Response to reviewer's comments

Anonymous Referee #2:

Major comments:

This study has analyzed data from multiyear measurements of the gaseous elemental mercury (GEM) concentration at a regional background site in eastern China and quantified the contribution of natural surface emission to GEM using the positive matrix factorization (PMF) model. The long-term observation data are valuable and the topic is of broad interests.

My major concern is the robustness of the PMF results. To what extent should we believe these results? The results need further verification. Figure 5 is one of the most important yields from this study. Suppose Figure 5 is basically correct, we can draw some important conclusions from this figure:

(1) Although cement production is believed to be one of the most important emission sources in China, it seems to contribute very little to GEM at this site. Could this be true?

(2) The current Hg emission inventories haven't considered ship emissions, but this emission source should be considered in the Hg emission inventory development, especially for coastal areas. This could be a very important finding if it is true.

(3) Iron and steel production has a large contribution to GEM concentration as well. Is this site under the influence of many large iron and steel plants (e.g., Baogang)?

If the contributions from different anthropogenic sources could be verified to some extent, it would be much easier for the readers to believe the contribution from natural sources. One possible approach for the verification that I can think of is to use the PSCF model to identify the potential GEM source regions from 2015 to 2018. If the key source regions for the monitoring site are consistent with the above conclusions (e.g., do not have many cement plants; have potential ship emissions from the seas or the rivers; have many iron and steel production activities; etc.), the robustness of the PMF model could be verified.

Overall, I think this manuscript is worth publishing on Atmospheric Chemistry and Physics after major revision.

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.

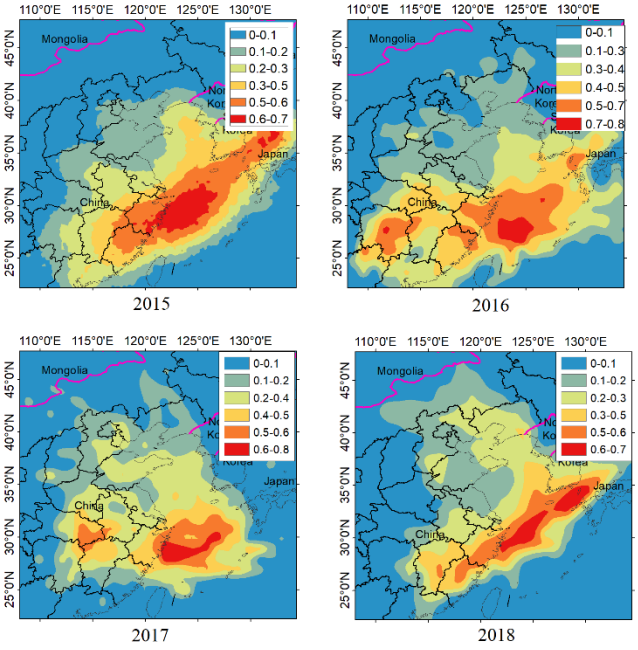
Specific comments:

1. Although cement production is believed to be one of the most important emission sources in China, it seems to contribute very little to GEM at this site. Could this be true?

Response: We agree with the reviewer that cement production is one of the most important mercury sources in China. According to the emission inventories, the annual GEM emission from cement production in the YRD region is around 2.3 tons/year, accounting for about 13% of its total anthropogenic emissions (Tang et al., 2018). By considering the natural sources of GEM (Zhu et al., 2016), the contribution of cement production to total GEM emissions should be lower than 13%. In this study, the seasonal contribution of cement production to the ambient GEM was estimated to be in the range of 2% - 10% at the study site. Hence, the PMF modeling results were generally consistent with the emission inventories.

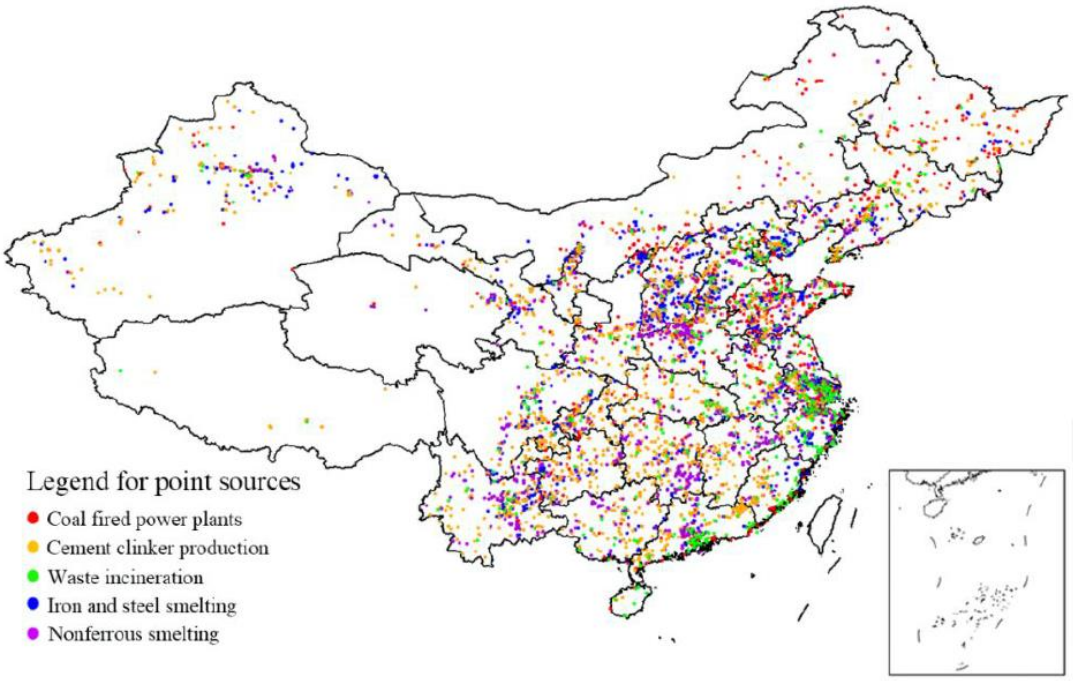
2. The current Hg emission inventories haven't considered ship emissions, but this emission source should be considered in the Hg emission inventory development, especially for coastal areas. This could be a very important finding if it is true.

Response: Thanks for the comment. Shipping emissions are indeed important sources of air pollutants for the coastal areas, especially the East China Sea (Liu et al., 2017;Fan et al., 2016). However, as current Hg emission inventories haven't considered ship emissions as the reviewer mentioned, it is hard to verify the results of this study against the emission source data.
Instead, we plotted the PSCF maps of GEM contributed from shipping emissions extracted from the PMF modeling results as shown in the figure below. The results showed strong PSCF signals from the coastal and oceanic areas, indicating the shipping factor resolved in this study is valid. Again, this should be verified when shipping mercury emission inventory is available in the future.



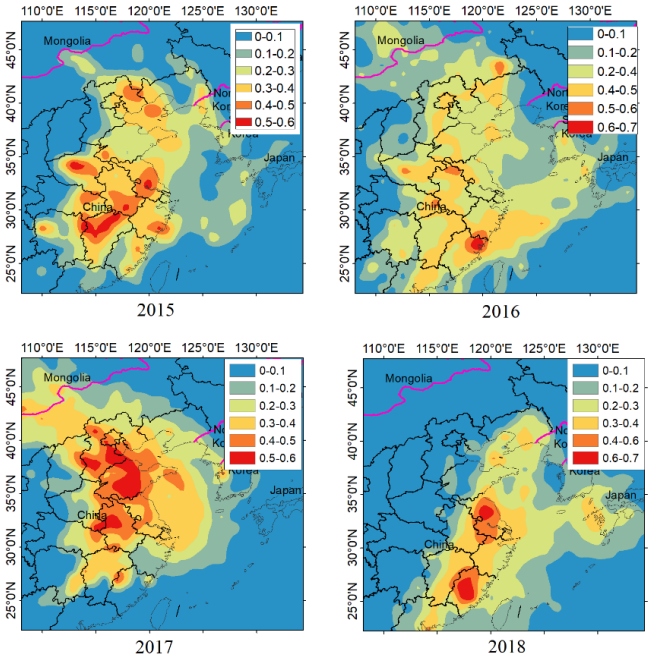
3. Iron and steel production has a large contribution to GEM concentration as well. Is this site under the influence of many large iron and steel plants (e.g., Baogang)?

Response: The figure below exhibit the geographical distribution of point sources in 2017 in China (Liu et al., 2019), which show that there are indeed many large iron and steel sites around our site (e.g., Baogang, Nangang, and Hanggang). According to the recent emission inventories, the contribution of iron and steel production accounts for about 7% of total anthropogenic GEM emissions (Tang et al., 2018). The seasonal contribution of iron and steel production to GEM ranged from 1% to 17% from 2015 to 2018 according to the PMF results. We believe that this site is under the influence of many large iron and steel plants.

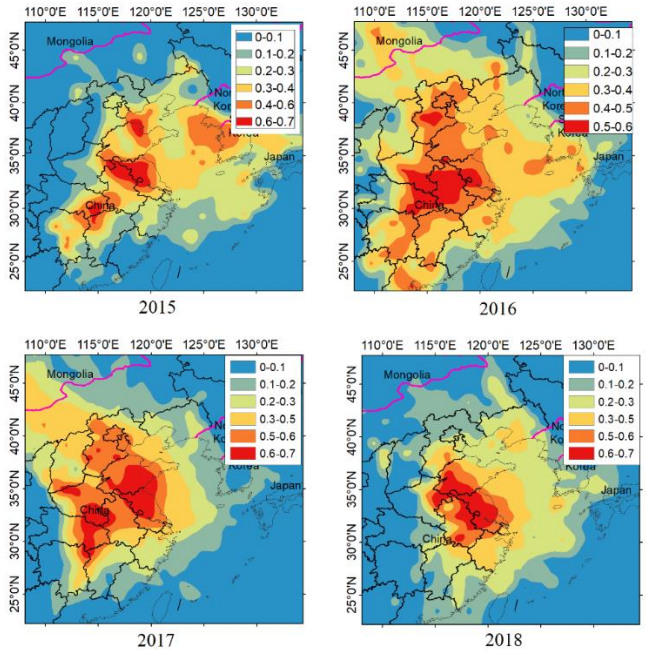


4. One possible approach for the verification that I can think of is to use the PSCF model to identify the potential GEM source regions from 2015 to 2018. If the key source regions for the monitoring site are consistent with the above conclusions (e.g., do not have many cement plants; have potential ship emissions from the seas or the rivers; have many iron and steel production activities; etc.), the robustness of the PMF model could be verified.

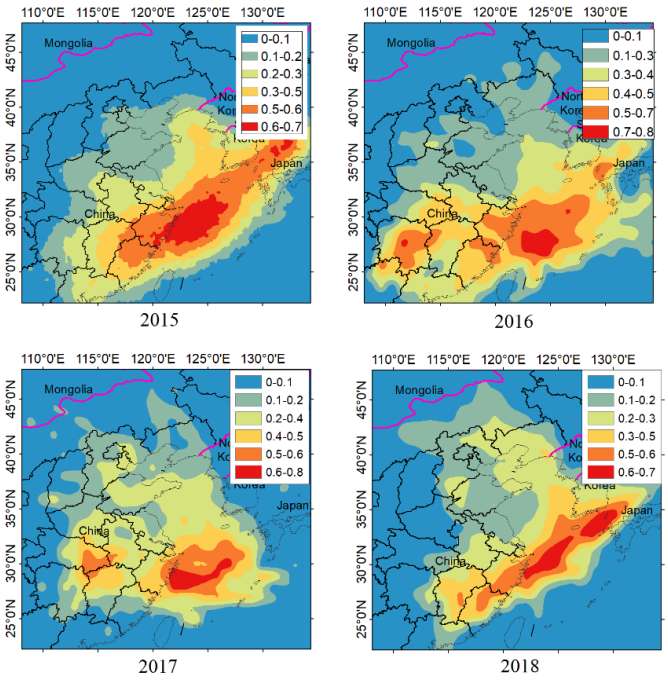
Response: According to the reviewer's suggestion, we have identified the potential source regions of the PMF modeled GEM from cement production, iron and steel production, and shipping activities during 2015 - 2018, respectively. As shown in the figures below, the PSCF signals of GEM from cement production in the YRD region are relatively weak, while there are substantial high PSCF signals for iron and steel production GEM in Eastern China. As for GEM from the shipping sector, most high PSCF signals are from the coastal and oceanic areas. These results suggest that the PMF results in this study are credible.



Potential source regions of GEM from cement production during 2015 - 2018



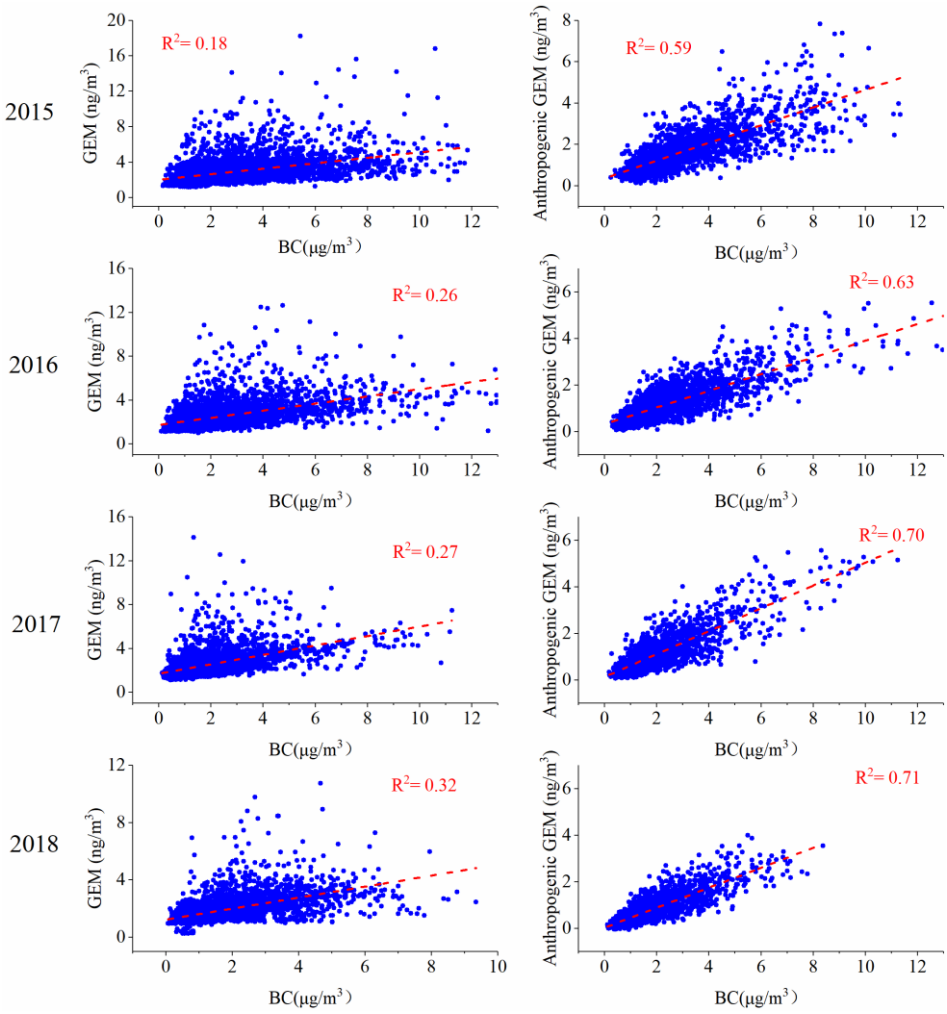
Potential source regions of GEM from iron and steel production during 2015 - 2018



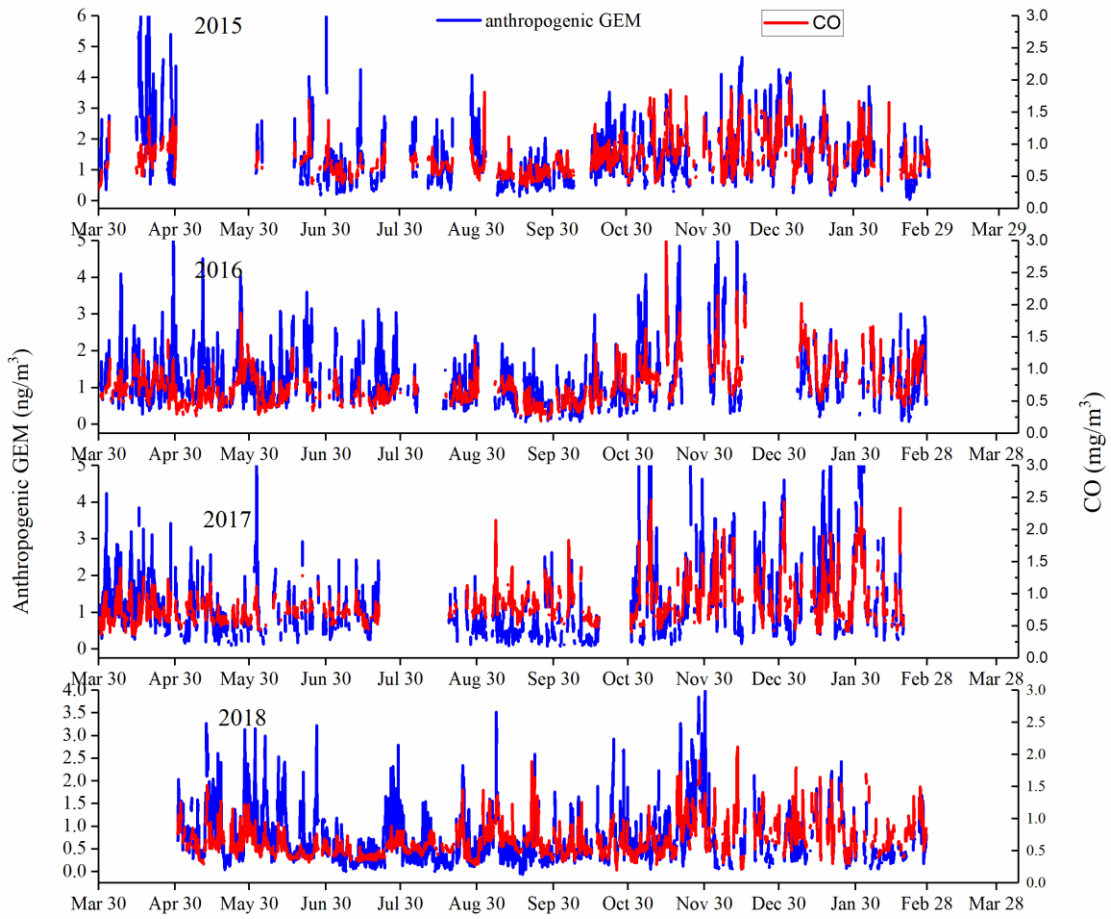
Potential source regions of GEM from shipping activities during 2015 - 2018

As Reviewer#1 also raised similar concerns, we added additional analysis about the verification of PMF results as below.

We verified whether the separation of natural and anthropogenic GEM was credible or not, which is also the main focus of this study. To achieve this, the relationship between particulate black carbon (BC) and GEM concentrations was investigated. On the one hand, BC mainly derives from various combustion processes, which are also the main anthropogenic sources of atmospheric mercury. On the other hand, BC was never introduced into the PMF modeling. As shown in the figure below, the observed total GEM concentrations and BC concentrations only showed weak correlations. This was mainly due to the fact that besides anthropogenic sources, natural sources also contributed significantly to GEM. As a comparison, anthropogenic GEM concentrations (extracted from PMF results) showed much stronger correlations with BC from 2015 to 2018. In addition, the time series of anthropogenic GEM concentrations generally varied consistently with CO (shown in the figure below), which is also a tracer of fuel combustion. This suggests that the PMF results are credible and the separation of anthropogenic and natural GEM has been successfully achieved.

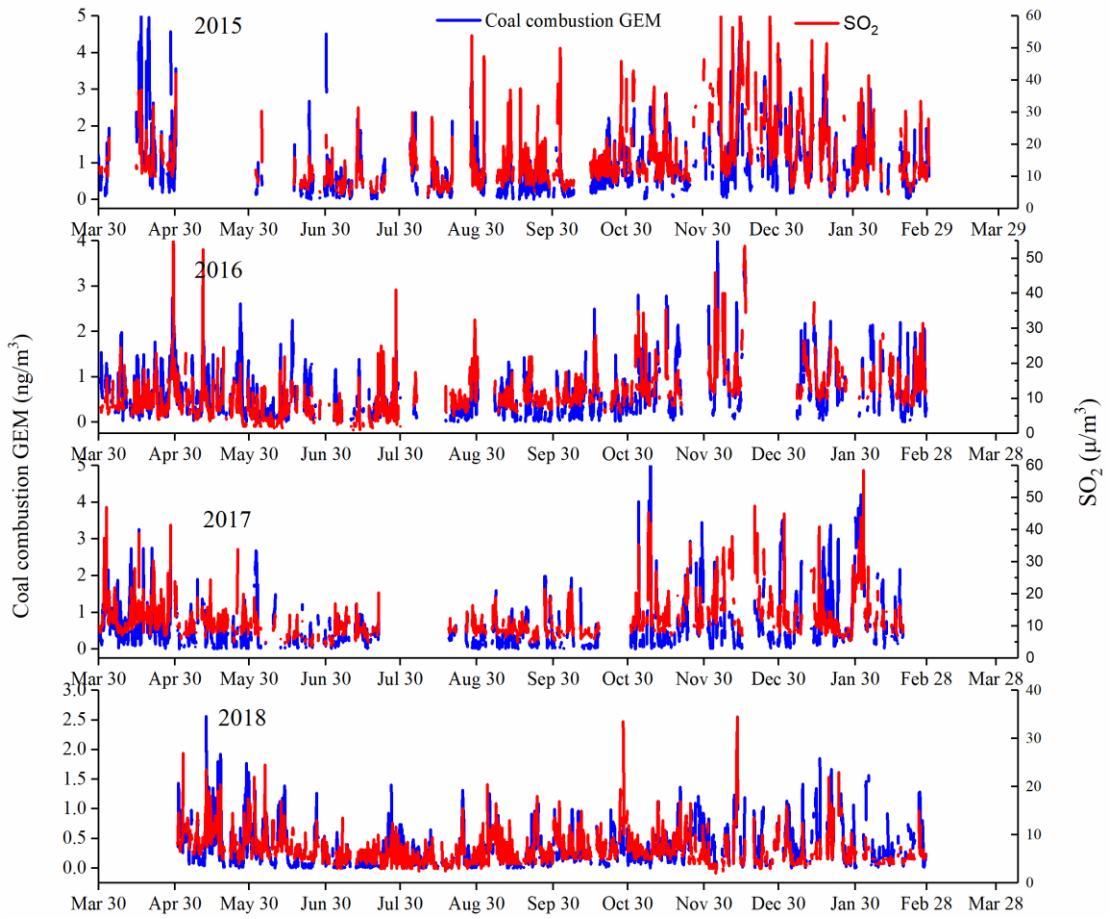


The relationship between observed GEM and BC, anthropogenic GEM (extracted from PMF results) and BC during 2015 – 2018



Time series of anthropogenic GEM and CO concentrations

Furthermore, as shown in the figure below, we examine the time series of coal combustion GEM (extracted from PMF results) and observed SO_2 from 2015 to 2018. It is found that the trend of coal combustion GEM is basically consistent with that of SO_2, which indicates that the coal combustion factor resolved by PMF is credible.



Time series of coal combustion GEM and SO_2 concentrations

In the revised manuscript, we have added a paragraph about the verification of PMF results as below.

"In addition, the relationship between particulate black carbon (BC) and GEM concentration was investigated. On the one hand, BC mainly derived from various combustion processes, which were also the main anthropogenic sources of atmospheric mercury. On the other hand, BC was never introduced into the PMF modeling. As shown in Figure 5, the observed total GEM and BC concentrations only showed weak correlations. This was mainly due to the fact that besides anthropogenic sources, natural sources also contributed significantly to GEM. As a comparison, anthropogenic GEM concentrations (extracted from PMF results) showed much better correlations with BC from 2015 to 2018. In addition, the time-series of anthropogenic

GEM concentrations generally varied consistently with CO, which was also a tracer of fuel combustion (Figure S28). All the evidences above corroborated that by using temperature and NH_3 as tracers for PMF modeling, the separation of anthropogenic and natural GEM can be successfully achieved.

As for the specific anthropogenic mercury sources extracted from PMF results, Figure S29 shows that the time-series of coal combustion GEM also varied consistently with SO_2, indicating that the coal combustion factor resolved by PMF was credible. As shown in Figure S30, the potential source regions of shipping GEM were found mainly over coastal and oceanic areas, indicating the shipping factor resolved in this study was also valid. Figure S31 and Figure S32 show that the PSCF signals of cement production GEM were relatively weak in the YRD region, while there were substantial high PSCF signals for iron and steel production GEM in Eastern China. All the results above collectively confirmed that the PMF results were robust.“

5. Lines 47–48: It should be “non-ferrous metal smelters” instead of “non-ferrous smelters”.

Response: The statement “non-ferrous smelters” has been change as “non-ferrous metal smelters” in the revision.

6. Section 2.2: How many valid GEM data were included in the analysis?

Response: The sentence “In this study, the number of valid GEM data was 16266” has been added in the revision.

7. Lines 195–196: This statement is not accurate and lacks evidence. Some of the anthropogenic emission sources vary significantly from season to season. For example, coal combustion for residential use has a much higher level in winter.

Response: Thanks for pointing out this inaccurate statement. the sentence “Considering that seasonal variations of anthropogenic emission are minimum” has been revised as “Considering that the anthropogenic emissions were less temperature dependent, the different seasonal decreasing rates of GEM between the warm and cold seasons should be mostly caused by the seasonal-dependent emission amounts from natural sources” in the revision.

8. Lines 208–209: The p values for all the correlations should be given here.

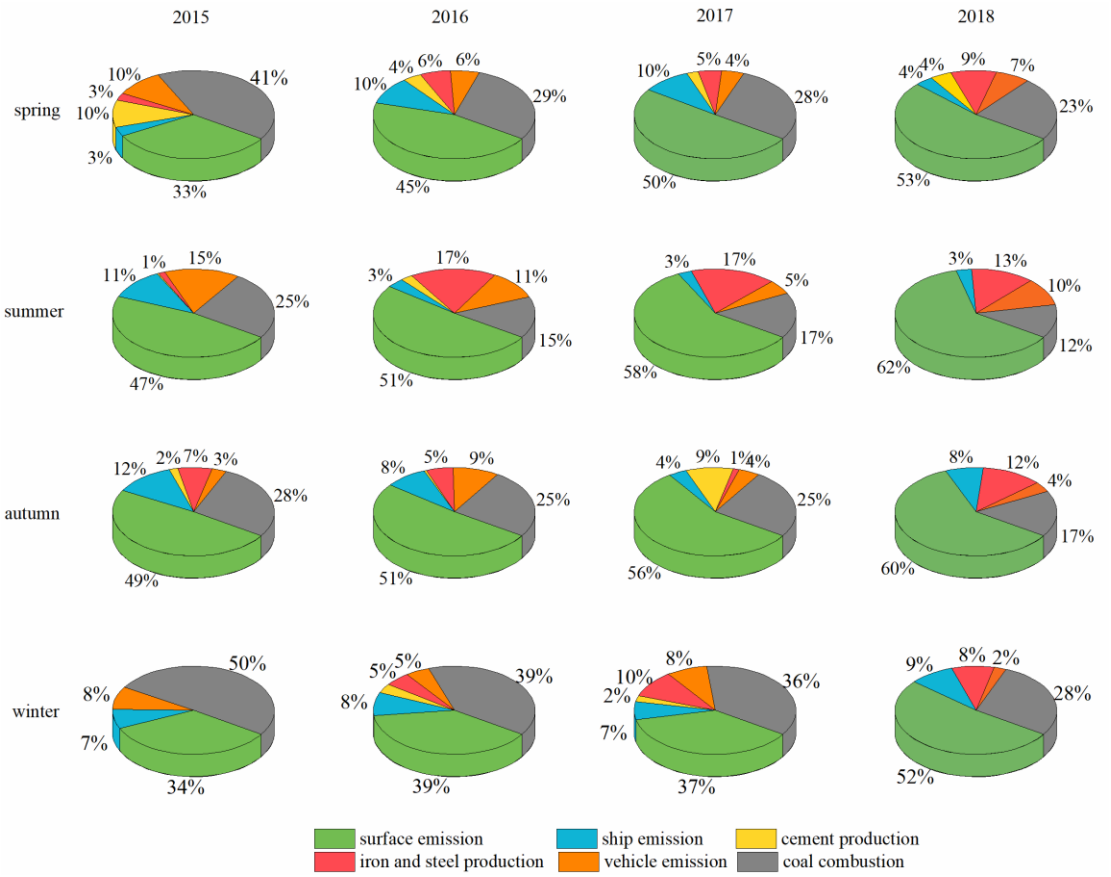
Response: The p values for all the correlations have been added in the revision.

9. Have the authors investigated the correlations between GEM and solar radiation? Solar radiation and temperature could have collinearity to a certain extent. It is possible that the diurnal GEM trend has a more significant correlation with solar radiation. Solar radiation is related to the photoreduction process of Hg in soil, which could be the major natural GEM source in the study area.

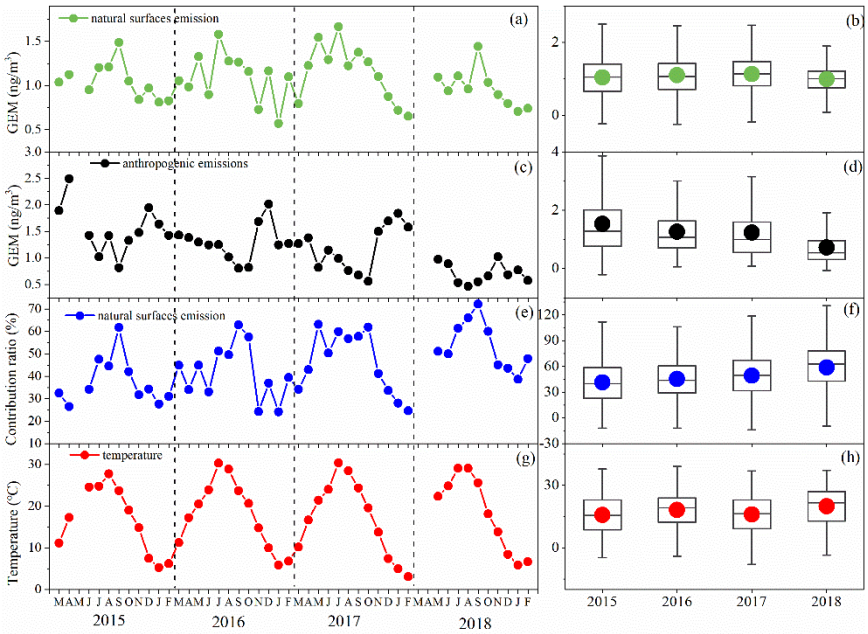
Response: Thanks for this valuable suggestion. We quite agree with the reviewer that solar radiation is a key factor of the photoreduction process of Hg in soil and the diurnal GEM trend likely has a significant correlation with solar radiation. However, due to that solar radiation was not measured in this study, we cannot carry out the corresponding analysis. We will certainly consider the investigation of the relationship between GEM and solar radiation in the future field experiments.

10. Lines 241–245: The choices of NH3 and O_3 as tracers should be more carefully examined. These two tracers are not directly linked to natural emission sources, but indirectly through temperature. If temperature is already chosen as a tracer for PMF and NH3 and O_3 are only linked to natural sources through temperature, what is the point of choosing NH3 and O_3? The authors should pay attention to the other links between NH_3/O_3 and natural sources. Say the links through solar radiation, land surface type, and so on. Moreover, the PMF method usually chooses primary air pollutants as tracers, e.g., VOC species profiles, ions on particles, heavy metal profiles, etc. Secondary air pollutants, such as O_3, are usually avoided to be used as a tracer for PMF, because all the coefficients resulting from the PMF model need to be positive while it is not always the case for secondary air pollutants like O_3, not to mention that O_3 and GEM are potentially not independent variables. O_3 might act as an oxidizer for GEM under certain conditions (e.g., high humidity), although this mechanism is not clear so far. Therefore, the authors should either remove O_3 as a tracer or explain why in this case O_3 is applicable from PMF.

Response: After considering the reviewer's insightful suggestion, we agree that O_3 is not suitable as the tracer of natural emission and shouldn't be used as a tracer for PMF modeling. Hence, we have removed O_3 and re-run the PMF model for the whole multi-year dataset. The new modeling results are shown in the following figures. We found that after the removal of O_3, the contributions of natural and anthropogenic sources to GEM from 2015 to 2018 didn't change much, hence the major conclusion hasn't been affected. In general, the contributions of natural sources to GEM increased slightly. For example, before removing O_3, the relative contribution of natural surface emissions to GEM increase from 36% in 2015 to 53% in 2018. After removing O_3, its contribution increases from 41% in 2015 to 57% in 2018. In the revision, we replace Figure 5 and Figure 6 with the following two figures, and modified the corresponding specific contribution values.



Contributions of natural surface emissions and anthropogenic sources to atmospheric GEM in the four seasons during 2015 – 2018.



The monthly and annual GEM concentrations contributed by natural surface emissions (a-b) and anthropogenic emissions (c-d) from 2015 to 2018. (e-f) The monthly and annual contribution of natural surface emissions to GEM concentrations from 2015 to 2018. (g-h) The corresponding ambient temperature from 2015 to 2018.

References:

Fan, Q., Zhang, Y., Ma, W., Ma, H., Feng, J., Yu, Q., Yang, X., Ng, S. K. W., Fu, Q., and Chen, L.: Spatial and Seasonal Dynamics of Ship Emissions over the Yangtze River Delta and East China Sea and Their Potential Environmental Influence, Environmental science & technology, 50, 1322-1329, 10.1021/acs.est.5b03965, 2016.

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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.

Zhu, W., Lin, C.-J., Wang, X., Sommar, J., Fu, X., and Feng, X.: Global observations and modeling of atmosphere–surface exchange of elemental mercury: a critical review, Atmospheric Chemistry and Physics, 16, 4451-4480, 10.5194/acp-16-4451-2016, 2016.