Response to reviewer's comments

Anonymous Referee #1:

Major comments:

The manuscript entitled "Assessing contributions of natural surface and anthropogenic emissions to atmospheric mercury in a fast developing region of Eastern China from 2015 to 2018", investigated the temporal variations of GEM, and developed a receptor model based method to quantify the contribution of natural surface mercury emission. The quantification of emission sources are significant to understand global mercury cycle. The development of the receptor model is one significant output of this study. However, the approach and the results is doubtful.

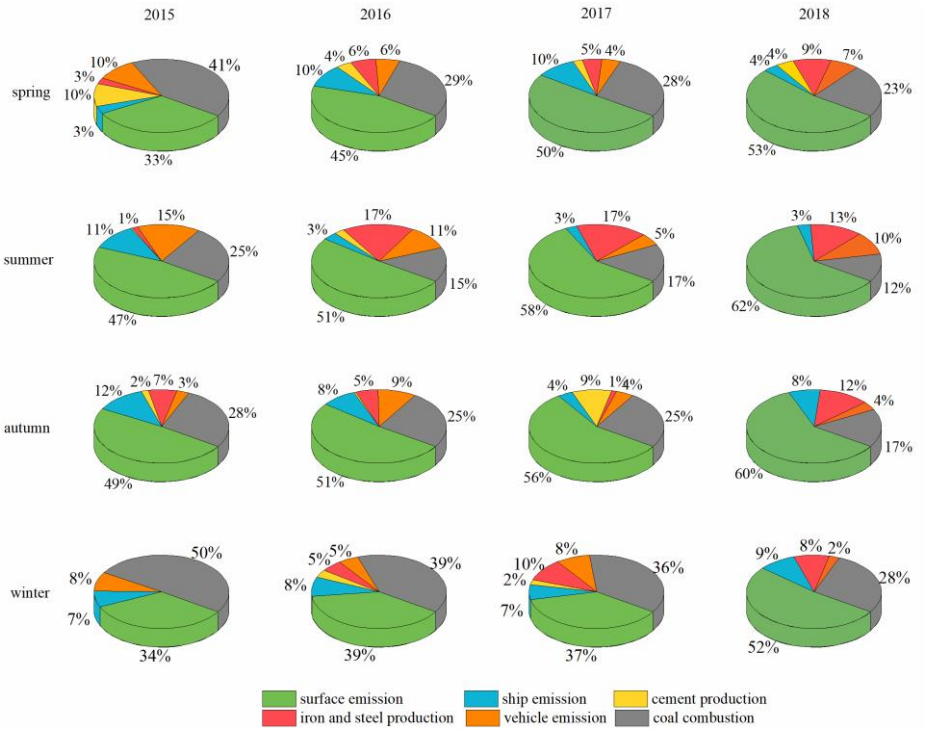
We sincerely thank for the reviewer's in-depth comments and helpful suggestions on this manuscript. Based on the specific comments, we have responded to all the comments point-by-point and made corresponding changes in the manuscript as highlighted in red color. The reviewer has raised a number of issues 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:

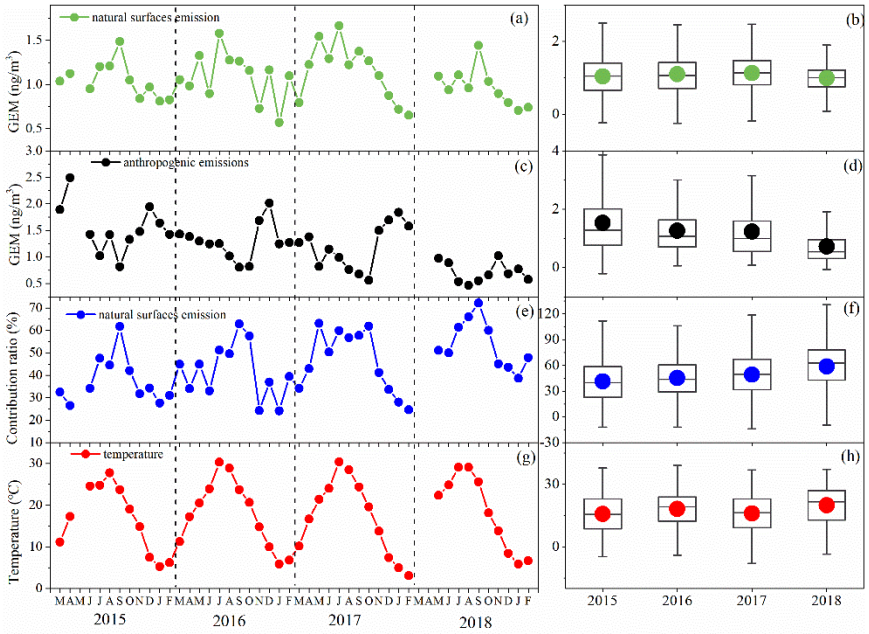
1. It is true that when temperature increase, we can observe high GEM and NH_3 emissions from natural sources. O_3 is a typical secondary pollutant formed from VOCs and NOx, which mainly originates from photochemical reactions of anthropogenic pollutants and is impacted by temperature. The increase of temperature can also promote the generation of O_3 as well. But the simultaneous changes of these three are not entirely the contribution of natural source emissions. Take a simple example. Both NH_3 and mercury can participate between gas and particle. The increase of temperature will promote the generation of both NH3 and GEM. In addition, high temperature in summer generally promote the generation of O_3. Thus, the simultaneous increase of NH_3, O_3, and GEM may occur due to atmospheric reaction process. Therefore, using O_3 and NH_3 as tracers of the natural emission of GEM will introduce a relative large uncertainty. The problem is that we do know how large the uncertainty will be, because we cannot exhaust this kind of examples considering the variable sources and generation pathways of these three air pollutants and the complicated impact from temperature

Response: Thanks a lot for the reviewer's insightful suggestion. We agree that O_3 is not suitable as the tracer of natural emission as it is a typical secondary pollutant 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.

2. The results are also confusing. The author stated that "As for the other resolved factors, ... of Pb and SO_4^{2-}" (Line 255-261). The explanation of the factors is too arbitrary and lacks enough support.

Response: We agree with the reviewer that the explanation of the factors is not sufficient. In the revision, we revised the sentences as " As for the other resolved factors, the factor with high loadings of V and Ni evidently represented shipping emissions, because Ni and V have been considered as typical tracers of heavy oil combustion which has been commonly used in marine vessels (Viana et al., 2009). The factor with high loading of Ca was assigned to cement production as the raw materials used in cement production contain a large amount of calcium compounds. Moderate loadings of multiple species including Cr, Mn, and Fe were found in one factor which was identified as iron and steel production. The factor with high loading of NO was identified as vehicle emissions, as the major source of NOx in the YRD region is mobile oil combustion (Tang et al., 2018). And the last factor was identified as coal combustion due to the high loadings of As and Se, and moderate contributions from Pb and SO_4^{2-}. As, Se, and Pb were all typical tracers of coal combustion and the precursor of SO_4^{2-} (i.e. SO_2) also mainly derived from coal combustion."

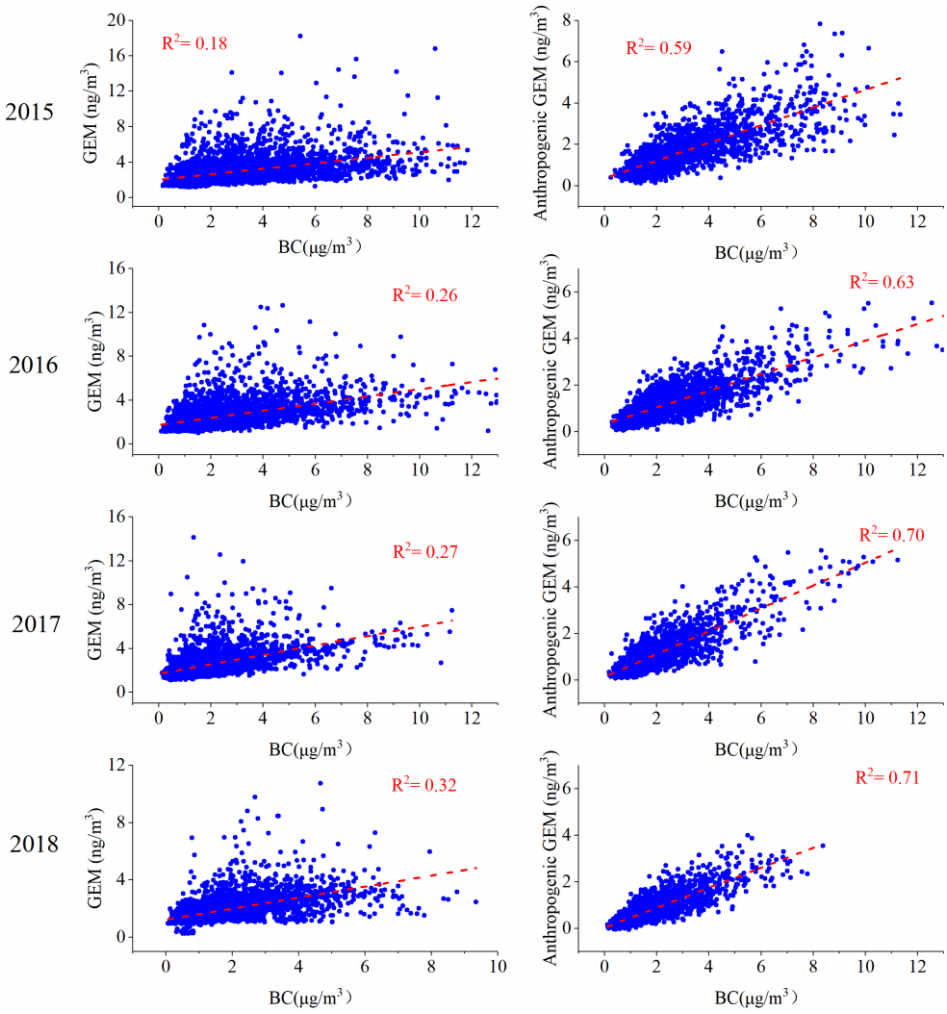
3. For example, the authors pointed out that the factor with high loadings of Ca was assigned to cement production. However, there are several anthropogenic Ca emission sources if the authors investigated the heavy metal emission inventory, such as the ferrous metal smelting. Ferrous metal smelting is also one significant emission sources around Shanghai. From this aspect, the anthropogenic sources resolved by using the developed model cannot be supported by the emission inventory.

Response: Thanks for the comment. According to the emissions inventories of China, non-ferrous metals smelting plants are mainly concentrated in Hunan, Yunnan, and Henan provinces (Liu et al., 2019). Hg emissions from non-ferrous metals smelting gradually decreased since 2004 in China, benefitting from the elimination of small-scale smelters and stringent SO_2 emission control measures (Wu et al., 2016). As for the YRD region, the recent emissions inventories show that the main emission sectors of GEM include coal-fired power plants, coal-fired industrial boilers, residential coal combustion, cement clinker production, iron and steel production, and mobile oil combustion, but very little from non-ferrous metal smelting (Tang et al., 2018). 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.

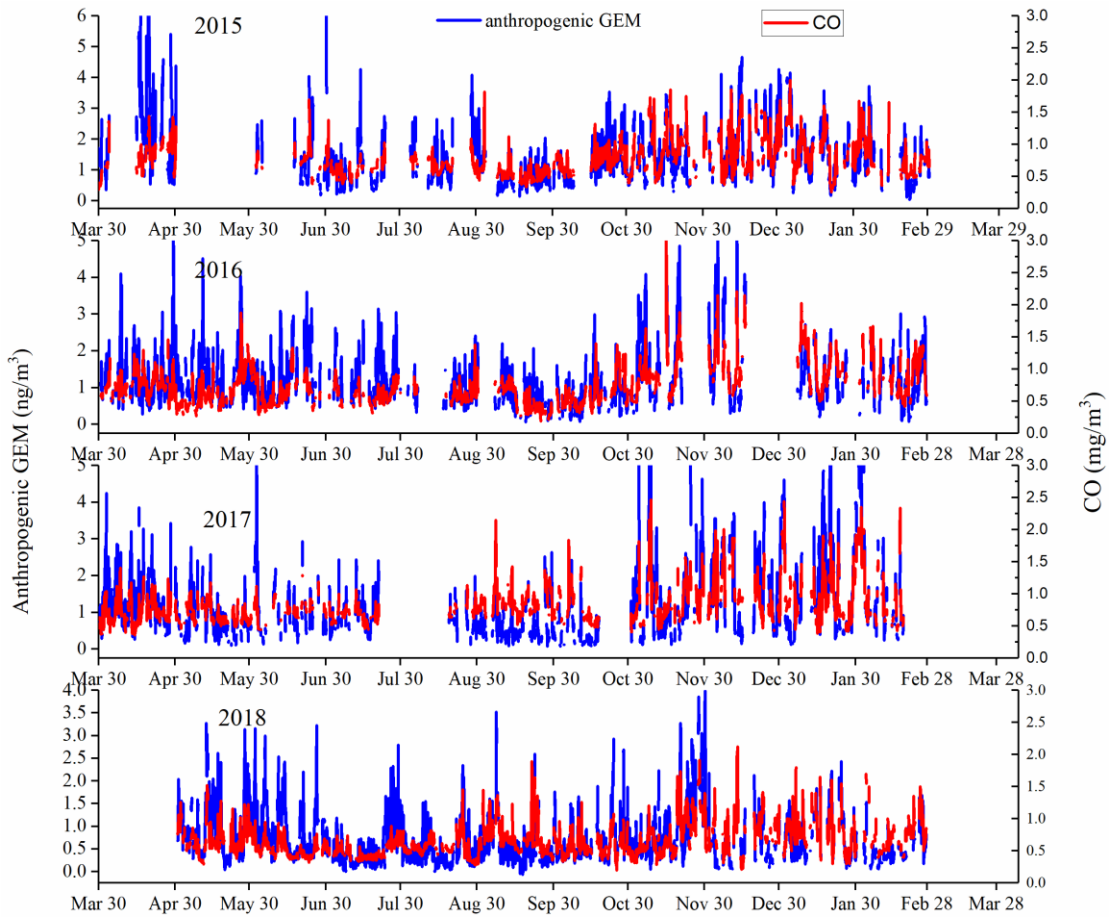
4. Due to the question of current receptor model and their definition of different factors, I think the authors need to carefully verify their results or use other source resolution methods to determine the sources.

Response: Thanks for the comments and we do agree with the reviewer that the results should be carefully verified. In this regard, we have conducted more analysis to verify the results of PMF model from several aspects.

First, we verified whether the separation of natural and anthropogenic GEM was credible or not, which was 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 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 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.

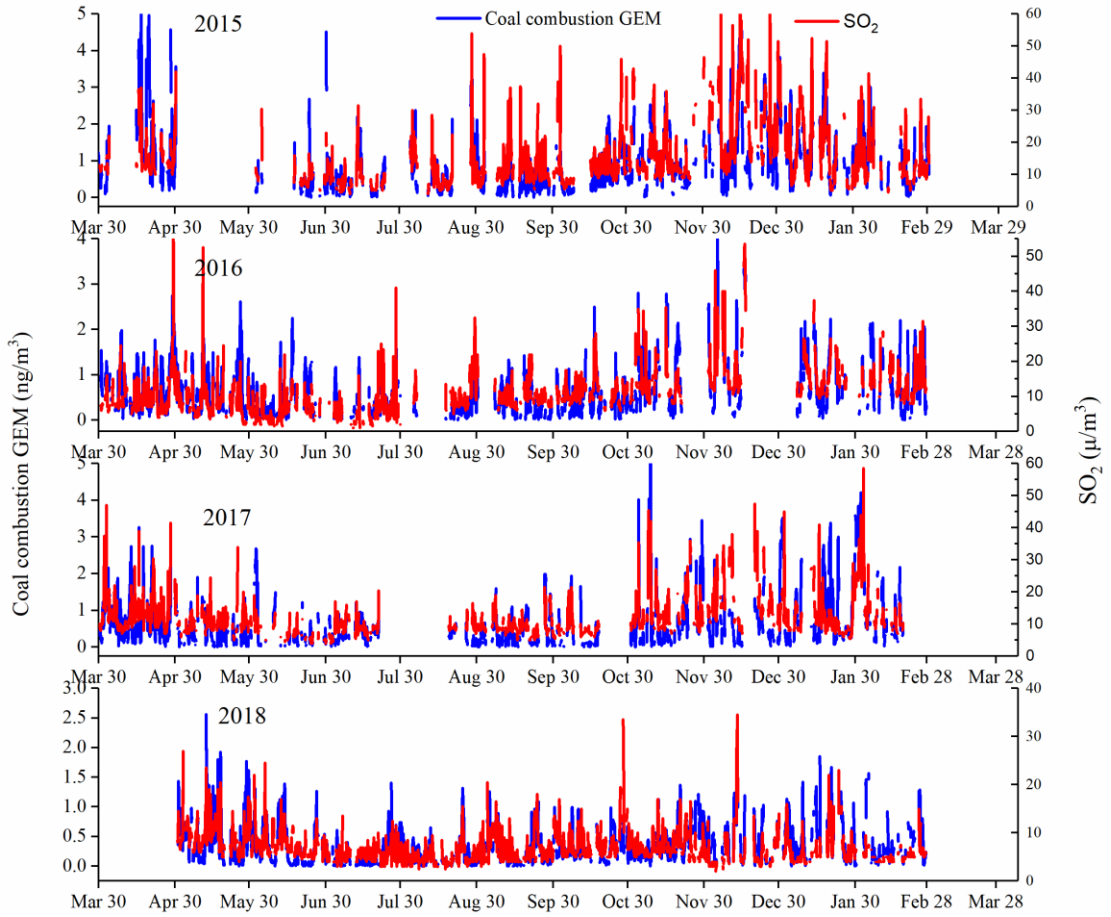


The relationship between observed GEM and BC, anthropogenic GEM (extracted from PMF results) and BC during 2015 – 2018



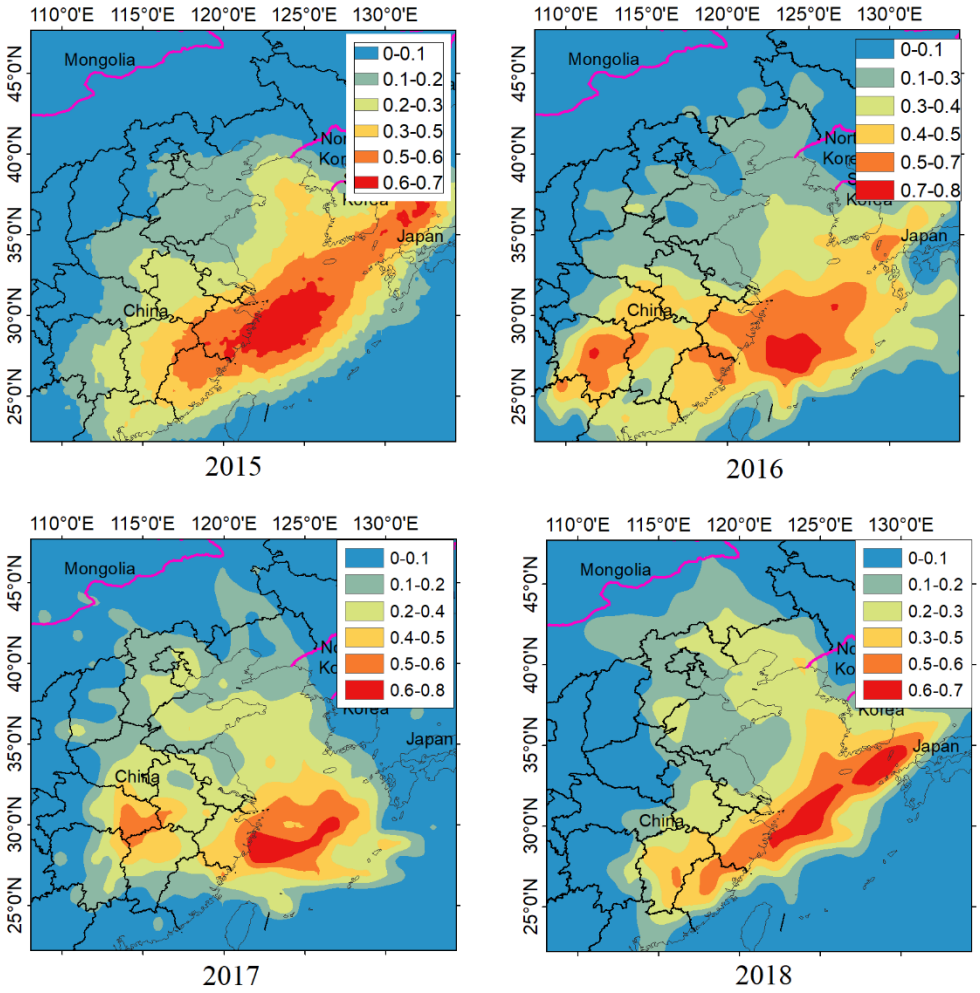
Time series of anthropogenic GEM and CO concentrations

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

To verify the resolved shipping emission factor from PMF modeling, we using the PSCF model to identify the potential source regions of the shipping GEM (extracted from PMF results) from 2015 to 2018. As shown in the figures below, the potential source regions are mainly located over coastal and oceanic areas, which suggests that the shipping factor resolved by PMF is credible.



Potential source regions of shipping GEM from 2015 to 2018

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.“

References:

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