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Mass-dependent and mass-independent fractionation of mercury isotopes in precipitation from Guiyang, SW China



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ABSTRACT

The isotopic composition of mercury (Hg) is increasingly used to constrain the sources and pathways of this metal in the atmosphere. Though China has the highest Hg production, consumption and emission in the world, Hg isotope ratios are rarely reported for Chinese wet deposition. In this study, we examined, for the first time outside North America, both mass-dependent fractionation (MDF, expressed as $\delta^{202}\text{Hg}$) and mass-independent fractionation of odd (odd-MIF, $\Delta^{199}\text{Hg}$) and even (even-MIF, $\Delta^{200}\text{Hg}$) Hg isotopes in 15 precipitation samples collected from September 2012 to August 2013 in Guiyang (SW China). All samples displayed significant negative $\delta^{202}\text{Hg}$ ($-0.44 \sim -4.27\%$), positive $\Delta^{199}\text{Hg}$ ($+0.19$ to $+1.16\%$) and slightly positive $\Delta^{200}\text{Hg}$ (-0.01% to $+0.20\%$). Potential sources of Hg in precipitation were identified by coupling both MDF and MIF of Hg isotopes with a back-trajectory model. The results showed that local emission from coal-fired power plants and cement plants and western long-range transportation are two main contributing sources, while the contribution of Hg from south wind events would be very limited on an annual basis. The relatively lower $\Delta^{200}\text{Hg}$ values in Guiyang precipitation may indicate a dilution effect by local sources and/or insignificant even-MIF in the tropopause contribution of this subtropical region. Our study demonstrates the usefulness of isotope fractionation, especially MIF for tracing sources and pathways of Hg in the atmosphere.

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1. Introduction

Mercury (Hg) is a hazardous metal with high toxicity and extreme mobility. The bioaccumulation and biomagnification of its toxic form mono-methylmercury (MMHg)

in aquatic food webs may pose significant threats to human health and the environment (Sonke et al., 2013). The atmosphere plays a critical role in the global biogeochemical cycle of Hg and is an important reservoir of Hg; for example, more than 6×10^9 g of mercury were found in the single troposphere (Blum, 2011; Lin and Pehkonen, 1998; Slemr et al., 1985; Strok et al., 2015). Hg could be naturally released or re-emitted into the atmosphere by volcanic eruptions, forest fires, sea salt

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spray, wind-blown soil particles, and biogenic aerosols. Mercury can also be emitted into the atmosphere by human activities, such as coal combustion, cement production, non-ferrous metal smelting and waste incineration (Streets et al., 2005; Wang et al., 2014b). Anthropogenic emission is about three times that resulting from natural processes (Blum et al., 2014; Mason et al., 1994) and could reach remote areas, such as Tibet and Arctic areas (Douglas et al., 2008; Huang et al., 2012). Hg mainly exists as gaseous elemental Hg (Hg^0), divalent reactive gaseous Hg ($\text{Hg}(\text{II})$) and particle-bound Hg (Hg_p) in the atmosphere. Hg^0 is relatively inert and has a residence time of several months to one year, which allows for long-distance transport (Schroeder and Munthe, 1998). However, both $\text{Hg}(\text{II})$ and Hg_p are of high water solubility and thus deposit easily (Schroeder and Munthe, 1998). These atmospheric mercury species undergo complex physical and chemical processes, which make it challenging to identify the sources and pathways of Hg in the atmosphere and to evaluate its impact on surface ecosystems after deposition (Fu et al., 2010, 2012; Sonke, 2011; Wang et al., 2014b, 2006).

Mercury isotope signature is a useful tool for understanding Hg sources and the potential processes that Hg has undergone in the aqueous environment including precipitation and surface waters (Sonke and Blum, 2013). The advent of MC-ICP-MS has allowed for accurately measuring Hg isotopic composition, which sheds light on the global Hg cycle (Chen et al., 2012; Point et al., 2011; Sherman et al., 2011; Yin et al., 2014). Previous studies have reported both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF) of Hg isotopes in nature. Laboratory experiments showed that MDF could occur in almost all kinetic and equilibrium reactions (Blum et al., 2014), while MIF of odd Hg isotopes (odd-MIF, $\Delta^{199}\text{Hg}$) could only be triggered by special processes, such as photochemical reduction of $\text{Hg}(\text{II})$, photochemical degradation of MMHg, equilibrium evaporation, and abiotic dark reduction (Bergquist and Blum, 2007; Estrade et al., 2009; Zheng and Hintelmann, 2010b; Zheng et al., 2007). MDF has been proven to largely expand our understanding of the processes that constrain Hg distribution in various environments (Bergquist and Blum, 2009). The observation of odd-MIF greatly amplified the utilization of Hg isotopes because MIF could serve as the fingerprint of specific chemical pathways. Intriguingly, recent studies also reported MIF of even Hg isotopes (even-MIF, $\Delta^{200}\text{Hg}$) in mainly atmospheric samples, highlighting the importance of investigating Hg isotopes in atmospheric deposition, by which Hg enters into terrestrial ecosystems (Chen et al., 2012; Gratz et al., 2010; Sherman et al., 2010, 2011). However, due to the very low concentration (ng/L level), Hg isotopes in precipitation are rarely reported (Chen et al., 2012; Gratz et al., 2010; Sherman et al., 2010, 2011).

China is the largest coal producer and consumer in the world, and is considered as the largest global atmospheric Hg contributor (Fu et al., 2010; Wang et al., 2014b; Yin et al., 2014). However, Hg isotopic characteristic in precipitation from China remains unknown. Guiyang is the capital city of the province of Guizhou (SW China), and

possesses a large amount of coal and mercury mines, and is considered as an important Hg emission area in China (Feng and Qiu, 2008). Investigation of Hg isotopic signatures in this region could thus provide useful information on national Hg emission and deposition budgets in China. In this study, we determined the isotopic composition of Hg in precipitation from Guiyang collected from September 2012 to August 2013. This is the first study on Hg isotopic ratios in Chinese precipitation. The objectives of this study are:

- to characterize mercury isotopic signatures in precipitation in China;
- to identify the possible sources of Hg in Guiyang precipitation;
- to verify whether the observation of odd-MIF and even-MIF in North America precipitation results from a global phenomenon.

2. Materials and methods

2.1. Materials and reagents

All reagents (BrCl , HNO_3 , HCl , L-cysteine, $\text{NH}_2\text{OH}\cdot\text{HCl}$, SnCl_2) used in this study were analytical grade and prepared in the clean room. The water was 18.2 M Ω /cm ultrapurified Milli-Q water (Millipore). The vessels were of glass or Teflon, and were consecutively washed with 2% BrCl (for two days), 20% HNO_3 (for one day) and Milli-Q water. Then, all the high borosilicate glass vessels were heated in a muffle furnace at 500 °C for an hour to remove trace Hg before their use. All the samples were collected using “U”-type Teflon board (surface area $\sim 1.5\text{ m}^2$ each) connected with a large glass beaker (volume of 5 L each). Before sampling, the samplers were cleaned using 10% HNO_3 then with Milli-Q water. The blank of the whole collecting system was accessed by processing 1 L of Milli-Q water and was about 15 pg ($n=4$). The anion-exchange resin AG1-X4 (200–400 mesh, Bio-rad[®]) was used for pre-concentrating Hg from precipitation samples (Chen et al., 2010). NIST SRM 3133 Hg and two other Hg standards (Fluka and UM-Almadén, provided by J. Wiederhold and J. Blum) solutions were used as reference materials (also see Bergquist and Blum, 2007; Blum and Bergquist, 2007; Chen et al., 2010, 2012; Jiskra et al., 2012).

2.2. Field settings and sampling

The sampling site is shown in Fig. 1. Fifteen precipitation samples were collected on a building roof at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS, 26.35°N, 106.73°E), Guiyang, Guizhou, China, from September 2012 to August 2013. Guiyang is located in a subtropical region of the Yunnan–Guizhou Plateau. In general, our sampling site was constrained by two primary wind directions: west, southeast, with west wind dominated for most of the sampling period (from 9/2012 to 5/2013). Owing to low Hg concentration in precipitation (Table 1), a large volume of samples was needed to obtain

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