

11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

## Large variation of mercury isotope composition during a single precipitation event at Lhasa City, Tibetan Plateau, China

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### Abstract

This study examined for the first time the Hg isotope composition in rain samples from a single precipitation event at Lhasa City (China) on the Tibetan Plateau, the “world’s third pole”. Large variations of both mass-dependent fractionation (MDF,  $\delta^{202}\text{Hg}$  from -0.80‰ to -0.42‰) and mass-independent fractionation (MIF,  $\Delta^{199}\text{Hg}$  from 0.38‰ to 0.76‰) were observed, with the latter increasing with time. Our results demonstrated that the large variation of Hg isotope ratios likely resulted from mixing of locally emitted Hg and long-term transported Hg, which were characterized by different Hg isotope signatures and mainly leached by below-cloud scavenging and in-cloud scavenging processes, respectively. Our findings demonstrated that Hg isotopes are a powerful tool for investigating the dynamics of precipitation events and emphasized the importance of systematic monitoring studies of the chemical and isotope variability of Hg and other elements during rainfall events.

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Peer-review under responsibility of the scientific committee of AIG-11

**Keywords:** Hg isotopes; single precipitation event; mass-dependent fractionation; mass-independent fractionation; Lhasa; Tibetan Plateau

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### 1. Introduction

Recently developed isotope methods have opened up a new avenue for studying the global biogeochemical cycle

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of mercury (Hg). Previous studies have reported both mass-dependent fractionation (MDF,  $\delta^{202}\text{Hg}$ ) and mass-independent fractionation (MIF) of Hg isotopes in the nature, with MIF of odd atomic weight Hg isotopes (odd-MIF,  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ) as an important novel observation<sup>1-3</sup>. Odd-MIF was mainly produced in special biogeochemical processes, such as divalent Hg photoreduction or abiotic dark reduction, methylmercury (MMHg) photodegradation and elemental Hg evaporation<sup>1,3</sup>. It is noteworthy that these specific processes can lead to different  $\Delta^{199}\text{Hg} / \Delta^{201}\text{Hg}$  ratios, which is very useful for differentiating the transformation processes of Hg in nature. More importantly, recent studies have found the intriguing MIF of even atomic weight Hg isotopes (even-MIF,  $\Delta^{200}\text{Hg}$ ) mainly in atmospheric samples, rendering Hg as a unique heavy metal having "three-dimensional" isotope systems<sup>4</sup>. The nuclear volume effect (NVE) and magnetic isotope effect (MIE) are thought to be the main causes for odd-MIF<sup>1,2,5,6</sup>, the mechanism triggering even-MIF remains unknown<sup>4,6</sup>.

Up to now, only a few studies reported Hg isotopic composition in precipitation samples<sup>4,6-8</sup>. Due to the low Hg concentrations in rainfall, all these samples were collected as bulk samples from at least one entire rainfall event or even multiple rainfall events. This approach may conceal detailed information about the influence of numerous parameters on the evaluation of Hg physicochemistry and its isotope composition during one single dynamic precipitation event<sup>9</sup>. In this paper, we present the first study on Hg concentration and isotope composition of rainfall samples collected from one single precipitation event at Lhasa, the largest city on Tibetan Plateau (TP) in China. The specific objectives are (1) to determine Hg isotopic composition in precipitation from TP, and (2) to evaluate Hg concentration and its isotope composition during a single rainfall event.

## 2. Methods

Lhasa is located in a narrow west-east valley in the southern part of the TP with a central area of 51.4 km<sup>2</sup>. The population density of Lhasa (5837 people per km<sup>2</sup>) is significantly higher than the mean population density (2.5 persons per km<sup>2</sup>) in the TP. During the monsoon season (July through September), the low pressure over the TP brings warm air masses from the Indian Ocean to the plateau, while during the rest of the year the large-scale atmospheric circulation patterns over the Tibetan Plateau are mainly dominated by westerly winds<sup>10</sup>. Due to the low Hg content, only four rain samples were collected with a tilted "V" type Teflon board of large area (~2.2m<sup>2</sup>) during a single precipitation event from the night of 31<sup>st</sup> August to the early morning of 4<sup>th</sup> September, 2013 at the campus of the Institute of Tibetan Plateau Research, Lhasa Branch (ITPR-LB) (29°38'N, 91°01'E, 3640 m a.s.l.), situated in the western part of Lhasa. The samples were filtered and Hg was pre-concentrated from the aqueous matrix using a chromatography column<sup>11</sup>. Hg isotope ratios were measured using multiple-collector ICP-MS (Nu Instruments) with Tl added for mass bias correction. The detailed description of Hg pre-concentration and isotope analysis can be found in previous studies of our group<sup>8,11,12</sup>. The MDF ( $\delta^{202}\text{Hg}$  in ‰) and MIF ( $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ) of Hg isotopes were defined using the equations given in Blum and Bergquist (2007)<sup>13</sup>. Our repeated measurements of the secondary standard UM-Almadén Hg gave long-term (n = 42) average  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  values of  $-0.56 \pm 0.12$ ,  $-0.02 \pm 0.07$ ,  $0.01 \pm 0.06$  and  $-0.04 \pm 0.06$  (2SD), respectively, in accordance with the previous studies<sup>4,13</sup>. The obtained 2SD were considered as the typical uncertainties for the four samples that were measured only once.

## 3. Results and Discussion

### 3.1. Variation of Hg concentration and isotopic composition

Volume weighted Hg concentrations in samples varied from 3.1 ng L<sup>-1</sup> (R4 in Fig. 1a) to 8.3 ng L<sup>-1</sup> (R1 in Fig. 1a) and displayed a progressive decline with time during the single precipitation event (Fig 1). These values were similar to those (generally low than 10 ng L<sup>-1</sup>) previously reported for precipitation of the same region<sup>10</sup>, of Guiyang in China<sup>8</sup> and Peterborough in Canada<sup>4</sup>, but lower than those of Florida (4.0~140 ng L<sup>-1</sup>, average 51.80 ng L<sup>-1</sup>)<sup>7</sup> and the Great Lake region in USA (6.9~29.3 ng L<sup>-1</sup>, average 10.48 ng L<sup>-1</sup>)<sup>6</sup>.

As shown in Fig. 1, precipitation samples were characterized by negative  $\delta^{202}\text{Hg}$ , with the highest value of -0.42‰ for R3 and the lowest value of -0.80‰ in R1 (Fig. 1b). These values are similar to those in precipitation from Guiyang in China, and from Peterborough, Florida and the Great Lake region in the North America (Fig. 2a)<sup>4,6-8</sup>. Interestingly, the four samples from this single precipitation event displayed a large variation of odd-MIF ( $\Delta^{199}\text{Hg}$

from 0.38‰ for R1 to 0.76‰ for R4), and a progressive increase with time (Fig. 1c). These  $\Delta^{199}\text{Hg}$  values are similar to that of rain samples from Guiyang and Peterborough, but relatively higher than that of Florida and the Great Lake region (average  $\leq 0.3\%$ ) (Fig. 2b)<sup>4,6-8</sup>. All four samples had positive even-MIF, with  $\Delta^{200}\text{Hg}$  varied from 0.10‰ to 0.15‰ (average 0.13‰), similar to the wet precipitation samples collected in Guiyang, Florida and the Great Lake region (generally below 0.20‰)<sup>6-8</sup>, but lower than that from Peterborough (0.21 ~ 1.24‰)<sup>4</sup>.

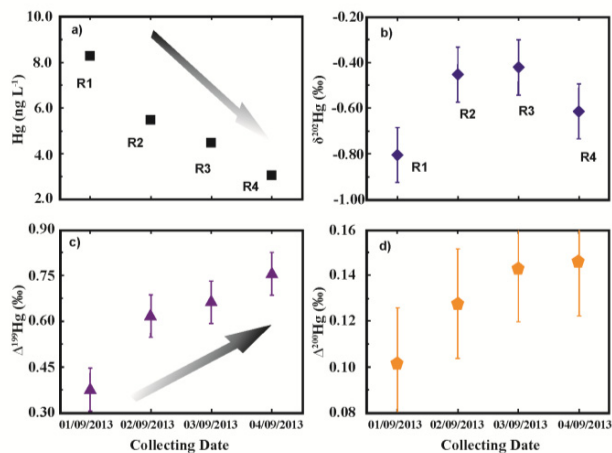


Fig. 1. Variation of Hg concentration (a),  $\delta^{202}\text{Hg}$  (b),  $\Delta^{199}\text{Hg}$  (c) and  $\Delta^{200}\text{Hg}$  (d) during single precipitation event.

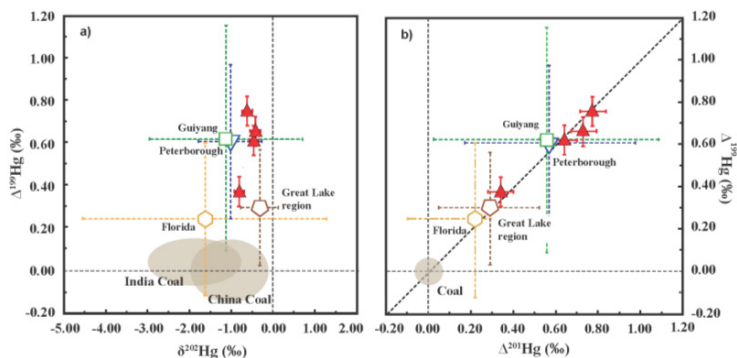


Fig. 2.  $\Delta^{199}\text{Hg}$  vs  $\delta^{202}\text{Hg}$  (a) and  $\Delta^{199}\text{Hg}$  vs  $\Delta^{201}\text{Hg}$  (b) for rain samples of the precipitation event. Hg isotope data (average  $\pm 2\text{sd}$ ) reported in previous studies<sup>4,6-8</sup> for precipitation from Peterborough, Great Lakes region, Florida and Guiyang are also given for comparison. The isotope data for coals of China and India are from Sun et al. (2014)<sup>14</sup>.

### 3.2. Below-cloud scavenging of local emitted Hg

Local sources may contribute to Hg in our precipitation samples. In fact, the air quality of the sampling campus is mainly influenced by emissions from industrial sources including a coal-fired power plant (CFPP, located on the south-west of sampling site) and surrounding cement production facilities<sup>10</sup>. Hg(II) is the main form of Hg emitted into the atmosphere by CFPP and cement plants, which may be easily scavenged into water droplets (and particles) in the atmosphere. Since pollutants released by human activities mainly reside and accumulate in the atmosphere boundary layer (generally  $< 1000\text{m}$ ), anthropogenic Hg emitted by local sources would thus be principally leached down at the beginning of the precipitation event by below-cloud scavenging processes<sup>9,10,15</sup>. Hg is also contained in

cloud water droplets. The rapid deposition of these droplets at the first precipitation phase would largely incorporate below-cloud Hg as well, inducing high Hg content at the beginning stage of rainfall.

Unfortunately, Hg isotope ratios of local emission were not analyzed in this study. According to a previous study, Hg emitted by two kinds of main anthropogenic sources (CFPP and cement plant emissions) is characterized by negative  $\delta^{202}\text{Hg}$  (about -1.46‰ and -1.33‰, respectively) and  $\Delta^{199}\text{Hg}$  close to zero<sup>8</sup>. Thus, anthropogenic Hg had different isotopic composition from the rain sample R1 for both MDF and odd-MIF. There are two possibilities to explain this difference: 1) post-emission processes modified the initial Hg isotope signature and 2) anthropogenic Hg was mixed with Hg from another source that displayed significant odd-MIF.

Actually, atmospheric Hg species could undergo complex physical and chemical processes. In this study, the four rain samples plot on the 1:1 line in  $\Delta^{199}\text{Hg}$  versus  $\Delta^{201}\text{Hg}$  figure (Fig. 2b), consistent with the result of previous photo-reduction experiment<sup>16</sup> and precipitation studies<sup>1,4,6-8</sup>. This suggests that odd-MIF in precipitation from Lhasa was likely triggered by Hg(II) photo-reduction in water droplets in the atmosphere boundary layer<sup>4</sup>. Based on the previous experiment<sup>16</sup>, we can calculate the variation of Hg isotopic composition caused by post-emission photochemical reactions using a Rayleigh model<sup>8</sup>. The results showed that, with respectively 13% or 15% of initial Hg(II) photo-reduced and released into air, the final  $\Delta^{199}\text{Hg}$  would be 0.38‰ for the remaining solution for Hg emitted from China coal and cement plants, and the corresponding  $\delta^{202}\text{Hg}$  in the ultimate atmospheric phase would be -0.93‰ and -1.21‰. These values are very close to those of R1. This suggests that local emission by human activities is a possible contributing source to Hg in the precipitation. However, the initial emitted Hg did not have even-MIF and the post-emission processes could not induce any  $^{200}\text{Hg}$  anomaly, which was contrast to what we observed in rain samples ( $\Delta^{200}\text{Hg} > 0.10\text{‰}$ ). As a result, rather than the post-emission processes, the higher  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  values in precipitation sample R1 more likely reflect a mixing of locally emitted Hg with another source, possibly the long-term transported Hg.

### 3.3. In-cloud scavenging of long-term transported Hg

The progressive decrease of Hg concentration and the inverse increase in odd-MIF may be a result of Hg(II) photo-reduction that leads to high  $\Delta^{199}\text{Hg}$  in the remaining solution. Considering that R1 and R4 are respectively the initial and the final solutions, the calculation using the Rayleigh model (see above) shows that  $\delta^{202}\text{Hg}$  and  $\Delta^{199}\text{Hg}$  of remaining solution would be -0.05‰ and 3.10‰ respectively, much higher than that of R4, suggesting that the in-cloud photo-reduction itself couldn't explain the large variation of both MDF and MIF of Hg isotopes.

Alternatively, mixing of local Hg with another source having significant odd-MIF (and even-MIF) is the most possible explanation. India was likely such a significant atmospheric Hg contributor to TP<sup>8,17</sup>. In fact, the four samples were collected during the monsoon season when the low pressure would bring warm air masses from India to the plateau. A NOAA-HYSPLIT back trajectory of air masses with initial heights of 500m, 1000m and 3000m above ground level (AGL) showed that the air mass from the north of India could arrive at Lhasa city in about ten hours. The higher  $\Delta^{199}\text{Hg}$  value in precipitation samples (e.g. 0.76‰ in R4, Table 1) may result from the extended photo-reduction during the long-term transportation<sup>4</sup>. Based on the data ( $\delta^{202}\text{Hg}$  of -1.87‰ and  $\Delta^{199}\text{Hg}$  of 0.04‰) reported for Indian coals<sup>15</sup>, we calculated using a simple Rayleigh fractionation model<sup>16</sup> that when 23% of initial Hg(II) was photo-reduced the remaining Hg would have a  $\Delta^{199}\text{Hg}$  value of about 0.76‰, close to that of R4. High  $\Delta^{199}\text{Hg}$  values should be also found for long-term transported Hg emitted by Indian cement plants<sup>8</sup>. Thus, the long-term transported Hg derived from Indian emission was generally characterized by high  $\Delta^{199}\text{Hg}$  values.

The long-range transported Hg (mainly Hg(II)) with large odd-MIF would be leached by in-cloud scavenging processes. Thus, Hg in the precipitation samples would be a mixture of variable proportions of local and long-term transported Hg. At the beginning of single rainfall event, the water droplets containing long-term transported Hg would scavenge locally originated Hg below the cloud parcel, inducing high Hg concentration. If Hg and its isotopic composition were homogeneous in the whole cloud cell, the Hg leached by in-cloud scavenging would have identical concentration and isotope ratios due to the continuous supply. However, the content of locally emitted Hg would considerably decrease due to below-cloud scavenging. As a result, the Hg concentration in precipitation decreased with time (Fig. 1a), while odd-MIF ( $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ) progressively increased towards the  $\Delta^{199}\text{Hg}$  value (e.g.  $> 0.76\text{‰}$  of R4) of the long-term transported Hg at the later stage of the event (Fig. 1c). The slight increase of  $\Delta^{200}\text{Hg}$  (Fig. 1d) during the event would imply that Hg having even-MIF, which had been probably

derived from the high atmosphere<sup>4</sup>, was largely incorporated into water droplets during long-range transport.

#### 4. Conclusion

In this study, we reported for the first time large variation (up to 0.38‰) of both MDF and MIF of Hg isotopes in four rain samples collected during one single precipitation event on the Tibetan Plateau, China. All samples had negative MDF, significant positive odd-MIF and slightly positive even-MIF, again, showing a general characteristic of Hg isotopic composition in worldwide precipitation. Hg concentrations displayed a progressive decline with time, while odd-MIF and even-MIF increased at the later stage of the event. Our results demonstrated that the large variation of Hg isotope ratios could not be explained by in-situ photo-reduction, but more likely resulted from mixing of locally emitted Hg and long-term transported Hg, which were leached by below-cloud scavenging and in-cloud scavenging processes, respectively. Our findings demonstrated that Hg isotopes are a powerful tool for investigating the dynamic of precipitation event and the related cloud movement, and emphasized the importance of systematic monitoring studies on the chemical and isotope variability of Hg during rainfall events in order to better characterize the chemistry and the flux of elements in wet precipitation.

#### Acknowledgements

This research was funded by National “973” Program (2013CB430001), Natural Science Foundation of China (41273023, U1301231), “Strategic Priority Research Program” (No. XDB05030302) and “hundred talent” project of Chinese Academy of Sciences.

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