



Sequential samples reveal significant variation of mercury isotope ratios during single rainfall events

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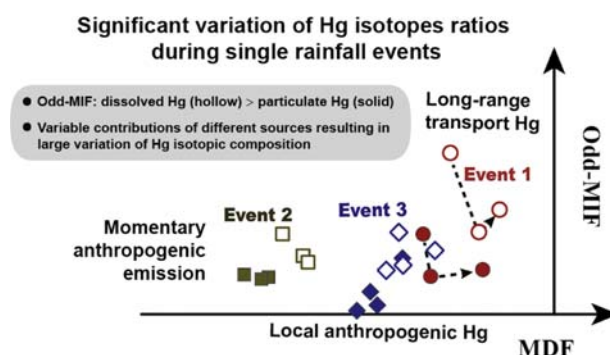
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HIGHLIGHTS

- Hg isotope ratios were measured in sequential precipitation for 3 events.
- Contribution of different sources was observed due to meteorological conditions.
- Particulate Hg and filtered rainwater Hg showed different isotopic compositions.
- Isotopic composition was sensitive to a brief anthropogenic incense burning event.

GRAPHICAL ABSTRACT



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ABSTRACT

Although the investigation of mercury (Hg) isotopes in precipitation has largely improved our knowledge of the source and transformation of Hg in the atmosphere, rainwater investigated in previous studies were integrated samples collected over an event and could obscure key information about the physiochemical transformation and deposition dynamics of Hg (and its isotopes) in short precipitation events. In this study, we investigated Hg isotopic composition of filtered (Hg_F) and particulate Hg (Hg_{PM}) in sequential rain samples from three single rainfall events in Guiyang, China. All samples showed a decrease of total Hg concentration, as well as Hg_F and Hg_{PM} with time in each rainfall event, and large variation of both mass-dependent fractionation (MDF) and mass-independent fractionation of odd Hg isotopes (odd-MIF) for both phases. Isotopic data indicated variable contributions of different sources triggered by the instant change of meteorological conditions, rather than internal atmospheric processes. The rapid response of MDF and odd-MIF of precipitation samples to the incense burning on the Tomb Sweeping Day implied that Hg isotopic composition was very sensitive to the momentary anthropogenic emission, which could have at least a regional short-lived effect and should be taken into account in future studies. Hg isotopes are a powerful tool for investigating both atmospheric transformation and instant deposition dynamic of Hg, and like stable H and O isotopes, could provide useful information about local or regional meteorological changes.

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1. Introduction

Mercury (Hg) is a globally transported contaminant (Giang and Selin, 2015). The atmosphere is both a receptor of naturally and anthropogenically emitted Hg, and a crucial contributing source of Hg in surface ecosystem through both wet (mainly in reactive gaseous Hg (RGM) and particulate Hg (PHg)) and dry deposition (mainly in PHg and gaseous elemental Hg, GEM) (Enrico et al., 2016, 2017; Landing et al., 2010; Lynam et al., 2014; Marumoto and Matsuyama, 2014; Obrist et al., 2017; Sanei et al., 2010; Schroeder and Munthe, 1998). Previous studies have shown that the majority of atmospheric Hg is transported to the surface through wet deposition, because RGM and PHg are both prone to scavenging (Lynam et al., 2014; Seo et al., 2012). Inorganic Hg derived from the atmosphere is converted into methylmercury (MeHg) that impacts the health of humans and biota (Giang and Selin, 2015; Walters et al., 2015). Thus, understanding Hg deposition dynamics is important for deciphering the biogeochemical cycling of Hg in surface terrestrial ecosystems. Although significant progress has been made on the understanding of atmospheric Hg deposition through investigation of Hg concentration, species and transport models, some aspects of the deposition flux and dynamics remain unclear (Brunke et al., 2016; Gratz et al., 2009; Huang et al., 2012; Seo et al., 2012; White et al., 2013).

Measurement of Hg isotopes has proven useful for investigating the transformation and the flux of Hg between different reservoirs (Blum et al., 2014). Recent studies have reported both mass-dependent fractionation of Hg isotopes (MDF, $\delta^{202}\text{Hg}$) and mass-independent fractionation of odd Hg isotopes (odd-MIF, $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$) in both natural samples (sediments, soils, food web and precipitation) (Blum et al., 2014; Sun et al., 2014, 2016) and in laboratory experiments (Bergquist and Blum, 2007; Zheng and Hintelmann, 2009, 2010). Odd-MIF is mainly induced by specific biogeochemical processes, such as divalent Hg photo-reduction, abiotic dark reduction, MeHg photo-degradation, and elemental Hg evaporation, and is triggered by either the magnetic isotope effect (MIE) or the nuclear volume effect (NVE) (Bergquist and Blum, 2007; Blum et al., 2014; Sun et al., 2016; Zheng and Hintelmann, 2009, 2010). Though the exact mechanisms remain unclear, MIF of even Hg isotopes (even-MIF, $\Delta^{200}\text{Hg}$) has also been recently determined in atmospheric samples or natural materials mainly related to the atmosphere, such as GEM (Demers et al., 2015; Rolison et al., 2013), precipitation Hg (including both RGM and PHg) (Chen et al., 2012; Gratz et al., 2010; Sherman et al., 2012; Z. Wang et al., 2015; Yuan et al., 2015), mosses (Cai and Chen, 2016), sediments and soils (Demers et al., 2013; Gray et al., 2013, 2015). This renders Hg a unique heavy metal having a “three-dimensional” isotope system (Cai and Chen, 2016; Chen et al., 2012).

Hg isotopes have been successfully used to trace atmospheric Hg sources and transport. The studies on the integrated precipitation samples (mixing the samples of successive precipitation events over days or even weeks) from USA showed that Hg isotopic compositions could serve as an efficient tracer of local and regional emission (Gratz et al., 2010; Sherman et al., 2012, 2015). Two studies of precipitation in China and Canada demonstrated that Hg isotopes could be used for tracking long-range transport as well (Chen et al., 2012; Z. Wang et al., 2015). Moreover, Hg isotopes could be employed in much more complex systems for assessing sources or behaviors of its subspecies (Demers et al., 2013, 2015). Interestingly, even isotope anomaly has been observed in all atmospheric samples and could be used as a conservative tracer of upper atmosphere chemistry (Cai and Chen, 2016; Chen et al., 2012, 2016; Demers et al., 2013, 2015; Gratz et al., 2010; Sherman et al., 2012, 2015; Z. Wang et al., 2015; Yuan et al., 2015). These studies demonstrated that both odd-MIF and even-MIF could serve as the Hg deposition tracer from atmosphere to earth surface.

Due to the need of enough mass of Hg for high-precision isotope measurement, the precipitation samples investigated in the above studies are all integrated samples collected from an entire precipitation event or from multiple events, over a relatively long period. This sampling

scheme obscures some key information about the physiochemical transformation of Hg (and its isotopes) related to the washout curve. For example, studies with high frequency sequential sampling has reported the great variability of Hg concentration in intra-rainfall events (White et al., 2009, 2013), which might be caused by the changes of meteorological conditions, source contribution and/or other potential factors (White et al., 2013). These changes would also induce large variation of isotope ratios, as demonstrated in previous studies for other stable isotopes (e.g. $\delta^2\text{H-H}_2\text{O}$, $\delta^{18}\text{O-H}_2\text{O}$, and $\delta^{15}\text{N-NO}_3^-$) (Coplen et al., 2008; Felix et al., 2015; Li et al., 2015; Munksgaard et al., 2012). Similarly, in our previous study, variation of both MDF and MIF of Hg isotopes were also observed in one single rain event at the Lhasa City on the Tibetan Plateau (Yuan et al., 2015) that likely resulted from the contribution of variable Hg sources characterized by different isotopic compositions (Chen et al., 2012; Gratz et al., 2010; Sherman et al., 2012; Z. Wang et al., 2015; Yuan et al., 2015). This observation motivated further systematic study of changes in Hg isotopes during intra-precipitation events and the relative influence of contributory factors in other geographic regions.

Here, we conducted a systematic study of Hg concentration and isotopic variations in sequential samples collected from three intra-rainfall events at Guiyang City, China. The potential factors causing these variations were carefully investigated by coupling Hg, oxygen and hydrogen isotopic signatures, meteorological data, and air-mass back trajectory calculation. Because the particulate phase could occupy a large proportion of total Hg (Huang et al., 2012, 2013), we collected and measured Hg concentrations and isotopic ratios in filtered rainfall (Hg_r) and on particles (Hg_{PM}) separately. Many previous studies investigated bulk unfiltered rainfall only. The specific objectives are 1) to investigate the variation of Hg concentration and isotopic composition in the particulate and filtered phases during single rainfall events; 2) to identify the potential factors controlling these variations; and, 3) to test the possibility of tracing meteorological changes using Hg isotopes.

2. Materials and methods

2.1. Materials and reagents

All reagents, including HCl, HNO_3 , KBr, KBrO_3 , L-cysteine, $\text{NH}_2\text{OH}\cdot\text{HCl}$ and SnCl_2 , were analytical grade (Sinopharm Chemical Reagent Co., Ltd., China) and were prepared in an ultra-clean room at the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). 18.2 M Ω Milli-Q water (Millipore, USA) was used for preparation all aqueous solutions. Concentrated HCl and HNO_3 were double-distilled. A 0.2 M BrCl solution was prepared by mixing the concentrated HCl with preheated (250 °C, 12 h) KBr and KBrO_3 powders. Two SnCl_2 solutions of 0.20 and 0.03 g/mL were prepared by dissolving the solid in 1 M HCl and were used for online reduction of Hg during the concentration and isotope measurement steps, respectively. For neutralizing the excess BrCl, a 0.25 g/mL $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution was prepared and bubbled for 6 h with Hg-free N_2 to remove trace levels of Hg vapor. The NIST SRM 3133 Hg and UM-Almadén Hg were used as international standards and measured regularly to control the accuracy and quality of isotope analysis (Blum and Bergquist, 2007; Chen et al., 2010), and also served for the method validation coupling with Yellow-Red Soil GBW07405 (National Center for Standard Materials, Beijing, China) (Huang et al., 2015). The NIST SRM 997 thallium solution (20 ng/mL Tl in 3% HNO_3) was used for instrument mass-bias correction. The anion-exchange resin AG-1X4 (200–400 mesh, Bio-Rad®) was used for pre-concentrating Hg from precipitation samples (Chen et al., 2010). All vessels were made either of glass or of Teflon. Borosilicate glass bottles were acid-cleaned by soaking in 10% HNO_3 solution for 24 h followed by rinsing three times with Milli-Q water, then baked for 4 h at 460 °C in a muffle furnace. The vessels in Teflon were cleaned similarly and air dried for 24 h in a laminar fume hood. For rainwater collecting, a 1.2 m \times 1.0 m Teflon board (3 mm thick) was deformed into a “U”-type sampler (surface area of $\sim 0.9\text{ m}^2$) and fixed through four Nylon sticks at 1.5 m above ground. The rainwater

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