Response to Anonymous Referee #1

RC- Reviewer's Comments; AC – Authors' Response Comments

RC1: This manuscript described seasonal variations of Hg isotopes in TGM from 10 Chinese urban sites, and addressed the importance of urban surface emissions to both concentration and isotopic compositions of urban TGM. The provided concentration and isotopic data are precious for enhancing our understanding to the re-emission of Hg legacy in building surfaces or urban soils. The data was archived and presented well. In general, I recommend the publication of this article after the following revisions.

AC1: We greatly appreciate the reviewer for recognizing the merits of this work and for providing the valuable suggestions. We have made revisions following the comments (corrections are marked in blue fonts in the revised manuscript), and the response are shown below.

RC2: L110-112: To my knowledge, the effect of emission and re-emissions of GEM from urban surfaces was frequently neglected because we thought the flux was low in these processes, but not the poor understanding of isotopic signatures of that.

AC2: We agree that the traditional thought of primary anthropogenic Hg emissions is the dominant source of atmospheric Hg in urban areas is one the most important reason to neglect the effect of land surface GEM emissions. We have revised the statement to highlight the anthropogenic emissions in line 111-113 in the revised manuscript, which read: "whereas the effect of emission and re-emission of GEM from urban surfaces was frequently neglected mainly because of the strong primary anthropogenic Hg emissions and poor understanding of emission flux and isotopic signatures of GEM from land surfaces in urban areas".

RC3: L112-115: If we accept anthropogenic emissions as the most important component to urban GEM, which has been proved by many speciation observations in China, the observed d202Hg in TGM should be linked with that in local coal rather than an averaged value from publications. According to Liu et al. Chemical Geology, 2019, d202Hg in stack emission was similar with feed coal used in CFPPs.

AC3: We read that Liu et al. (2019) estimated the isotopic compositions of total Hg in coal burning flue gas and added this citation in line 87-88 in the revised manuscript. Since isotopic compositions of the total Hg were estimated by this study, we use the fractionation of Hg isotope between GEM and GOM to estimate the GEM isotope signature. In addition to coal fire power plant, many other anthropogenic activities are also important GEM sources in China (Zhang et al., 2015). Therefore, it is needed to use the GEM isotopic signature of all anthropogenic emissions to interpret our observations, which have been estimated by Sun et al. (2016). We agree that isotopic compositions of Hg in feed coal would affect, but currently we do not have this kind of information.

RC4: L213: Did the authors present 204Hg data in this study?

AC4: Yes, some of our samples were measured with δ204Hg signatures, which are presented in the supporting information Table S4. For the rest of the samples, we did not measure δ204Hg signatures because of the limitation of instrumental collector designs.

RC5: L359-367: It's a little arbitrary to evaluate the contribution from urban surface using averaged values from only 3 studies of various surface emissions. The authors should emphasize that.

AC5: Agree. We show that our estimate has large uncertainties as well as their reasons, which is shown in line 371-374 in the revised manuscript, which reads: "We caution that, due to the fact that the isotopic signatures of GEM emitted from many anthropogenic sources and land surfaces in China have not been well constrained, such a preliminary assessment should have large uncertainties".

RC6: L414-416: These study sites are all located in monsoon area in China. How about the effect from monsoon climate? Cities in east part of China, especially in north China plain, are largely controlled by north wind from Siberian in winter. The continental monsoon originates from low human active areas, with low GEM concentration, high d202Hg, and low D199Hg in air parcels. This could also be indicated from Figure 4 in this manuscript. I suggest the influences from monsoon be discussed in this study.

AC6: Yes, the effect of monsoon is discussed in line 421-429 in the revised manuscript, which reads: "Prevailing wind directions during the wintertime and summertime sampling campaigns were similar Jinan, Lanzhou, Zhengzhou, and Shanghai, but were different in other remaining cities (Figure S6). Variations in predominant wind directions would change the relationships between receptor and regional anthropogenic emissions, which could further influence the TGM levels and isotopic compositions in these cities. Given the similarity in wintertime and summertime prevailing wind directions in some cities and consistent summertime lower CO concentrations in most cities, it is postulated that the variations in local anthropogenic emissions and transport of regional anthropogenic emissions were not likely the main cause for the seasonal variations in TGM concentrations and isotopic compositions".

References:

Sun, R. Y., Streets, D. G., Horowitz, H. M., Amos, H. M., Liu, G. J., Perrot, V., Toutain, J. P., Hintelmann, H., Sunderland, E. M., and Sonke, J. E.: Historical (1850–2010) mercury stable isotope inventory from anthropogenic sources to the atmosphere, Elem. Sci. Anth, 4, 1-15, http://doi.org/10.12952/journal.elementa.000091, 2016.

Zhang, L., Wang, S. X., Wang, L., Wu, Y., Duan, L., Wu, Q. R., Wang, F. Y., Yang, M., Yang, H., Hao, J. M., and Liu, X.: Updated Emission Inventories for Speciated Atmospheric Mercury from Anthropogenic Sources in China, Environmental Science & Technology, 49, 3185-3194, Doi 10.1021/Es504840m, 2015.

Response to Anonymous Referee #2

RC- Reviewer's Comments; AC – Authors' Response Comments

RC1: The manuscript presents data of TGM concentrations and their isotopic compositions in 10 large cities, many of them considered mega cities, in China. Documentation of such data in open literature is valuable, the data quality is good and the scientific presentation is sound. The primary weakness of the manuscript is a deterministic scientific argument based on the relatively scattered data, which is difficult for a study of this nature since the sampling was perform at different time (and perhaps by different sets of researchers) at different locations. Given the level of data scattering, it is somewhat uncertain to provide a clear scientific finding, which seemed to be the main criticisms of Reviewer #3 in the previous round of peer review.

Other than a lack of deterministic scientific conclusion, the reasoning and interpretation of data appear to be sound. One interesting feature of the conclusive remarks made by the author group is the attribution of mercury source and the TGM concentration variation primarily to soil evasion, which is somewhat counter-intuitive to the intensive human activities in large cities. The measured TGM concentrations in those cities are highly elevated (Figure 4). Previous work has attributed the elevated concentrations to human activities and the seasonal variation to meteorological factors, which seems reasonable and intuitive. Although this work present additional mercury isotope data, the level of data scattering does not seem justified to rule out the past attribution to human activities and meteorology. Perhaps the authors should at least make an attempt to strengthen the arguments described in their conclusion.

AC1: We greatly appreciate the reviewer for recognizing the value of our study and for providing constructive comments, which would help us improve the manuscript.

We understand the concerns of this reviewer regarding the interpretation of the factors influencing the TGM concentrations and isotopic compositions in our investigated sites. Actually, we have not ruled out the effect of anthropogenic emissions and meteorology on our measurements. For example, we roughly estimated that primary anthropogenic emission is of similar importance as land surface emission in atmospheric Hg emission budget in our investigated cities (line 371 in the revised manuscript). In this study, we are trying to use multiple evidences (including the unique Hg isotope data) to show that the land surface emission likely played a dominant role in regulating the seasonal variations in TGM isotopic compositions and concentrations. We have strengthened this arguments by a comparison of GEM emission fluxes between land surface and primary anthropogenic sources in line 374-379 in the revised manuscript, which reads: "However, our estimate is overall consistent with pervious studies on GEM emission fluxes from land surfaces and anthropogenic sources in Chinese urban areas. For example, Previous studies on GEM emission fluxes from urban surfaces in China showed a mean value of 83.2 ± 170 ng m^{-2} h^{-1} (1σ, n = 39) (Fu et al., 2012;Feng et al., 2005;Wang et al., 2006;Fang et al., 2004), which was relatively higher than the mean anthropogenic GEM flux (48.4 ± 48.1 ng m^{-2} h^{-1}, 1σ, n = 10) in the ten investigated cities (Table S5) (AMAP/UNEP, 2013)".

There are also several other areas that can use additional clarity:

RC2: The selection of the ten city sites needs to be justified and the characteristics can be more detailed. Was the selection by design or by incident? If it is by design, discussion should be provided for the intended scientific goals. If it is by incident, discussion should be provided to argue why the data collected from the 10 sites can sufficiently support the conclusion.

AC2: These cities were selected by design, and the intended scientific goals are added in line 132-137 in the revised manuscript, which reads: "These cities are located in different geographical regions of China, which were potentially characterized by specific source emission patterns, climate, and atmospheric chemistry. The designated investigations in these cities may therefore provide a comprehensive information on the variations of TGM concentrations and isotopic compositions in mega cities of China, and help to explore the major factors influencing the atmospheric Hg in Chinese cities".

RC3: Since the samples were collected at different times and locations where the chemistry of various urban airshed could be substantially different such that the samplers may behave inconsistently. Based on the description in the method section, it seems that the sampling was not duplicated but the analysis was repeated. Some discussion in regard to the consistency of the carbon trap samplers will ensure the confidence on the data quality.

AC3: We are confidential that the collections of TGM using the carbon trap would not be biased by various atmospheric chemistry. This method has been used successfully in free troposphere, marine boundary layer, arctic, and forests by many previous studies (Fu et al., 2019;Fu et al., 2016;Obrist et al., 2017;Yu et al., 2020), and the data quality have been proven by these studies. In the present study, we investigated the blanks (n = 27), breakthrough (n = 10), and standard addition of Hg(0) vapor to carbon trap (n = 11), which showed good results (more details in Section 2.3 and 2.4) and suggest our carbon trap method could measure the TGM concentrations and isotopic composition precisely.

RC4: The 10 city sites have drastically different meteorological patterns other than the generic seasonal patterns described in the manuscript. It is possible that there are local processes forcing the observed isotopic characteristics? This is not clear in the manuscript.

AC4: We agree that the local meteorological patterns would be a potential factor in some cities, but we suppose they are not a dominant cause to drive the consistent seasonal variations in the ten investigated cities. The reason of this argument is added in line 421-429 in the revised manuscript, which reads: "Prevailing wind directions during the wintertime and summertime sampling campaigns were similar Jinan, Lanzhou, Zhengzhou, and Shanghai, but were different in other remaining cities (Figure S6). Variations in predominant wind directions would change the relationships between receptor and regional anthropogenic emissions, which could further influence the TGM levels and isotopic compositions in these cities. Given the similarity in wintertime and summertime prevailing wind directions in some cities and consistent summertime lower CO concentrations in most cities, it is postulated that the variations in local anthropogenic emissions and transport of regional anthropogenic emissions were not likely the main cause for the seasonal variations in TGM concentrations and isotopic compositions".

RC5: It will be useful if the authors can specify what statistical criteria is considered significant for using the relatively scattered data to draw the conclusion.

AC5: The statistical method used in this study is specified in line266-267 in the revised manuscript, which reads: "Linear regression analysis was performed with IBM SPSS Statistics using the forced entry method".

RC6: Overall, the manuscript is considered acceptable after revisions on the scientific arguments and editorial improvements.

AC6: The reviewers' and editorial comments have been addressed and revisions have been made accordingly.

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