Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., author comment AC2
https://doi.org/10.5194/acp-2021-493-AC2, 2021

Reply on RC2

Lingling Xu et al.

Author comment on "Mercury isotopic compositions in fine particles and offshore surface seawater in a coastal area of East China: implications for Hg sources and atmospheric transformations" by Lingling Xu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-493-AC2, 2021

The proposed paper described Hg isotope variation of $PM_{2.5}$ sample collected from urban and mountain area of East China to test Hg isotope as the tracer of source and process of particulate Hg in atmosphere. Since Hg isotope of particulate Hg is still scarce, the data provided by this study surely contribute to better understanding of Hg chemistry in the atmosphere. The authors well cover the previous monitoring and experimental studies, and they tried to interpret their data set through comparing the relevant works. Nevertheless, two points have to be considered to evaluate this work correctly. Firstly, description of methodology section is insufficient. As authors mentioned, the technical difficult is accurate measurement of trace amount of particulate Hg in $PM_{2.5}$ sample. I cannot validate quality of the data only from the provided information in methodology section (see specific comments). Secondly, missing of Hg0 data makes all interpretation rather speculative. Gaseous elemental Hg is the predominant form of Hg in atmosphere, while gaseous oxidizing Hg and particulate Hg (likely contribution of Hg(II) is high) occupy minor pool. Conversion of Hg species from large to minor pool potentially causes large isotope fractionation. I think authors should mention the isotopic variation of GEM in China more carefully to interpret their data. The specific comments are as below.

Response: We appreciate for your valuable comments and suggestions which helped us to improve the quality of the article. According to your comments, we have given more information about sample treatments and measurements in the methodology section, and considered the isotopes of GEM when interpreting the MIF of Hg isotopes in $PM_{2.5}$. The specific responses to the comments are as follows.

L66. Despite HgPM level expressed here being volume based, their own results are expressed as mass basis. It makes comparison difficult.

Response: In addition to volume based Hg_{PM} level, we have compared the contribution of Hg_{PM} to total Hg between industrial and uncontaminated areas in the manuscript (lines 64-69).

"Previous studies indicated that Hg_{PM} concentrations in urban and industrial areas could reach up to hundreds even thousands of pg m^{-3}, relative to tens of pg m^{-3} in uncontaminated remote areas (Fu et al., 2015; Mao et al., 2016). In addition, Hg_{PM} can account for up to 40% of atmospheric Hg in industrial areas, relative to < 5% in uncontaminated areas (Guo et al., 2022□Schroeder and Munthe, 1998)."

L92. ~1.0 for photo-reduction of Hg(II); L93. ~1.6 for photo-oxidation of Hg(0)

Response: We have revised the sentence as "…~1.0 for photo-reduction of Hg^{2+} and ~1.6 for photo-oxidation of Hg(0)".

L144. What is "regional emission"? It should be specified.

Response: The "regional emissions" are mainly industrial activities and coal combustion in the Yangtze River Delta and the neighboring region of Anhui, Jiangsu, and Zhejiang Provinces (Yu et al., 2015). We have specified the regional emissions in the manuscript (lines 152-155).

L147. Although I thought seawater data is rather minor focus in this paper, more oceanographic background should be provided to help data interpretation, such as temperature and primary productivity.

Response: Thank you for the suggestion. We have presented the salinity and pH of the seawater samples in the manuscript (lines 158-160).

"The salinity of the seawater samples ranged from 21.2‰ to 29.5‰. The pH of the seawater samples was in the range of 5.7 ~ 8.5, with the mean value of 7.5 ± 0.6."

L200. This means, authors pooled 10 samples to be one? If so, it should be written accordingly.

Response: Nope. Individual $PM_{2.5}$ samples with sufficient Hg mass were chosen for Hg isotopes analysis. There were 10 samples in total for each site.

L202~. Recovery through this combustion process should be given at the last of this paragraph. Careful operation is often required for complete recovery using dual combustion furnace.

Response: Thank you for the suggestion. We have presented a detail operation and given the Hg recovery of the dual-stage protocol accordingly (lines 220-229)."

The combustion procedure was run with no samples in the furnace quartz tube before $PM_{2.5}$ sample treatment every day to remove residual volatiles. The released Hg was transferred by O_2/Ar gas (30%/70%) at a flow rate of 20 mL min^{-1} and then trapped by a 10 mL of 40% inverse aqua regia (2: 4: 9 ratio of 10 M HCl, 15 M HNO_3 and ultra-pure water) in a designed glass bottle. In advance of $PM_{2.5}$ sample analysis, the accuracy of dual-stage combustion method was assessed by the analysis of the standard NIST SRM 3133 Hg (dripped on blank filters) and the certified reference material GBW07434. The Hg recovery efficiency of the dual-stage protocol was in the range of 87.6% ~ 103.3% (mean: 95.0 ± 5.1%, n = 6)."

L214 Concentration of SnCl2 should be given.

Response: We have given the concentration of $SnCl_2$ (200 g/L) in the manuscript.

L220-227. The description of MC-ICP-MS analysis is poor although they cited one reference paper. The method here is CV-MC-ICP-MS? If so, it should be noted. In which aqueous Hg concentration did author choose to the isotope analysis? Did author match the Hg signal of sample and standard? The UM-Almaden values were obtained by exactly same level to the sample? Since sample measurements were made only one time, the information are important to validate data quality.

Response: Yes, the method here is CV-MC-ICP-MS. The pre-concentration solutions were measured in Xiamen University (Xiamen, China) with the method described in a recently published paper (Huang et al., 2021). According to the suggestion, we have given more information of sample measurements (lines 241-253) and data quality assurance (lines 261-265) in the manuscript as follows. In addition, after careful consideration, we have deleted ^{204}Hg data due to its low natural abundance.

"Hg isotopic compositions were measured by a multi–collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Instruments Ltd. UK) equipped with an introduction device following the protocols presented in previous studies (Huang et al., 2015; Huang et al., 2021□Lin et al., 2015). The introduction device includes a modified cold-vapor generator (CVG) and an Aridus III nebulizer for respective Hg and Tl introduction. Between standard and sample, the CVG was rinsed with 3% (v/v) HNO_3 solution to ensure the Hg signal returned to the background level. Instrument mass bias was corrected using both an internal standard (NIST 997 Tl) and a strict sample-standard bracketing method (NIST 3133 Hg). A reference material NIST 8610 was measured repeatedly for quality control. The pre-concentration solutions were diluted to about 1.5 ~ 3.0 ng mL^{-1} and the NIST 3133 and NIST 8610 were kept at 2.0 ng mL^{-1} during the analysis period."

"The repeated measurement of NIST 8610 during the analysis session yielded δ^{202}Hg and Δ^{199}Hg values of -0.60 ± 0.15‰ and -0.02 ± 0.06‰ (2σ, n = 7). In addition, a well-known reference material UM-Almaden showed a long-term average of δ^{202}Hg = -0.59 ± 0.10‰ and Δ^{199}Hg = -0.03 ± 0.07‰ (2σ, n = 25), which are well consistent with those in previous studies (Blum and Bergquist, 2007; Huang et al., 2015)."

L246. Again, why the author showed only mass-based concentration. Besides, there are no data of total mass of particle on the filter. Without this value, readers cannot calculate concentration of Hg in final solution used for the isotope analysis. If the author used hydride generation system such as CETAC HGX-100, >2.5 ng is required for the precise data analysis.

Response: We showed only mass-based concentration because the mass-based concentration is more appropriate for discussion of reaction processes and isotope fractionation. As you suggested, we have presented the mass and the volumetric concentrations of $Hg_{PM2.5}$, and the concentration of $PM_{2.5}$ in the manuscript (Table 1). We used a modified CVG for Hg introduction in the isotope analysis. All of the pre-concentration solutions were diluted to approximately 1.0~3.0 ng mL^{-1} (at least 1.0 ng mL^{-1}). The internal precision of δ^{202}Hg for each measurement was determined as about 0.035‰ ~ 0.055‰ corresponding to the concentration of 1.0~3.0 ng mL^{-1} (Lin et al., 2015).

L249. Again, what is the regional emission?

Response: As you suggested, we have specified the regional emissions (lines 281-283) in the manuscript.

L300. remarkably positive odd-MIF

Response: We have revised the related sentence.

L302. L299-302. I couldn't understand the reasoning here. What is the enhanced photo[1]reaction? Hg0 reduction? Or MMHg demethylation? The δ202Hg vs Δ199Hg of DMS in Fig. 2 seems positively correlated with slope being ca. 0.4. Does this trend support author's interpretation?

Response: We did not state this question clearly. The significant positive Δ^{199}Hg and the

near-unity slope of Δ^{199}Hg vs. Δ^{201}Hg in the study region indicate that odd-MIF in $PM_{2.5}$ was impacted by photo-reduction of Hg^{2+}. The correlation of δ^{202}Hg and Δ^{199}Hg at the DMS (Fig. 4c) was consistent with the experimental results of photo-reduction that generally showed positive correlation for the residual Hg pool (here aerosols). The result supports the interpretation that photo-reduction of Hg^{2+} was the important source of the odd-MIF of Hg_{PM} at the DMS. This issue was discussed in more detail in Section 3.3 (lines 464-475).

Here, we have revised the content as follows focusing on the comparison of Δ^{199}Hg values (lines 324-332).

"The significant positive Δ^{199}Hg in this study are similar to those observed in coastal areas (Rolison et al., 2013; Yu et al., 2020) and in remote areas in China (Fu et al., 2019), but distinguishable from those in urban and industrial areas with near-zero values due to anthropogenic emissions (Das et al., 2016; Huang et al., 2016, 2018, 2020; Xu et al., 2019; Yu et al., 2016). A laboratory study has indicated that photo-reduction of Hg^{2+} restrains odd Hg in reactants (aerosols here) in priority, which shifts Δ^{199}Hg values positively (Bergquist and Blum, 2007). Thus, it's reasonably supposed that the positive odd-MIF of HgPM in the study region was associated with photo-reduction of Hg^{2+} in aerosols."

L349. A prior study estimated that…of coal feeds based on the mass balance model (Sun et al., 2014).

Response: We have revised the sentence as "A prior study estimated that emitted Hg_{PM} has a shift of -0.5‰ relative to δ^{202}Hg of coal feeds based on the mass balance model (Sun et al., 2014)."

Figure 4. I am afraid poor data quality from the rather scattered correlation of Δ199Hg and Δ 201Hg.

Response: Thank you for the suggestion. We have compared the correlation coefficient of Δ^{199}Hg and Δ^{201}Hg of this study with other public studies. We found that the correlation of Δ^{199}Hg and Δ^{201}Hg of this study was comparable with those conducted on Chinese urban areas (r^2 = 0.81~0.92 in Beijing, Huang et al., 2019; r^2 = 0.92 in Beijing, 0.73 in Changchun, and 0.76 in Chengdu, Xu et al., 2019), and better than the study conducted during three cruises to Chinese seas ($p > 0.05$, Yu et al., 2020). Thus, we thought that the rather scattered correlation of Δ^{199}Hg and Δ^{201}Hg was probably because the Hg contents in environmental samples are low and they are affected by complex factors. In addition, according to the above suggestions, we have given more information about sample measurements and the results of quality control in the methodology section to validate the data quality.