Responses to the Reviewers' Comments

First Observation of Mercury Species on an Important Water Vapor Channel in the Southeast Tibetan Plateau

Dear editor and reviewer,

We greatly appreciate the useful comments and suggestions from the editor and reviewers. We think the novelty and importance of this study have been acknowledged by the reviewers. We have revised the manuscript thoroughly based on the reviewers' comments. Detailed point by point responses are provided below. All the revisions have been highlighted in blue in the revised manuscript. We hope the revised manuscript could meet the standard of ACP. Thanks again for your considerations.

Anonymous Referee #1

Comment #1

General comment

The manuscript by Lin et al. carried out a half-year of continuous measurements of speciated atmospheric Hg as well as a year of measurements of gaseous elemental Hg using a passive sampling technique at a high-altitude station in the eastern Tibetan Plateau. This study combined field observations with backward trajectory analysis, criteria pollutants and a PCA source identification approach, which are used to understand the sources and transport of atmospheric Hg in the eastern Tibetan Plateau. This study is valuable for the atmospheric Hg research topic especially in the pristine Tibetan Plateau where could be potentially impacted by long-range transport of Hg from surrounding anthropogenic Hg source regions. The authors have provided detailed explanations for the variations in the atmospheric Hg, and I broadly agree with the interpretation and hypothesis. The manuscript is overall well organized and written. I therefore suggest a publication of this manuscript in ACP after addressing the following minor to moderate issues.

Response #1

We appreciate the reviewer for dedicating time to review our manuscript and provide constructive comments. We have updated the cited references, extended discussion content, redrawn some figures and addressed other concerns from the reviewer in the revised manuscript. All the revisions

have been highlighted in blue. Detailed responses to the comments are provided as follows.

Specific comments

Comment #2

Line 67-68: the authors mentioned that numerous studies have been conducted in Europe and North America. As I know, atmospheric Hg studies in China have also obtained many advances in recent years, which should be also mentioned here (instead of using a citation of mercury emission study in China).

Response #2

Thanks for the suggestion. We agree with the reviewer that scientists in China have also conducted studies on the behavior of atmospheric Hg and have obtained many advances in recent years. We have added some literature to the introduction section.

Comment #3

Line 80-83: I would suggest to cite Hg emission inventories developed in China and worldwide directly. Note that coal combustion is not the exclusive sources of atmospheric Hg in China.

Response #3

Thanks for the suggestion. We have added a sentence to exhibit the Hg emission in Asia, as follow: '**South Asia, and East and Southeast Asia accounted for 10.1% and 38.6% of global emissions of mercury, respectively (UNEP, 2018; Zhang et al., 2015b).** '

Comment #4

Line 84-111: I saw the authors introduced many studies on air pollutants in the Tibetan Plateau, and I agree this is useful for highlighting the need of the present study. However, I would suggest the authors to make a general description of previous atmospheric Hg studies in the Tibetan Plateau, which would help the authors figure out the knowledge gaps in this study area and strengthen the importance of this study in this research topic.

Response #4

Thanks for the suggestion. We have added some general description of previous atmospheric Hg studies in the Tibetan Plateau, as follow: '**In the case of atmospheric Hg, monitoring in marginal**

areas depicted the basic spectrum of atmospheric Hg in the Tibetan Plateau. Monitoring of atmospheric Hg at Shangri-La, Nam Co, Qomolangma, Mt. Gongga, Mt. Waliguan and Mt. Yulong have illustrated atmospheric Hg concentrations and transport patterns in the Tibetan Plateau from multiple perspectives, all of which also indicated the effects of transboundary transport on the atmospheric Hg concentrations in the Tibetan Plateau (Zhang et al., 2015a; Yin et al., 2018; Lin et al., 2019; Fu et al., 2008; Fu et al., 2012; Wang et al., 2014). For example, our previous study in the QNNP, on the southern border of the Tibetan Plateau, proved that atmospheric Hg from the Indian subcontinent can be transported across high-altitude mountains, and directly to the Tibetan Plateau under the actions of the Indian monsoon and local glacier winds (Lin et al., 2019). Studies of water vapor mercury and wet deposition of Hg in cities such as Lhasa have demonstrated higher concentrations of Hg species than expected (Huang et al., 2015; Huang et al., 2016b; Huang et al., 2016a). But the monitoring of atmospheric Hg speciation is still rare.'

Comment #5

Line 135: is the rain depth at SET station much higher than the mean in the Tibetan Plateau? Could the author tell something regarding the seasonal patterns in rain depth at SET (noticeable difference between the PISM and ISM)?

Response #5

Thanks for the suggestion. We have added the precipitation data in the revised manuscript, as follow: **'The average annual precipitation is approximately 700-1000 mm at the SET station, much higher than the annual precipitation in Tibet (596.3 mm in 2019). The precipitation at the SET station is 47.7 mm during the period of PISM, and is 528.5 mm during the period of ISM in 2019.'**

Comment #6

Section 2.3: the study by McLagan et al., 2018 (ACP) should be cited. I suggest the author to briefly introduce how to use the passive technique to calculate the atmospheric GEM concentrations. The current information is not very clear to me.

Response #6

Thanks for the suggestion. In view of the length of the article, only literature citations are given in the text and no detailed calculations are given. We have added the following information accordingly: '**Hg concentrations in the atmosphere are then calculated from the mass of sorbed Hg according to the equation obtained from our previous work (Guo et al., 2014).**' and '**Similar passive sampling methods for Hg have been widely used worldwide (McLagan et al., 2018).**'

Comment #7

Line 202: why did the authors choose a ending height of backward trajectory of 1000 m agl. A height of 1000 m is almost above the PBL.

Response #7

Thanks for the comment. The relative high trajectory arrival height was set mainly due to concerns that the complex topography of the Tibetan Plateau might cause significant disruptions to the trajectory. We reviewed the data and found that the average boundary layer height in Nyingchi is 457 m (data from Global Data Assimilation System (GDAS)). In the revised manuscript, we have recalculated all trajectories and redone all the simulations associated with the trajectories. The arrival height was set at 200 m a.g.l., which is about half of the boundary layer height. Considering that a longer simulation time will bring higher trajectories uncertainty, and 120 hours are sufficient for trajectories transmission over longer distances, every backward trajectory was simulated for 120 hours at 3 hours intervals. Also, we examined the effect of arrival height on the trajectories using different arrival heights (20m, 50m, 200m and 500m, respectively) in June 2019. The results showed that the calculated trajectories of the air masses are almost the same when the arrival height is below 500m. The figure below shows the trajectories to Nyingchi in June 2019 with different air masses arrival height. We also added these results in the support information in the revised manuscript.

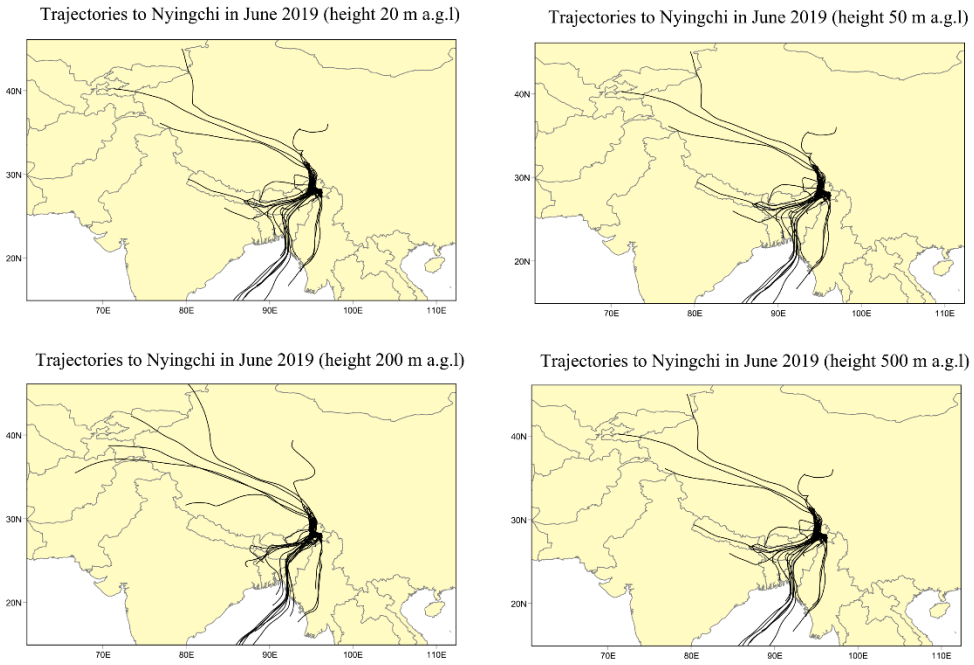

Figure Trajectories to Nyingchi in June 2019 with different air masses arrival height

We have changed the describe of the backward trajectory simulations in the revised manuscript to make it clear: '**The trajectory arrival height was set to 200 m a.g.l., which is about half of the boundary layer height. We examined the effects of arrival height on the trajectories using different arrival heights (20m, 50m, 200m and 500m, respectively) in June 2019. The results show that the calculated trajectories of the air masses are almost the same when the arrival height is below 500m (Figure S3). Each backward trajectory was simulated for 120 hours at 3 hours intervals for GEM, which can cover China, Nepal, India, Pakistan, and the majority of western Asia.**'

Comment #8

Line 206-212: the description of PSCF is not clear to me. A least, the authors should mention the arbitrarily set criterions in GEM concentrations used for different sampling period.

Response #8

Thanks for the comment and suggestion. The criterion level was set based on the average GEM concentration during the whole monitoring campaign with Tekran instrument. However, we agree with another reviewer that the PSCF analysis does not provide gainful information in this

manuscript. So we have decided to delete the PSCF related discussion in the revised manuscript.

Comment #9

Line 235-237: rain depth is a good proxy for the changes of monsoons. However, I would suggest the authors to show the air mass sources and transport pathways in different monitoring periods. This would help to better show the changes in monsoons.

Alternatively, the authors may provide the Indian monsoon index to support the changes in ISM.

Response 9

Thanks for the suggestion. We have added the Indian Monsoon Index for 2019 in the supporting information (Figure S1), with the Indian monsoon starting to break out in May, 2019 and becoming the dominant wind field. We have also calculated trajectories for different seasons and added a discussion of the sources of trajectories in section 3.3 to calculate transport pathways' changes.

Comment #10

Line 395-252: the authors did not show the GEM, GOM and PBM during the ISM3 period. The ISMS is characterized by elevated GEM and decreasing GOM and PBM. Would these observations be explained by wet deposition removal processes?

Response #10

Thanks for the comment. We have added a discussion for the ISM3 period. The wet deposition removal process is one of the reasons for the decrease of GOM and PBM, but not the only reason, as GOM and PBM concentrations continue to decline when precipitation declines from ISM2 to ISM3. This may indicate that less GOM and PBM were transported to the SET station or with fewer local sources during ISM3.

Comment #11

Line 255: the mean GEM measured by Tekran instrument should be presented.

Response #11

Thanks for the suggestion. We have added the mean GEM measured by Tekran instrument here accordingly.

Comment #12

Figure 4: this figure contains to many information and I can only read the diurnal GEM trend clearly. I would suggest to redraw these figures by separating some of the observations in different figures (some maybe in SI). Also, these figures are lacking of Y axis.

Response #12

Thanks for the suggestion. We agree with the reviewer that the figures contain too much information. We have redrawn the diurnal variation figures, keeping only GEM and error range, GOM, PBM and wind speed information.

Comment #13

Section 3.2: the authors presented the diurnal patterns in criteria pollutants in Figure 4, but they did not use these data to explain the sources and factors regulating the atmospheric Hg. I would suggest to use the CO (or NO2) to strengthen their hypothesis.

Response #13

Thanks for the suggestion. We agree with the reviewer that the use of CO (or NO_2) could facilitate the understanding of the changing patterns of GEM. However, the relations between the pollutants and atmospheric Hg are extremely complicated, and due to the word limit, we didn't make very detailed expansion on the manuscript. For example, the relationships between GEM and other pollutants may be significantly affected by the complex topography and precipitation conditions at Nyingchi. The presence of abundant vegetation may also affect GEM concentrations.

Comment #14

Figure 5: these figures are difficult to read. I would suggest the authors to add tables in these figures, which may include the relative fractions, travelling height, mean GEM, GOM and PBM concentrations for the grouped clusters. Alternatively, they can show these information by text directly in the figures (information using thickness and color of the lines are difficult to obtain)

Response #14

Thanks for the suggestion. We agree with the reviewer that the figures presented here are difficult to obtain useful information. We have redrawn the trajectory and showed detailed information concerning the cluster number, GEM concentration and ratio on the trajectory edges by text directly

in the figures in the revised manuscript. We hope the new version can provide these information clearly.

Comment #15

Line 410-417: would the transport of Hg from southwestern China contribute to the elevated GEM during ISM3?

Response #15

Thanks for the suggestion. The old version trajectories showed that the transport of Hg from southwestern China might contribute to the elevated GEM during ISM3. However, after we re-calculate the backward trajectories in lower arrival height, we didn't found trajectories from southwestern China.

Comment #16

Section 3.3: the authors mainly use backward trajectories to show the sources and transport pathways. I suggest the authors to add an analysis of wind dependence distribution of GEM, GOM, and PBM. This would help to support the findings using trajectories (trajectory has many uncertainties especially for mountainous monitoring sites.)

Response #16

Thanks for the suggestion. We agree with the reviewer that trajectory analysis for mountainous monitoring sites could be affected and have higher uncertainties. We didn't show the wind dependence distributions of GEM, GOM, and PBM in this paper, mainly because of the complex topography of the SET station. The final arrival wind direction may be influenced by local vegetation or small local topography, and may not reflect the true atmospheric transport trend.

Comment #17

Line 420: are these PSCF figures showing the sources of GEM, or GOM and PBM? Overall, the authors did not well explain the sources and transformation of GOM and PBM, neither combined them with GEM to propose the atmospheric processes (or sources) of atmospheric Hg in the high-altitude regions.

Response #17

Thanks for the suggestion. The PSCF figures show the sources of GEM. As we mentioned above, we agree with another reviewer that the PSCF analysis does not provide gainful information in this manuscript. So we have decided to delete the PSCF related discussion in the revised manuscript.

Comment #18

Line 465: would GOM be emitted from land surfaces? The elevated GOM accompanied by increasing solar radiation many indicate in situ oxidation of GEM?

Response #18

Thanks for the suggestion. We agree with the reviewer that strong solar radiation in Tibet may indicate in situ oxidation of GEM. We did find that intense solar radiation may be associated with extremely high GOM concentrations. We have added some discussions at the end of section 3.1: '**Table S3 shows the variations of Hg species, meteorological factors and other pollutants from June 1 to 4, 2019. High GOM concentrations were observed on June 2 and 3, and very high solar radiation and UV Index were also observed in these days. PBM concentrations, relative humidity and O_3 were low during this period. The solar radiation was nearly twice the mean value of the ISM1 phase (162.79 W m^{-2}, Table S2), and thus higher solar radiation might contribute to the higher GOM concentrations. Some of the PBM might be converted to GOM, but the decrease in PBM concentration was less than the increase in GOM concentration. Generally, high O_3 concentrations should be observed at high solar radiation (Kondratyev et al., 1996), but low O_3 concentrations were found at Nyingchi, suggesting that O_3 may be involved in the formation of GOM. The oxidation of GEM by OH and O_3 to generate GOM has been discussed in previous studies with model simulation (Sillman et al., 2007), which may explain the reduced concentration of O_3, while OH radicals may be associated with high solar radiation. The mechanism of GOM formation should be further explored in future studies.**'

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