Spatial distribution of mercury in topsoil from five regions of China

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Abstract The concentrations and distributions of mercury (Hg) in topsoil from four provinces and one municipality in China were investigated. A total of 1,254 samples were collected and analyzed. The average concentrations of Hg were 0.064 mg kg^{-1} for Liaoning Province, 0.100 mg kg^{-1} for Jiangsu Province, 0.110 mg kg^{-1} for Zhejiang Province, 0.154 mg kg^{-1} for Sichuan Province, and 0.098 mg kg^{-1} for Chongqing Municipality. Although differences were found among the ranges of Hg concentrations, the average values for each region were similar with other published data. The concentrations of Hg in topsoil varied largely upon the sampling locations. More than 80 % of the soil samples from Liaoning Province, Jiangsu Province, Zhejiang Province, and Chongqing Municipality, were ranked Grade I by the China Environmental Quality Standard for Soils, which can be considered as not contaminated by Hg. The concentrations of Hg in 0.3–0.4 % of soils collected from Jiangsu Province, Zhejiang Province and Chongqing Municipality exceeded the limitation for Grade III, indicating the contamination of Hg in these sites. The sources and potential risks of Hg in these sites should be brought to attention and further investigated.

Keywords Mercury · Soil · Spatial distribution · China

Introduction

As a toxic and global pollutant, mercury (Hg) has been of wide public health concern during the last century. Although there are some natural emissions of Hg from volcanoes, forest fires and evaporation from soil and water, anthropogenic emissions are considered the main sources for the global Hg contamination. Currently, there are more than 2,000 tonnes of Hg emitted every year by human activities, such as coal combustion, mining and smelting, and industrial usage of Hg in batteries, electric lighting, medical devices, and more (Pirrone et al. 2010; Streets et al. 2011).

China has a long history of mining and using of Hg. With the rapid economic development in the past decades, the amount of Hg consumed and released also increased significantly (Feng 2005; Jiang et al. 2006). The total demand of Hg from different sectors exceeded 1,500 tonnes in 2007, about 40 % increase compared with that in 2004 (Jian et al. 2009). Almost all the 11 categories and 59 sub-categories of emission sources defined by the *UNEP Toolkit for Identification and Quantification of Mercury Release* (UNEP 2010) are present in China. Although there is still a large uncertainty, the amount of Hg emitted from China was estimated in the range of 600–700 tonnes/year (Pacyna et al. 2006; Wu et al. 2006), accounting for about 30 % of the global emission. However, the fate of these emitted Hg was little studied and is not clear until now.

Besides aquatic system, soil is another important sink and source of Hg. As a natural element, Hg is widely present in soils at a certain level since the Earth was formed. Hg could also be introduced and accumulated in soil through various pathways, such as dry and wet deposition from atmosphere, release from waste products, and application of fertilizers and pesticides containing Hg. As a result, the content of Hg in soil may increase with growing anthropogenic activities. On the other hand, Hg in soil could be evaporated to the atmosphere,

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leached by water, or accumulated in plant. Thus, soil becomes an important source of Hg. Recent studies in Guizhou Province, southwestern China, have showed that rice is the major pathway for methylmercury (MeHg) exposure to humans, in which MeHg is mainly accumulated from soil (Meng et al. 2010, 2011; Qiu et al. 2008; Zhang et al. 2010). Therefore, monitoring the concentrations of Hg in soil is important for understanding the geochemical cycle of Hg in the environment.

Investigations from different countries showed that the Hg concentrations is in the range of 0.01–1 mg kg⁻¹ in soils without known nearby contamination sources and 0.1–10 mg kg⁻¹ in urban and industrial soils, while very high values were found in soils close to Hg mines (Tipping et al. 2011). A survey conducted by the China National Environmental Monitoring Center in 1990 showed that the national average concentrations of Hg in topsoil were 0.065 mg kg⁻¹ (Wei et al. 1991). However, there have been little available update data since the survey. Our recent studies in Pearl River Delta, one of the most industrialized and urbanized region in China, has shown that the concentrations of Hg in the sediments increased with the economic development in the last three decades (Shi et al. 2007, 2010). Studies also found high concentrations of Hg in the air and soil of some cities (Fang et al. 2004; Feng et al. 2003; Zhang et al. 2004; Zhang and Wong 2007).

The aim of this work was to investigate the levels of Hg in topsoil of four provinces and one municipality of China. A total of 1,254 samples were collected and analyzed. The spatial distribution of Hg in these regions was then further discussed.

Materials and methods

Sample collection

The map of the study regions and the locations of sampling sites are shown in Fig. 1. Four provinces (Liaoning, Jiangsu,

Zhejiang and Sichuan) and one municipality (Chongqing) were selected for sample collection. These regions are located in northeast (Liaoning), east (Jiangsu and Zhejiang), and southwest (Sichuan and Chongqing) of China, representing different conditions of climate, soil property, and Hg emission and deposition. The basic information of the sampling regions is shown in Table 1.

A total of 1,254 samples were collected in 2010, which included 147 samples from Liaoning Province, 231 from Jiangsu Province, 311 from Zhejiang Province, 239 from Sichuan Province, and 326 from Chongqing Municipality. The sampling sites covered the whole regions except for Sichuan Province, where all the sampling sites were distributed in the central province. Therefore, the concentrations of Hg obtained for Sichuan Province may not be representative for the whole province, but can nevertheless provide a useful reference for further studies.

Topsoil samples (0–20 cm) were collected using clean stainless steel spades. The geographic location and land utilization for each sampling site were recorded. The samples were kept in polyethylene bags at –20 °C after collection. In the laboratory, the soils were freeze-dried at –45 °C, and ground to fine particles.

Analysis

The concentrations of total Hg in soil samples were determined with AFS-8120 cold vapor atomic fluorescence spectrometry (CVAFS, Beijing Titan Instruments Co., Ltd., China) after acid digestion. Approximately 0.05–0.1 g of soil was weighted and added into a 20 mL ampule, and 2 mL of HNO₃ and 1 mL deionized water were added. After predigesting for 30 min, the ampule was then sealed using a RFJ model manual ampule sealer (Jishou Zhongcheng Pharmacy Machine Co., Ltd., China). The ampule was heated for 2 h at 105 °C in an autoclave. After the solution was cooled down to room

Fig. 1 Map of study regions. Red circles indicate sampling sites

Table 1 Basic information of the sampling regions

Sampling sites	Location	Area ($\times 10^4$ km ²)	Population (million)	Total Hg emission in 2003 (tonnes) ^a	Number of samples
Liaoning	118°53′–125°46′E 38°43′–43°26′N	14.59	43.75	45.9	147
Jiangsu	116°18′–121°57′E 30°45′–35°20′N	10.26	78.66	23.6	231
Zhejiang	118°01′–123°08′E 27°01′–31°10′N	10.18	54.43	21.0	311
Sichuan	97°21′–108°31′E 26°03′–34°19′N	48.43	80.42	37.5	239
Chongqing	105°11′–110°11′E 28°10′–32°13′N	8.24	31.44	–	326

^aData from Wu et al. (2006)

temperature, the ampule was opened and 1 mL of digested solution was pipetted into a 15-mL polyethylene terephthalate vial containing 9 mL of deionized water. The solution was mixed to homogeneity and then determined with CVAFS.

For the analytical quality control, reagent blanks, certified reference materials (CRMs), and sample replicates were also included in the analytical protocol. The determined concentrations of Hg in two sediment CRMs (0.286 ± 0.016 mg kg⁻¹ in GBW07310 and 0.060 ± 0.005 mg kg⁻¹ in GBW07312, $n=5$) were both in good agreement with their certified values (0.280 ± 0.040 mg kg⁻¹ in GBW07310 and 0.056 ± 0.008 mg kg⁻¹ in GBW07312), indicating the accuracy and reliability of the method.

The total organic carbon (TOC) contents were determined on a TOC analyzer (O.I Analyzer, College Station, TX, USA). About 0.1 g of soil was weighed and loaded into a quartz combustion cup. Prior to combustion, the sample was wet with 5 % phosphoric acid and heated at 250 °C for 1 min to purge the inorganic carbon.

For pH analysis, 4 g of soil was weighed into a 25 mL beaker and 10 mL KCl solution (1 mol L⁻¹) was added. The suspension was stirred at regular intervals for 30 min. The pH was recorded with a pH meter (ORION 3 STAR, Thermo Scientific).

Geochemical mapping

In order to study the spatial distribution of Hg, the software ArcGIS 10 was used to produce the contour maps by applying the Kriging method for the geospatial interpolation of the Hg data.

Results and discussion

The concentrations of Hg

The concentrations of Hg in soil samples are shown as box-plots in Fig. 2. The concentrations of Hg were in the range

0.001–1.075 mg kg⁻¹ (average, 0.064 mg kg⁻¹) for Liaoning Province, 0.006–2.758 mg kg⁻¹ (average, 0.100 mg kg⁻¹) for Jiangsu Province, 0.002–1.946 mg kg⁻¹ (average, 0.110 mg kg⁻¹) for Zhejiang Province, 0.003–0.708 mg kg⁻¹ (average, 0.154 mg kg⁻¹) for Sichuan Province, and 0.001–3.102 mg kg⁻¹ (average, 0.098 mg kg⁻¹) for Chongqing Municipality.

The average concentration of Hg in soils from Liaoning Province was similar to the national average of 0.065 mg kg⁻¹ of Hg in soil (Wei et al. 1991), while the other provinces exhibited higher average levels. Comparisons with published data on Hg in the study regions are shown in Table 2. The studies in tea garden soil from Sichuan Province and vegetable field soil from Chongqing Municipality were significantly different from this work, possibly because of the specific sampling areas in those studies. In addition, differences were also found among the ranges of Hg concentrations. However, as a whole, the average values for each region were similar with previously published data, indicating no significant changes of Hg concentrations in topsoil of the study regions.

Table 2 Comparison of published concentrations of Hg in study regions (mg kg^{-1})

Type of samples	Number of samples	Liaoning	Jiangsu	Zhejiang	Sichuan	Chongqing	Reference
Agricultural soil	2256	0.076 (0.014–0.438) ^a					Hou et al. 2011
Agricultural soil	908			0.130 (0.020–1.240)			Cheng et al. 2007
Topsoil	24186		0.082 (0.005–8.090)				Liao et al. 2009
Tea garden soil	510				0.039 (n.d.–0.368)		Tan et al. 2005
Agricultural soil	455					0.092 (0.017–0.546) ^b	Yang et al. 2006
Vegetable field soil	144					0.196 (0.028–0.669)	Huang et al. 2003
Topsoil	1254	0.064 (0.001–1.075)	0.100 (0.006–2.758)	0.110 (0.002–1.946)	0.154 (0.003–0.708)	0.098 (0.001–3.102)	This work

^a Collected from Shenyang City area

^b Collected from Three Gorges Reservoir area

Spatial distribution

The concentrations of Hg were used as input data for contour mapping with the software ArcGIS 10. The spatial distributions of Hg concentrations in topsoil of Liaoning

Province, Jiangsu Province, Zhejiang Province, and Chongqing Municipality are shown in Fig. 3. The contour map for Sichuan Province was not drawn because the sampling sites did not cover the whole region. As shown in Fig. 3, the concentrations of Hg in topsoil varied largely

Fig. 3 The spatial distribution of Hg in topsoil (in milligrams per kilogram). **a** Liaoning, **b** Jiangsu, **c** Zhejiang, and **d** Chongqing

Table 3 Correlations of Hg concentrations, TOC contents, and pH values

Sampling sites	TOC (%)	pH	$R_{\text{Hg, TOC}}$	$R_{\text{Hg, pH}}$
Liaoning ($n=50$)	2.66 (0.07–6.96)	6.0 (4.0–8.0)	0.504*	−0.153
Jiangsu ($n=50$)	1.91 (0.66–3.41)	6.5 (4.0–7.0)	0.307	−0.537*
Zhejiang ($n=50$)	1.74 (0.19–5.97)	6.2 (5.4–7.0)	0.446*	−0.092
Sichuan ($n=50$)	2.30 (0.13–3.99)	6.2 (3.4–7.0)	0.394*	−0.204
Chongqing ($n=50$)	1.59 (0.29–6.08)	6.0 (3.1–7.0)	0.379*	0.014
Total ($n=250$)	2.04 (0.07–6.96)	6.2 (3.1–8.0)	0.317*	−0.085

* $p=0.99$, significantly correlated

upon the sampling locations, and some high-Hg hotspots were found. The concentrations of Hg could be affected by numerous factors such as soil property, natural abundance of Hg, the input and output of Hg in soil, human activities, and more. Therefore, further study is necessary to identify the sources of those significantly high-Hg areas.

The estimated amounts of Hg emitted from study regions in 2003 have been shown in Table 1. Liaoning emitted the largest amount of Hg but the average concentration of Hg in topsoil was the lowest. The Hg emitted from Sichuan was less than Liaoning, but it had the highest Hg level in topsoil. The amounts of Hg emitted from Jiangsu and Zhejiang were low, and the levels of Hg in topsoil were in the middle. Therefore, as a whole, the average concentrations of Hg in topsoil of study regions were not correlated with Hg emission. But it should be noticed that the contents of Hg in soil could be affected by Hg emissions in some specific sites, especially in sites near coal-burning plants and Hg mining areas.

In order to investigate the correlations of Hg concentrations, TOC contents and pH in soils, 50 samples were chosen for each region and the TOC and pH were analyzed. The samples were selected mainly based on their geographic locations and even-distributed in study regions. The average and ranges of TOC and pH of selected soils are shown in Table 3. The TOC contents ranged from 0.07 to 6.96 % with an average of 2.04 %. The pH values were between 3.1 and 8.0 with an average of 6.2. In Jiangsu, the concentrations of Hg were not correlated with TOC but significantly correlated with pH. However, the concentrations of Hg were significantly correlated with TOC contents but not correlated with pH in other four regions. The same correlations were also found when taking all the samples together. This indicated that the influence of TOC on Hg concentrations is more significant than that of pH in collected samples.

According to China Environmental Quality Standard for Soils GB15618-1995 (NSPRC 1995), soils can be divided into three grades on the basis of pH, metals (Cd, Hg, As, Cu, Pb, Cr, Zn and Ni), and organic pollutants (HCHs and DDTs). Soils of Grade I are considered uncontaminated and are suitable for natural reserves, pasture lands and other protected soils. Grade II is suitable for agriculture soils, and Grade III is for mining areas or industrial soils. The limitations of Hg concentration for each grade are described in Table 4. The percentages of Hg concentrations in collected soils for each grade were calculated. About 99 % of all soil samples were classified as Grade I and Grade II. More than 80 % of soils from Liaoning Province, Jiangsu Province, Zhejiang Province, and Chongqing Municipality, ranked Grade I, which can be considered as uncontaminated by Hg. Although only 54.0 % of soils collected from Sichuan Province ranked Grade I, all the others were in the range of Grade II, indicating they were still safe for agricultural use. However, the concentrations of Hg in 0.3–0.4 % of soils collected from Jiangsu Province, Zhejiang Province and Chongqing Municipality exceeded the limitation for Grade III, indicating contamination of Hg in these sites. The sources and potential risks of Hg in these sites should be considered and further studied in detail.

Conclusions

Although differences were found among the ranges of Hg concentrations, the average values for each region were similar with previously published data. The concentrations of Hg in topsoil varied largely upon the sampling locations, which could be attributed to environmental and geographical factors. The concentrations of Hg in 0.3–0.4 % of soils collected from

Table 4 Distribution of collected soil samples among different grades based on Hg concentrations (GB 15618-1995, NSPRC 1995)

Grade	Ranges (mg kg ^{−1})	Liaoning (%)	Jiangsu (%)	Zhejiang (%)	Sichuan (%)	Chongqing (%)
I	≤0.150	93.9	86.6	82.6	54.0	86.5
II	0.150–1.000	5.4	13.0	16.7	46.0	12.9
III	1.000–1.500	0.7	0.0	0.3	0.0	0.3
>III	>1.500	0.0	0.4	0.3	0.0	0.3

Jiangsu Province, Zhejiang Province, and Chongqing Municipality exceeded the limitation for Grade III, indicating contamination of Hg in these sites. Further studies on the potential sources and environmental risks of Hg in these sites are warranted.

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