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Reply on RC1

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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-AC1, 2021

The Manuscript entitled 'Mercury isotopic compositions in fine particles and offshore surface seawater in a coastal area of East China: Implication for Hg sources and atmospheric transformations' investigated the Hg isotopic composition of fine aerosols (PM2.5) sampled from industrial and mountain sites in a coastal area if East China. In addition, the authors also evaluated the Hg isotopes in surface seawater close to the Industrial area. The authors aimed to obtain the roles of anthropogenic sources and atmospheric transformations in particulate Hg isotopic compositions. Stable Hg isotopes have become a useful proxy for the identification of Hg sources, particularly as a result of improvements in high-precision analytical methods. Limited data are available on the stable isotopes of Hg or their application in source apportionment in atmospheric aerosols. Therefore, studies on atmospheric Hg and its isotopic compositions are important for understanding the atmospheric concentrations, sources, transport mechanisms, and fate of particulate Hg and the data are important to the broad scientific community. The manuscript is well written and the results are discussed in detail, although, some of the latest studies are not reviewed. Hence, I suggest the acceptance of this manuscript in ACP after minor suggestions below are addressed.

Response: We appreciate for your overall positive evaluation of the manuscript. We have revised the manuscript carefully according to the suggestions. The "point to point" responses are as follows.

A little more on atmospheric particulate mercury (PBM) and it scenario (literature review) is need in the introduction section. The motivation to carry out this study must me made clear with more gaps identified.

Response: As you suggested, we have indicated the role of Hg_{PM} in the cycling of Hg in the manuscript (lines 79-82). In addition, we made a literature review of Hg_{PM} isotopes and elaborated the motivation of this study more clearly (lines 105-121 and 128-132). The main revisions are as follows.

"In addition, Hg_{PM} has a residence time of several weeks as it can transport and deposit at a regional scale (Selin, 2009). The research has suggested that atmospheric Hg_{PM} is

generally a combined result of anthropogenic emissions and atmospheric processes, which plays a crucial role in the global cycling of Hg."

"East China is densely populated and one of the heaviest industrialized area in China. The concentration of Hg_{PM} in this region has been well characterized (Hong et al., 2016; Xu et al., 2020□Yu et al., 2015), but only two studies conducted at the remote sites have referred to Hg_{PM} isotopes (Fu et al., 2019□Yu et al., 2016). To the best of our knowledge, there is no report on the isotopic compositions of Hg_{PM} from urban areas of East China. Likewise, the effect of atmospheric processes on the fractionation of Hg isotopes in the coastal region has not been well elucidated."

"The objectives of this study are (1) to differentiate the Hg isotopes in $PM_{2.5}$ from the two neighboring industrial and mountain sites; (2) use the Hg isotopes to explore the influence of anthropogenic sources on the Hg_{PM}; (3) to reveal the role of atmospheric transformations in varying Hg_{PM} isotopic compositions."

Line 98-112: The literature review missed some of the recent works on PBM isotopic ratios of atmospheric samples (e.g., Source identification of atmospheric particle-bound mercury in the Himalayan foothills through non-isotopic and isotope analyses; Atmospheric particle-bound mercury in the northern Indo-Gangetic Plain region: Insights into sources from mercury isotope analysis and influencing factors).

Response: We have introduced the recent works on the application of Hg_{PM} isotopes in sources or transboundary Hg transport identification (e.g., Fu et al., 2019EST; Guo et al., 2021EP, 2022GF, lines 108-115) in the manuscript.

Line 246-249: The authors presented the Hg mass in PM2.5, however I did not find the PBM concentrations presented and discussed. The Hg mass can also suggest the source is from natural or anthropogenic. When assessing Hg enrichment and sources, the PBM/PM ratio may be useful if we have Hg concentrations for natural and anthropogenic components (e.g., soil and coal) in the region of interest? Please check it for the two studied sites.

Response: We have added the discussion of Hg_{PM} volumetric concentration in the manuscript (lines 272-277). In addition, we agree that PBM/PM ratio (i.e. Hg mass concentration) could indicate that the source is from natural or anthropogenic. We did not find the Hg mass for natural and anthropogenic components in the study region, so we addressed this issue based on the national data (lines 283-296). We found that the Hg contents of $PM_{2.5}$ in the study region are higher than those of natural sources (e.g., dust and topsoil; 0.056 ~ 0.30 μg g^{-1}; Schleicher et al., 2015) and those of coals in China (mean: 0.22 μg g^{-1}; Yin et al., 2014b).

Line 258: Spearson correlation? Should be Spearman?

Response: Sorry for the typo. The "Spearson" should be "Spearman".

The Hg isotope data presented here does not seem to be able to distinguish between different sources. For example, Hg isotopes (Figure 2) show urban, remote and near sources, however, the clear sources e.g., coal, industrial emission, traffic and soils are all possible source of particulate Hg? This is not clear and not discussed clearly. Distinguishing between these sources seems difficult based on isotope alone. Thus I am not sure why the authors conclude anthropogenic sources (what are the sources) is not clear.

Response: We agree that we could not identify the specific sources of $Hg_{PM2.5}$ solely based on Hg isotopes, because the $\delta^{202}Hg$ values of potential sources are not

distinguishable. We have revised the content and clarified this point as follows (lines 305-313).

"The δ^{202}Hg values at the CX basically overlap those for PM in urban areas of China (mean: from -1.60‰ to -0.42‰), as well as those for major source materials such as coal combustion, smelting, and cement plants (mean: -1.10‰, -0.87‰, and -1.42‰ respectively, Huang et al., 2016) and those for PM near anthropogenic emissions such as industry, landfill, traffic, and coal-fired power plants (mean: from -2.41‰ to -0.58‰) (Fig. 2). The result likely indicates an important contribution of anthropogenic sources to the CX $Hg_{PM2.5}$. However, the δ^{202}Hg values of above mentioned potential sources are not distinguishable, thus we could not identify the specific sources of $Hg_{PM2.5}$ solely based on Hg isotopes."

Line 343: Why the authors directly start with numbering 1. Coal combustion, this may break the flow and so on?

Response: Thank you for the suggestion. We have revised the section 3.2 to make the text more concise and fluent.

Similarities or differences in Hg isotope ratios at the two sites need to be described and the different seasons of their collection reported. The authors should see if their results plotted on a coherent mixing line on an inverse Hg concentration plot (i.e. d202Hg vs 1/HgP). Soils and values for PM from other locations in China might also be informative on such a plot. More broadly, Hg isotope ratios in aerosols from coastal sites should be compared with those in aerosols from other locations in Asia. This may be placed in Supplementary document.

Response: (1) As you suggested, we have presented the ratios of Δ^{199}Hg to Δ^{201}Hg at the both sites and compared them with the ratios in aerosols from coastal site and from other locations in Asia in the manuscript (lines 449-454) as follows. On the other hand, we did not present the Hg isotopes ratios among seasons, because the number of the samples in each season was not large enough.

"The slope of Δ^{199}Hg versus Δ^{201}Hg yielded from the data of each site was 1.16 (R^2 = 0.92) at the CX and 0.63 (R^2 = 0.85) at the DMS, respectively. The data over the two sites defined a straight line with a slope of 0.92 (R^2 = 0.83, $P < 0.01$; Fig. 4a). The near-unity slope of Δ^{199}Hg versus Δ^{201}Hg was widely observed in particles from coastal site and from other locations in Asia (Fu et al., 2019; Rolison et al., 2013; Huang et al., 2016, 2019; Xu et al., 2019). The $\Delta^{199}Hg/\Delta^{201}$Hg ratios of this study are more consistent with the indicative ratio of aqueous photo-reduction of inorganic Hg^{2+} (~1.0, Bergquist and Blum, 2007; Zheng and Hintelmann, 2009), but different from the ratios of other processes, like photo-oxidation (1.64 by Br· and 1.89 by Cl·, Sun et al., 2016) and photo-demethylation (1.36, Bergquist and Blum, 2007)."

(2) We have plotted a line on δ^{202}Hg vs. Hg_{PM} concentration in Fig. 3a and the relevant discussion was showed as follows (lines 369-371). As you suggested, we have plotted the relationship of δ^{202}Hg with $1/Hg_{PM}$ for this study and for other locations in China and Asia. The relationships of δ^{202}Hg with $1/Hg_{PM}$ were similar to those with Hg_{PM} concentration. The linear relationship was basically insignificant for the DMS, the CX and over the total data. For above reasons, we did not discuss the relationships of δ^{202}Hg with $1/Hg_{PM}$ further.

"The result was supported by the correlation between δ^{202}Hg values and $Hg_{PM2.5}$ concentrations which was insignificant at the DMS, but significant at a loose level at the CX (Fig. 3a)."

Plot of Δ199Hg (‰) vs. δ202Hg (‰) is not presented. Hg-MIF (Δ199Hg) signatures are

also valuable for distinguishing Hg contamination pathways because Hg2+ photo-reduction in aerosols. The authors discussed on the slope, however, it is important to show the figure to clearly understand the atmospheric transformation and photochemical process.

Response: The plot of Δ^{199}Hg vs. δ^{202}Hg has already been presented in Fig. 4c in the submitted manuscript. We agree that Hg-MIF (Δ^{199}Hg) signatures are valuable for distinguishing Hg contamination pathways and the relevant discussion is presented in the section 3.1 (lines 323-332) as follows. In addition to the slope of Δ^{199}Hg vs. δ^{202}Hg, we also presented the relationships of Δ^{199}Hg with δ^{202}Hg and Hg content to reveal the role of photo-reduction in aerosols (Fig. 4bc, lines 463-478). We found an inverse relationship between Δ^{199}Hg and $Hg_{PM2.5}$ content and a positive correlation between Δ^{199}Hg and δ^{202}Hg at the DMS, which suggest a key role of photo-reduction of Hg^{2+} in isotopic fractionation of $Hg_{PM2.5}$. In contrast, the variation of Δ^{199}Hg at the CX was not associated with $Hg_{PM2.5}$ contents or δ^{202}Hg. The result suggests an insignificant impact of photo-reduction relative to anthropogenic sources on MDF and Hg content in $PM_{2.5}$ at the CX.

"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 Hg_{PM} in the study region was associated with photo-reduction of Hg^{2+} in aerosols."

Line 421-424: This statement needs more thought. Photo-reduction of Hg2+ mostly results in positive D199Hg in reactant Hg.

Response: The reactant here is aerosols. To clarify it, we have revised the sentence.

"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)."

Line 530-532: Please show in figure as suggested previously.**Response:** As you suggested, we presented the plot of Δ^{199}Hg vs. Δ^{201}Hg as Fig. S3 in the supplementary document.The detailed revisions are needed before publications.

Response: We have checked and revised the whole manuscript carefully before re-submission.