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Mercury drop trend in urban soils in Beijing, China, since 1987

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ABSTRACT

Mercury (Hg) concentration and its change trend in soils was investigated at different periods in Beijing. An Hg-enriched area with 1000 $ng \cdot g^{-1}$ Hg concentration was delineated within the Third Ring Road of the city, where the capital of the Ming Dynasty was situated approximately 500 years ago. The Hg concentration was attributed to the historical use of Hg and coal burning. The geometric mean of Hg concentration in Beijing was 714 $ng \cdot g^{-1}$ in 1987, 375 $ng \cdot g^{-1}$ in 2000, 294 $ng \cdot g^{-1}$ in 2005, and 251 $ng \cdot g^{-1}$ in 2009, indicating a drop in Hg concentration in the soil since 1987. The results show that the environmental quality of the soil Hg in Beijing had been significantly improving since 1987. The average topsoil Hg density (0 cm to 20 cm) decreased from 411 $mg \cdot m^{-2}$ in 1987 to 178.0 $mg \cdot m^{-2}$ in 2005, with an annual decrease of 4661 kg and an annual average drop rate of 3.15%. The sharp decrease in soil Hg content is attributed to tight emission controls implemented by the Beijing Government since 2000 and Hg emission from topsoil. However, the amount of Hg emission from urban soils is comparable with the value of Hg emission from fuel coal, oil, and natural gas in Beijing, implying that natural Hg emissions from the soil are another important atmospheric Hg source expected for emissions from fuel combustion.

1. Introduction

Mercury (Hg) is a persistent, toxic, and bio-accumulative heavy metal. Hg concentrations in the atmosphere, water, and soil at the global level were two to five times of those before industrialization, resulting in serious dangers to the environment and human health. Moreover, elemental mercury (Hg^0) is highly volatile; therefore, it could be exchanged bidirectionally between the soil and atmosphere (i.e., deposition and evasion), thus undergoing long-range transportation and global cycling (Lindberg et al., 2007; Schroeder and Munthe, 1998). The amount of mercury cycling among the land, atmosphere, and ocean has increased by a factor of three to five (Selin, 2009). Hence, Hg geochemical behavior and its potential risks, especially in urban areas, have received increasing scientific attention at present (Kelly et al., 1996; Mielke et al., 1999).

In China, Hg contamination is seen as a serious problem in urban areas (Jiang et al., 2006; Zhang and Wong, 2007). A systematic soil geochemical survey shows that over 100 cities in China were observed with high concentrations of Hg in soils (Cheng et al., 2008). Beijing and its Hg concentration has been the focus of numerous studies over the past decade, owing to the city's big population and function as the economic and cultural center of China. Hg-enriched soils have been found mainly in the downtown of the city (Cheng et al., 2008). Cinnabar (HgS), the predominant form of Hg in soils, was more widely distributed in the heavily Hg-polluted area (Cheng et al., 2008; Zhu et al., 2005). Results of sequential fractionation show that Hg in the water-soluble, ion-exchangeable, Fe–Mn oxide-bound, and organic phases in topsoil accounted for 0.78%, 0.18%, 0.25%, and 3.42%, respectively (Li et al., 2010), indicating the low mobility and bioavailability of Hg in topsoil. However, the risk of atmospheric Hg from soils should not be ignored.

The changing trend of soil Hg in urban areas has not been reported previously. The data for soil Hg concentrations in Beijing in 1987, 2000, 2005, and 2009 are presented in this work to study the spatial distribution and changing trend of topsoil in the different periods. The affecting factors are discussed to provide a scientific basis for understanding Hg geochemical behavior and assessing Hg ecological risks in cities.

2. Materials and methods

2.1. Study area

Beijing is situated at the northern tip of the roughly triangular North China Plain, with its center located at 39.9N and 116.4E. The

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city is surrounded by mountains on the West, North, and Northeast and extends to the seashore of the Bohai Sea on the southeast. Beijing has a typical monsoon-influenced climate characterized by hot, humid summers attributed to the East Asian monsoon and generally cold, windy, dry winters attributed to the vast Siberian anticyclone. Its annual mean temperature is 12.1 °C, with an extremely high temperature reaching 41.9 °C, and an annual mean precipitation of 588 mm since 1951. Soil types in Beijing are mainly silt, silt loam, loam soil, clay, silt clay, and silt clay loam (Cheng et al., 2008). The topsoil is slightly alkaline, with a median pH of 8.32, and the total organic carbon in the topsoil ranges from 0.22% to 6.94% (Chen et al., 2010).

The central portion of the city features a higher population and larger number of vehicles, as well as many ancient buildings (i.e., Forbidden City). With rapid development, Beijing's urban area has expanded from approximately 360 km^2 in 1987 to over 1000 km^2 in 2005. The suburban region outside of the Fourth Ring Road is notorious as an area of heavy industry, with such facilities as the Shoudu Steel Iron Company, the Beijing Chemistry Factory, and the Beijing Coking Factory, which have been closed or moved between 2005 and 2007. The rural region in the southern portion is a well-known agricultural area.

2.2. Sample collection

Systematic geochemical surveys were conducted in the urban areas of Beijing in 1987, 2000, and 2005. Topsoil samples at a depth of 0 cm to 20 cm were collected using the gird random sampling method for the surveys (Xie and Ren, 1991; Xie et al., 1989a). One or two topsoil subsamples were taken from the gardens, green belts, residential areas, or factories within each 1 ×1 km grid (Fig. 1).

In 1987, a total of 552 samples were obtained downtown at 360 km^2, with an average sample density of 1.55 samples per km^2 (Fig. 1). Each sample was sent for analysis; all analytical data within a 4-km^2 grid were averaged to represent the soil Hg concentration in the grid for comparison with data obtained in the following surveys.

In 2000 and 2005, 1140 samples and 1395 samples, respectively, were collected from the entire city, which has an area of 1044 km^2 (Fig. 1). Four topsoil samples within a 4 km^2 grid were composited to a sample for chemical analysis, thereby resulting in the creation of 210 composite samples in 2000 and 261 composite samples in 2005.

From December 2008 to November 2009, topsoil samples were also collected along a 32 km North–South (NS) transect and a 38-km East–West (WE) transect (Fig. 1). Sampling sites were equally spaced with a sampling interval of 1 km. Soils on each site were sampled each month during the sampling period.

Soils were taken from a soil profile of 210 cm in the old city, with a sampling interval of 15 cm. Samples were also obtained from another profile of 475 cm in the Western suburb with an interval of 25 cm (Fig. 1).

2.3. Sample preparation and analysis

Soil samples were prepared according to the standard procedure in the guidebook for soil geochemical survey (MLR, 1994). The soil samples were air dried in the dark at room temperature. Impurities, such as stones and tree leaves, were removed. Coarse soil particles (>0.84 mm) were crumbled by a wooden hammer, and the samples were sieved to < 0.84 mm after drying using a nylon screen; 80 g samples < 0.84 mm were ground with an agate mortar to < 0.074 mm, then sealed in amber glass sample containers, and stored at −4 °C until analysis.

The prepared soil samples were digested with HNO_3 and HCl-aqua regia (concentrated HNO_3:concentrated HCl = 1:3 by volume), after which total Hg was determined using cold-vapor atomic fluorescence spectrometry (XGY-1011A) at the Analytical Center of the Institute of Geophysical and Geochemical Exploration (IGGE).

Standard reference materials (SMR) and duplicate samples were used to control the analytical quality (Ye, 2005). Four SMRs of the GSS series (GSS-1, GSS-2, GSS-3, and GSS-8), produced by IGGE in China (Xie et al., 1985, 1989b), were inserted blindly into each of the 50 soil samples and analyzed simultaneously with the samples. The logarithmic difference ($\Delta \lg C_{SRM}$) between the analytical value and the standard value of each determination was then calculated to monitor the accuracy of the sample analyses and the between-batch bias as follows:

$$\Delta \lg C_{SRM} = |\lg C_d - \lg C_s|$$

where C_d is the determined concentration, and C_s is the standard reference concentration.

Analyses were considered acceptable if the $\Delta \lg C_{SRM}$ was <0.12 for samples with concentrations within three times the detection limit and <0.10 for samples with concentrations over three times the detection limit.

Duplicate samples, equaling 5% of the total number of samples, were inserted randomly to evaluate the precision of the analyses. The percent relative deviation (RD) was calculated as follows:

$$RD(\%) = [(C_1 - C_2)/((C_1 + C_2)/2)] \times 100$$

where C_1 is the first determination, and C_2 is the second determination. Analyses were considered acceptable if the RD was $-40\% \le RD \le 40\%$.

The logarithmic difference of the GSS series ranged from 0.00 to 0.035 (Table 1), the precision obtained from replicate analysis varied from −24.72% to 17.95%, with an average RD of 4.89% in 1987, 4.65% in 2000, 0.00% in 2005, and 3.77% in 2009 (Table 1).

3. Results and discussion

3.1. Hg in urban soils

3.1.1. Hg concentration in urban soils

Although the distribution of soil Hg concentration in Beijing is strongly skewed (Table 2), the log-transformed data passed the Kolmogorov–Smirnov test for normality (K–S, $p > 0.05$); thus, the geometric mean was used to illustrate the whole data set. As shown in Table 2, the geometric mean value of Hg concentration at different periods are significantly higher than the background values in 1984 (Chen et al., 1991; Li and Xu, 1984), revealing an evident Hg accumulation in Beijing's urban topsoil.

Urban soils in Beijing show intermediate Hg concentrations (mean 410 $ng \cdot g^{-1}$ in 2005) higher than the average concentration in Shenyang, Changchun (Yang et al., 2011), Shenzhen, Taiyuan, Shanghai, Tibet, and Urumqi; Avellino, Benevento, Caserta, Salerno, and Napoli, Italy (Cicchella et al., 2008a, 2008b); Berlin, Germany (Birke and Rauch, 2000); and Norway (Tijhuis et al., 2002). However, the Hg concentrations were lower than those in Guiyang, Chongqing, and Guangzhou (Zhang and Wong, 2007); Central Jordan (Banat et al., 2005); and Sicily, Italy (Manta et al., 2002).

3.1.2. Distribution of Hg in topsoil

As shown in Fig. 2, the high Hg anomalies at different periods were distributed in the downtown of the city. This site was the location of the capital of the Ming Dynasty approximately 500 years ago; hence, numerous historical buildings can be found in the area, which has the highest population density in the city. Unlike to the center of the city, the Hg concentration in Beijing shows a decreasing trend from the center of the city to its suburb (Figs. 3 and 4). If we set 1000 $ng \cdot g^{-1}$ as the guideline value for the residential area designated as UK (DEFRA and Environment Agency, 2009), an area of 48 km^2 has been delineated