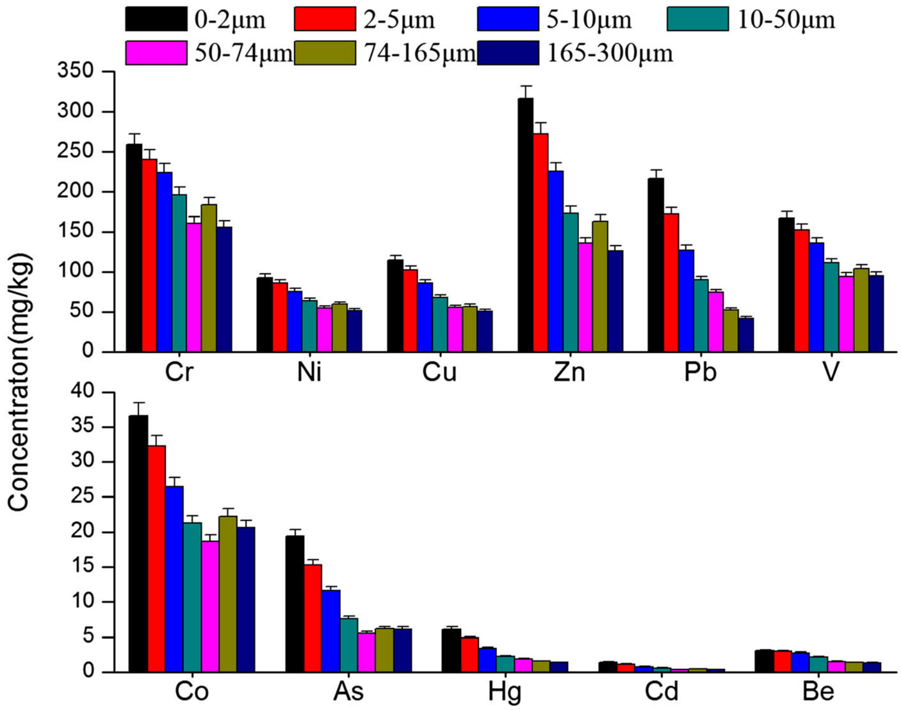


Fig. 5 The mean heavy metal concentrations (mg kg−1) in the different soil particle size fractions (μm) (*n*=8)

background concentrations in the larger particle size fractions, indicating that their sources were the parent materials of the soil, but they were found at higher concentrations in the fine particle size fractions (<10 μm), probably because of agricultural activities (Li et al. 2013). The long-term unreasonable use of chemical fertilizer, pesticide, and plastic film could cause heavy metal contamination in soils. The Co, Ni, and V concentrations in most of the particle size fractions were slightly higher than the background concentrations and there was little evidence of dispersion, so we concluded that they were derived from

Table 4 The values of mean element concentrations ((mg kg−1) and standard error in different soil particle size fractions (μm)

Fractions		Cr	Ni	Cu	Zn	Pb	V	Co	As	Hg	Cd	Be
0–2	Mean	258.88	92.68	114.79	316.13	215.84	167.25	36.63	19.41	6.15	1.44	3.08
	Error	12.94	4.63	5.74	15.81	10.79	8.36	1.83	0.97	0.31	0.07	0.15
2–5	Mean	240.13	85.45	101.93	272	171.89	152.13	32.21	15.26	4.85	1.14	2.97
	Error	12.01	4.27	5.1	13.6	8.59	7.61	1.61	0.76	0.24	0.06	0.15
5–10	Mean	223.5	75.18	85.75	224.88	127.11	136	26.44	11.62	3.41	0.8	2.75
	Error	11.18	3.76	4.29	11.24	6.36	6.8	1.32	0.58	0.17	0.04	0.14
10–50	Mean	195.88	63.81	67.4	173.08	89.79	110.93	21.29	7.58	2.28	0.6	2.14
	Error	9.79	3.19	3.37	8.65	4.49	5.55	1.06	0.38	0.11	0.03	0.11
50–74	Mean	160.38	54.48	55.35	135.84	74.09	94.29	18.66	5.57	1.89	0.4	1.51
	Error	8.02	2.72	2.77	6.79	3.7	4.71	0.93	0.28	0.09	0.02	0.08
74–165	Mean	183.33	59.4	56.45	162.63	51.95	103.49	22.27	6.16	1.57	0.45	1.38
	Error	9.17	2.97	2.82	8.13	2.6	5.17	1.11	0.31	0.08	0.02	0.07
165–300	Mean	155.69	51.51	50.58	125.98	41.78	94.74	20.62	6.13	1.37	0.34	1.35
	Error	7.78	2.58	2.53	6.3	2.09	4.74	1.03	0.31	0.07	0.02	0.07

Table 5 Correlation coefficients between the heavy metal concentrations in the bulk soils and the different soil particle size fractions

	Be	V	Cr	Co	Ni	Cu	Zn	Cd	Pb	As	Hg
Be	1										
V	0.528**	1									
Cr	0.472**	0.569**	1								
Co	0.437**	0.862**	0.589**	1							
Ni	0.490**	0.684**	0.741**	0.791**	1						
Cu	0.603**	0.533**	0.630**	0.700**	0.697**	1					
Zn	0.656**	0.584**	0.720**	0.472**	0.548**	0.622**	1				
Cd	0.572**	0.241*	0.689**	0.346**	0.504**	0.742**	0.692**	1			
Pb	0.487**	0.030	0.566**	0.192	0.412**	0.715**	0.512**	0.866**	1		
As	0.724**	0.482**	0.362**	0.598**	0.416**	0.732**	0.487**	0.498**	0.471**	1	
Hg	0.409**	0.244*	0.541**	0.378**	0.489**	0.628**	0.594**	0.765**	0.657**	0.407**	1

*$P<0.05$ correlation is significant (two-tailed); **$P<0.01$ correlation is significant at (two-tailed)

the parent materials of the soil, transportation, and mineral exploitation. The Cr, Cu, and Zn concentrations were higher than the background concentrations in most of the particle size fractions, and their concentrations were particularly high in the finest particle size fraction. The sources of Cr, Cu, and Zn may, therefore, have been transportation, atmospheric deposition, and mineral exploitation. The Cd, Hg, and Pb concentrations varied with the TOC content, and the metal concentrations in all of the particle size fractions in several samples were only slightly higher than the background concentrations, while the metal concentrations in the fine particle size fractions (<10 μm) in some of the samples were very much higher than the background concentrations, with a wide concentration range. The sources of Cd, Hg, and Pb could, therefore, be divided into two groups, the sources in the first group being the parent materials of the soil and agricultural activities, and the sources in the other group being transportation, atmospheric deposition, and mineral exploitation. For Hg, in particular, the wide use of the amalgamation technique and the cyanide leaching process in gold smelting in the study region will have led to the serious enrichment of Hg in all soil particle size fractions, especially in the <10 μm fraction. On the whole, there was little evidence of dispersion between the concentrations of the metals and the TOC content in coarse-grained soils, while there was higher dispersion in fine particle size fractions. In conclusion, heavy metals in the coarse grained soils (>10 μm) mainly originated from the parent materials of the soil, and the heavy metal distribution was greatly affected by the particle surface area and the amounts of clay minerals and organic matter in the soil. However, the high concentrations of metals in the fine particle size fractions (<10 μm) were influenced to a significant degree by anthropogenic activities, such as ore treatment processes, leading to metal transportation and atmospheric deposition.

Principle component analysis

PCA was used to identify the sources of the metal pollutants. Table 6 shows the principal component factor loadings and the eigenvalues from the varimax rotation method using the element concentrations in the soil samples. A 3-D factor PCA loading plot is shown in Fig. 8. Three PCs together accounted for 83.394 % of the total variance in the data. PC1 was dominated by Cd, Hg, and Pb and accounted for 59.684 % of the total variance, with high positive factor loadings for Cd, Hg, and Pb. Cu, Zn, Cd, Hg, and Pb were grouped closely in the 3-D PCA loading plot (Fig. 8), which suggests that these five elements were strongly correlated and had common sources. PC2 explained 15.369 % of the total variance and was dominated by Co, Cr, Ni, and V. Cr and Ni, and V and Co were grouped closely in the 3-D PCA loading plot, which suggests that these pairs had common sources. PC3 described 8.341 % of the total variance and was dominated by As and Be.

Cluster analysis

The CA results for the heavy metals in the soil samples are shown as a dendrogram in Fig. 9. There were three

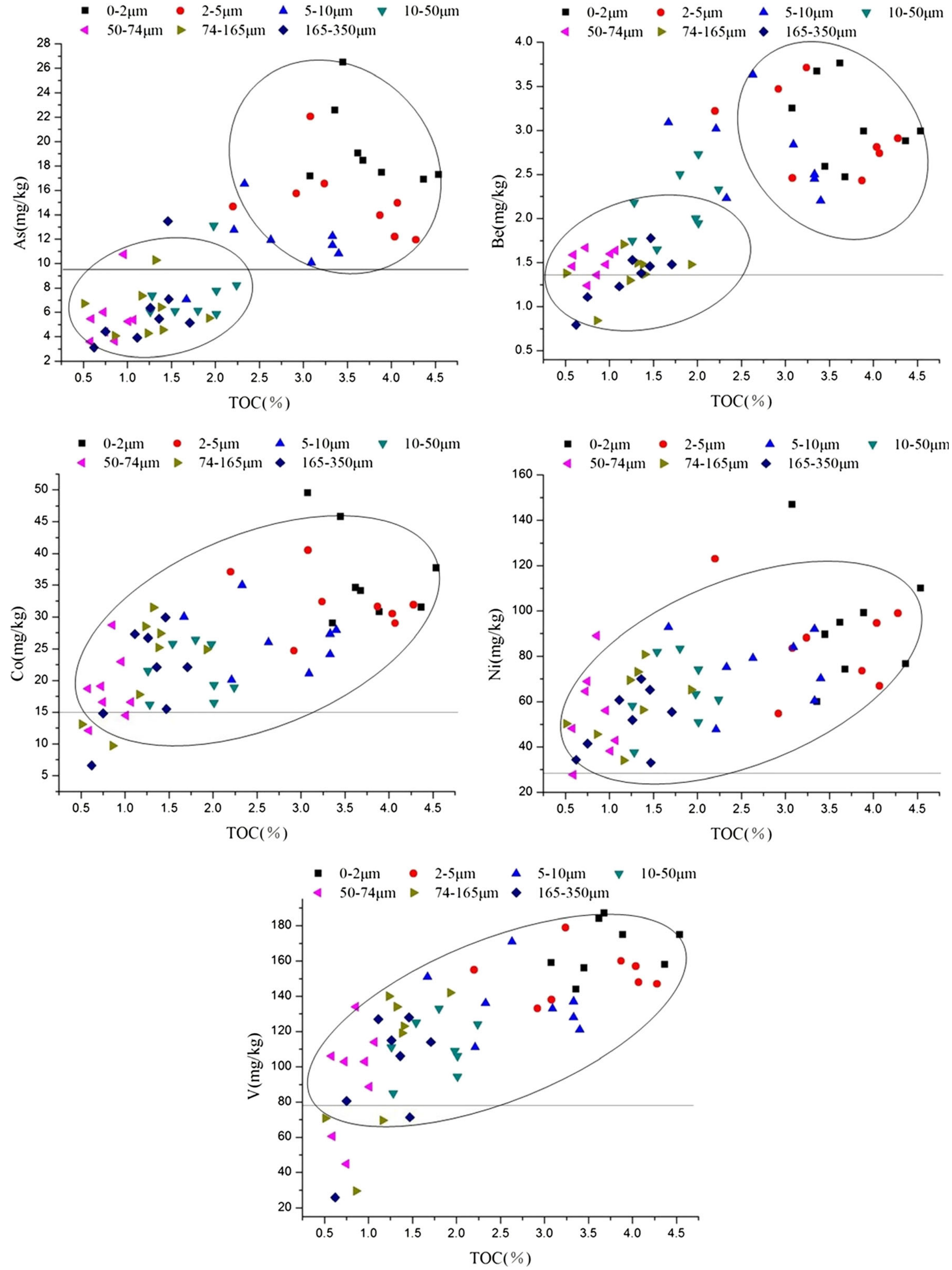


Fig. 6 The correlation scatter diagram of As, Be, Co, Ni, V, and TOC in seven particle size fractions (the straight line indicates the background value)

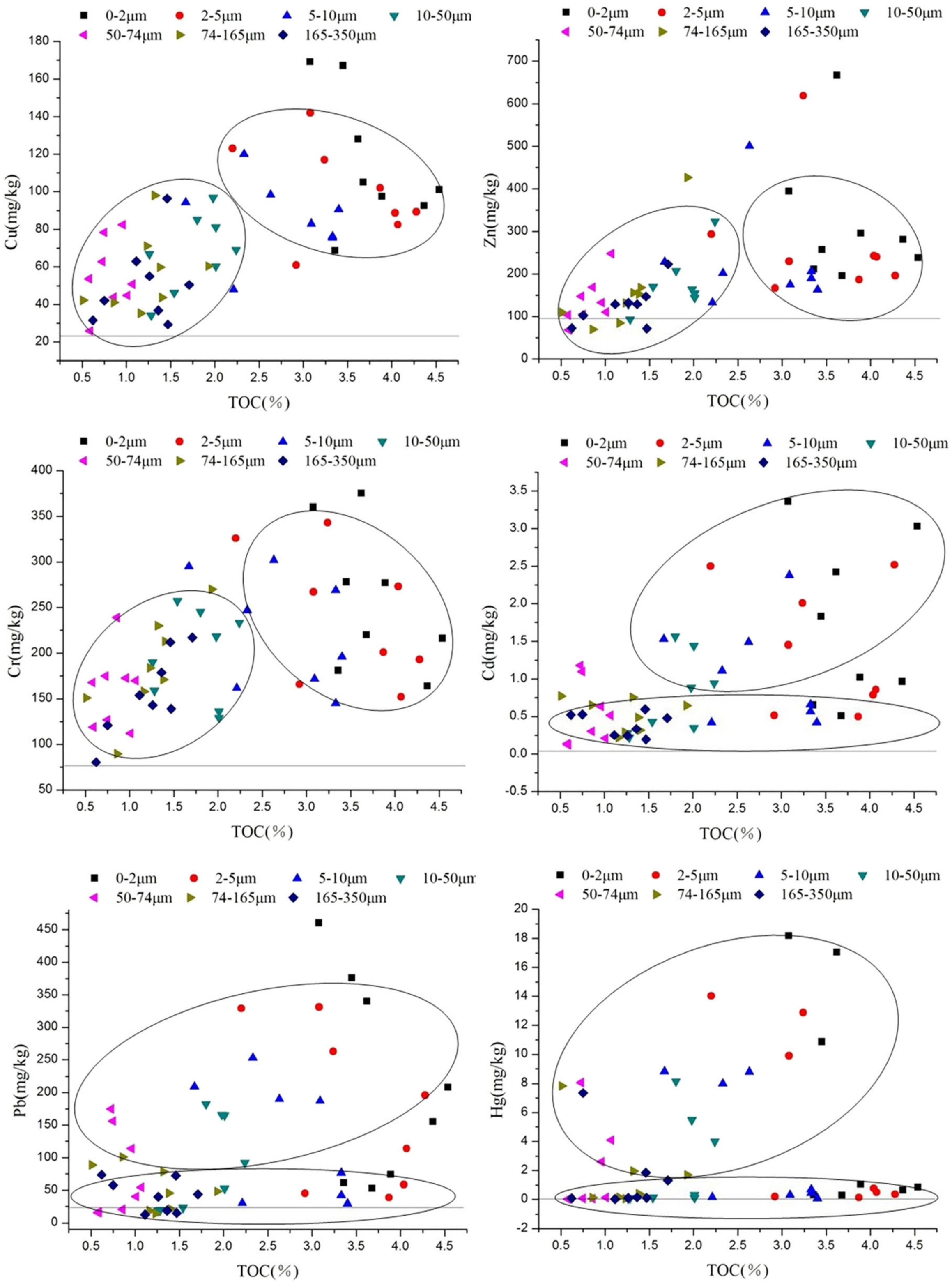


Fig. 7 The correlation scatter diagram of Cd, Cr, Cu, Hg, Pb, Zn, and TOC in seven particle size fractions (the straight line indicates the background value)

Table 6 Total variance explained and component matrixes

Component	Initial eigenvalues			Element	Rotated component matrix		
	Total	% of variance	Cumulative (%)		PC1	PC2	PC3
1	6.565	59.684	59.684	Be	0.341	0.285	0.764
2	1.691	15.369	75.053	V	−0.022	0.900	0.331
3	0.918	8.341	83.394	Cr	0.643	0.648	0.020
4	0.630	5.725	89.119	Co	0.109	0.874	0.338
5	0.411	3.741	92.859	Ni	0.403	0.807	0.122
6	0.274	2.487	95.346	Cu	0.594	0.457	0.512
7	0.177	1.609	96.956	Zn	0.587	0.476	0.315
8	0.137	1.244	98.199	Cd	0.903	0.163	0.284
9	0.088	0.797	98.996	Pb	0.895	−0.038	0.296
10	0.069	0.631	99.627	As	0.241	0.261	0.882
11	0.041	0.373	100.000	Hg	0.802	0.216	0.146

clusters of elements, the first containing Cd, Hg, Pb, and Zn, the second containing Co, Cr, Ni, and V, and the third containing As, Be, and Cu.

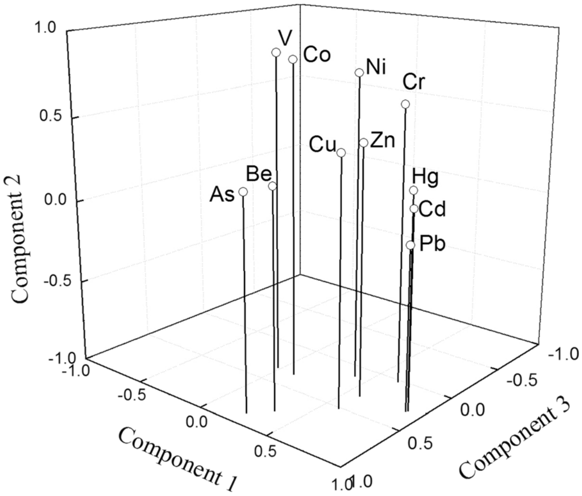


Fig. 8 PCA loading 3-D plot (PC1 vs. PC2 vs. PC3) for heavy metals

Analysis of the potential risk assessment

Enrichment factor analysis

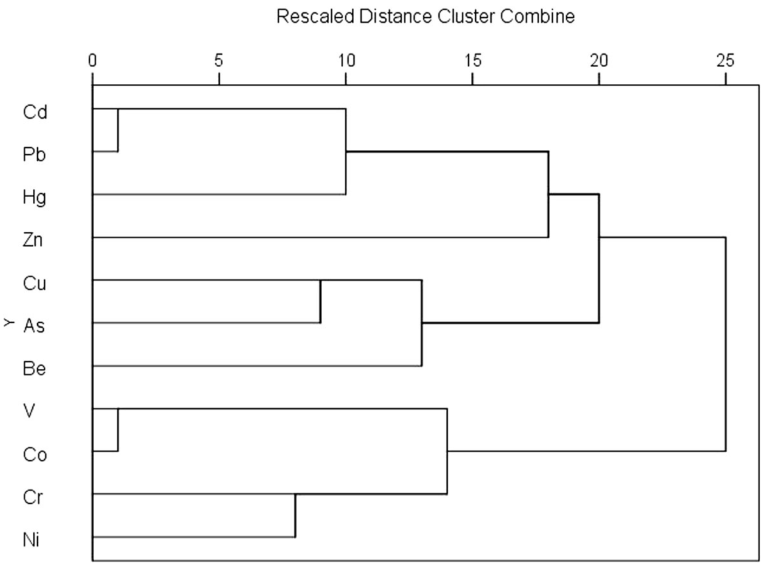
The mean heavy metal EFs in the bulk soil and the seven particle size fractions in the eight selected samples are shown in Fig. 10, and these were calculated by normalizing the selected metals to the reference element, Sc. The data of Sc was presented in Table 7. All of the heavy metals except As and Be had mean EFs of more than 1 in the bulk soils (Fig. 10). As and Be had EFs close to unity, further confirming that they had natural sources. The other elements in the bulk soil had different EFs, with Co, Cr, Cu, Ni, Pb, V, and Zn having mean EFs of more than 1, Cd having an EF of more than 5, and Hg having an EF of more than 20, indicating that the soils were strongly contaminated with Cd and very strongly contaminated with Hg. Our results were consistent with the results of previous studies of metal contamination in gold mining areas (Boamponsem et al. 2010; Yang and Wang 2013). In particular, Hg contamination in soils in gold mining areas should be a cause of great concern.

The EFs for the different particle sizes are shown in Fig. 10. The EFs for Cd, Cu, Hg, and Pb in the 0–2 μm fraction were more than 2 while the EFs for Cd and Cu in the bulk soil were less than 2. Furthermore, the EF for Cd increased from 5.1 in the bulk soil to 12.5 in the finest particle size fraction, the Pb EF increased from 1.4 to 4.0, and the Hg EF increased from 20.1 to 50.0.

Accumulation factor analysis

The AFs for selected metals in each soil particle size fraction are shown in Figs. 11 and 12. The AFs show that the heavy metals accumulated more in the finer fractions than in the coarser fractions, and that the heavy metals mainly accumulated in the clay (0–2 μm) and silt (2–50 μm) fractions. The heavy metal AFs in the silt fractions were higher than 1, indicating that the heavy

Fig. 9 Dendogram for metal elements obtained by hierarchical cluster method



metal concentrations were higher in the fine particles than in the bulk soil. The mean heavy metal AFs in the clay fractions were higher than 1.6, especially for Cd (4.0), Pb (5.0), and Hg (7.9), showing that the heavy metals accumulated to a significant degree in the clay fraction. However, the heavy metal AFs in the sand (>50 μm) fraction were approximately 1, which may have been caused by the low clay mineral and organic matter contents in the sand fraction. From the discussion above, the high metal concentrations in the fine particle size fractions were, therefore, caused by the high surface area, the presence of clay minerals and organic matter (Hardy and Cornu 2006; Li et al. 2011), and the ore treatment processes (Silvia et al. 2010).

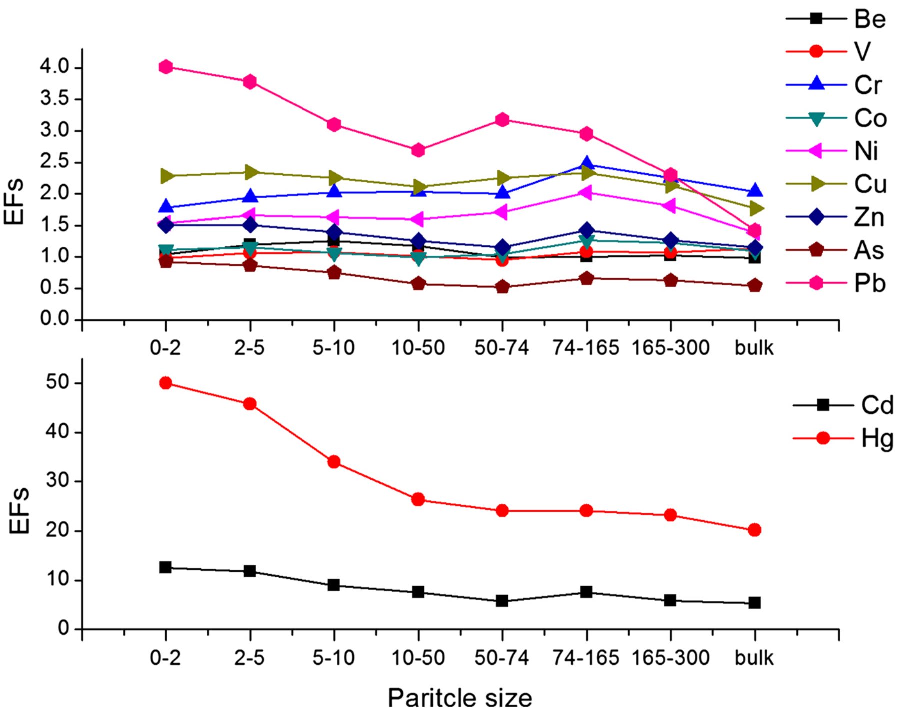


Fig. 10 The mean heavy metal EFs in the bulk soil and the seven particle size fractions (μm) in the eight selected samples

Table 7 The concentrations (mg kg−1) of Sc in bulk soils and seven particle size fractions in selected samples

Selected samples	Size fraction and bulk							
	0–2 μm	2–5 μm	5–10 μm	10–50 μm	50–74 μm	74–165 μm	165–300 μm	Bulk
S2	27.7	23.5	21.9	27.9	31.7	28.1	21.3	18.8
S3	25.8	20.9	16.2	12.2	8.59	9.6	8.81	10.68
S4	24.1	20.3	17.5	15.7	13.3	14.4	13.8	14.25
S11	22.7	20.1	17.3	14.9	16.2	17.8	15.9	11.3
S16	32.7	26.7	23.3	18.8	18.3	19.9	20.2	20.3
S18	23.9	21.6	19.8	15.7	15.9	16.8	14.0	16.3
S19	20.7	17.2	17.2	16.9	14.7	8.11	8.91	13.2
S23	23.8	18.7	15.6	11.1	5.63	3.68	3.52	13.0

Our results agree with the results of previous studies, with the preferential partitioning of heavy metals to fine soil particle size fractions, and, in particular the dominant accumulation of some heavy metals in the clay fraction of the soil, being found (Ljung et al. 2006a, b; Ajmone-Marsan et al. 2008; Madrid et al. 2008; Luo et al. 2011). Acosta et al. (2009) reported that, except for clay minerals and organic matter, the high dolomite and calcite contents in fine soil particle size fractions could serve as major sinks for metals. Metals such as Pb and Zn readily react with CO32− to form metal–carbonate complexes/minerals on the surfaces of dolomite and calcite crystals. Banat et al. (2005) reported that the proportion of heavy metals in carbonate forms in soils from Jordan were Cd=33 %, Pb=16 %, Zn=5.0 %, and Cr=1.0 %.

Compared with the results about particle size distributions of heavy metals in urban soils (Ajmone-Marsan et al. 2008; Luo et al. 2011; Li et al. 2011), the heavy metals in soils polluted by gold mining mainly accumulated in the clay (0–2 μm) and silt (2–50 μm) fractions, this is not only due to the high surface area, the presence of clay minerals and organic matter, but also because heavy metals in the fine particle size fractions (<10 μm) were mainly influenced by anthropogenic activities.

Analysis of potential ecological risk index

The ecological risk index results for the heavy metals are shown in Table 8. The mean Eir was less than 40 for As, Be, Co, Cr, Cu, Ni, V, and Zn in all of the particle size fractions, indicating that these metals posed only slight ecological risks. The mean Pb Eir was more than 40 in the clay (0–2 μm) fraction, presenting a moderate ecological risk. The mean Cd Eir was 320 in the clay (0–2 μm) and silt (2–50 μm) fractions, showing that Cd posed strong ecological risks, and the Cd Eir in the sand (>50 μm) was between 160 and 320, showing that it posed very strong ecological risks. The Hg Eir was more than 320 in all of the particle size fractions, indicating that it posed extremely strong ecological risks, which should be of public concern. It is important to note that the RI was higher than 600 in all of the particle size fractions, showing that the metals posed very strong ecological risks, and most of that risk was attributed to Hg. The results showed that the potential ecological risk index for the individual metals (Eir) and for all of the metals (RI) increased as the particle size decreased. This conclusion is consistent with the conclusion made from the AF and EF analyses.

Implications for potential risk assessments

The soils from around the gold mines upstream of the Miyun Reservoir have been influenced by anthropogenic activities, especially the fine soil particles that can be easily resuspended and transported by air flows generated by wind or traffic. The fine particles can, therefore, easily migrate to the surrounding environment and significantly contribute to the atmospheric particulate loads, such as PM10 (particles with aerodynamic diameters <10 μm), PM2.5 (particles with aerodynamic diameter <2.5 μm), and TSP (total suspended particulates <100 μm; Luo et al. 2011), which is a major environmental concern in many cities. Such particle resuspension can also allow contaminated

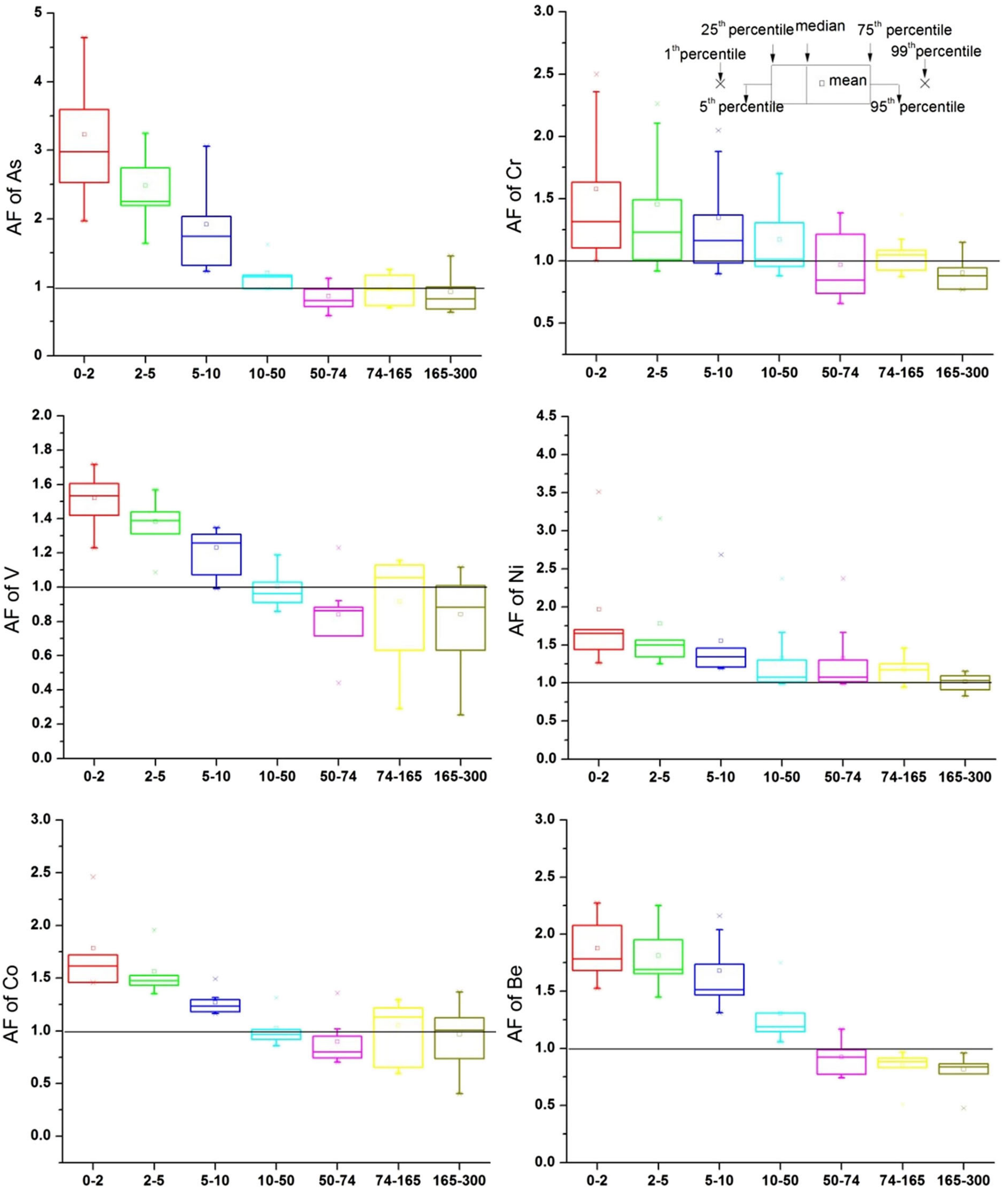


Fig. 11 The AFs for As, Be, Co, Cr, Ni, and V in each soil particle size fraction (μm)

soils to give rise to contaminated ambient airborne particulate, indoor dust, and wetland systems, posing potential risks to human and ecosystem health (Cho et al. 2009; Gerlofs-Nijland et al. 2009). Once inhaled, fine silt particles (2–10 μm) can deposit in the upper respiratory tract, while the finest clay particles

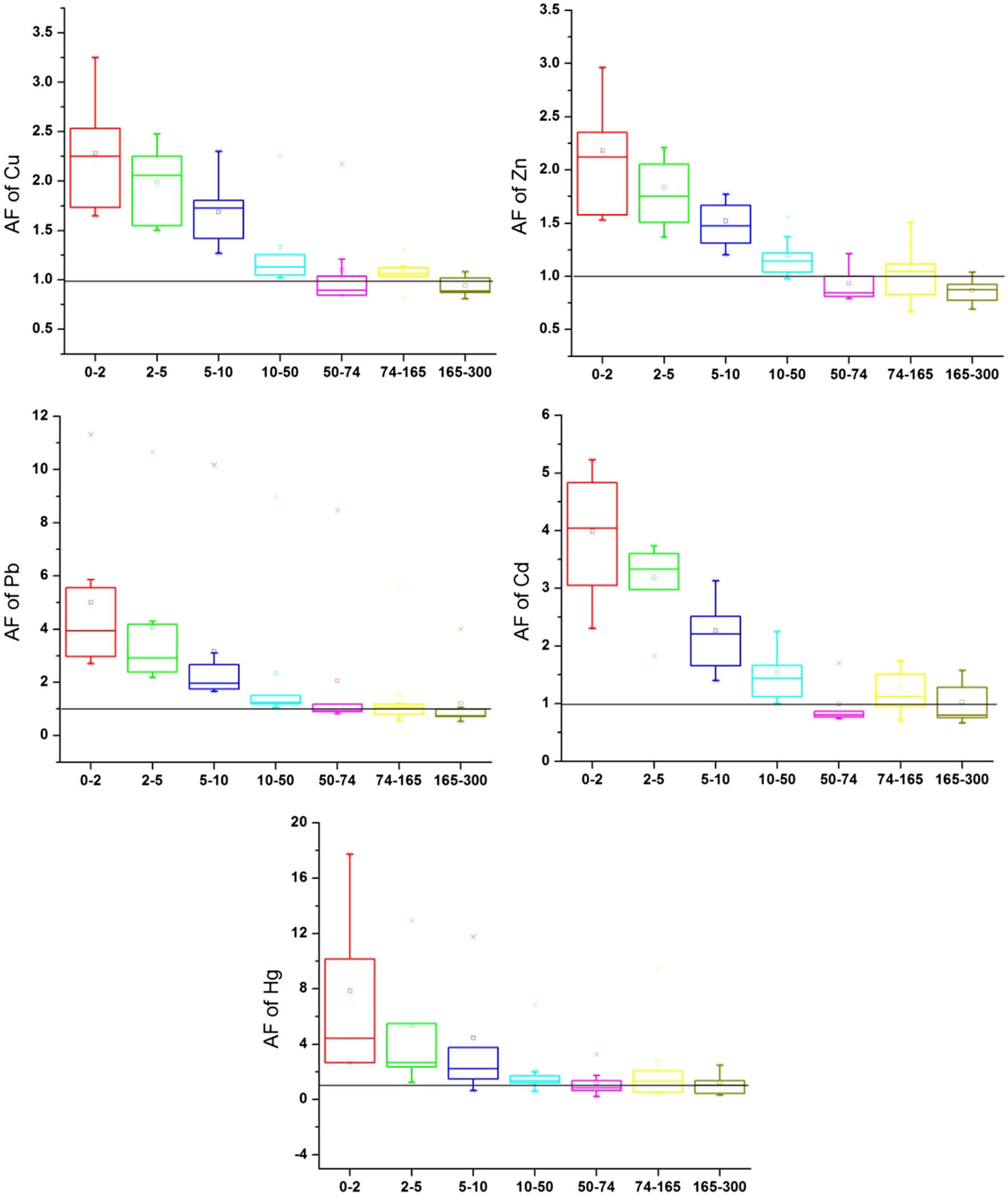


Fig. 12 The AFs for Cd, Cu, Hg, Pb, and Zn in each soil particle size fraction (μm)

(0–2 μm) are mainly deposited in the alveolar regions of the lung, causing pulmonary and cardiovascular diseases (Dominic et al. 2006; Vallejo et al. 2006). If these particles are rich in heavy metals, they will affect lung physiology because of the lung's high efficiency for absorbing trace elements.

Table 8 Potential ecological risk index results for the heavy metals in the different soil particle size fractions

Size fraction	Statistics	Be Eir	V Eir	Cr Eir	Co Eir	Ni Eir	Cu Eir	Zn Eir	Cd Eir	Pb Eir	As Eir	Hg Eir	RI
<2 μm	Mean	2.28	2.16	7.76	12.21	16.43	24.85	3.25	808.08	43.69	20.65	4,271.70	5,213.06
	Min	1.83	1.86	4.92	9.67	10.62	14.85	1.91	285.96	10.63	17.97	201.39	577.62
	Max	2.79	2.42	11.24	16.50	26.06	36.58	6.85	1,887.64	93.12	28.16	12,625.00	14,722.47
	SD	0.35	0.20	2.34	2.46	4.92	7.98	1.59	568.28	32.02	3.61	5,494.29	6,089.41
2–5 μm	Mean	2.20	1.97	7.20	10.74	15.15	22.06	2.80	641.36	34.80	16.23	3,364.58	4,119.09
	Min	1.80	1.72	4.56	8.23	9.70	13.20	1.72	279.21	7.81	12.72	90.28	449.64
	Max	2.75	2.31	10.28	13.50	21.81	30.74	6.37	1,404.49	67.00	23.47	9,750.00	11,314.68
	SD	0.34	0.18	2.17	1.61	3.74	5.41	1.50	429.89	25.26	3.38	4,348.64	4,800.63
5–10 μm	Mean	2.03	1.76	6.71	8.81	13.33	18.56	2.31	451.83	25.73	12.36	2,368.06	2,911.48
	Min	1.63	1.43	4.35	6.70	8.46	10.37	1.37	133.71	5.93	7.51	48.61	354.10
	Max	2.69	2.21	9.06	11.67	16.45	25.97	5.15	859.55	51.21	17.59	6,125.00	7,096.68
	SD	0.37	0.24	1.87	1.61	2.75	4.52	1.18	283.61	18.56	2.84	2,956.13	3,251.61
10–50 μm	Mean	1.58	1.43	5.88	7.10	11.32	14.59	1.78	337.15	18.18	8.06	1,587.67	1,994.73
	Min	1.22	1.10	3.87	5.40	6.67	7.36	0.96	80.90	3.74	6.24	41.67	226.25
	Max	2.02	1.72	7.71	8.80	14.79	20.93	3.32	876.40	36.84	13.95	5,652.78	6,627.60
	SD	3.92	3.55	14.65	17.68	28.14	36.61	4.46	883.70	47.59	20.28	4,515.27	5,553.08
50–74 μm	Mean	1.12	1.22	4.81	6.22	9.66	11.98	1.40	225.35	15.00	5.93	1,311.63	1,594.31
	Min	0.92	0.58	3.36	4.03	4.91	5.61	0.71	61.80	3.24	3.83	13.89	131.76
	Max	1.24	1.73	7.17	9.57	15.80	17.86	2.55	662.92	35.43	11.47	5,611.11	6,356.61
	SD	0.11	0.37	1.24	1.73	3.46	4.05	0.56	207.45	13.16	2.43	2,038.50	2,250.39
74–165 μm	Mean	1.03	1.34	5.50	7.42	10.53	12.22	1.67	251.97	10.52	6.55	1,090.28	1,399.01
	Min	0.63	0.38	2.69	3.24	6.05	7.64	0.72	56.74	2.85	4.33	41.67	196.41
	Max	1.27	1.83	8.10	10.50	14.33	21.21	4.39	434.27	20.45	10.95	5,437.50	5,926.96
	SD	0.18	0.54	1.65	2.60	2.77	4.50	1.15	143.33	6.86	2.19	1,829.95	1,937.89
165–350 μm	Mean	1.00	1.22	4.67	6.88	9.13	10.95	1.30	190.96	8.46	6.52	953.13	1,194.20
	Min	0.59	0.33	2.41	2.19	5.85	6.34	0.74	53.48	2.61	3.31	20.83	153.41
	Max	1.32	1.65	6.51	9.97	12.41	20.84	2.29	334.83	14.92	14.35	5,104.17	5,443.84
	SD	0.22	0.46	1.38	2.61	2.48	4.73	0.49	98.79	5.00	3.44	1,743.66	1,809.76

Our data show that heavy metal EFs were relatively low in the bulk soil, but reached high values in the 0–2 μm size fractions. The AFs showed that heavy metal mainly accumulated in the finest size fraction. The potential ecological risk index was relatively high for the fine particle fractions, especially for Pb (Eir=44), Cd (Eir=808), and Hg (Eir=4,272) in the 0–2 μm fractions. Our results show that the distribution of heavy metals in fine particle size fractions deserves attention when assessing potential risks. Finer soil particles tend to readily adhere to human hands, and fine clay particles (0–2 μm) can be incorporated into the surface of the skin through dermal absorption, because they are of a similar roughness to the surface of the skin, and become resistant to washing off (Luo et al. 2011). The high heavy metal concentrations in the fine soil particle size fractions can be released into surface and ground water through runoff and leaching, affecting drinking water quality. The accumulation of heavy metals in fine soil particle fractions could, therefore, cause risks to the environment and to human health in different ways.

Conclusions

Gold mining activities upstream of Miyun Reservoir have caused the soils in that area to become seriously contaminated with heavy metals. This is especially true for Cd, Hg, and Pb, for which observed concentrations were much higher than the background concentrations (the mean Hg concentration was 30 times higher than the background concentration). The heavy metal concentrations and TOC contents in the soil particle fractions generally increased as the particle size decreased. Correlation analysis showed that there were significant positive correlations between most of the heavy metal concentrations and the TOC contents. The highest metal concentration was found in the fine particle size fractions because of their high surface areas, high clay mineral and organic matter contents, and ore treatment processes. Statistical analyses (PCA, CA, and correlation analysis) and selected metal concentrations allowed three heavy metal sources to be identified: (1) Cd, Cu, Hg, Pb, and Zn were derived from anthropogenic sources; (2) Co, Cr, Ni, and V had mixed anthropogenic and natural sources; and (3) As and Be were mainly derived from natural sources. The elevated metal AFs (>1.5), EFs (>2.0), and ecological risk indices (Eir>40) in fine fractions suggested that heavy metals in fine particles should be considered when assessing potential risks to human health. These risks were particularly important for Cd, Pb, and Hg, the AFs of which reached 4.0, 5.0, and 7.9, respectively, in clay fractions. In the study area, the inhalation of resuspended airborne soil particles (PM10 or PM2.5), and the ingestion of adhered soils through the hand-to-hand pathway may impose health hazards. One application of our results is in assessing risks associated with soils on playgrounds where children can unknowingly ingest and inhale dust. These conclusions are important to the monitoring and assessment of heavy metal pollution in mining areas, and critical for the formulation of policies for protecting drinking water sources for Beijing.

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