



Mercury concentrations in forest soils and stream waters in northeast and south China



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HIGHLIGHTS

- Atmospheric deposition in China has led to elevated Hg in forest soils and streams.
- Soil Hg concentrations are less in northeast China than those in south.
- Stream water concentrations are higher in the northeast compared to the south.
- High-concentration DOC in streams in northeast China facilitates Hg mobility.

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ABSTRACT

Atmospheric deposition of mercury (Hg) is generally higher in China than in North America and Europe. Transport and methylation of Hg deposited in forest ecosystems may cause health risks to humans. We collected water samples from 117 small streams, and soil samples from 25 sites in forested areas in northeast and south China during 2011–2013 to investigate the spatial distribution of Hg. Results showed that Hg concentration in surface soil (0–5 cm in depth) was generally higher in south China ($97.8 \pm 36.0 \mu\text{g}/\text{kg}$) than that in the northeast ($44.0 \pm 14.1 \mu\text{g}/\text{kg}$). In contrast, the Hg concentration in stream water was higher in northeast China ($17.2 \pm 11.0 \text{ ng}/\text{L}$) than that in the south ($6.2 \pm 6.4 \text{ ng}/\text{L}$). Hg concentrations in surface soil were positively correlated with Hg concentrations in the overlying litter Oe/Oa horizon ($r^2 = 0.84$). Hg concentrations in stream water were positively correlated to DOC (dissolved organic carbon) concentrations ($r^2 = 0.43$) and to the Hg concentration in the litter Oe/Oa horizon ($r^2 = 0.69$). Because the litter Oe/Oa horizon represents Hg accumulated by foliage, the positive correlations indicate that atmospheric Hg deposition was an important factor affecting Hg concentrations in soils and stream water.

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1. Introduction

Elemental mercury (Hg^0) can be transported globally and deposited in remote ecosystems (Fitzgerald et al., 1998) due to its long residence time (approximately 6–24 months) in the atmosphere (Schroeder et al., 1998). In aquatic ecosystems, Hg pollution is of great concern because Hg can be methylated and biomagnified (Morel et al., 1998). Because of the larger geographical area, forests receive more atmospheric Hg deposition than the lakes and rivers that surround the forests (Grigal, 2002). Deposited Hg may initially be retained in forest soil, but it will ultimately be transported into the aquatic ecosystem through stream and/or ground waters (Aastrup et al., 1991; Swain et al., 1992) or re-emitted into the atmosphere (Xiao et al., 1991).

China is currently the world's top emitter of anthropogenic Hg (Pirrone et al., 2010; Wang et al., 2010; Wu et al., 2012), which results in relatively higher atmospheric Hg deposition in China than in North America and Europe (Fu et al., 2012). Recent estimates using the mercury model of the USEPA Community Multi-scale Air Quality modeling system (CMAQ-Hg) showed that the dry deposition of Hg in the northeast and south of China in 2005 was generally greater than $40 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ and that wet deposition was greater than $20 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ (Lin et al., 2010), which are considerably greater than the total deposition of Hg in northeastern North America ($21.3 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$; Miller et al., 2005) and Japan ($20.8 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$; Sakata and Marumoto, 2005). To evaluate the health risks associated with the high deposition of Hg in China, it is important to investigate the spatial distribution of Hg in forest soil and stream water, and the factors that affect the accumulation of Hg. However, recent reports on the Hg pollution of soil and surface waters in China were related to local sources, such as Hg mines, zinc smelters and chlor-alkali factories, rather than the long-range

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transport of Hg (Feng, 2005; Qiu et al., 2005; S. Wang et al., 2009). Shi et al. (2013) conducted a regional investigation on topsoil (0–20 cm) in five provinces in China. In that study, a grid sampling method was applied, i.e., the land use and soil type were not differentiated during sampling, which biased soil sampling to agricultural fields. To our knowledge, no study has yet observed the larger-scale distribution of Hg in forest soil and stream water in remote areas in China, which could be influenced by the increasing long-range transport and deposition of atmospheric Hg.

Studies on the spatial distribution of Hg in forest soil and stream water at a regional scale are also limited globally. Obrist et al. (2011) performed a systematic investigation on the distribution of Hg in 14 forests across the contiguous U.S. and attributed the Hg spatial patterns to the organic matter concentration in the soil rather than atmospheric Hg deposition. Similar results were obtained in Norway (Låg and Steinnes, 1978). In contrast, Nater and Grigal (1992) reported that the regional and local sources of atmospheric Hg inputs resulted in Hg enrichment in litter and surface soil across a 1000-km transect in the north-central U.S. These conflicting results of previous studies indicate the need for additional regional investigations.

In this study, we investigated the Hg concentrations in forest soils and small streams in the northeast and south of China. Due to the lack of field observations of wet and dry Hg deposition in China and to the large uncertainty in the model simulation of atmospheric Hg deposition, the Hg concentration in the litter O_e/O_a horizon of soil was used as an indicator of accumulated Hg deposition. The objective of the present study was to investigate the spatial pattern of Hg in forest soils and small streams at a regional scale in China and factors that potentially influence these patterns, such as soil TOC (total organic carbon), stream DOC (dissolved organic carbon), and atmospheric Hg deposition.

2. Materials and methods

2.1. Soil and water sampling

Soil and stream sampling sites were selected in forested areas and at locations far (at least 50 km) from obvious anthropogenic Hg emission sources in the northeast and south of China. The investigation area of our study covered 6 provinces, and the only area that overlapped with the study of Shi et al. (2013) was Chongqing. A specific forested area included several soil sampling sites and small streams (different streams) to represent the Hg concentrations in the soil and stream in each area. Soil samples of different layers from 25 sites and water samples from 117 small streams (with 9 sites and 42 streams in the northeast and 16 sites and 75 streams in the south) were collected during 2011–2013 (Fig. 1).

At each soil sampling site, 3 sampling points were selected to conduct the vertical layered sampling, and 3 samples of the same layer were mixed to yield one sample. Litter samples were visually separated into two layers to collect undecomposed litter (O_i) and moderately decomposed litter/humus (O_e/O_a) using clean latex gloves and a stainless steel spade. Mineral soil samples were collected at depth intervals of 0–5 cm, 5–15 cm and 15–30 cm using a soil auger. The thickness of the horizon of soil A was generally less than 5 cm in all sampling sites. The 15–30 cm soil layer was in the horizon of soil B and represented soil that was minimally influenced by direct Hg deposition. All soil samples were immediately placed in plastic bags and stored in an insulated box with ice bags until being transported to the laboratory. In the laboratory, all soil samples were air dried at room temperature. Soil samples of mineral soil layers (0–5 cm, 5–15 cm, and 15–30 cm) were first roughly milled, and the large inorganic and organic particles were removed, such as gravel, pebbles, twigs, and branches. Then, the soil samples were milled to 100-mesh before chemical analysis.

To ensure that the collected water samples had percolated through the soil, i.e., to minimize the effect of directly transported Hg deposition to the stream water via surface flow, we avoided sampling during rain

or immediately after a heavy rainfall. Water samples were collected using a plastic 1.5 L jug. The jug was acid washed in the laboratory and was washed three times using stream water before sampling. A 50 mL water sample was poured into a PET (polyethylene terephthalate) centrifuge tube and then acidified with 0.4% HCl (v/v) and stored in the insulated box with ice bags to avoid the transformation and adsorption of Hg (Parker and Bloom, 2005). Three new PET tubes were randomly selected to check for contamination in the laboratory prior to the field investigation, and no contamination was found.

2.2. Sample analysis

Total Hg concentration in the solid samples (soil and litter) was analyzed using a direct Hg analyzer (DMA80, Milestone Inc., Italy). Total organic carbon (TOC) of the solid samples was measured using a wet chemistry method (Schumacher, 2002). Before the soil TOC measurement, carbonates in the mineral soil were removed using HCl (1 N) if carbonates were present. Soil samples were digested using potassium dichromate (K₂Cr₂O₇) and concentrated H₂SO₄ and boiled at 150 °C for 30 min to ensure that the oxidation reaction was completed. Then, ferrous ammonium sulfate [Fe(NH₄)₂(SO₄)₂·6H₂O] was used to titrate the solution after it had cooled. Water samples were filtered through a 0.45-μm glass fiber filter, and the total Hg concentration in these samples was measured using cold vapor atomic fluorescence spectrometry (CVAFS) (Tekran model 2600 system, Tekran Inc., Canada), following the U.S. EPA Method 1631 guideline (revision 1.20, July 2001) (Holmes and Lean, 2006). Dissolved organic carbon (DOC) in water was analyzed using a total organic carbon analyzer (TOC-VCPH, Shimadzu Inc., Japan).

For quality control, all containers (Teflon tubes/bottles and glassware) for the chemical analyses were acid cleaned prior to use. Every sample was analyzed in duplicate, and analyses were repeated when the difference exceeded 10%. The differences between duplicates were generally less than 7% (90% of the data). Blanks were checked, and standard samples were measured after every 8–10 samples. According to the U.S. EPA Method 1631 guideline for measuring the concentration of Hg in water, some reagents added to the water samples may contain Hg, and this amount was determined using reagent blanks (using ultra-pure water rather than water sample). The Hg concentration in blanks was less than 1 ng/L. A Hg²⁺ standard solution was prepared from a reference standard (1000 μg·mL⁻¹ in 3% HNO₃, Ricca Chemical Company). Solid standard reference materials (GBW07410 and GBW10015) were purchased from the National Research Centre for Reference Materials of China. When the measured values deviated by more than 5% from the standard values, the analyzers were recalibrated. The recovery percentages from spiked samples ranged from 90% to 110% for Hg in water samples, and ranged from 95% to 105% for Hg in soil samples.

2.3. Statistical analysis of data

SPSS (Statistical Product and Service Solutions) was used to perform statistical analysis. The significance of differences was analyzed according to a one-way ANOVA (analysis of variance), and the differences were considered to be significant when $p < 0.05$. Linear regression analysis was used to obtain r^2 values.

2.4. Atmospheric Hg deposition modeling

Atmospheric total Hg deposition (wet deposition + dry deposition) in China in 2009 was calculated using the GEOS-Chem model (Bey et al., 2001) with the Hg emission inventory of China in 2007 (Wang et al., 2014). The simulation results with a spatial resolution 0.5° × 0.667° (approximately 40 km × 50 km) agreed well with the observed background GEM (gaseous elemental mercury) concentrations (1.6–4.0 ng·m⁻³) in the atmosphere in China.

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