



Speciation and distribution of mercury in soils around gold mines located upstream of Miyun Reservoir, Beijing, China



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ABSTRACT

Long-term mining and smelting activities have contaminated gold mine soils and sediments close to Miyun Reservoir. Several studies have reported concentrations of mercury (Hg) in the Miyun Reservoir area, but this paper presents the first comprehensive study of the distribution and speciation of Hg in this area. The gold mines upstream of the Miyun Reservoir were selected for study. Our results indicate that the total Hg contents in soils (average of $9.57 \text{ mg} \cdot \text{kg}^{-1}$) were higher in the study area than background values for Beijing surface soils. Samples suggest that Hg distributed as from a point source around the tailings, suggesting that tailings are the major sink for anthropogenic Hg in the study area. Total Hg had a negative correlation with cation exchange capacity, while pH and total organic carbon showed little correlation with total Hg. Hg in soils existed mainly in residual form, with bioavailable Hg accounting for only 0.30% of total Hg. High pH conditions were conducive to the formation of Fe–Mn oxide-bound Hg in mine soils. The Müller geoaccumulation index used to assess pollution indicates that Hg had very serious pollution levels within the study area, requiring urgent management to prevent residual Hg becoming exchangeable through humic acid conversion and entering the watershed.

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1. Introduction

Mercury (Hg) is a highly toxic and non-essential element for life. However, elemental Hg and its compounds have high volatility, and can easily migrate into environments, entering the food chain, which can cause irreversible harm for human and animal life.

The soil is both a potential source and sink of Hg in the global Hg cycle (Kim and Lindberg, 1995). The presence of Hg in soil comes from natural and anthropogenic sources (Bose-O'Reilly et al., 2010; Zhang and Wang, 2007). The biggest anthropogenic Hg sources include coal combustion and industrial chloralkali processes. Large-scale Hg and gold mining/smelting activities, artisanal and small-scale mining are also major contributors to Hg emissions (Veiga et al., 2006; Dai et al., 2013; Solgi et al., 2014; Ohki et al., 2014). Artisanal and small-scale gold mining often use rudimentary technologies that involve amalgamation with Hg in the extraction processes (Spiegel and Veiga, 2010). During amalgamation, large quantities of noxious atmospheric mercury (Hg^0) are emitted, as well as significant amounts of metallic Hg. It was estimated that 1000 t of Hg have been lost to the environment from such amalgamation processes (Swain et al., 2007).

Miyun Reservoir is the only surface water source in Beijing. Its water quality directly affects the safety of drinking water for Beijing residents. However, upstream of the Miyun Reservoir there are some small-scale gold mines. Most of these gold mines have used amalgamation with Hg in their extraction processes (Huang et al., 2013). Such processes have caused damage to vegetation and stripped the surface soil, causing soil and water loss, as well as erosion. Toxic elements in mining wastes, deposited in the open air, will weather rapidly under rain, causing acidification with possible toxic elements run-off into the reservoir. This is a potential threat to the water quality of Miyun Reservoir, and its surrounding plants, animals, and human residents.

Research and monitoring of Hg pollution areas have been undertaken using water, fish, and estuarine sediment samples in different parts of the world (Nyanza et al., 2014; Abdolash et al., 2014). However, at present, baseline data on the distribution and speciation of Hg around the Miyun Reservoir of Beijing is scarce. Only a few studies have reported concentrations and distributions of Hg in soils and estuarine sediments around the Miyun Reservoir (Li et al., 2013; Qin et al., 2013; Huang et al., 2013). These data are too limited to define the distribution and speciation of Hg in this area. Such data also do not describe the speciation of Hg in gold mine soils, which are critical to determining the toxicity and bioavailability or potential risk assessment of Hg in these soils. Speciation is dependent on soil properties and composition (e.g., pH, organic matter content, cation exchange capacity (CEC), oxidation–reduction potential, grain size), as well as Hg loading

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(Richardson et al., 2013; Zhang et al., 2014a, 2014b; Zhang et al., 2015). Hence, a geochemical study of Hg in these soils will contribute to a deeper understanding of the sources of Hg, as well as its migration, transformation and bioavailability. It will also provide reference information to manage heavy metal contamination in the soils and water sources around Beijing.

Nowadays, a broad spectrum of techniques are used to examine Hg metal fractionations in the soil solid and soil solution phases, including many submicroscopic techniques (e.g., X-ray absorption fine structure, XAFS; X-ray absorption near edge structure, XANES; near edge X-ray absorption fine structure, CNEXAFS). In addition, improvements in nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and pyrolysis provide better understanding of the binding of metals in complexes in soils (Weber and Karczewska, 2004; Peacock and Sherman, 2004; Rasmussen et al., 2008). Classical sequential extraction procedures (SEPs) also are still used widely (Tessier et al., 1979; Gómez-Ariza et al., 2000; Chakraborty et al., 2014). Using a modified Tessier sequential extraction, different forms of Hg in our soil samples were extracted to determine the concentration and spatial distribution of Hg in soil around gold mines upstream of the Miyun Reservoir. From these data, we evaluated the relationship between the different species of Hg in these soils using multivariate statistics and assessed the potential risks to human health, and ecological systems.

2. Materials and methods

2.1. Study area description

The study area is located in the north of Miyun County, Beijing, China, upstream of the Miyun Reservoir (Fig. 1). The Miyun Reservoir is situated northeast of Beijing, between $40^{\circ}31'–40^{\circ}45'N$ and $115^{\circ}56'–117^{\circ}10'E$, with a watershed area of about 15,788 km². Since 1997, it has been the biggest and the only surface drinking water reservoir for Beijing. The Miyun basin is bordered by the Yanshan mountains; hence, northwest elevations are higher than southeast ones, with elevations ranging between 150 and 1730 m above sea level. This region has a temperate semi-humid and semi-arid continental monsoon climate, with annual average temperatures below 10 °C, and annual precipitation around 600–700 mm. Rainfall is uneven, with 80% of rainfall occurring in June to September.

Miyun Reservoir is mainly fed by the Chaohe and Baihe Rivers. The Sheyuchuanhe, Baimaguanhe, Mangniuhe, and Qingshuihe Rivers also flow into the Miyun Reservoir.

The gold resources are situated upstream of the Miyun Reservoir; there are a dozen small gold mines, although most have now been closed. Their earlier mining activities have affected the soil and water in the study area. A gold mine cluster (including Xiangshuiyu, Xituogu,

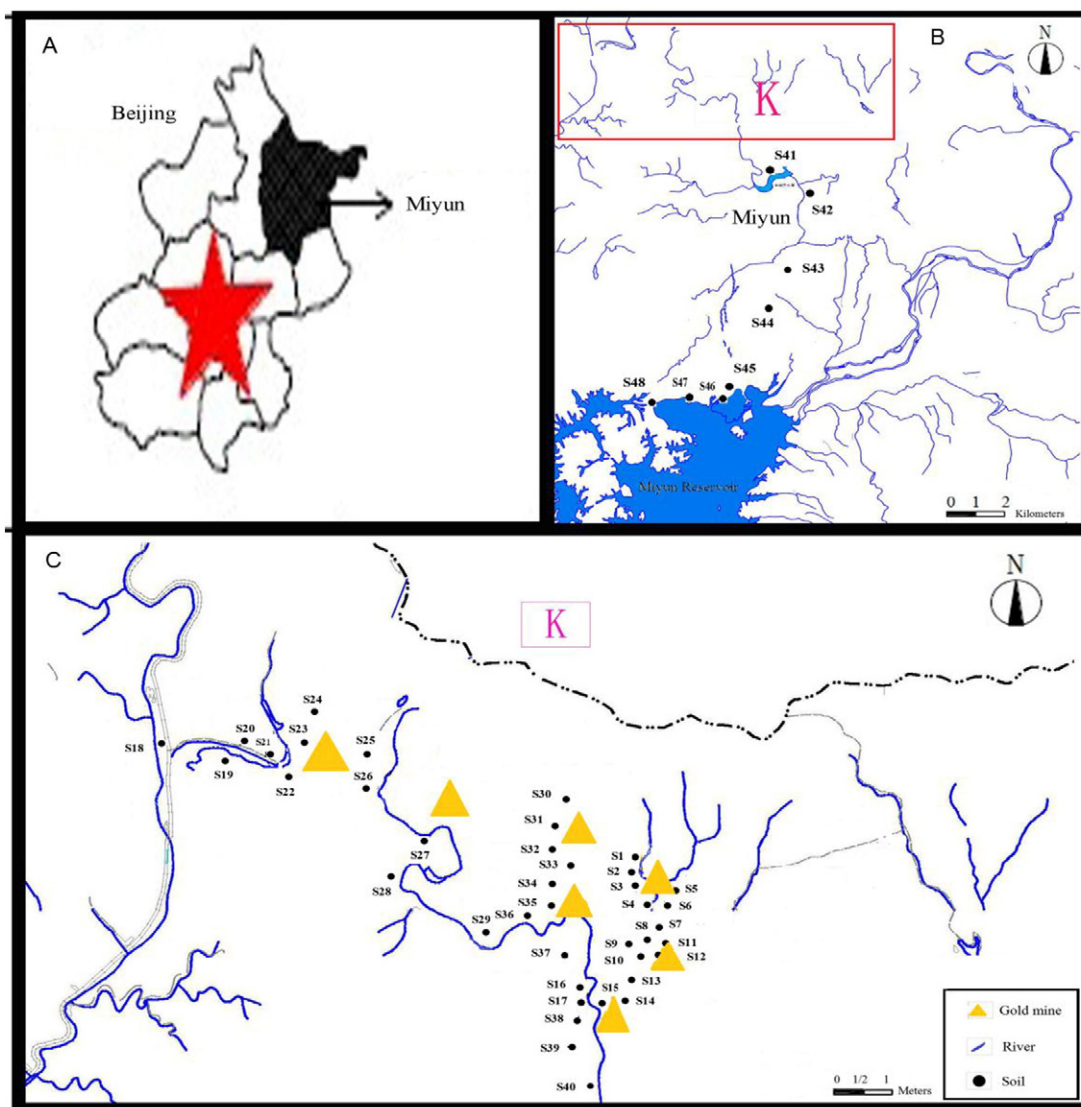


Fig. 1. Location of Miyun county in Beijing (A), sampling location and whole study area (B), sampling location and gold mine area (C).

Table 1
Physical and chemical properties of soil.

| | | pH | TOC (%) | CEC (cmol·kg ⁻¹) | Total Hg (mg·kg ⁻¹) |
|-----------------------------------|-----------|------------|-------------|------------------------------|---------------------------------|
| Gold mine area (n = 40) | Range | 2.9 ~ 8.0 | 0.26 ~ 4.54 | 0.01 ~ 101.26 | 0.06 ~ 63.79 |
| | Mean ± SD | 6.6 ± 1.10 | 1.52 ± 0.99 | 28.49 ± 20.79 | 9.57 ± 13.25 |
| Surroundings of reservoir (n = 8) | Range | 5.1 ~ 7.90 | 0.73 ~ 3.28 | 19.29 ~ 109.88 | 0.13 ~ 0.35 |
| | Mean ± SD | 7.1 ± 0.81 | 1.35 ± 0.79 | 52.65 ± 29.43 | 0.22 ± 0.07 |

Yangpodi, Dongtuogougoumen, Chenjiayu, and Daqiao-tongzi gold mines) was selected for study. Soil samples were collected along the Mangniuhe River basin, from the gold mine cluster to the Miyun Reservoir.

2.2. Sample collection and preparation

Forty-eight soil and tailing samples were collected from around the gold mines and reservoir (Fig. 1); sample set (S1–S40) are from the gold mines, while sample set (S41–S48) are control samples. At each sampling site, a composite soil sample composed of three subsamples to 20-cm-depth was collected using a stainless steel spade. During sampling, a bamboo blade was used to strip the soil surface in contact with metal. The locations of all samples were determined by GPS, and environmental conditions for each sample were recorded. All samples were sealed in polyethylene bags. In the laboratory, samples were air-dried, gently crushed and ground in an agate mortar, and sieved before carrying out analyses.

2.3. Analysis of soil physical and chemical properties

The pH of the soil was measured in a 1 M KCl solution for a soil-to-solution ratio of 1:5 using a pH meter (Leici PHS-3C, Shanghai INESA

Scientific Instrument Co., Shanghai, China). The amount of total organic carbon (TOC) was determined using the TOC analyzer (Elementar Analysensysteme GmbH, Germany). CEC was measured using the barium chloride–sulfate compulsive exchange method (Zhang et al., 2010). To prepare samples for Hg analysis, 0.5 g of soil was digested in a water bath (95 °C) using 10 mL (1 + 1) of aqua regia (HCl:HNO₃:water, 3:1:4,v/v/v), then made up to a volume of 50 mL with a preservation solution (0.5 g L⁻¹ K₂CrO₄ + 5%HNO₃) (Zhu et al., 1996). The concentration of Hg in the digested solution and in all leachates derived from the SEP described below were measured using atomic fluorescence spectroscopy (AFS-920, Jitian Instruments Co. Ltd., China).

2.4. Sequential extraction procedure

The modified Tessier sequential extraction procedure determines Hg as belonging to one of seven fractions: soluble and exchangeable (fraction 1), humic acid (fraction 2), fulvic acid (fraction 3), carbonate-bound (fraction 4), Fe/Mn oxide-bound (fraction 5), organic-bound (fraction 6), and residual (fraction 7). To extract the soluble and exchangeable Hg (fraction 1), about 2 g of soil was mixed with 10 mL of 0.5 M MgCl₂ (pH = 7), while shaking at a speed of 22 ± 3 rpm for 3 h at room temperature. This solution was then centrifuged at 3000g for

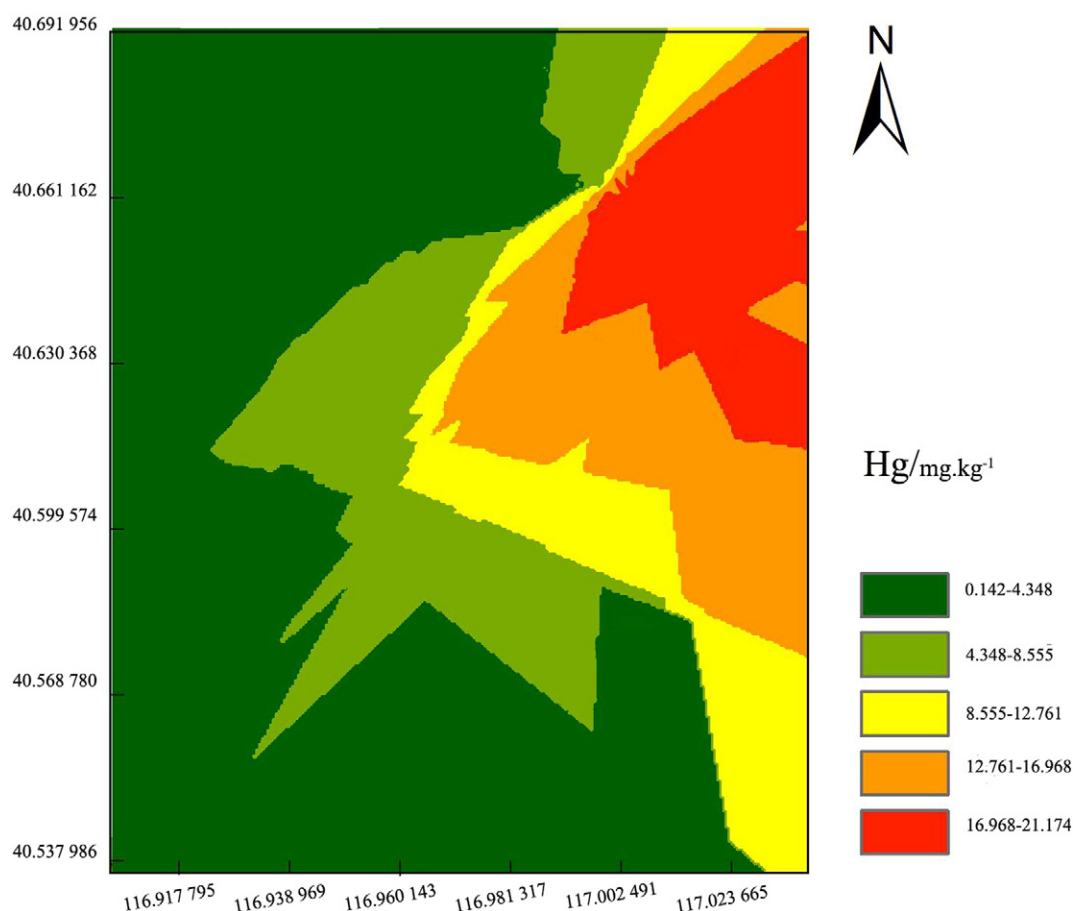


Fig. 2. Spatial distribution of Hg in study area.

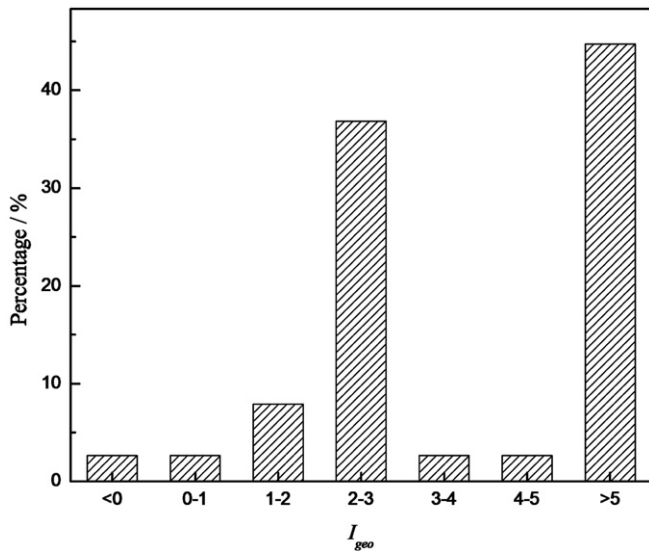


Fig. 3. I_{geo} of Hg in gold mine soils: <0, 0–1, 1–2, 2–3, 3–4, 4–5 and >5, represent uncontaminated, slightly polluted, moderately polluted, moderately to highly polluted, highly polluted, highly to very highly polluted and very seriously polluted, respectively.

20 min, and the supernatant separated by passing the solution through a 0.45- μ m microfilter. This residue was washed with 5 mL of double de-ionized water before the next step. To determine the humic and fulvic acid fractions (Hg fractions 2 and 3), the washed residue from fraction 1 was extracted by 10 mL of 0.1 M NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ at room

temperature overnight, followed by shaking for 2 h, and centrifuging for 20 min as in step 1. The resulting supernatant was used to determine these two fractions, while the washed residue was used for the next step. The supernatant was adjusted to pH = 3 using HCl, then centrifuged; this supernatant was used for determining the humic acid Hg (fraction 2), while its acid residue was used for analysis of the fulvic acid Hg (fraction 3), the acid residue was digested and determined as for the total Hg measurement. To determine the carbonate-bound Hg (fraction 4), the washed residue from step 2 was extracted with 10 mL of 1 M CH_3COONa (adjusted to pH = 5 with acetic acid), followed by shaking for 4 h at room temperature, and centrifuging for 20 min as in step 1. The supernatant from this step was used to analyze Hg from carbonates, while the washed residue was retained for the next step. To determine the Fe/Mn oxide-bound Hg (fraction 5), the washed residue from fraction 4 was extracted by 15 mL of 0.04 M $\text{NH}_2\text{OH HCl}$ in 25% CH_3COOH (v/v), followed by shaking for 6 h at room temperature, and centrifuging for 20 min as in step 1. The supernatant was used to analyze Hg bound with Fe/Mn oxide, while the washed residue was retained for the next step. To determine the organic-bound Hg (fraction 6), the washed residue from fraction 5 was extracted with 8 mL of 30% H_2O_2 (adjusted to pH = 2 with HNO_3) for 2 h at 85 °C in a water bath. After 2 h, an additional 2 mL of 30% H_2O_2 (adjusted to pH = 2 with HNO_3) was added, the temperature was maintained for another 3 h at 85 °C in the water bath; the resulting supernatant was used to analyze organic-bound Hg, while the residue was used for determining fraction 7. The final residue Hg (fraction 7) was digested and determined, as for the total Hg measurement.

Before carrying out atomic fluorescence spectroscopy, all supernatants were brominated by adding 1 ml of concentrated hydrochloric

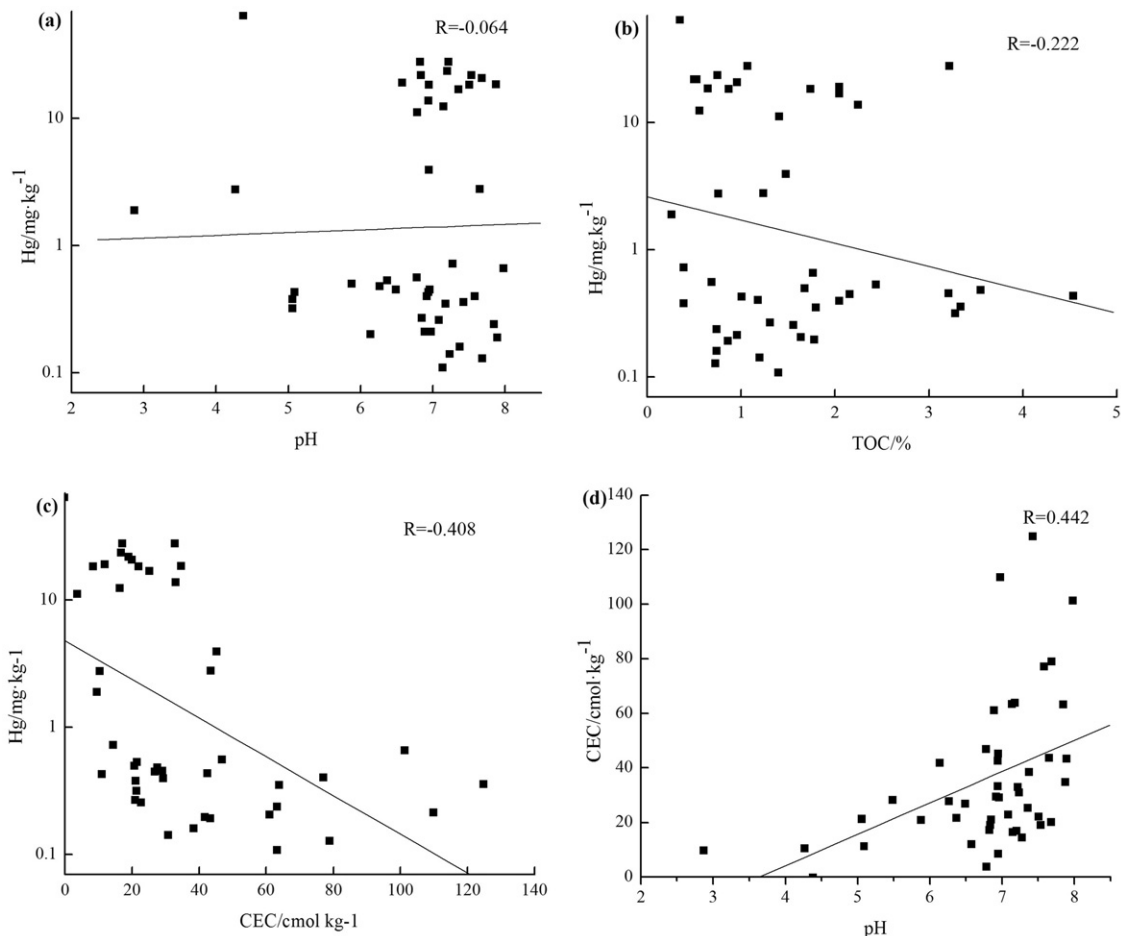


Fig. 4. Correlation coefficients for total mercury with pH (a), TOC (b), CEC (c) and pH with CEC (d).

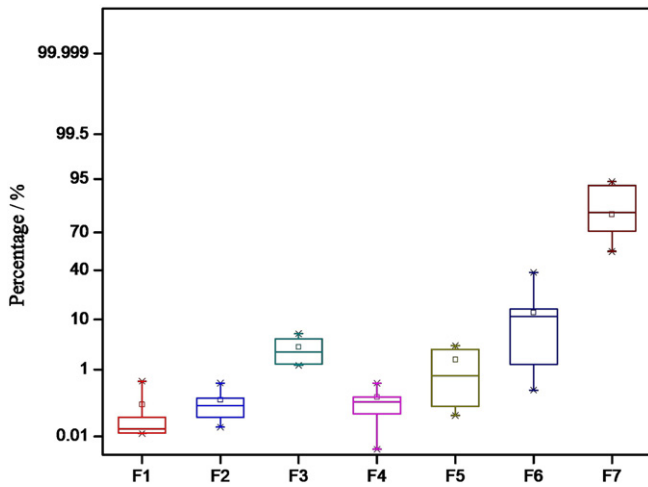


Fig. 5. The percentage of different forms of Hg.

acid together with 1 ml of bromide agent ($2.784 \text{ g L}^{-1} \text{ KBrO}_3 + 10 \text{ g L}^{-1} \text{ KBr}$). These solutions were placed for 1 h at room temperature, before adding hydroxylamine hydrochloride-sodium chloride solution ($120 \text{ g L}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}-120 \text{ g L}^{-1} \text{ NaCl}$) to clear their yellow color.

2.5. Quality control and quality assurance

Quality assurance and quality control were carried out using a system of method blanks, duplicates, and certified reference materials (GSS-3, Beijing, China; the Center of National Standard Reference Material of China). The relative standard deviation was <5%. The relative percentage difference between sample duplicates was <7%. The accuracy of the modified sequential extraction procedure was quantified using the parameter “recovery”, which is defined as the sum of extracted Hg fractions divided by the independently measured total Hg concentration (Wang et al., 2014). The recovery ranged between 86% and 108%, which was similar to reported studies for Hg of modified sequential extraction procedure (Hou et al., 2005, 2011; Wang et al., 2014).

2.6. Data analysis

Descriptive statistics for soil Hg concentrations and soil properties were calculated using SPSS 21.0 for windows (IBM, USA). Spatial distribution of total Hg in soils was described by the Kriging interpolation method in ArcGIS (Esri, CA, USA). Correlative relationships between Hg concentration and soil properties were investigated using multivariate statistical methods. We used Pearson’s correlation coefficient analysis, principal component analysis (PCA), and corresponding analysis (Han et al., 2006; Astel et al., 2011).

3. Results and discussion

3.1. Soil physicochemical property

Table 1 presents the physical and chemical properties of soils from the study area. In the gold mine area, soil pH varied from 2.9 to 8.0, with an average of 6.6. The lowest pH value (2.9) was found in the tailing sample (S15) from the Chenjiayu gold mine. In the control area, the soil pH was higher than the mine soils, varying from 5.1 to 7.9, with an average of 7.1. The control area soil pH was similar to the pH of surrounding waters (7.8 to 8.1) (Li et al., 2014). The lower pH values in the mine soils are due to acidic wastewater from the abandoned gold mine tailings (Jiménez-Rodríguez et al., 2009). The TOC content of soils varied little from the gold mine area to the control area, ranging from 0.26% to 4.54%. The highest TOC content was measured in sample S32, a surface soil from an orchard, and may be related to the use of organic fertilizer. The range in CEC values was larger, with higher average values in the mining area ($52.65 \text{ cmol kg}^{-1}$) compared with the control area ($28.49 \text{ cmol kg}^{-1}$). Compared with the current agricultural soil CEC control standard (Yu et al., 2014), the soils in this study area had strong fertilizing ability, with a high soil buffer capacity and self-purification ability.

3.2. Total mercury contents of soils

3.2.1. Distribution and assessment of total mercury content in soils

The contents of total Hg in soils varied greatly (Table 1). Average concentration of total Hg in soils collected from the mining area was higher than for the control area. The mean value of Hg concentrations in gold mine soils ($9.57 \text{ mg}\cdot\text{kg}^{-1}$) was 166 times the background values for Beijing surface soils ($0.058 \text{ mg}\cdot\text{kg}^{-1}$) (Li et al., 2013). However, the average concentration of total Hg in this study area was lower than concentrations found in the Andacollo Cu–Au–Hg mines, Chile (Higuera et al., 2004), Wangshan Hg mines, China (Qiu et al., 2005), and the Chatian Hg mine, China (Li et al., 2009). Nevertheless, it was higher than concentrations found at the Wanzhuang gold mines, China (Zhang et al., 2014a, 2014b).

The spatial distribution of total Hg in this study was interpolated using the Kriging method in ArcGIS, as shown in Fig. 2. Clearly, the tailings had the highest Hg contents, with Hg distributed as from a point source around the tailings. Hg concentrations decreased with increasing distance from the tailings. The high Hg levels in tailings are attributed to the amalgamation process used for gold extraction, resulting in much Hg released into the local environment. Typically, ore tailings produced by selecting or smelting and low grade ores contain a lot of heavy metals (Huang et al., 2012; Korte and Coulston, 1995).

The index of geoaccumulation (I_{geo}) developed by Muller (1979) was used to assess Hg contamination in the gold mine soils:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right), \tag{1}$$

Table 2
The concentrations of Hg speciation in soil ($\text{mg}\cdot\text{kg}^{-1}$).

| Stations | F1 | F2 | F3 | F4 | F5 | F6 | F7 | Summation of each fraction | Total Hg by single digestion | Recovery% |
|----------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|----------------------------|------------------------------|------------|
| S4 | 0.0031 | 0.0195 | 1.1543 | 0.016 | 0.0198 | 2.2465 | 16.6801 | 20.1393 | 21.7931 | 92.4 |
| S12 | 0.0023 | 0.0314 | 0.9174 | 0.0006 | 0.0094 | 0.0532 | 17.26 | 18.2743 | 19.0443 | 96.0 |
| S24 | 0.0005 | 0.0029 | 0.0853 | 0.0046 | 0.0194 | 0.0511 | 2.5546 | 2.7184 | 2.7767 | 97.9 |
| S29 | 0.0005 | 0.0039 | 0.172 | 0.0022 | 0.0187 | 0.0499 | 3.528 | 3.7752 | 3.93 | 96.1 |
| S30 | 0.0001 | 0.0001 | 0.0065 | 0.0009 | 0.0157 | 0.0549 | 0.4001 | 0.4783 | 0.483 | 99.0 |
| S18 | 0.0018 | 0.0008 | 0.0072 | 0.0016 | 0.0100 | 0.0512 | 0.2806 | 0.3532 | 0.3508 | 100.7 |
| S41 | 0.0001 | 0.0001 | 0.0028 | 0.0003 | 0.0075 | 0.0535 | 0.1565 | 0.2208 | 0.2559 | 86.3 |
| S48 | 0.0004 | 0.0007 | 0.0038 | 0.0006 | 0.0044 | 0.0589 | 0.085 | 0.1538 | 0.1417 | 108.5 |
| Mean | 0.0011 | 0.0074 | 0.2937 | 0.0034 | 0.0131 | 0.3274 | 5.1181 | 5.7642 | 6.0969 | 97.1 |
| SD | 0.0011 | 0.0116 | 0.4662 | 0.0053 | 0.0060 | 0.7754 | 7.4241 | 8.4160 | 8.9749 | 6.4155 |
| Range | 0.0001–0.0031 | 0.0001–0.0314 | 0.0028–1.1543 | 0.0003–0.0160 | 0.0044–0.0198 | 0.0499–2.2465 | 0.0850–17.260 | 0.1538–20.139 | 0.1417–21.793 | 86.3–108.5 |

Table 3
Correlation coefficients between different Hg forms in soil.

| | F1 | F2 | F3 | F4 | F5 | F6 | F7 | pH | TOC |
|-----|---------|---------|---------|---------|--------|--------|--------|----------|--------|
| F2 | 0.778* | | | | | | | | |
| F3 | 0.871** | 0.915** | | | | | | | |
| F4 | 0.664 | 0.360 | 0.691 | | | | | | |
| F5 | 0.182 | 0.092 | 0.293 | 0.612 | | | | | |
| F6 | 0.707 | 0.419 | 0.746* | 0.964** | 0.447 | | | | |
| F7 | 0.842** | 0.966** | 0.986** | 0.583 | 0.262 | 0.629 | | | |
| pH | 0.220 | −0.118 | 0.090 | 0.549 | 0.202 | 0.417 | 0.020 | | |
| TOC | −0.403 | −0.180 | −0.368 | −0.588 | −0.102 | −0.533 | −0.305 | −0.883** | |
| CEC | −0.209 | −0.611 | −0.592 | −0.198 | −0.119 | −0.339 | −0.601 | 0.285 | −0.024 |

* Significant p -values ($p < 0.05$) (2-tailed).

** Significant p -values ($p < 0.01$) (2-tailed).

where C_n is the measured concentration of a given element in the soil, B_n is the geochemical background value of this element, and the factor 1.5 is included to address differences in the background values because of lithology. I_{geo} has seven grades, ranging from uncontaminated to very seriously polluted. In this study, B_n was the background value of Hg in Beijing surface soils ($0.0576 \text{ mg} \cdot \text{kg}^{-1}$).

The I_{geo} values and contamination levels based on Hg in the gold mine soils are shown in Fig. 3. Clearly, the majority of soils at the gold mine area were very seriously polluted, followed by moderately to highly polluted and moderately polluted. The fractions of moderately polluted, moderately to highly polluted, and very seriously polluted soils at the mine area were 7.89%, 36.84% and 44.74%, respectively.

3.2.2. Factors determining the distribution of mercury

Fig. 4 shows the correlation between Hg concentration and various soil properties: pH, TOC and CEC. A weak negative correlation was found between the total Hg content and pH at this study area ($R = -0.064$, $p < 0.005$) and TOC ($R = -0.222$, $p < 0.005$), while a stronger negative correlation was observed for CEC ($R = -0.408$, $p < 0.005$). The correlation between CEC and TOC was also weak, but CEC showed a strong positive correlation with pH (Fig. 4(d)), which increased with the increasing soil pH. Hence, pH is an important factor affecting the variable charge produced by soil solid surface adsorption or medium-to-medium release of ions (such as H^+) (Costa et al., 2001). In this study, changes in soil pH clearly affected the CEC (Fig. 4).

3.3. Speciation of mercury in soils

Contents of the various forms of Hg found in soils are shown in Table 2. In general, the sum of extracted Hg fractions was slightly lower than the independently measured total Hg content, giving recovery rates between 86 and 108%. This may be caused by volatile loss of Hg in the SEP (except for the residue), and incomplete bromide digestion. However, linear analysis showed that values obtained through sequential extraction of various forms of Hg and independently measured total

Hg had a correlation of 0.999 ($y = 1.0661x - 0.0483$, $R^2 = 0.9995$). This indicates that the modified Tessier sequential extraction method effectively extracted different forms of Hg in the soils.

The fractions of various forms of Hg in the soils from highest to lowest were residual (81.74%) > strong organic-bound (12.89%) > humic acid (3.20%) > Fe–Mn oxide-bound (1.72%) > carbonate-bound (0.19%) > fulvic acid (0.15%) > soluble and exchangeable (0.11%) fractions (Fig. 5). In the study area, Hg occurred mainly in residual form, accounting for more than 80% of the total Hg, consistent with the findings of Gómez-Ariza et al. (2000) and Aldea et al. (2005) for other locations.

In any environmental consideration of heavy metals in the soil, the greatest concern is the transfer of the metal from soil to plants, allowing it to enter the food chain and pose a threat to human health. The residues of heavy metals exist in a soil lattice of silicates, and other primary and secondary minerals. In this form, the metal is stable, and not easily absorbed by plants. In contrast, bioavailable Hg easily migrates and is absorbed by plants (Wallschläger et al., 1998). Generally, bioavailable Hg is defined as soluble and exchangeable, as well as the carbonate-bound fractions (Li et al., 2009). In this study, bioavailable Hg accounted for only 0.30% of the total Hg content, with the soluble and exchangeable, and carbonate-bound fractions comprising 0.11% and 0.19% of the total Hg content, respectively. Hg in the fulvic acid and humic acid fractions occurs in active functional groups, with Hg^{2+} forming coordination complexes through redox reactions. The ratio of Hg combined with humic acid was higher than with fulvic acid, accounting for 3.20% and 0.15% of the total Hg content, respectively. This is because the migration ability of Hg in the soil is different for various types of humic acids. Fulvic acid bound Hg in has higher activity in the environment, while humic acid has an inhibiting effect (Yao et al., 2000). The mean ratio of Fe–Mn oxide-bound Hg in mining samples (S4, S12, S18, S24, S29, S30) is 1.2%, which was lower than in control area soils (S41, S48) of 3.2%. The higher pH value of the control soil forces Hg to strong binding sites in the Fe–Mn oxide, forming thermodynamically stable complexes. Han and Banin (1996, 2000) pointed out that soil pH and redox conditions have important effects on the Fe–Mn oxide-bound

Table 4
The results of PCA of different Hg forms in soil.

| Component | Initial eigenvalues | | | Rotation sums of squared loadings | | | Speciation | Rotated component matrix | |
|-----------|---------------------|---------------|-------------|-----------------------------------|---------------|-------------|------------|--------------------------|--------------|
| | Total | % of variance | Cumulative% | Total | % of variance | Cumulative% | | PC1 | PC2 |
| 1 | 4.881 | 69.725 | 69.725 | 4.881 | 69.725 | 69.725 | X1 | 0.861 | 0.325 |
| 2 | 1.378 | 19.689 | 89.415 | 1.378 | 19.689 | 89.415 | X2 | 0.971 | 0.004 |
| 3 | 0.560 | 8.000 | 97.414 | | | | X3 | 0.925 | 0.362 |
| 4 | 0.165 | 2.352 | 99.766 | | | | X4 | 0.413 | 0.881 |
| 5 | 0.016 | 0.223 | 99.989 | | | | X5 | −0.032 | 0.841 |
| 6 | 0.001 | 0.011 | 100.00 | | | | X6 | 0.505 | 0.779 |
| 7 | 6.629E−006 | 9.470E−005 | 100.00 | | | | X7 | 0.950 | 0.252 |

Extraction method: principal component analysis.

Rotation method: varimax with Kaiser normalization.

Numbers in bold are factor loadings of Hg speciation.

Hg, with high pH and redox potential conducive to the formation of Fe–Mn oxides. Clearly, gold mining had a huge effect on the distribution of Fe–Mn oxide-bound Hg at this study area. Strong organic-bound Hg accounted for 0.29–38.30%, with a mean value of 13%, which is lower than for Miyun Reservoir sediments (16.07%) (Liu et al., 2005).

3.4. Relationship between different forms of mercury in the soil

Soil is a complex system, where different and independent forms of Hg are influenced directly or indirectly by various environmental factors. Study of these interactions supports a clearer understanding of the migration of Hg in soil environments, and better remediation practices.

3.4.1. Correlation analysis

Correlations between various forms of Hg in our soil samples are shown in Table 3. The fulvic acid (fraction 2), humic acid (fraction 3) and residual Hg (fraction 7) were clearly related to the soluble and exchangeable Hg (fraction 1), suggesting these species have similar trends. The fulvic acid (fraction 2) and humic acid Hg (fraction 3) both had a strong positive correlation ($p < 0.01$), indicating that their formation mechanisms were similar under the same environmental conditions at this study area. The marked correlation between the humic acid (fraction 3) and the organic-bound Hg (fraction 6) showed that humic acid and macromolecular organisms both combined easily with Hg, and were fixed in the soil. The carbonate-bound (fraction 4) and the organic-bound Hg (fraction 6) also showed a significant correlation ($p < 0.01$). Compared with other forms, carbonate-bound and the organic-bound Hg had stronger correlation with pH and TOC, indicating that these two forms may depend on soil properties. Finally, the Fe–Mn oxide-bound Hg (fraction 5) had no significant correlation with any other Hg form, which may be related to its low content in the soil.

The results of correlation analysis showed that there is a dynamic equilibrium of adsorption–desorption and conversion between various forms of Hg, involving physical, chemical, and biological processes in the soil. In this study, correlation was not significant between most forms of Hg, suggesting that changes in one form are not simply related to transformation of another form, but are also influenced by the ambient environment. When the soil environment changes, the distribution of Hg in each phase (solid, liquid, and organisms) also changes. Adsorbed Hg is not invariable, and may combine with stronger adsorbents or be transformed.

3.4.2. Principal component analysis

PCA is commonly used to distinguish the possible sources of heavy metals and pathways in soils (Facchinelli et al., 2001; Zheng et al., 2008; Chabukdhara and Nema, 2012). The factor loadings were carried out with a varimax rotation as well as with the cumulative percentage of variance (Table 4). The forms of Hg were represented by the first two principal components (PC), which accounted for over 89% of the total variance.

PC1 was the most important principal component and was dominated by the exchangeable, fulvic acid, humic acid and residual forms of Hg. It accounted for 69.72% of the total variance. The contents of humic acid and residual Hg were relatively high in study area soils. Given their stable states, these forms of Hg reflected the total amount of Hg in the soil. PC2 was dominated by the carbonate-, Fe–Mn oxide-, organic-bound

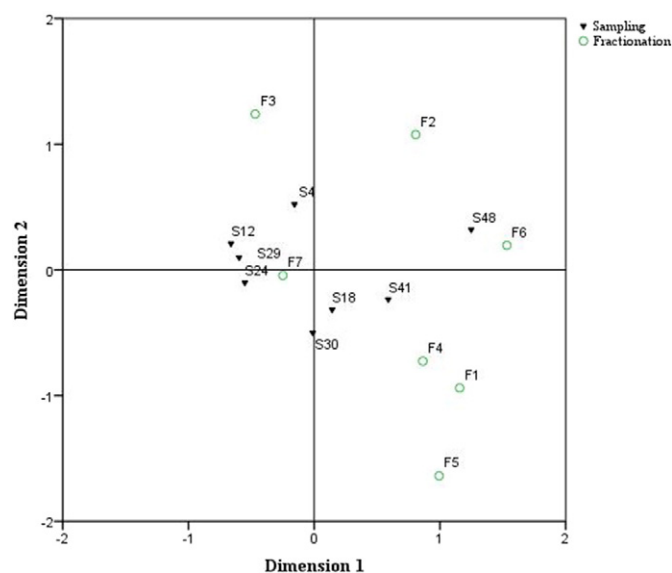


Fig. 6. Map of samples and variables in corresponding analysis.

Hg, accounting for 19.69% of the total variance. Carbonate-bound and Fe–Mn oxide-bound heavy metals are sensitive to pH. Under high pH conditions, free heavy metals precipitate with carbonates, as a function of the redox soil potential. With decreasing redox potential, the contents of heavy metals in high oxidation states decrease significantly and organically bound heavy metals increase. Thus, each form of Hg is affected differently by changing soil properties between the mine and control areas.

3.4.3. Correspondence analysis

Correspondence analysis is a multivariate statistical method to study the relationship between samples and other variables. We used this analysis to explore the relationship between the distributions of various forms of Hg and sampling points, using the percentage compositions of various forms of Hg in samples (Table 5 and Fig. 6). Two dimensions explained most of the data. The first dimension explained 90.9% of the corresponding analysis contingency table information, while the second dimension explained 7%, with a cumulative variance contribution rate of 97.9%.

The sampling points (S18, S41, S48) located in the first and fourth quadrants are far away from the gold mine area, while sampling points (S4, S12, S24, S29) in the gold mine area were mostly located in the second and third quadrants (Fig. 6). The sample S18 is in Xiaying village, which distance the Xiangshuiyu gold mine 3 km. This illustrates that the Hg distribution in the soil was affected by human activities, such as gold mining. The sampling point S48 gets close to fulvic acid and organic-bound Hg (fractions 2 and 6), indicates that Hg in the Miyun Reservoir soil was easily adsorbed onto soil organic matter. The sampling points (S4, S12, S24, S29) gets close to humic acid and residual Hg (fractions 2 and 7), show poor mobility of Hg, which has important implications for storage of Hg in these soils. The sampling points (S18, S30, S41) show that Hg in their soils was easy to form soluble and exchangeable, carbonate- or Fe–Mn oxide-bound Hg; all these forms are

Table 5

The results of corresponding analysis.

| Dimension | Singular value | Inertia | Proportion of inertia | | Confidence singular value | |
|-----------|----------------|---------|-----------------------|------------|---------------------------|---------------|
| | | | Accounted for | Cumulative | Stand deviation | Correlation 2 |
| 1 | 0.381 | 0.145 | 0.909 | 0.909 | 0.034 | 0.025 |
| 2 | 0.106 | 0.011 | 0.070 | 0.979 | 0.034 | |

easily absorbed and used by plants, and play an important role in the mobility of Hg in soil.

4. Conclusions

This study showed that the total Hg contents in the study area were higher than the background values for Beijing surface soils; generally, values were higher in mine soils relative to control soils. Mercury pollution was serious in the gold mine area, where tailings were the major sink of anthropogenic Hg. This suggests that urgent measures are required to deal with these tailings. We found that soil physico-chemical parameters were the limiting factors for the presence of Hg in these soils.

In our study area, Hg was mainly residual in the soil, accounting for more than 80%. Bioavailable Hg accounted for only 0.26%, including the soluble, exchangeable, and carbonate-bound fractions. These fractions still pose a potential threat to human health. Gold mining activities in the study have had a significant effect on elevating the Fe–Mn oxide-bound Hg in soil; the higher pH at these sites rapidly transforms Hg into Fe–Mn oxide-bound Hg.

Soil is a complex system, with chemical changes arising through interaction and transformation of its components, as well as in response to changes in the environment. The concentration and distribution characteristics of Hg in different forms is clearly connected to Hg content as well as soil properties. Therefore, to determine the transport, transformation, and fate of Hg in soils.

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