Response to Reviewer #2's Comments

Anonymous Referee #2:

The paper analyzed speciated Hg concentrations at a site in eastern China and applied various data analysis methods, including potential source contribution function (PSCF) and positive matrix factorization (PMF), to examine the sources and transformation processes involved. The speciated Hg concentrations collected at this site are likely some of the highest that have been observed worldwide including within Asia, and this warrants a detailed investigation into the causes in order to address the Hg pollution issue in China. However, I did not get a clear understanding of the sources contributing to such high speciated Hg concentrations. I think this is partly due to incomplete understanding of Hg emissions in China, which leads to uncertainties in the interpretation of the sources. The omission of the PMF analysis for GOM and PBM is also contributing to a lack of understanding of the anthropogenic sources. The alternative explanation in the paper for the extremely high GOM concentrations is the oxidation of GEM. However, the discussion seems too speculative, as it doesn't account for the many physical and chemical parameters that are involved in the Hg transformation process. This is a complicated process, and the way that it is examined in the paper (methodology and data) does not further the understanding of GEM oxidation. Considering the high levels of anthropogenic Hg emissions across China, I suggest focusing your analysis on anthropogenic sources and making sure that all of these sources have been carefully considered.

We sincerely thank for the reviewer's in-depth comments and helpful suggestions on this manuscript. Based on the specific comments, we have responded to all the comments point-by-point and made corresponding changes in the manuscript as highlighted in red color. The reviewer has raised a number of issues and we quite agree. We feel the substantial revisions based on the reviewer's comments have greatly improved the quality of this manuscript. Please check the detailed responses to all the comments as below.

Specific comments:

1. Line 26: what is meant by quasi-local? Please explain what local sources were affecting this site.

Response: The sampling site is located in the suburbs of Shanghai. At the scale of the Yangtze River Delta (YRD) region, the main emission sectors of GEM were coal-fired power plants, coal-fired industrial boilers, residential coal combustion, cement clinker production, and mobile oil combustion (Wang et al., 2016). We also calculated the total mercury emissions in a region of $0.4° \times 0.4°$ covering the sampling site based on the EDGAR emission inventory. The emissions for GEM were around 105 kg/yr, indicating that no strong mercury emissions are around this site. The major emission sectors are from the power industries and cement production.

Usually local emissions refer to the scale of one city. Since the sampling site is located at the conjunction of Shanghai, Jiangsu, and Zhejiang provinces, quasi-local mean the emissions around the site covering multiple cities in Shanghai, Jiangsu, and Zhejiang. In the revised manuscript, we have defined it more clearly.

2. Lines 29-30: "Besides the common anthropogenic emission sectors…" I think that it is better to list the anthropogenic sources in the abstract because it informs stakeholders about the major sources of Hg in China so that appropriate policies can be developed to manage Hg pollution.

Response: Thanks for the suggestion. This sentence is revised as "Besides the common anthropogenic emission sectors (i.e., industrial and biomass burning, coal combustion, iron and steel production, cement production, and incineration), …" in the revision.

3. Line 55: "mercury will experience the chemical and physical speciation and its forms were essential to understand its biogeochemical cycle". I suggest revising this to, "mercury undergoes speciation which plays an important role in its biogeochemical cycle."

Response: Thanks for the suggestion. This sentence has been revised as "mercury undergoes speciation which plays an important role in its biogeochemical cycle." in the revision.

4. Line 76: The treaty name is Minamata Convention on Mercury.

Response: The treaty name has been corrected as "Minamata Convention on Mercury" in the revision.

5. Lines 77-79: "the situation of mercury pollution is still grim, especially in Asia, which contribute about half of the global mercury emissions (Wu et al., 2006)" I suggest changing this to "the mercury pollution issue is still grim especially in Asia,: : :" Could you use a more recent reference to describe the current Hg emissions in Asia?

Response: Thanks for the reviewer's suggestions. The reference has been updated and the sentence has been revised as "However, the mercury pollution issue is still grim especially in Asia, which contribute about half of the global mercury emissions (Pacyna et al., 2016)." in the revision.

6. Lines 83-85: I've seen several papers analyzing the sources and processes of speciated Hg in China. Could you discuss the major findings from these studies and explain how this paper is different or builds on the current knowledge?

Response: Thanks for the suggestion and we have added the major findings from some recent papers about the sources and processes of speciated Hg in China as below.

     "Early field measurements in urban Shanghai found that the sources of TGM were most likely derived from coal fired power plants, smelters and industrial activities (Friedli et al., 2011). The study in urban Nanjing indicated that natural sources were important while most sharp peaks of TGM were caused by anthropogenic sources (Zhu et al., 2012). Modeling of atmospheric mercury in eastern China simulated by the CMAQ-Hg model showed that natural

emissions were the most important source for GEM in eastern China with a contribution of 36.6% (Zhu et al., 2015). One study at Chongming (an island belonging to Shanghai) observed a downward trend for GEM concentrations from 2014 to 2016 due to the reduction of domestic emissions (Wang et al., 2016). Studies conducted in Changbai Mountain (Wan et al., 2009) and Xiamen (Xu et al., 2015) used Principal Components Analysis (PCA) to identify potential sources of atmospheric mercury, but the specific contributions of each source couldn't be quantified due to the limitation of the PCA method. Overall, studies with respect to the specific sources and their quantified contribution to atmospheric mercury in the suburbs of East China and the formation and transformation processes among Hg species in the atmosphere are still lacking." in the revision.

7. Line 128: Did you perform any quality control on the speciated Hg data, e.g. determining field blanks? Some of the 2-h GOM and PBM concentrations were extremely high; I wonder if they may be outliers? You mentioned that the air inlet is on the rooftop of a building. What kind of building is this and is there the possibility that ventilation exhaust from the building caused the high Hg concentrations? Depending on the building, indoor air can be very polluted.

Response: Yes, a series of work have been done to ensure the quality of the measurement. Before sampling, denuders and quartz filters were prepared and cleaned according to the methods in Tekran technical notes. The Tekran 2573B instrument routinely undergoes automated daily calibrations using internal GEM permeation source and external manual calibration when necessary. Two-point calibrations (including zero calibration and span calibration) were performed separately for each pure gold cartridge. Manual injections were performed to evaluate these automated calibrations using the standard saturated mercury vapor. We noticed that sometimes the concentrations of GOM and PBM were extremely high. After ascertaining that the instrument was in normal operation during those episodes, we find that these high values are continuous, but not suddenly rising or falling. Thus, we think the data under these conditions are valid. We did find some extremely high values, which were about several times higher than the previous hour. As for these data, we think they are outliers and have already been excluded in the data analysis.

The Tekran instrument along with other instruments were set up on the top roof of a four-story building. This supersite is carefully maintained by SEMC. The building is purely used for atmospheric monitoring without any other usage. There are no human activities inside the building except that when the maintenance people enter the building. There is only routinely one guard responsible for the running of the building and he doesn't live inside the building. Thus, we can say that there are almost no emissions inside the building and the ventilation exhaust shouldn't be the cause of high Hg concentrations.

In the revised manuscript, we have added more description about the supersite in Section 2.

8. Line 166: "we set the threshold concentration as the mean value of the whole sampling period." Are these the mean Hg concentrations and what are the values?

Response: Yes, the mean concentrations of GEM, PBM, and GOM are used. We added the sentence "The mean GEM, PBM, and GOM concentrations were 2.77 ng/m^3, 60.8 pg/m^3, and 82.1 pg/m^3, respectively." in the revision.

9. Line 167: Please describe how the back trajectories were calculated and the relevant model inputs and parameters.

Response: We have added more detailed description about the simulation of back trajectories as below.

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is applied for calculating air mass backward trajectories (Draxler and Rolph, 2012). The model was run online at the NOAA ARL READY Website using the meteorological data archives of Air Resource Laboratory (ARL). The meteorological input data used in the model was obtained from NCEP (National Centers for Environmental Prediction)'s global data assimilation system (GDAS) with a horizontal resolution of 0.5° × 0.5°. In this study, 72-hours back trajectories were calculated at 500m AGL (above ground level) and the cell size was set as 0.5°×0.5°

10. Line 187: The description of the PMF analysis is overly general; there needs to be a more detailed description of the model runs. Did you perform only a single run or multiple runs with different number of factors to come up with the optimal solution? How did you decide how many factors to keep? Did you do any analysis to assess the performance of the model? The quality of the PMF results depends on the input data and other considerations. Were there any procedures followed to ensure the quality of the input data?
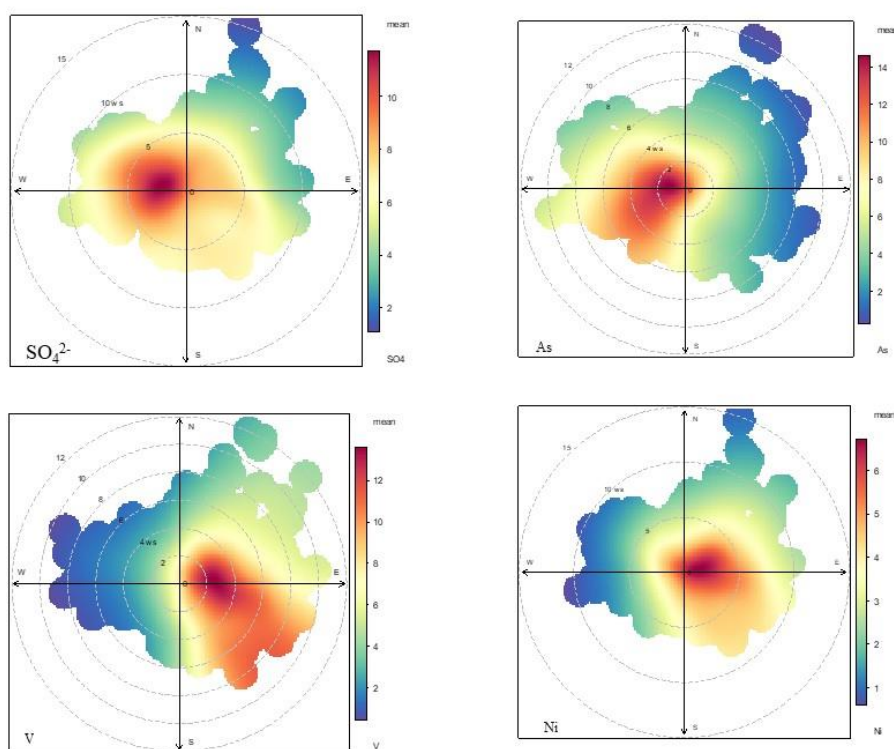
Response: We have added more detailed description of the PMF running as suggested in Section 2.5.
"In this study, the number of factors from 3 to 8 was examined with the optimal solutions determined by the slope of the Q value versus the number of factors. For each run, the stability and reliability of the outputs were assessed by referring to the Q value, residual analysis, and correlation coefficients between observed and predicted concentrations. Finally, a 6-factor solution, which showed the most stable results and gave the most reasonable interpretation, was chosen. Before running the model, a dataset including unique uncertainty values of each data point was created and digested into the model. The error fraction was assumed to be 15% of concentrations for GEM and 10% of concentrations for the other compounds (Xu et al., 2017), the missing data were excluded and the total number of samples was 3526."

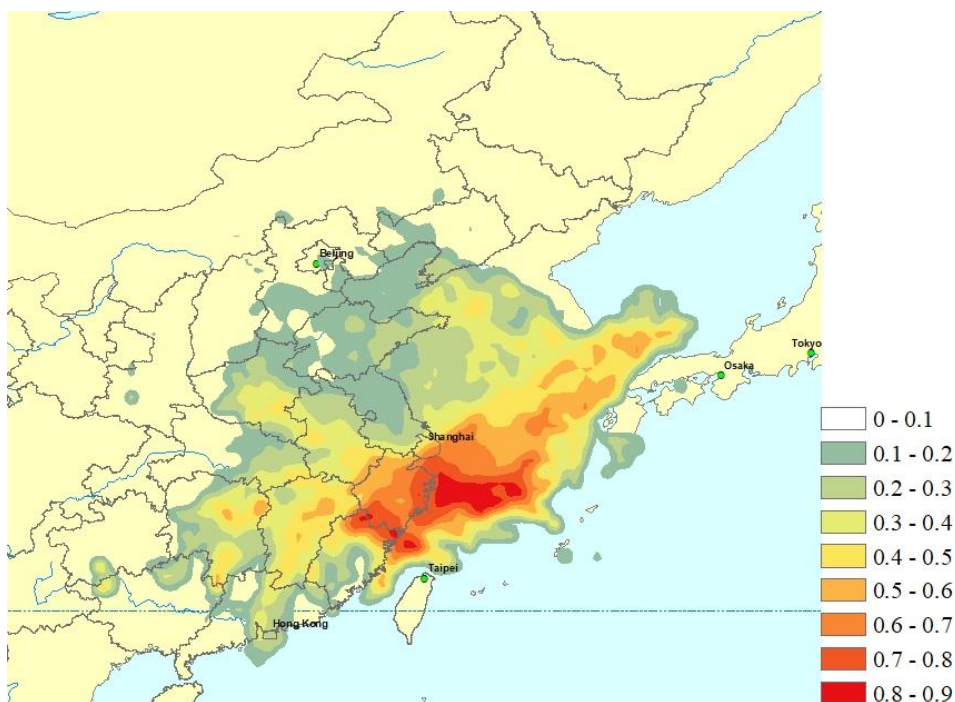We added additional analysis to assess the performance of the model as below.

（1）In order to validate the PMF results, wind roses of SO$_4^{2-}$, As, Ni, and V are plotted in the figure below. SO$_4^{2-}$ and As shared similar patterns with high concentrations mainly from the southwest. SO$_4^{2-}$ and As are tracers for coal combustion. PMF identified combustion is the biggest source of GEM. Thus, this confirmed that the major sources of GEM are located in the southwest region. Ni and V showed similar patterns with high concentrations mainly from the

northeast, east, and southeast. PMF identified a shipping source from the ocean. The wind rose plots of Ni and V also confirmed the identification of the shipping factor.

(2) In order to determine whether factor 2 represents shipping emissions, the time-series of GEM concentrations from the shipping factor based on the PMF modeling were extracted and digested into the PSCF modeling. The figure below showed the potential sources regions were mainly located over the East China Sea, which indicated factor 2 from PMF should be representative of the shipping sector. At the same time, we recognized oil combustion in motor vehicle and shipping emissions over the Dianshan Lake certainly contributed to Hg pollution, but the existing ships in Dianshan Lake are far from being comparable to that of the adjacent East China Sea, and the proportion of mobile oil combustion is relatively small in YRD (5.34%)(Tang et al., 2018), thus we think that factor 2 should be likely related to ship emission over the offshore and open areas of the East China Sea as well as oil combustion in motor vehicles and inland shipping activities.

In the revised manuscript, we have made clarification about the explanation of factor 2 by PMF modeling.

11. Lines 192-193: Please include the standard deviation for the concentrations.

Response: The standard deviation for the concentrations have been included, the sentence has been revised as "The annual average concentrations of GEM, PBM, and GOM at DSL were 2.77±1.36 ng/m^3, 60.8±67.4 pg/m^3, and 82.1±115.4 pg/m^3, respectively." in the revision.

12. Lines 203-205: "The abnormally high GOM concentrations observed in this study were likely attributed to both strong primary emissions and secondary formation" I am skeptical that this is due to secondary formation because as discussed in the seasonal concentrations in the next paragraph, it is the winter concentrations that were much higher than other seasons. During the winter, secondary formation from GEM oxidation is likely not significant. I suggest focusing on primary emissions during the wintertime and determining the major sources (e.g. coal combustion, oil combustion, residential wood burning, etc.) and conditions during winter that could lead to strong pollution episodes (e.g. stagnant atmosphere, changes in air mass patterns, etc.). Is DSL a high elevation area? If so, could transport from the free troposphere contribute to the extremely high GOM concentrations?

Response: Thanks for the comment. We do agree with the reviewer that high GOM concentrations are dominated by primary emissions, especially in wintertime. We revised the sentence as "The abnormally high GOM concentrations observed in this study were likely dominated by strong primary emissions." in the revision.

The DSL site is not a high-altitude site (~ 14 meter above sea level), so we don't think transport from the free troposphere can significantly contribute to the atmospheric mercury concentrations under most circumstances. However, we do appreciate for this comment on the possibility of mercury transport from the free troposphere in the future studies.

13. Lines 227-228: Have you ruled out other possible reasons, e.g. forest fire emissions, combustion and industrial emissions, etc.? The lower concentrations in summer compared to winter could be simply due to increased atmospheric mixing, wet deposition (have you analyzed rainfall data?), dry deposition, changes in air mass patterns, etc. More detailed analysis is needed before arriving at the conclusion that GEM oxidation is causing the high GOM concentrations.

Response: Thanks for the comments and we do agree with the reviewer that we didn't fully consider the factors influencing the concentrations of GOM. As for the reviewer's concern, forest fire emissions were not the emission source in the Yangtze River Delta region. Combustion and industrial emissions were the major emission sectors in the Yangtze River Delta region. Those emissions are almost constant among the 12 months (Tang et al., 2018). Thus, the lower concentrations of GOM in summer compared to winter should be largely due to the more favorable meteorological conditions as the reviewer mentioned. At the same time, GOM concentrations in summer were higher than spring and autumn, which should be partly ascribed to the secondary transformation from GEM. In this Section, we just generally describe the seasonal pattern of Hg species. More detailed analysis of the impact of meteorological conditions on Hg species and the related formation mechanisms are presented in the following sections.

In the revised manuscript, this sentence is changed as "GOM concentrations in summer were much lower than that in winter, which were largely due to the more favorable meteorological conditions. However, GOM concentrations in summer were higher than spring and autumn, which should be partly ascribed to the secondary transformation from GEM. More detailed analysis of the impact of meteorological conditions on Hg species and the related formation mechanisms are presented in the following sections.".

14. Lines 238-240: Do these sites have similar/different characteristics as the DSL site? What about the distance between the listed sites and DSL? I think these factors may explain the diurnal variations.

Response: The listed sites are all urban site, of which the site in Nanjing also belongs to the Yangtze River Delta region and is about 300km from the DSL site. The similar meteorology and emission characteristics within the Yangtze River Delta region may explain the similar diurnal patterns of Hg species between DSL and Nanjing. As for Guiyang, and Guangzhou, they are much far away from DSL with distances of around 1000 – 2000km. Different meteorology and emission characteristics may explain the different diurnal patterns between those sites and DSL. In the revised manuscript, we have explained more clearly about the comparison of diurnal patterns among various sites.

15. Lines 240-245: It appears GEM and GOM have similar diurnal variations and both peaked at 10 AM. This suggests they were affected by the same sources. Could you elaborate what are the stronger emissions from both human activities and natural releases in this area that are causing the high GEM concentrations? Did you consider traffic emissions as a potential source because of higher traffic volumes in the morning which is consistent with the morning peak in the concentrations? I also think more investigation is needed before you can state that the high GOM concentrations are the result of GEM oxidation. To support this statement requires

additional data on the oxidants of GEM and model simulations of the chemical reactions. Based on the diurnal variation, the 10 AM peak does not seem consistent with GEM oxidation because the photochemistry is driven by solar irradiance which peaks at noon. The GOM peak would likely be at noon or later, but in your case, the peak occurs earlier than noontime. Also, have you considered all possible sources of Hg and are there any unknown sources (sources that are not reported in the emissions inventory)?

Response: Thanks for the comments. According to the emissions inventory in the YRD region, the main anthropogenic emission sectors of GEM included coal-fired power plants (39.33%), coal-fired industrial boilers (27.53%), residential coal combustion (1.12%), cement clinker production (13.2%), iron and steel production (6.46%), and mobile oil combustion (5.34%) (Tang et al., 2018). Natural emissions included primary natural release and re-emission of legacy Hg stored in the terrestrial and water surface (Cheng et al., 2014). According to the emissions inventory, traffic emissions only accounted for 5.34% of the total GEM annual emission in the YRD region (Tang et al., 2018). We did consider whether the traffic emissions cause the morning peak of Hg concentrations, however, if it is true, Hg concentrations should also rise during the evening rush hours, which is not shown in the figure. We agree with the reviewer that more investigation is needed before we can draw the conclusion that the high GOM concentrations are the result of GEM oxidation. Thus, we revised the description as "GOM and GEM showed similar diurnal variations and both peaked at 10:00, probably suggesting that GOM and GEM were affected by common sources (e.g. coal-fired power plants and industrial boilers)." in the revision.

16. Lines 253-257: Both GEM and GOM appeared to be 2 and 8 times higher, respectively, when winds came from the southwest quadrant than other directions. I think more analysis is needed to identify the sources from this southwest region that is causing the mean GOM concentrations to increase to 100 pg/m^3. Since wind speed and wind direction data were used, the sources are likely local which narrows down the area of investigation.

Response: According to the PMF source apportionment results, industrial and biomass burning (47.8%) was the biggest source of GEM at the sampling site. When referring to the emissions inventory in the YRD region, the main anthropogenic emission sectors of GEM were coal-fired power plants and coal-fired industrial boilers, accounting for 66.9% of the total GEM emissions in YRD (Wang et al., 2016). Thus, it is reasonable to conclude that the high GEM and GOM concentrations from the southwest were caused by coal-fired power plants and coal-fired industrial boilers.

17. Lines 262-265: This is too general. I think that you need to extract the relevant details from this reference, e.g. Hg flux data from the southwest region vs. north/northwest regions. Did the reference discuss what is causing the Hg in the soil, e.g. local contamination, atmospheric deposition, etc.?

Response: Thanks for the suggestion. According to the study of (Wang et al., 2016), it could be seen that the mean annual Hg air-soil flux in the southwest region of our sampling site (e.g. Zhejiang province) ranged from 8.75 to 15 ng m^{-2} h^{-1}, while that in the north/northwest region (e.g. Jiangsu province) ranged from 2.5 to 8.75 ng m^{-2} h^{-1} (left figure). The reference didn't discuss in details about the factors affecting the levels of Hg in soil, but mentioned that soil Hg

contents in forest ecosystems are 2-4 times higher than that in grassland and cropland. The land type of the southwest region is mainly mountain forests while that of the north/northwest region is mainly flat cropland and grassland. This may partly explain the relatively high mercury concentrations observed from the southwest.
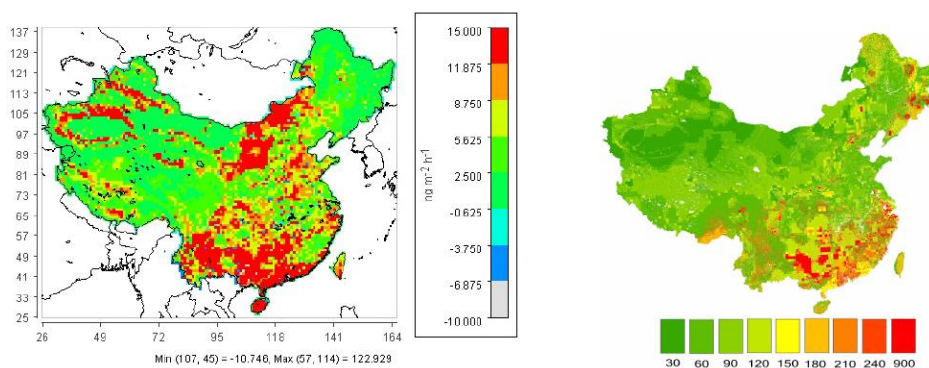

Figure R1. (left) mean annual air–soil flux; (right) Hg concentrations (ng g-1 in surface soil (0–20 cm) of China.

In the revised manuscript, we added the sentence "A modeling study simulated that the mean annual Hg air-soil flux in the southwest region of our sampling site (e.g. Zhejiang province) ranged from 8.75 to 15 ng m^{-2} h^{-1}, while that in the north/northwest region (e.g. Jiangsu province) ranged from 2.5 to 8.75 ng m^{-2} h^{-1} (Wang et al., 2016). Hence, emissions from natural sources, such as soils, vegetations and water, should play an important role in the observed high atmospheric Hg concentrations from the south and southeast." in the revision.

18. Lines 270-271: "This relationship between GEM and temperature can only be interpreted as the impact of natural source emissions." I think this is one possible interpretation, but not the only interpretation. Temperature can co-vary with other parameters. Also, natural source emissions should be revised to surface emissions because it may have originated from anthropogenic sources by process of deposition.

Response: Thanks for the comment and we agree that this is just a possible interpretation but not the only one. And we have changed the term "natural source emissions" as "surface emissions" and elsewhere throughout the manuscript. We revised the description as "This relationship between GEM and temperature can be likely interpreted as the impact of surface emissions." in the revision.

19. Lines 275-277: "The GOM concentration showed a clearly positive correlation with temperature in summer. This should be related to the in situ oxidation of GEM under high temperature" The correlation between GOM and temperature does not necessarily indicate oxidation of GEM. Temperature is only one parameter involved in Hg chemistry; there are many other physical and chemical parameters that are influencing the chemistry but they have not been considered in this analysis.

Response: Thanks for the comment and we do agree with the reviewer that the conclusion cannot be drawn based on inadequate evidence. Given the limited parameters measured in this study, it is difficult for us to investigate other physical and chemical parameters that impact the mercury chemistry. When higher temperature occurs, the atmospheric oxidation ability is usually enhanced due to enhanced solar radiation, thus resulting a larger extent of GEM oxidation. Thus, we think the positive relationship between GOM and temperature may imply the oxidation of GEM to GOM to some degree. But of course, GOM has a significant source of direct emissions as mentioned by the reviewer above. Thus, we revised the description as "The GOM concentration showed a clearly positive correlation with temperature in summer. Higher temperature in summer in the Yangtze River Delta region is mostly associated with ozone pollution days (Lu et al., 2018), thus implying higher GOM could be partially related to the in situ oxidation of GEM in addition to its sources from direct emissions. " in the revision.

20. Lines 293-295: "However, as shown in Fig. 1, southern provinces such as Zhejiang and Jiangxi were estimated to release only 25 tons/yr atmospheric Hg from anthropogenic activities, being far less than the northern provinces such as Jiangsu and Shandong (77 tons/yr)… If only the anthropogenic emissions of GEM were considered, the occurrence of stronger PSCF signals in southern provinces seemed unreasonable." 25 tons/yr of Hg emissions from anthropogenic sources is still very high if you were to compare that to emissions in North America and Europe. I don't think you can rule out the impact of anthropogenic Hg sources in the southern region on this site, even though the PSCF values are higher in the northern region. Also, have you considered possible transport of GOM from the free troposphere especially when the trajectory endpoints reach high altitudes?

Response: Thanks for the comments. In this discussion, we are not trying to rule out the impact of anthropogenic Hg sources. What we wanted to clarify is that in addition to the direct emissions from anthropogenic sources, surface emissions are also important. As the sampling site is not a high-altitude site, we did not consider the impact of possible transport GOM from the free troposphere. But this suggestion is of great valuable, and inspiring for our future work.

In the revised manuscript, we have deleted the term "only" to avoid any misunderstandings.

21. Lines 297-298: "In this regard, the re-emission of GEM from natural surfaces in southern areas should be a crucial source, corroborating the discussion in Section 3.2." How do you know this when you don't have the Hg emissions from natural surfaces to compare against anthropogenic emissions? More data are needed before you can arrive at this conclusion.

Response: Thanks for the comments and suggestions. Based on the study by (Wang et al., 2016), the mean annual Hg air-soil flux in the southwest region of our sampling site ranged from 8.75 to 15 ng m^{-2} h^{-1}. By using this value, we can estimate that the total Hg emissions from soils were in the range of 6.9 - 13.9 tons/yr for Zhejiang province. As for the anthropogenic Hg emission of Zhejiang in 2014, it was approximately 15tons/yr (Wu et al., 2016). Thus, the magnitude of mercury from natural surfaces is comparable to that from anthropogenic sources.

In the revised manuscript, we have added more discussions to support this conclusion.

22. Lines 315-316: "the potential source regions of GOM were more from southern China rather than from northern China, which might be due to the higher atmospheric oxidants levels in the southern regions." This is highly speculative and needs to be supported with data.

Response: Thanks for the comments. We deleted this sentence and changed the description as "The PSCF patterns of GOM were similar with that of GEM but different from that of PBM." in the revision.

23. Lines 322-328: "…leading to the formation of GOM dominated by mainland oxidants rather than the ocean oxidants." This discussion needs to be revised because I don't think you can differentiate between mainland oxidants (i.e. ozone) and oceanic oxidants (i.e. bromine). There are many potential oxidants of GEM aside from ozone and bromine. Modeling studies indicate that oxidation of GEM by bromine can occur globally not just in the marine regions. I feel there is too much speculation on the discussion of GEM oxidation. Instead of this reason, have you considered that GOM may have originated from mainland and then was transported into the sea before arriving at the site?

Response: Thanks for the comments. We do agree with the reviewer that mainland oxidants and oceanic oxidants were not differentiated and this paragraph is speculative. Hence, we deleted the sentence "It should be noted that the signals from the ocean in summer were weaker than in the other seasons. This was likely due to the particularly high ozone concentrations over land in summer (Lu et al., 2018), leading to the formation of GOM dominated by mainland oxidants rather than the ocean oxidants." to avoid inappropriate conclusion.

24. Lines 367-369: "This corroborated the discussion above that the GOM/PBM ratio was a reliable tracer for assessing the relative importance of regional/long-range transport vs. local atmospheric processing." I am skeptical about this because of the mixing between regionally-transported air masses and local air. I think it is more complicated, and there are many processes affecting GOM and PBM concentrations at a particular site.

Response: Thanks for the comments and we do agree that there are too many processes affecting the formation of GOM and PBM. As for the ratio of GOM/PBM, it has been used to investigate the relative importance of local sources relative to regional transport in a number of studies based on the fact that the atmospheric residence time of GOM is generally regarded to be shorter than that of PBM (Lee et al., 2016;Zhang et al., 2013;Zhu et al., 2014). However, the GOM/PBM ratio can be only regarded as a qualitative tracer but not a quantitative method for identifying the relative importance of long-range transport vs. local sources.

In Section 3.3.2, by introducing more atmospheric species such as CO and SNA, we found that all the evidences were consistent. But still, this section didn't aim to sort out the complicated processes that affect GOM and PBM.

25. Line 388: "six-factor solution was selected based on the results of multiple model runs". The details of these model runs should be included in the methods.

Response: The details of model runs have been included in the methods. We added the sentences "In this study, the number of factors from 3 to 8 was examined with the optimal

solutions determined by the slope of the Q value versus the number of factors. For each run, the stability and reliability of the output were assessed by referring to the Q value, residual analysis and correlation coefficients between observed and predicted concentrations. Finally, a 6-factor solution, which showed the most stable results and gave the most reasonable interpretation, was chosen. Before running the model, a dataset including unique uncertainty values of each data point was created and inserted into the model, the error fraction was assumed to be 15% of concentrations for GEM and 10% of concentrations for other compounds (Xu et al., 2017), the missing data were excluded and the total number of samples was 3526." in the revision.

26. Lines 391-392: "since no tracers for the natural emissions (e.g. soils, vegetations, and ocean) were available in this study, the identification of natural mercury sources was not possible." What about Na and Cl ions for identifying marine sources and Ca and K for soil and vegetation?

Response: Thanks for the comment. We have tried multiple runs by setting up different number of factors. However, the model didn't resolve specific factors for natural emissions. We think the possible reasons are as below. Na has sources from soil dust, road dust, and industrial fly ash in addition to marine sources. Cl is significantly impacted by coal burning and waste incineration. Ca and K both have sources from construction activities. Hence, the miscellaneous sources of those elements precluded the PMF model to resolve the natural sources of mercury.

As suggested by another reviewer, we applied the PCA (Principal Component Analysis) to identify the potential sources of GEM by adding temperature. Four factors are resolved, which totally explained 75.32% of the variance as shown in the table below.

Factor 1 accounted for 34.15% of the total variance with high loadings for SO_2, SO_4^{2-}, NH_4^+, K^+, Pb, Se, and As, which is explained as coal combustion mixed with biomass burning. Factor 2 accounted for 14.85% of the total variance with high loadings for temperature, O_3, and NH_3, which is explained as surface emissions. Factor 3 explained 13.43% of the total variance, showed high loading of Ni and V, which indicated the contribution of ship emissions. Factor 4 explained 12.89% of the total variance, with high loading of Fe and Ca, indicating the contribution of cement production.   Table R2 PCA factor loading for GEM at DSL.

	Factor 1	Factor 2	Factor 3	Factor 4
GEM	0.50	0.25	0.11	0.07
SO_2	**0.69**	-0.20	-0.18	0.35
NO_2	0.38	-0.49	0.35	0.39
SO_4^{2-}	**0.84**	0.13	0.15	0.00
NH_4^+	**0.88**	-0.12	0.18	0.07
K^+	**0.77**	-0.25	0.04	0.39
Pb	**0.80**	-0.17	0.04	0.32
Se	**0.87**	-0.05	0.01	0.29
As	**0.82**	-0.23	0.06	0.33
O_3	0.06	**0.79**	-0.30	0.03
NH_3	0.03	**0.73**	0.36	-0.04
Temperature	-0.23	**0.82**	0.17	-0.03
Ni	0.24	-0.02	**0.85**	0.22
V	-0.03	0.11	**0.90**	-0.05
Fe	0.50	-0.12	0.24	**0.74**
Ca	0.26	0.08	0.00	**0.90**
Explained variance %	34.15	14.85	13.43	12.89

27. 3.3.3. Source apportionment by PMF: Why was the PMF analysis only performed on GEM data and not GOM and PBM? I think GOM and PBM needs to be included due to the extremely high concentrations at this site. Anthropogenic emissions of GOM and PBM should not be ruled out. One of the major goals of the Minamata Convention is to reduce anthropogenic Hg emissions. Thus, it seems logical to carry out source apportionment analysis on GOM and PBM and attempt to identify the sources contributing to such high concentrations.
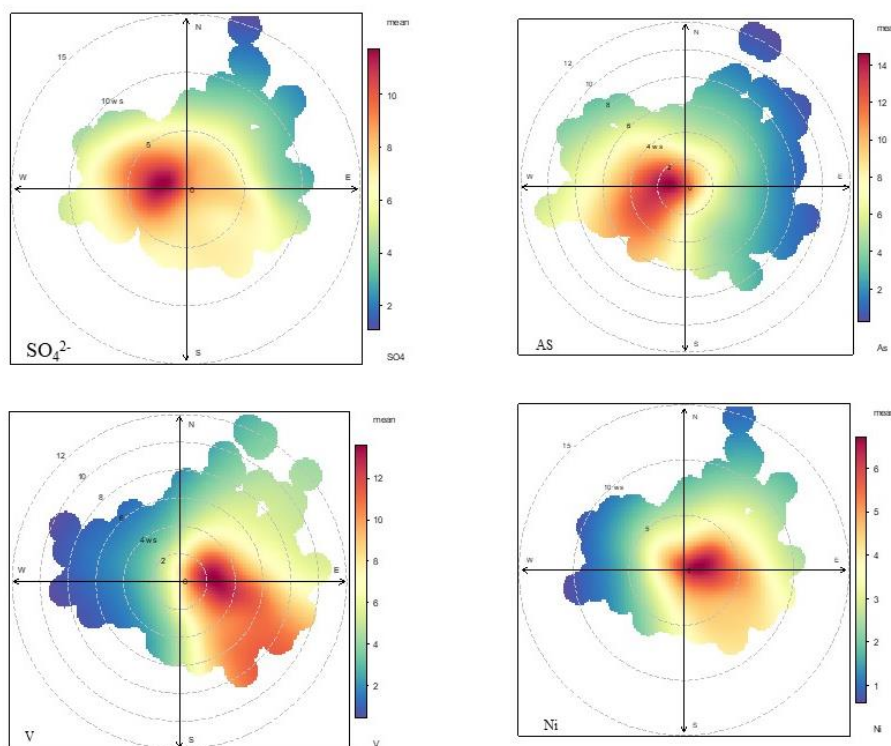
Response: Thanks for this good suggestion. Actually, we've tried hard to apportion the major sources of PBM and GOM by using PMF. However, we found the results difficult to explain. We think that the possible reasons are that the concentrations of PBM and GOM fluctuated much stronger than other atmospheric species such as soluble ions, organic/elemental carbon,

and elements. Due to the relatively short residence time in the atmosphere, it seems not suitable by digesting PBM and GOM into the PMF analysis. Thus, we didn't include source apportionment of PBM and GOM in this study.

28. Another suggestion is to confirm whether the sources identified from PMF are located in the southwest region, where you previously identified as the wind direction sector associated with the highest concentrations. Aside from using the ions and trace metals data for PMF analysis, the data can be used in the previous wind direction and PSCF analyses and also in the time-series analyses with speciated Hg. The concentration spikes in GOM (800-1000 pg/m^3 at times) as shown in the time-series plots are very concerning, and I would look further into what is the cause of this.

Response: Thanks for the suggestion. In order to discuss where the sources identified from PMF came from, wind roses of SO_4^{2-}, As, Ni, and V are plotted in the figure below. SO_4^{2-} and As shared similar patterns with high concentrations mainly from the southwest. SO_4^{2-} and As are tracers for coal combustion. PMF identified combustion is the biggest source of GEM. Thus, this confirmed that the major sources of GEM are located in the southwest region.

Ni and V showed similar patterns with high concentrations mainly from the northeast, east, and southeast. PMF identified a shipping source from the ocean. The wind rose plots of Ni and V also confirmed the identification of the shipping factor.

29. Lines 435-438: "Accordingly, as an anthropogenic emitting tracer, the concentration of carbon monoxide was basically stable and even showing a downward trend, which suggested that anthropogenic activities were not the main driving force for the increase of GOM." I am skeptical about this. Is CO a tracer for all types of industries or only those involving combustion? The point that CO was stable and not increasing with GOM doesn't necessarily imply no

anthropogenic influence. CO is stable likely because it is continuously supplied by the high density of combustion activities in this region.

Response: Thanks for the comments. CO is generally regarded as a tracer for industries involving combustion. According to the inventory of Hg emissions in the YRD region, the main sources of Hg were related to the industries involving coal combustion (Wang et al., 2016).Thus the level of CO concentration could be used to represent the intensity of anthropogenic emissions to some extent. We agree with the reviewer that CO was stable and not increasing with GOM doesn't necessarily imply no anthropogenic influence. In Figure 11, although GOM didn't co-vary with CO, we didn't mean to say "no anthropogenic influence". In the revised manuscript, this sentence is revised as "Accordingly, as an anthropogenic emitting tracer, the concentration of carbon monoxide was basically stable and even showing a downward trend, which suggested some other factors accounted for the increase of GOM in addition to the anthropogenic emissions" to avoid any misunderstandings.

30. Lines 438-469: The discussion on GEM oxidation by ozone is too speculative. As mentioned, there are many potential oxidants of GEM, but they were not analyzed in this work. I think the understanding of Hg transformation is very complicated, and this discussion does not really acknowledge that

Response: Thanks for the comments. Severe ozone pollution frequently occurred in the YRD due to strong anthropogenic emission intensities (Lu et al., 2018). In this study, high GOM concentrations were observed (Fig. 2). GOM concentration showed a clearly positive correlation with temperature in summer, the summer mean GOM concentration was higher than spring and autumn, a clear positive correlation between GOM and O_3 were also observed in both statistical analysis (Fig. 12) and episode events (Fig. 11). In this regard, we think that the atmospheric oxidants should play an important role in GEM oxidation. But of course, we understand that the formation mechanism of GOM is complicated and we are not trying to elucidate it based on limited measured parameters. In the revised manuscript, we have revised the title of Section 3.4 as "Factors affecting the formation and transformation of mercury species". In the context of this section, we have adjusted the writings to focus on the crucial factors affecting the formation and transformation of mercury species but not the intrinsic mechanisms.

References

Cheng, I., Zhang, L. M., Mao, H. T., Blanchard, P., Tordon, R., and Dalziel, J.: Seasonal and diurnal patterns of speciated atmospheric mercury at a coastal-rural and a coastal-urban site, Atmospheric Environment, 82, 193-205, 10.1016/j.atmosenv.2013.10.016, 2014.

Draxler, R. R., & Rolph, G. D. (2012). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD. http://ready.arl.noaa.gov/HYSPLIT.php. Accessed March 2012.

Friedli, H. R., Arellano, A. F., Geng, F., Cai, C., and Pan, L.: Measurements of atmospheric mercury in Shanghai during September 2009, Atmospheric Chemistry and Physics, 11, 3781-3788, 10.5194/acp-11-3781-2011, 2011.

Lee, G.-S., Kim, P.-R., Han, Y.-J., Holsen, T. M., Seo, Y.-S., and Yi, S.-M.: Atmospheric speciated mercury concentrations on an island between China and Korea: sources and transport pathways, Atmospheric Chemistry and Physics, 16, 4119-4133, 10.5194/acp-16-4119-2016, 2016.

Lu, X., Hong, J., Zhang, L., Cooper, O. R., Schultz, M. G., Xu, X., Wang, T., Gao, M., Zhao, Y., and Zhang, Y.: Severe Surface Ozone Pollution in China: A Global Perspective, Environmental Science & Technology Letters, 10.1021/acs.estlett.8b00366, 2018.

Pacyna, J. M., Travnikov, O., De Simone, F., Hedgecock, I. M., Sundseth, K., Pacyna, E. G., Steenhuisen, F., Pirrone, N., Munthe, J., and Kindbom, K.: Current and future levels of mercury atmospheric pollution on a global scale, Atmos. Chem. Phys., 16, 12495-12511, 10.5194/acp-16-12495-2016, 2016.

Tang, Y., Wang, S. X., Wu, Q. R., Liu, K. Y., Wang, L., Li, S., Gao, W., Zhang, L., Zheng, H. T., Li, Z. J., and Hao, J. M.: Recent decrease trend of atmospheric mercury concentrations in East China: the influence of anthropogenic emissions, Atmospheric Chemistry and Physics, 18, 8279-8291, 10.5194/acp-18-8279-2018, 2018.

Wan, Q., Feng, X. B., Lu, J. L., Zheng, W., Song, X. J., Han, S. J., and Xu, H.: Atmospheric mercury in Changbai Mountain area, northeastern China I. The seasonal distribution pattern of total gaseous mercury and its potential sources, Environmental Research, 109, 201-206, 10.1016/j.envres.2008.12.001, 2009.

Wang, X., Lin, C.-J., Yuan, W., Sommar, J., Zhu, W., and Feng, X.: Emission-dominated gas exchange of elemental mercury vapor over natural surfaces in China, Atmospheric Chemistry and Physics, 16, 11125-11143, 10.5194/acp-16-11125-2016, 2016.

Wu, Q., Wang, S., Li, G., Liang, S., Lin, C.-J., Wang, Y., Cai, S., Liu, K., and Hao, J.: Temporal Trend and Spatial Distribution of Speciated Atmospheric Mercury Emissions in China During 1978–2014, Environmental science & technology, 50, 13428-13435, 10.1021/acs.est.6b04308, 2016.

Zhang, L., Wang, S. X., Wang, L., and Hao, J. M.: Atmospheric mercury concentration and chemical speciation at a rural site in Beijing, China: implications of mercury emission sources, Atmospheric Chemistry and Physics, 13, 10505-10516, 10.5194/acp-13-10505-2013, 2013.

Zhu, J., Wang, T., Talbot, R., Mao, H., Hall, C. B., Yang, X., Fu, C., Zhuang, B., Li, S., Han, Y., and Huang, X.: Characteristics of atmospheric Total Gaseous Mercury (TGM) observed in urban Nanjing, China, Atmospheric Chemistry and Physics, 12, 12103-12118, 10.5194/acp-12-12103-2012, 2012.

Zhu, J., Wang, T., Talbot, R., Mao, H., Yang, X., Fu, C., Sun, J., Zhuang, B., Li, S., Han, Y., and Xie, M.: Characteristics of atmospheric mercury deposition and size-fractionated particulate mercury in urban Nanjing, China, Atmospheric Chemistry and Physics, 14, 2233-2244, 10.5194/acp-14-2233-2014, 2014.

Zhu, J., Wang, T., Bieser, J., and Matthias, V.: Source attribution and process analysis for atmospheric mercury in eastern China simulated by CMAQ-Hg, Atmos. Chem. Phys., 15, 8767-8779, 10.5194/acp-15-8767-2015, 2015.

Xu, L. L., Chen, J. S., Yang, L. M., Niu, Z. C., Tong, L., Yin, L. Q., and Chen, Y. T.: Characteristics and sources of atmospheric mercury speciation in a coastal city, Xiamen, China, Chemosphere, 119, 530-539, 10.1016/j.chemosphere.2014.07.024, 2015.

Xu, X., Liao, Y., Cheng, I., and Zhang, L.: Potential sources and processes affecting speciated atmospheric mercury at Kejimkujik National Park, Canada: comparison of receptor models and data treatment methods, Atmospheric Chemistry and Physics, 17, 1381-1400, 10.5194/acp-17-1381-2017, 2017.