Response to Reviewer #1's Comments

Anonymous Referee #1:

This manuscript presents a year of continuous measurements of atmospheric Hg species at a suburban site in eastern China, which is an important anthropogenic Hg source region in China. This study combines the analysis of speciated Hg concentrations, local meteorology, receptor-based modelling, PMF and specific event, showing the sources and transformations of atmospheric Hg.

Major comments:

The authors discussed the impact of local emissions and long-range transport of Hg on observed atmospheric Hg. The analysis, however, do not generate a conclusion that which of these two processes were the dominant sources of the observations, and some of the conclusions from the analysis are contradictory to each other at times. The analysis of using PSCF model neglect the local meteorology. For example, when there is a shallow boundary layer formed at the sampling site, an analysis of long range transport could be not suitable because local to regional are more important in this case. This manuscript seems not have a clear motivating hypothesis. The authors made a brief introduction of Hg emissions in East Asia, but have not summarized the findings of many previous studies conducted in this region or in East Asia. They also have not addressed the scientific gaps existing after many previous studies in this region. Therefor, it is not clear to what extent that this study could contribute to the science. The descriptions of the materials and methods section are not clear. The collection of GOM and PBM at 2-hour interval indicates a GOM or PBM concentration could be obtained every 3 hours (1 hour thermal desorption and detection is needed after collection). This does not match the backward trajectories simulated every two hours. The operations of the speciated Tekran system did not followed the standard method very well. For example, a replacement of filter at a monthly interval is too longer under heavily PM pollution conditions. The calculation of backward trajectory is not clear. What is the arrival height used for the calculation of backward trajectories? What is the threshold concentrations of speciated atmospheric Hg and the reasons of the selection of the thresholds.

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 26-27: a conclusion of impact of the long-range transport and local emissions on observations is meaningless. All observations could be impacted by local and long-range sources.

Response: We agree with the reviewer that this sentence is redundant. This statement has been revised as "An application of the GOM/PBM tracer method and trajectory-based source region identification distinguished the relative importance of long-range transport from northern China and quasi-local emission sources on the magnitudes of Hg species." in the revision.

2. Line 46 and 48: the citations of references are not correct. Please check the similar errors throughout the manuscript.

Response: Thanks for pointing out this. The references have been checked throughout the manuscript.

3. Line 53: as for the anthropogenic mercury?

Response: The sentence has been revised as "As for the anthropogenic emission sources of mercury, coal combustion, non-ferrous smelters, cement production, waste incineration, and mining are considered to be the main sources." in the revision.

4. Line 71-72: are you sure that atmospheric transformations such as redox reactions could not impact atmospheric GEM. There are many evidences that transformations including oxidation of GEM and foliar uptake of GEM could significantly affect GEM observations.

Response: We agree with the reviewer that the redox reactions can indeed significantly affect GEM observations and our statement was not appropriate. we have revised the original sentence as "Generally, the levels of GEM could be affected by various emission sources, redox reactions, and foliar uptake, while the GOM species from the GEM oxidation and subsequent formation of PBM by adsorption on the particulate matters can significantly affect their ambient concentrations, especially in regions with high GEM levels." in the revision.

5. Line 75-85: a detailed introduction of previous studies in eastern China should be added here. You should also introduce the progress of atmospheric Hg observations and point out the remaining questions regarding sources and transformation in this region.

Response: Thanks for the suggestion. A detailed introduction of previous studies has been added in the revision. "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). One 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 with a contribution of 36.6% were the most important source for GEM in eastern China (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 contributions to atmospheric mercury in the suburbs of East China and the formation and transformation processes among Hg species in the atmosphere are still lacking."

6. Section 2.1: the authors declare that there is no large point sources within 20 km of the sampling site. This seems not correct. From the Chinese inventory and global inventory, I can calculate the total GEM emission reaches more than 10 tons within 0.4°×04° grid of the site (corresponding to a 20 Km cycle around the site). For such a strong local emission, is it suitable to use PSCF modelling to study the long-range transport. How could you separate the local emissions from long-range transport signals?

Response: Thank for the reviewer's carefully check on the emissions around the sampling site. Based on a mercury emission inventory of China in 2014 (Wu et al., 2016), the total GEM emission in Shanghai was approximately 5 tons/yr. Since our sampling site is located in Shanghai, it seems unlikely that the GEM emission within a 0.4°×04° grid of the site can reach more than 10 tons, even higher than the total of Shanghai. To clarify this, we checked the EDGAR (Emissions Database for Global Atmospheric Research) global emission inventory (http://edgar.jrc.ec.europa.eu/overview.php?v=4tox2), which included a variety of emission sectors as shown in the table below. We also selected a 0.4°×04° grid of the site as shown in the figure below. The latest year of the EDGAR mercury emission dataset is 2012.

It is calculated that the total GEM emissions in this grid box is about 105kg/yr, of which power industry and cement production are the major contributors. In this regard, the emissions around the sampling site is not significant.

The sampling site is located beside Dianshan Lake as seen in the photos below. No strong point sources and high buildings are around the site and could be regarded as an ideal suburban site in the YRD region.

Sector	Emissions (kg/yr)
Cement	28.49
Power-industry	53.87
Residential	10.05
Glass	0.03
Transportation	3.67
Waste	9.38
Total	105.49

7. Section 2.4: you should show the arrival heights of the backward trajectories and the threshold concentrations.

Response: Thanks for the suggestion. The last paragraph in Section 2.4 has been revised as "In this study, we set the threshold concentration as the mean value of the whole sampling period. 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. 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°.

8. Line 193: standard errors of the means should be also presented here. You should also define the characteristic of the site. Is it a remote site or suburban site? I would prefer a suburban characteristic of the sampling site. Then, comparisons between previous observations in urban, suburban and remote areas are meaningful.

Response: The standard errors of the means have been added and 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. The characteristic of the site has already been defined as suburban in Table 1.

9. Line 210: a description of elevated Hg concentrations in both cold and warm seasons is confusing. What is the statistical test for the seasonal variations?

Response: The table below shows the statistical test with the p-value among the four seasons for GEM concentration. It indicates the GEM concentration in autumn is statistically different from that of spring, summer, and winter (p<0.05), while there are no significant differences

among spring, summer, and winter (p>0.05). In this regard, we revised the description as "Statistical test showed that no significant differences of the seasonal variations of GEM concentrations among spring, summer, and winter were observed (Table S1). This was different from many urban and remote sites in China, such as Guiyang, Xiamen, and Mt. Changbai, where GEM showed significantly higher concentrations in cold seasons than those in warm seasons (Feng et al., 2004;Xu et al., 2015;Fu et al., 2012)." in the revision.

Table R1. P-value between seasons for GEM concentration

	spring	summer	autumn	winter
spring				
summer	p>0.05			
autumn	p<0.05	p<0.05		
winter	p>0.05	p>0.05	p<0.05	

10. Line 214-216: here references are needed.

Response: Thanks for the suggestion. The references have been added in the revision.

11. Line 224-225: does a highest GOM concentration observed in winter support the effect of atmospheric oxidation at the sampling site. Generally, modeling studies argued that the oxidation rate of GEM should be highest in summer. Also, GOM observed peaked in morning (10:00), similar to GEM. This is in contrast with many previous studies that showed highest concentrations at noon, which could support a strong transformation between GEM and GOM.

Response: Thanks for the comments. The atmospheric oxidation was lowest in winter due to the relatively weak solar radiation. Thus, the high GOM concentrations observed in winter probably were attributed to the influence of strong anthropogenic emissions (such as the enhanced coal combustion in winter) and unfavorable meteorological conditions.

As for similar peaks of GOM and GEM in this study, we think this is also likely attributed to the influence of anthropogenic emissions as GOM derived largely from anthropogenic emissions in addition to the secondary formation.

In the revised manuscript, we have stated more clearly about the diurnal pattern of mercury species.

12. Line 241: are there any previous studies showed the diurnal patterns of anthropogenic emissions. The difference in Hg concentrations between daytime and night needs a statistical test.

Response: To our best knowledge, no diurnal patterns of anthropogenic Hg emissions are available from previous studies. The figure below is the hourly profile of major emission sectors (including power plants, industries, residential and transportation) for allocating emissions in China (data from Prof. Qiang Zhang from Tsinghua University). It could be seen that all emissions peak during daytime, reflecting the strong influences from human activities. We also performed statistical analysis and confirmed that the difference of Hg concentrations between daytime and night was significant ($p<0.05$).
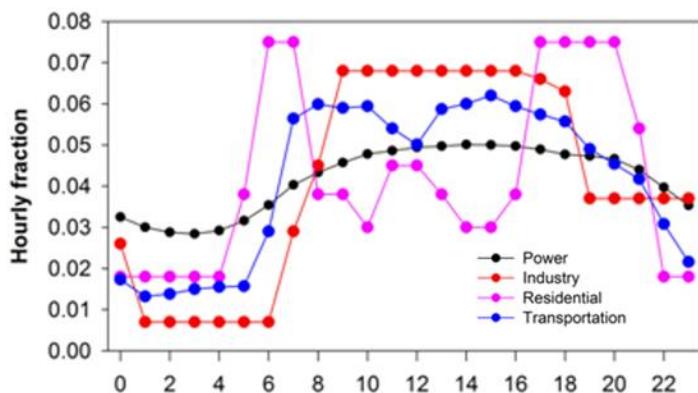
Figure R1. Hourly profile of major emission sectors in China

13. Line 257-258: PBM showed the highest in southwest, west and northwest winds, this is not consistent with the PSCF result. Please explain.

Response: Thanks for the comment. We think that there are two main reasons. 1) The wind rose plot was based on instantaneous wind directions, which revealed the relationship between PBM concentrations and wind direction/wind speed at a local scale. The PSCF analysis was based on three-days backward trajectories, which revealed the transport routes of air masses and potential sources regions at a much larger scale. Thus, it is possible that the wind rose plot and PSCF didn't show very consistent results. 2) As shown in Fig 5 (a), the frequency of the wind from southwest directions only accounted for about 6% of the total winds, which could impact the results of PSCF. As the PSCF analysis applied a weighting factor to reduce the uncertainty when a small number of trajectories crossed a particular cell. This might cause the PSCF values to be underestimated in the southwest, west and northwest wind directions.

14. Line 272: a description of PBL should be presented before the abbreviation. What methods did you use to determine the PBL? It is also appropriate to separate the shallow PBL from the PSCF analysis.

Response: We added the sentence "The data of the height of planetary boundary layer (PBL) were retrieved from the U.S. National Oceanic and Atmospheric Administration (https://ready.arl.noaa.gov/READYamet.php)." in Section 2 in the revision. When performing

the PSCF analysis, the starting heights were set as 500m, thus precluding the events under the shallow PBL conditions.

15. Line 300-301: I do not agree East China Sea is an important source region of the site given the PSCF values ranging from 0.2 to 0.4. There are also studies of atmospheric Hg in East China Sea, which highlighted that outflows of Hg from mainland China drive the increase of Hg concentrations.

Response: Thanks for the comment. The PSCF pattern in Fig. 7 of the original manuscript was based on an annual basis of Hg, indicating moderate PSCF values as the reviewer commented. If by referring to seasonal potential source regions of GEM as shown in the figure below, we did observe some high PSCF values (>0.5) over the East China Sea. We believe these signals imply the impact of ship emissions, but not the impact of ocean emissions. However, we do agree with the reviewer that East China Sea is not an important source region as the mainland evidently showed much higher and widespread PSCF signals. To avoid misunderstanding, we revised the sentence as "In addition, the East China Sea (including the offshore areas and open ocean) showed sporadic high PSCF signals of GEM in all four seasons (Fig. S1), indicating possible influences from shipping activities." in the revision.
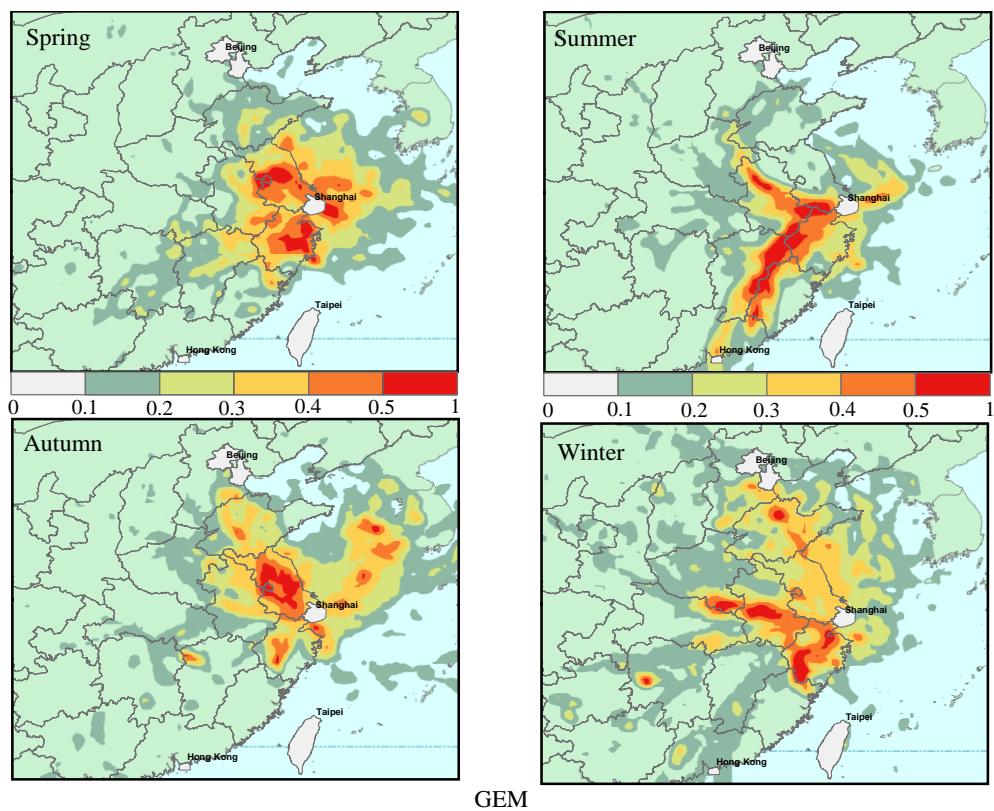
Figure S1. Potential source regions of seasonal GEM at the sampling site according to PSCF analysis.

16. Line 314-315: what I see from Figure 7 is that GOM and GEM share the similar source regions, and what is different is that of PBM.

Response: Thanks for pointing this out. We revised the description as "The PSCF pattern of GOM was as similar as that of GEM but different from that of PBM." in the revision.

17. Line 355-356: relative fraction of wind in south, southwest and west wind directions are similar in the four GOM/PBM groups, and why? Long-rang transport sources are also located in these directions.

Response: Thanks for the comment. We agree with the reviewer that the long-range transport sources could be also derived from the south, southwest and west directions. However, it is generally regarded that the long-range transport extent from the wind directions mentioned above was less than from northern China. Thus, this may explain that the frequency of south, southwest and west wind directions showed no clear trend as the GOM/PBM ratios increased. In this section, we have testified that the GOM/PBM ratio can be used as a quick tracer for identifying the relative importance of long-range transport vs. local sources. However, this is just a qualitative method, but not a quantitative solution for separating different sources. Explicit source apportionment should require chemical transport modeling, however, this is out the scope of this study.

In the revised manuscript, we have added in the end of this paragraph that "In general, the GOM/PBM ratio can be used as a qualitative tracer for identifying the relative importance of long-range transport vs. local sources. However, when the influences from long-range transport and local emission were close, the result could be ambiguous based on this method and this may require further efforts such as chemical transport modeling".

18. Line 359-382: low GEM concentrations were mostly related to high CO and SNA concentrations. Does this support that local-regional emissions are more important? This is contradictory to low GOM/PBM ratios, which indicates a progress of long-range transport.

Response: Thanks for the comments. In Shanghai, when high CO and SNA concentrations occurred, these events were generally related to the impact of long-range transport from northern China, especially in winter, but seldom from local emissions. In this study, GEM showed an increasing trend as the GOM/PBM ratios increased while both CO and SNA decreased. Thus, the low GEM concentrations were mostly related to high CO and SNA concentrations, suggesting the long-range transport from northern China was not the major cause of high GEM concentrations. In Fig. 9 of the manuscript, lower GEM concentrations corresponded to lower GOM/PBM ratios, further corroborating the influence of long-range transport was not crucial on GEM. Hence, there is no contradiction between the results based on different methods.

19. Section 3.3.3: why did not apportion the major sources of PBM and GOM?

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.

20. Line 401-406: factor 2 could be mostly related to oil combustion in motor vehicle in urban areas and shipping emissions over the Dianshan Lake.

Response: Thanks for the comment. 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.

21. Section 3.4.1: I do not agree variations of GEM and GOM concentration can support a strong conversion of GEM to GOM. Did you observe a strong negative correlation between GEM and GOM concentrations?

Response: Thanks for comments. Strong negative correlation between GEM and GOM concentrations were usually observed at remote and high-altitude sites, where the impact of anthropogenic emissions is weak. As a suburban site located in one of the most industrialized regions of China, it is difficult to see such a strong negative correlation between GEM and GOM as the reviewer mentioned. However, from Figure 11, we can still see that when GEM concentration began to decline from 6:00, the concentrations of GOM continued to rise until it reached the peak value at around 10:00, and the levels of ozone and temperature also kept rising during this period. This phenomenon has been repeatedly observed during the study period, revealing the acceleration of the conversion process of GEM to GOM under favorable atmospheric conditions of higher O_3 concentration and ambient temperature. However, we understand that GOM could be directly emitted from various emission sources and 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.

22. 452-469: Figure 12 is meaningless. Anyone could expect a similar trend between GOM concentrations and GOM/PBM ratios.

Response: Thanks for the comments. We do agree with the reviewer that the relationship between GOM concentrations and GOM/PBM ratios could be expected. Actually, Figure 12 more focus on the multi-relationship among GOM, GOM/PBM, O_3, and temperature. We intended to explore some crucial factors affecting the concentrations of GOM such as temperature and the levels of oxidants.

References:

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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.

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., Bieser, J., and Matthias, V.: Source attribution and process analysis for atmospheric mercury in eastern China simulated by CMAQ-Hg, Atmospheric Chemistry and Physics, 15, 8767-8779, 10.5194/acp-15-8767-2015, 2015.

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/m³, 60.8 pg/m³, and 82.1 pg/m³, 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 $0.5° \times 0.5°$. In this study, 72-hours back trajectories were calculated at 500m AGL (above ground level) and the cell size was set as $0.5° \times 0.5°$

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.

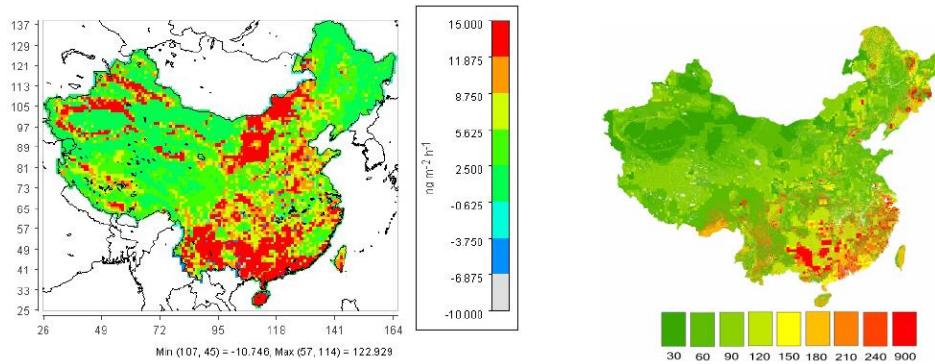



Figure R1. (left) mean annual air–soil flux; (right) Hg concentrations (ng g-1 in surface soil (0–20 cm) of China.

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

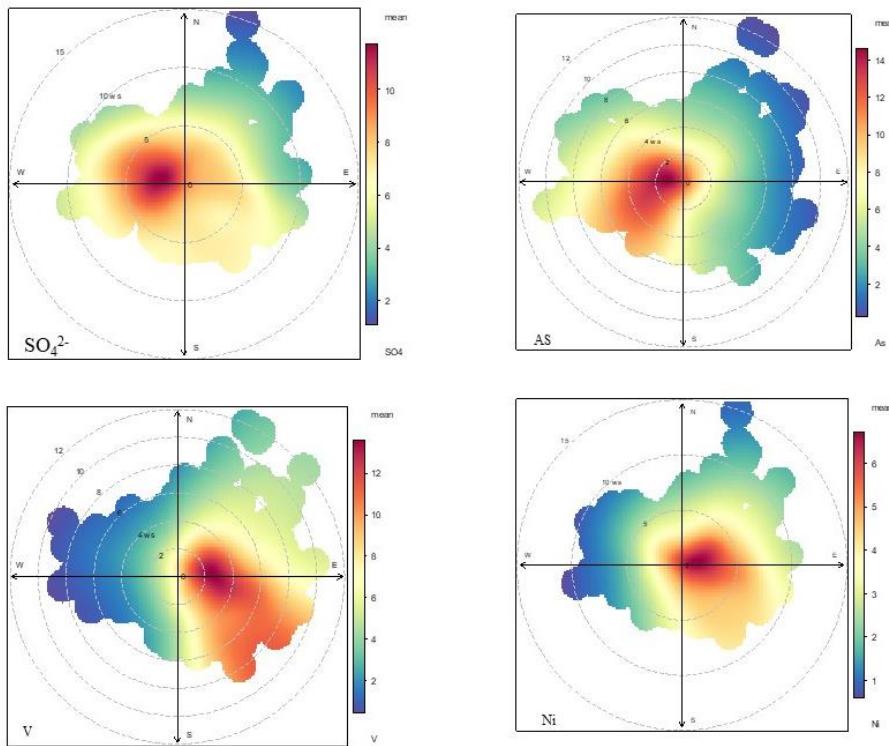
27. 3.3.3. Source apportionment by PMF: Why was the PMF analysis only performed on GEM data and not GOM and PBM? I think GOM and PBM needs to be included due to the extremely high concentrations at this site. Anthropogenic emissions of GOM and PBM should not be ruled out. One of the major goals of the 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.

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Response to Reviewer#3's comments

Anonymous Referee #3:

This manuscript presents an analysis of speciated atmospheric mercury (Hg), i.e. gaseous elemental mercury (GEM), particulate-bound mercury (PBM), and gaseous oxidized mercury (GOM), during June 2015 to May 2016 at the Dianshan Lake Station (DSL), Shanghai, east China. The topic is relevant to the Atmospheric Chemistry and Physics. However, the scientific contribution is hindered by a lack of methodology description in certain sections, some debatable analysis, some overreaching conclusions, and the quality of presentation. My specific comments and suggestions are listed below.

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.

1. re-emissions from surfaces.

It is concluded that "GEM at DSL exhibited high concentrations in both warm and cold seasons, which was due to the strong re-emission fluxes from natural surfaces in summer…" (L506) However, there is no quantitative analysis to support this claim. The authors pointed out that "It has to be noted that 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." (L390). The reviewer believes that temperature could be used to identify reemission with factor analysis approaches, such as Principal Component Analysis (PCA).

Response: Thanks for the suggestion. We applied the PCA 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 was explained as surface emissions. Factor 3 explained 13.43% of the total variance and showed high loadings for Ni and V, which indicated the contribution of ship emissions. Factor 4 explained 12.89% of the total variance and showed high loadings for Fe and Ca, indicating the contribution of cement production.

In the revised manuscript, we have added PCA analysis to perform source apportionment with PMF.

Table R1. PCA analysis 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

2. formation of GOM and PBM, local vs. regional events.

a. L359-369, CO and SNA concentrations were used to show that "GOM/PBM ratio was a reliable tracer for assessing the relative importance of regional/long-range transport vs. local atmospheric processing." (L368). Because CO and SNA concentrations are available, perhaps there is little need to use the GOM/PBM ratio, or GEM/CO ratio could be used as in previous studies of atmospheric Hg.

Response: Thank for the suggestion. We used CO and SNA to supplement the results based on the application of the ratio of GOM/PBM. The results by using CO and SNA or GOM/PBM are generally consistent, thus our study can be served as a reference that the GOM/PBM ratio could be used a tracer for assessing the relative importance of regional/long-range transport vs. local atmospheric processing even when data such as CO and SNA are not available.

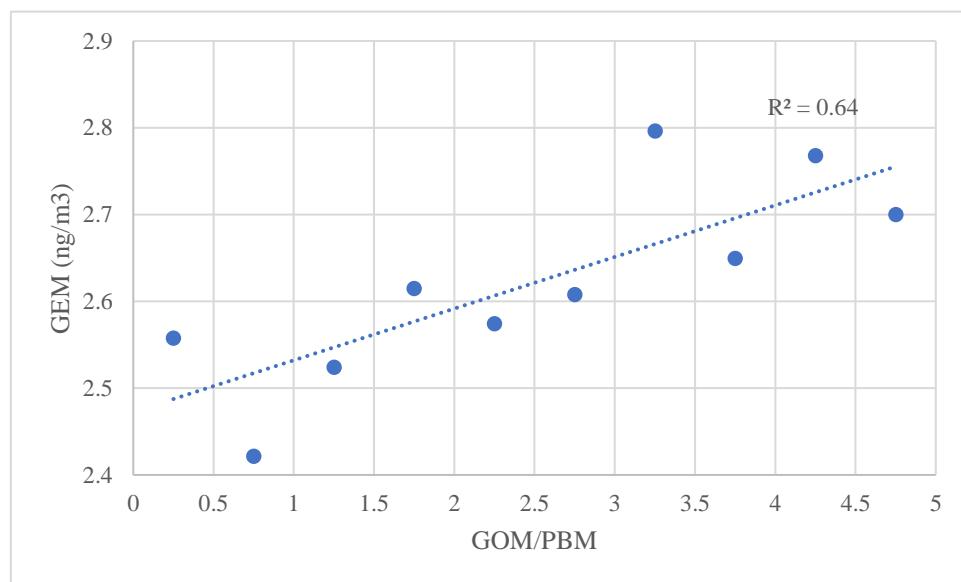
b. Local vs. regional events. The authors stated that "Fig. 12 also demonstrated the increases of GOM along with the ratios of GOM/PBM. The lower ratios of GOM/PBM were associated with lower temperature and O_3 concentrations, indicating the more. probable long range/regional events during the cold seasons with relatively weak photochemistry. On the contrary, the higher ratios of GOM/PBM were associated with higher temperature and O_3 concentrations, indicating the more probable local events during the warm seasons with relatively strong photochemistry." (L460) This reasoning seems to suggest that "long range/regional events" and "local events" dominate during the cold and warm seasons respectively. The authors may want to present evidence that the study site was shielded from long range transport in some seasons, because most receptors are under the influence of long-range transport all the time. In my view, air mass from all directions would have higher temperature and O_3 concentrations in summer thus "relatively strong photochemistry" than those in winter, regardless "local" or "long range/regional events". Therefore, higher temperature and O_3 concentrations in warm season would indicate "relatively strong photochemistry" but not "local events". Similarly, lower temperature and O_3 concentrations in cold season would indicate "relatively weak photochemistry" but not "long range/regional events". The authors may want to amend this section and the related conclusions.

Response: Thanks for the reviewer's in-depth comments and we totally agree. We revised the description as "Fig. 12 also suggested that the lower ratios of GOM/PBM were associated with lower temperature and O_3 concentrations, indicating relatively weak photochemistry during the cold seasons. On the contrary, the higher ratios of GOM/PBM were associated with higher temperature and O_3 concentrations, indicating relatively strong photochemistry during the warm seasons" in the revision.

c. GEM levels. It was concluded that "GEM as a function of the GOM/PBM ratios indicated that when the quasi-local sources dominated, GEM concentrations were relatively higher than those events under the regional/long-range transport conditions" (L522-524). L370-382, "In the GOM/PBM ratio bins of less than 2.5, GEM fluctuated with the mean values less than 2.6 ng/m^3. The mean GEM concentration increased from 2.61 ng/m^3 in the GOM/PBM ratio bin of 2.5-3.0 to 2.8 ng/m^3 in the bin of 3.0-3.5, and then remain relatively stable when the GOM/PBM ratio bins higher than 3.0." Indeed, this is the only noticeable increase in GEM (a 7% increase from the bin of 2.5-3.0 to that of 3.0-3.5) among 10 bins, while the change in GEM concentrations between the first and last bin is less than 5%. Nonetheless, the authors stated that "Generally, GEM showed an increasing trend as the GOM/PBM ratios increased while both SNA and CO decreased. The elevation of GEM concentrations tended to be associated with the impact of quasi-local sources. In contrast, under the high SNA and CO conditions when GOM/PBM ratios were lower, GEM was relatively low, suggesting its formation. was not favored via the regional/long-range transport." The authors may need to report the statistical trend (e.g. regression) if any, and clarity what type of GEM "formation was not favored via the

regional/long-range transport", and explain why GEM would change with the strength of photochemistry. In case GEM is high in summer due to re-emission when GOM is also high due to higher oxidant levels, then the common course is meteorological conditions, namely ambient temperature, an analysis taking into account seasonal trend of all variables involved could be more appropriate, instead of the seemingly speculative approach employed.

Response: Thanks for the insightful comments. The regression analysis between GEM and GOM/PBM was shown in the figure below. Correlation coefficients of the regression reached 0.64, suggesting the positive correlation between GEM concentrations and GOM/PBM ratios. By stating "GEM formation was not favored via the regional/long-range transport" in the original writings, we meant to say that when the impact of long-range transport was important, GEM concentrations were observed to be relatively low. The usage of the word "formation" might lead to misunderstandings here, so we revised the sentence as "In contrast, under the high SNA and CO conditions when GOM/PBM ratios were lower, GEM showed relatively low concentrations. This suggested the regional/long-range transport didn't favor the elevation of GEM concentrations.".

The seasonal relationship between temperature and Hg concentrations have been discussed in details in Section 3.1. Generally, the GEM concentrations increased as the temperature increased, which is interpreted to be likely from the surface emissions. GOM concentration showed a clearly positive correlation with temperature, which might be related to the in situ oxidation of GEM under high temperature.

3 PBM formation

1) L476, "Fig. 13 shows the statistical pattern of the variation of PBM and GOM in the ascending bins of PM2.5. It was obvious that the concentrations of PBM increased with the concentrations of PM2.5, which was due to both primary emissions and the subsequent process of Hg species adsorbed on particulate matters." The authors may want to provide more evidence or citation to support that increasing PBM with increasing PM2.5 concentrations "was due to

both primary emissions and the subsequent process of Hg species adsorbed on particulate matters"

Response: Thanks for the suggestion. Previous studies have shown that PBM can be emitted directly from various anthropogenic sources such as coal-fired power plants and industries (Liu et al., 2018;Wu et al., 2016). In addition, a number of studies concluded that gas-particle partitioning of TGM is an important pathway of PBM formation in urban areas of China (Shon et al., 2005;Fu et al., 2015). The high levels of particles in Eastern China probably facilitated the formation of PBM (Fu et al., 2015).

In the revised manuscript, we have added references in the related paragraphs in Section 3.4.2.

2)L480, "When PM2.5 concentrations were at relatively low levels under 75 µg/m3, GOM concentrations increased with PM2.5. However, when PM2.5 concentrations exceeded 75 µg/m3, GOM exhibited a slightly decreasing trend as PM2.5 increased. It seemed that when the concentration of PM2.5 reached a certain value, the formation of GOM was inhibited to some extent, which was likely due to the adsorption of GOM onto the particles." "Statistical analysis showed that when PM2.5 reached a certain value, GOM was inhibited to some extent due to the gas-particle partitioning process." (L34-35) Those statements/conclusions seem to be debatable. As seen in Fig 13, when PM2.5 concentrations exceeded 75 µg/m3, GOM decreased till PM2.5 reached 105µg/m3 then increased, instead of a slightly decreasing trend. The authors may need to report the statistical trend (e.g. regression) if any and rephrase the statements about inhibitive effects in discussion and conclusion, or omit this passage. Based on an analysis of a three-day episode (December 30, 2015 to January 1, 2016), the authors concluded that "Under high PM2.5 concentrations, high humidity and low temperature conditions, the gas-particle partitioning process was obvious at DSL, which might be an important pathway for the formation of PBM." (L532) The authors may want to provide more in-depth analysis of the reliance of PBM on PM2.5 concentrations when temperature and relative humidity levels favor formation of PBM, and justify the use of a three-day episode in winter to represent the year-long study period. My scan of Fig 6 suggests that only in autumn the PBM levels increase with decreasing ambient temperature, not in other three seasons including winter (the three-day episode).

Response: Thanks for the comments. We do agree with the reviewer that the description about the trends of GOM and PM2.5 seems to be debatable. Thus, the sentence has been changed as "However, when $PM_{2.5}$ concentrations increased to 75-105 $\mu g/m^3$, GOM exhibited as obvious decreasing trend as $PM_{2.5}$ increased." and added the sentences "when $PM_{2.5}$ concentrations exceeded 105 $\mu g/m^3$, GOM exhibited a slightly increasing trend as $PM_{2.5}$ increased. High $PM_{2.5}$ concentrations in China always related to severe anthropogenic emissions (Auzmendi-Murua et al., 2014), so the moderate increasing trend of GOM in these bins should be attributed to the impact of strong primary emissions." in the revision.

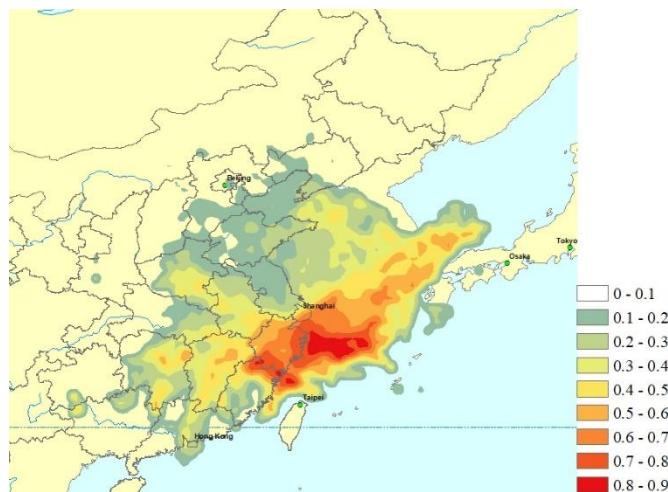
Previous study in an island between China and Korea has demonstrated that the partition coefficient of mercury gas-particle partitioning in atmosphere was negative correlated with atmospheric temperature and positively correlated with relative humidity (Lee et al., 2016). From the seasonal statistical analysis in Fig 6, the autumn PBM levels showed a clear decreasing trend with increasing ambient temperature, while the spring and winter PBM

showed a moderate decreasing trend with increasing ambient temperature. We think that this phenomenon can demonstrate the influence of gas-particle partitioning process and temperature on the PBM concentration during the whole study period to some extent.

3) contribution of the shipping sector

It is concluded that "shipping emissions" contributed to 20% of GEM based on PMF (L30, L526). However, there is a lack of data support. The authors may want to a) identify the port on Fig 1, b) find out the Hg emission value at and near this port (I believe that researchers from Tsinghua University have some related publications), and compare the shipping sector emission with emissions from other sources, c) for each sample, plot the time series of contribution to GEM by this factor and the wind or air mass direction to verify that this factor indeed represents the shipping sector.

Response: Thanks for the suggestion. The ports in the YRD region has been added in Fig 1. However, Hg emissions at the port level are not available as the public emission inventories are always grided.

As the reviewer suggested, we have extracted the time-series of GEM concentrations from the shipping factor based on the PMF modeling. We use this time-series 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.

2. The title reads, "Characteristics of atmospheric mercury in East China: implication on sources and formation of mercury species over a regional transport intersection zone". The authors may want to justify the use of data from a single site to represent 1) atmospheric Hg in East China, and 2) regional transport intersection zone, or rephrase the title. Similarly, some conclusions are a bit over-reaching, e.g. "shipping emission was found to be an important source (19.6%) of atmospheric mercury in East China" (L30)

Response: Thanks for the suggestion. The title is changed as "Characteristics of atmospheric mercury in the suburbs of East China: implication on sources and formation of mercury species over a regional transport intersection zone".

In the original abstract, the sentence before the writing "Besides the common anthropogenic emission sectors, shipping emission was found to be an important source (19.6%) of atmospheric mercury in East China" is "Six sources and their contributions to anthropogenic GEM were identified.". The PMF modeling only resolve source apportionment to anthropogenic mercury. However, based on the original data analysis and additional PCA analysis, we found the observed mercury has sources from natural emissions. Thus, the number 19.6% only pointed to anthropogenic emissions, but not all the mercury emissions. In the revised abstract, we have changed "atmospheric mercury" to "anthropogenic mercury" for clarification.

3. Seasonal trend of Hg species

The differences in seasonal mean TGM concentrations could be too small (max=2.88 ng/m3, min=2.63 ng/m3, the difference is 9%; summer 2.87 ng/m3, spring 2.73 ng/m3, difference 5%) and statistically not significant to support the conclusion of "GEM concentrations were elevated in both cold and warm seasons" (L21) and "GEM at DSL exhibited high concentrations in both warm and cold seasons, which was due to the strong re-emission fluxes from natural surfaces in summer and enhanced coal combustion for residential heating over northern China in winter." (L506). The authors may want to conduct comparison of multiple means (e.g. under ANOVA) for each of the three Hg species, and rephrase the discussion and conclusion in case the seasonal means are not statistically significant. Furthermore, please comment on the reasons of small difference among the four seasonal means if coal combustion for residential heating is enhanced in winter and re-emission fluxes from natural surfaces is strong in summer

Response: The table below showed the p-value by t-test between seasons for GEM concentrations, which suggested that the GEM concentration in autumn is statistically different from that of spring, summer, and winter (p<0.05), while there are no significant differences among spring, summer, and winter (p>0.05). In this regard, we revised the description as "Statistical test showed no significant differences of the seasonal variations of GEM concentrations among spring, summer, and winter were observed (Table S1). This was different from many urban and remote sites in China, such as Guiyang, Xiamen, and Mt. Changbai, where GEM showed significantly high concentrations in cold seasons than those in warm seasons (Feng et al., 2004;Xu et al., 2015;Fu et al., 2012). The relatively high GEM concentrations during the cold season in China should be attributed to the increases of energy consumption (Fu et al., 2015). In this study, GEM concentration in summer was comparable to that in winter, which was likely attributed to the strong natural mercury emissions (e.g. soils, vegetations, and water) due to elevated temperature in summer (Liu et al., 2016)" in the revision.

Table R1. P-value between seasons for GEM concentration

	spring	summer	autumn	winter
spring				

summer	p>0.05			
autumn	p<0.05	p<0.05		
winter	p>0.05	p>0.05	p<0.05	

4. Methodology is missing at numerous places. e.g. 1) please explain how to plot "Mean concentrations of (b) GEM, (c) PBM, and (d) GOM as a function of wind speed and wind directions" (L700) in the Method section and why Figures 5(b), (c) and (d) do not represent the frequency of wind directions shown in Figure 5 (a), in the Results section. 2) details of the backward trajectory simulation should be provided, including the model being use, run time, and start height, each with a justification, 3) where and how to use the "weighting function (wij)" (L162), 4) PMF, the treatment of missing data if any, and the total number of samples, 5) what is "the uncertainty of the jth pollutant on the ith measurement" (L187) in your study, 6) how to evaluate whether PMF is able to reproduce the observed Hg concentrations (e.g. time series and/or seasonal means), 7) how was hourly or bi-hourly PBL (assume it means Planetary Boundary Layer) height measured or estimated, 8) how was "secondary inorganic aerosols (SNA)" (L359) or "SNA (sulfate, nitrate, and ammonium) in PM2.5" (L715) monitored, 9) how to conduct analysis with bi-hourly Hg data and hourly data of meteorological parameters and other air pollutants.

Response:

1) Figure 5 (b), (c), and (d) were plot by the software R-studio. The radii of the circle in Figure 5 (b), (c), and (d) represent the value of wind speed. Figure 5 (b), (c), and (d) showed the relationship of Hg concentrations with wind speed and wind directions. As for Figure 5(a), the radii of the circle represent the frequency of wind directions but not the value of wind speed. In the revised manuscript, we have stated more clearly in the caption of Figure 5.

2) The details of the backward trajectory simulation have now been added into the Method section.

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 $0.5° \times 0.5°$. In this study, 72-hours back trajectories were calculated at 500m AGL (above ground level) and the cell size was set as $0.5°\times0.5°$.

3) w_{ij} is an empirical value to reduce the uncertainties of PSCF values in certain grid cells that are associated with a small number of endpoints. The values of wij have been shown in Eq. (2) in the manuscript and w_{ij} is multiplied by $PSCF_{ij}$ to derive the weighted PSCF values.

In this revision, we have stately clearly about the calculation.

4) we added the details of PMF model runs in the Method section. 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 data set 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 is 3526.

5) The error fraction was set as 15% of concentrations for GEM and 10% of concentrations for other compounds (Xu et al., 2017).

6) 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. These procedures guaranteed the PMF was able to reproduce the observed Hg concentrations.

7) The data of the height of planetary boundary layer (PBL) were retrieved from the U.S. National Oceanic and Atmospheric Administration (https://ready.arl.noaa.gov/READYamet.php).

8) Water-soluble inorganic anions (SO_4^{2-}, NO_3^-, Cl^-) and cations (K^+, Mg^{2+}, Ca^{2+}, NH_4^+) in $PM_{2.5}$ were simultaneously monitored by the Monitor for Aerosols and Gases in ambient Air (MARGA) at the temporal resolution of one hour. The details of the instrument have been described in the first paragraph of Section 2.3.

9) To conduct data analysis with bi-hourly Hg data and hourly data of meteorological parameter, we first converted hourly meteorological data to bi-hourly meteorological data. Briefly, the hourly meteorological data was converted into the X and Y vectors. Then wind speed at the X and Y vectors were averaged and final we can get the average wind speed and wind direction based on the trigonometric function.

5. GOM and PBM could be included in PMF source apportionment. The results (e.g. sample by sample GEM, GOM, PBM, CO, SNA etc contributions in each factor) might help the identification of age of the air mass, as well as sources and processes related with Hg.

Response: Thanks for this 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.

6. Interpretation of PMF results. This section could be improved by a more in-depth analysis and/or citation of existing literature. Overall, the analysis seems to be subjective at times, leading to invalid or overreaching statements/conclusions based on measurements at one site, a small difference in seasonal or binned concentrations, speculative approaches, or a short episode of a few days. It is recommended to clarify the meaning of local and regional events, whether "local" means local man-made emissions, local re-emission, local photochemical reactions, all of the above; or different item in different sections. Time series (Fig 2) or box plots (Fig 3) of temperature, relative humidity, CO, PM2.5 mass, SNA (sulfate, nitrate, and ammonium, or secondary inorganic aerosols), O3, and GOM/PBM ratios could be employed to depict seasonal trend of those variables, which may help to differentiate the association from causation.

Response: Thanks for the comments. In this study, local sources represented all emission sources in local area. GOM/PBM ratios together with CO, and SNA were used to reveal the relative importance of local sources vs. long-range transport.

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.

Clarification issues

1. The following items could be included in Fig 1, 1) location of the sampling site, 2) location of the shipping port, 3) the name of all provinces within e.g. 2000 or 3000 km of the sampling site, 4) a scale in the lower-right box, 5) the meaning of the upper-right box, 6) the meaning of the short black line.

Response: Thanks for the suggestion. Due to the conversion problems from text to pdf, some items in the figure were not properly shown in the original submission. Now we have corrected the errors and added marks as the reviewer suggested.

1) The location of the sampling site has been marked with a pentagram in Fig. 1.

2)The locations of the shipping ports has been marked by the purple triangle marks in Fig. 1.

3) The name of all provinces within e.g. 2000 or 3000 km of the sampling site have been added in Fig 1.

4) the plotting scale of the lower-right box has been added.

5) The upper-right box showed the compass of the map but failed to display, there must be an error in the file conversion.

6) That line was due to an error in file conversion and it is corrected now.

2. The provincial level Hg emissions in Wu et al. (2016) could be provided as supplemental information.

Response: The provincial level Hg emissions in Wu et al. (2016) have been provided as supplemental information in the revision.

3. Please provide the distance between the sampling site and the nearest coastal line, and comment on whether the sampling site is capable of capturing the land-sea circulation.

Response: The distance between the sampling site and coastal lines is about 50 km. One recent study reported that shipping emissions influenced the air quality in not only coastal areas but also the inland areas hundreds of kilometers away from the sea in China, as shown in the figure below (Lv et al., 2018). In this regard, our sampling site is well capable of capturing the land-sea circulation.

In the revised manuscript, we have added more descriptions about the sampling site.

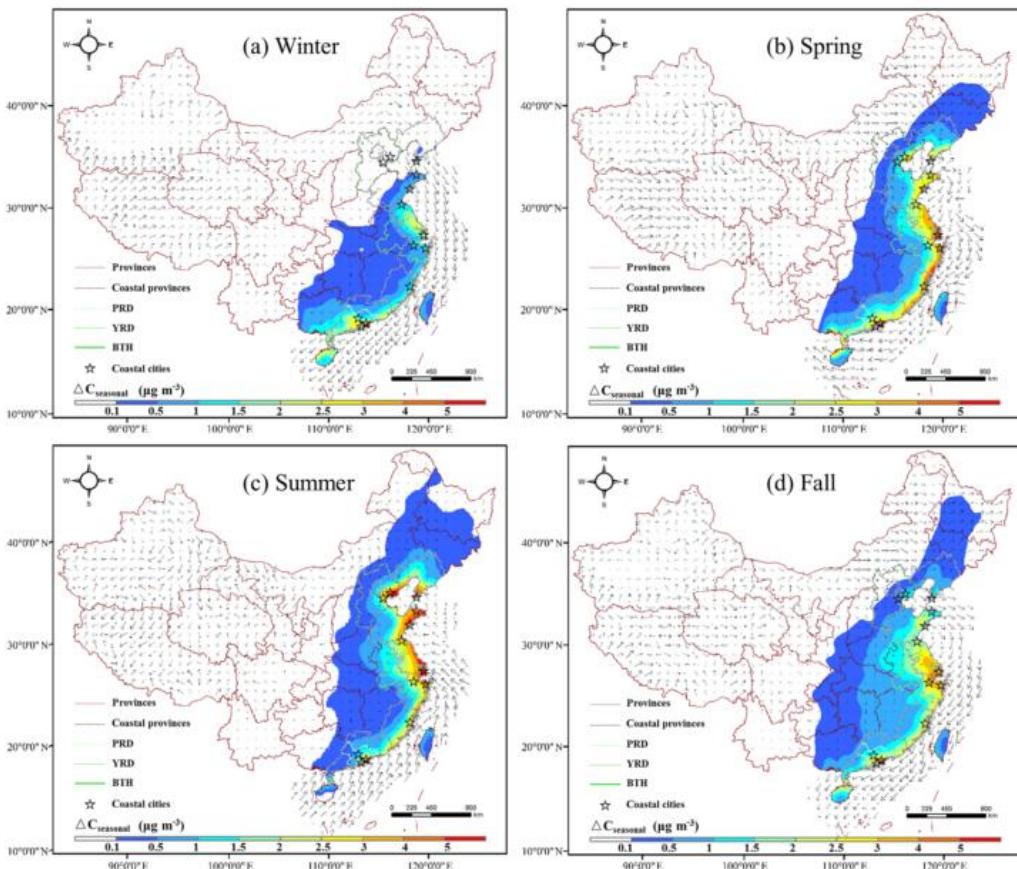



Figure 5. Contributions of shipping emissions to the seasonal mean PM$_{2.5}$ concentrations (base case- no ship case): **(a)** winter, **(b)** spring, **(c)** summer and **(d)** fall. Arrows represent the WRF modeled seasonal mean surface wind field.

4. L147, "meteorological data", please provide the height of the instrument about ground level, and comment on whether the instrument is capable of capturing the meteorological condition in the study area.

Response: The instrument was set up on the top roof of a four-story building, which is a supersite carefully maintained by Shanghai Environmental Monitoring Center (SEMC). The height of the instrument is about 14 m above the ground. The sampling site is located in the rural areas and beside the shore of Dianshan Lake. There are no tall buildings or mountains nearby, making sure that this site is capable of capturing the meteorological conditions in the study area.

5. L149, other pollutants, please provide the reporting or averaging intervals of CO, ozone and PM2.5 mass measurements.

Response: Thanks for the suggestion. The average intervals of CO, ozone, and $PM_{2.5}$ mass measurements were one hour. We revised the description as "Atmospheric ozone (O_3) concentration was continuously measured using Thermo Fisher 49i, which operates on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The ambient carbon monoxide (CO) and $PM_{2.5}$ concentrations were measured by Thermo Fisher 48Itle and Thermo Fisher 1405F, respectively. All data were averaged at the intervals of one hour." in the revision

6. L205 and L362, please explain what is "secondary formation".

Response: In Line 205, it means the oxidation process of GEM to GOM. In Line 362, it means secondary particle formation. We have expressed more clearly about this term in the revision.

7. L302-304, "The potential source regions of all year round PBM were mainly from northeastern China, including Jiangsu, Anhui, Shandong, and Hebei provinces." Please justify the classification that Jiangsu and Anhui belong to northeastern China.

Response: Thanks for the comments. The classification of the provinces in the original manuscript is not well defined. We revised the description as "The potential source regions of all year round PBM were mainly from the north of Jiangsu and Anhui provinces, and from northeastern China, including Shandong and Hebei provinces."

8. section 3.2.2 (L333), all eight wind directions should be included in the discussion. The authors many want to point out that there is little difference in the wind direction distribution between the GOM/PBM bins of 1-2 and 2-3.

Response: Thanks for the suggestion. We revised the sentence as "As shown in Fig. 8, the frequency of south, southwest, west, and northeast winds showed no clear trend as the GOM/PBM ratios increased." in the revision.

9. Figure 2, please explain the meaning of the red-dish line.

Response: The red-dashed line represented the mean concentrations of each season. We added the sentence "The red-dashed lines represent the mean concentrations of Hg species in each season." in the caption of Figure 2.

10. Figures 5 (b), (c), (d), what is the meaning of "15 ws"?

Response: "15 ws" in Figures 5(b), (c), (d) meaning the wind speed is 15 m/s. The radii of the circle in Figures 5 (b), (c), (d) represent the value of wind speed.

11. Figures 9 and 12, please explain the meaning of the bars.

Response: The bars in Figures 9 and 12 represent one standard error of the parameters in each bin. It has been clarified in the captions of the figures now.

12. Figure 12 caption, "Temperature as a function of the GOM/PBM ratios" Please explain why temperature would change with changing GOM/PBM ratios in the main body.

Response: This expression is not appropriate. We have changed it as "Temperature variations in each bin of the GOM/PBM ratios".

13. Figure 13, please explain the meaning of the shaded areas.

Response: The shaded areas in Figure 13 represented one standard error of GOM and PBM concentrations.

Editorial suggestions:

1. The significant number seems to be excessive at times, e.g. one decimal will suffice when presenting Hg concentrations.

Response: Thanks for the comment. We do agree with the reviewer that the significant number is excessive at times. After referring to a number of related papers, we revised the significant number as one decimal for GOM and PBM concentrations and two decimals for GEM concentrations in the revised manuscript.

2. Avoid the use of first person, i.e. "we".

Response: Thanks for the suggestion. All statements involving the use of first person have been revised in the revision.

3. Please define all abbreviations, e.g. PSCF, PBL, RH, in the main body instead of the headings.

Response: Thanks for the suggestion. All abbreviations have been defined in the main body instead of the headings in the revised manuscript.

4. Inconsistent expressions, e.g. "Equation 1" (L160), "as below" (L163), "shown as Eq. (3)" (L173); "secondary inorganic aerosols (SNA)" (L359), "SNA (sulfate, nitrate, and ammonium) in PM2.5" (L715); RGM (Figure 6).

Response: Thanks for the suggestions. All the inconsistent expressions have been revised in the revision.

5. There are quite a few awkward sentences, e.g. 34-35, L171-172, L268-270, L393 ("Se, As, and Pb, which were typical tracers of coal combustion"), L403-404, L443.

Response: Thanks for pointing it out. The awkward sentences have been adjusted.

6. There are quite a few awkward phrases, e.g. "obvious" (L35 and other places), "comprehensive" (L86, suggest to remove), "Xij is" (L175) should be "where Xij is", "about" (L305 and other places, suggest to replace with "approximately"), "As similar as Fig. 9" (L452), "CN" in Table 1 should be replaced with "China".

Response: Thanks for pointing it out. The awkward phrases have been replaced or removed according to the suggestions of the reviewer.

7. The manuscript could be shortened by 1) removing some unnecessary material (e.g. L170-186, those model descriptions could be removed by citing the Users Guide by USEPA or other publications), 2) condense the discussion and conduction sections.

Response: Thanks for the suggestions. We have revised the manuscript as suggested.

8. Figure 2, the seasons seem to be incorrect.

Response: Thanks for pointing this out. The seasons in Figure 2 have been corrected in the revised manuscript.

9. Figure 4 caption, suggest to remove "The red line and black line represented the corresponding diurnal variation of RH and wind speed, respectively." because there are legends to represent each and all variables.

Response: Thanks for the suggestion. The sentence has been removed in the caption of the figure.

10. Figure 6, the ranges should be, <13, 13-15, 15-17, etc.

Response: Thanks for the suggestion. The presenting of the ranges has been changed in the revision.

11. Figure 8, the ranges should be 0-1, 1-2, 2-3, >3.

Response: The presenting of the ranges has been changed according to the suggestion of the reviewer in the revision.

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1 **Characteristic of atmospheric mercury in the suburbs of East China: implication**

2 **on sources and formation of mercury species over a regional transport intersection**

3 **zone**

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15 **Abstract**

16 Mercury (Hg) is a global pollutant of great concern in East Asia, which is considered to be the largest

17 mercury-emitting region in the world. In this study, atmospheric gaseous elemental mercury (GEM),

18 gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM) were measured

19 continuously over a regional transport intersection zone in the suburbs of East China to reveal the

20 sources and formation of mercury species. The annual mean concentrations of GEM, PBM, and

21 GOM reached 2.77 ng/m³, 60.8 pg/m³, and 82.1 pg/m³, respectively. GEM concentrations were

22 elevated in winter, summer, and spring while lower in autumn. This seasonal pattern of GEM

23 suggested that the re-emissions from natural surfaces played a significant role in the fluctuation of

24 atmospheric mercury in addition to anthropogenic sources. Relationship between Hg species and

25 wind directions indicated the high Hg concentrations were related to winds from the south,

26 southwest, and north of the measurement site. An application of the GOM/PBM tracer method and

27 trajectory-based source region identification distinguished the relative importance of long-range

28 transport from northern China and quasi-local emission sources on the magnitudes of Hg species. It

29 was revealed that GEM concentrations were higher when quasi-local sources dominated compared

to the dominance of long-range transport events. Six sources and their contributions to anthropogenic GEM were identified. Besides the common anthropogenic emission sectors (i.e. industrial and biomass burning, coal combustion, iron and steel production, cement production, and incineration), shipping emission was found to be an important source (19.6%) of anthropogenic mercury in East China, where marine vessel shipping activities are intense. In addition, a considerable natural source of GEM was identified. Concurrences of high GOM concentrations with elevated O_3 and temperature, along with the lagged variation of GEM and GOM during daytime demonstrated the very high GOM concentrations were partially ascribed to the intense in situ oxidation of GEM. Statistical analysis showed that when $PM_{2.5}$ reached a certain threshold value, GOM was inhibited to some extent due to the gas-particle partitioning process. This process was controlled under the conditions of high $PM_{2.5}$ concentrations, high humidity, and low temperature.

1. Introduction

Mercury (Hg) is a global pollutant of great concerns for environment and human health. Based on its physical and chemical properties, atmospheric mercury is operationally divided into three forms, i.e. gaseous elemental mercury (GEM), particulate-bound mercury (PBM), and gaseous oxidized mercury (GOM). GEM is the predominant form in the atmosphere (>90%), while PBM consists of a small quantity of the total mercury as well as for GOM. Elemental mercury in the atmosphere is relatively stable, which means that it has a long lifetime of 0.5-2 year and can transport globally before they are oxidized and removed from the atmosphere via wet and dry depositions (Marsik et al., 2007). In contrast, GOM and PBM would be rapidly wiped out from the atmosphere after emission due to their significantly greater reactivity, deposition velocities, and water solubility .

Both natural processes and anthropogenic activities release mercury into the atmosphere. Natural sources of mercury include the ocean volatilization, volcanic eruption, evasion from soils and vegetation, geothermal activities, and weathering minerals (Pirrone et al., 2010;Simoneit et al., 2004). Re-emissions of mercury that previously deposited onto the environmental surfaces are also considered as natural source. As for the anthropogenic emission sources of mercury, coal combustion, non-ferrous smelters, cement production, waste incineration, and mining are considered to be the main sources. After being emitted into the atmosphere, mercury undergoes

60 speciation which plays an important role in its biogeochemical cycle. Previous studies suggest that

61 the oxidation of GEM in the terrestrial environments was generally initiated by O_3 and OH radicals

62 (Mao et al., 2016). Atomic bromine (Br) and bromine monoxide (BrO) are two additional oxidation

63 agents in the marine atmosphere (Xiao et al., 2018;Wang et al., 2016). Observational studies of

64 GOM in the polar regions (Choi et al., 2013;Ye et al., 2016) and in the subtropical marine boundary

65 layer (Cheng et al., 2014;Zhu et al., 2014) as well as atmospheric modeling studies about mercury

66 cycling (Feng et al., 2004;Shon et al., 2005) have considered Br to be an important oxidant of GEM.

67 (Wang et al., 2014) even reported that Br is the primary oxidant of GEM in tropical marine boundary

68 layer (MBL). However, it still remain unknown and controversial about the speciation and

69 quantification of the GEM+O_3 products, and the reaction of GEM+OH is still under huge debate

70 between theoretical and experimental studies due to the lacking of mechanisms consistent with

71 thermochemistry (Xiao et al., 2018). As the GEM converts into GOM, a part of GOM will be

72 adsorbed onto particulate matter since it has high water solubility and relatively strong surface

73 adhesion properties (Liu et al., 2010). GEM accounts for the vast majority of total mercury in the

74 atmosphere, and its concentration is an order of magnitude higher than that of GOM and PBM.

75 Generally, the levels of GEM could be affected by various emission sources, redox reactions, and

76 foliar uptake, while the GOM species from the GEM oxidation and subsequent formation of PBM

77 by adsorption on the particle matters can significantly affect their ambient concentrations, especially

78 in regions with high GEM levels.

79   Many efforts have been made by governments to reduce mercury emissions. In October 2013,

80 128 countries signed a global treaty "Minamata Convention on Mercury" in order to reduce mercury

81 emissions from anthropogenic activities (Zhu et al., 2016). However, the mercury pollution issue is

82 still grim especially in Asia, which contribute approximately half of the global mercury emissions

83 (Pacyna et al., 2016). Mainland China plays an important role in the biogeochemical cycling of

84 mercury, since approximately 27% of the global total atmospheric mercury exhausts are from this

85 area (Hui et al., 2017). The Yangtze River Delta (YRD) is one of the most industrialized and

86 urbanized regions in China. Early field measurements in urban Shanghai found that the sources of

87 TGM were most likely derived from coal fired power plants, smelters and industrial activities

88 (Friedli et al., 2011). One study in urban Nanjing indicated that natural sources were important while

89 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 with a contribution of 36.6% were the most important source for GEM in eastern China (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 contributions 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 this study, one-year measurements of GEM, GOM, and PBM were conducted at Dianshan Lake Station (DSL), a suburban site in Shanghai. DSL is located in the junction of Shanghai, Zhejiang, and Jiangsu provinces and is close to the East China Sea (ECS). Few local sources and multiple surroundings make DSL a unique location for studying the main pollution sources and transport pathways of Hg. In this paper, the relationship between Hg and meteorological conditions was revealed; and the oxidation process of GEM to GOM and the adsorption process of GOM on ambient particles were discussed. We also assessed the potential contributing sources of Hg, locating the high potential sources regions and identifying the specific source and their contributions. This study demonstrated the characteristics of atmospheric mercury over an intersection zone and provided insights into the formation of GOM and PBM, and revealed the considerable contribution from shipping activities over the coastal area.

2. Materials and methods

2.1. Site description

The field observation was conducted on the top of a four-story building (~ 14 m) at a super site which is located in the west of Shanghai, and nearby the Dianshan Lake in Qingpu district (Fig. 1). This supersite is carefully maintained by Shanghai Environmental Monitoring Center (SEMC). The building is purely used for atmospheric monitoring without any other usage. DSL lies at suburbs of Shanghai and there are no large point sources around within 20 kilometers, ensuring this site is capable of capturing the meteorological conditions in the study area. Beside the measurement site

is Dianshan Lake, which is the largest freshwater lake in Shanghai with a total area of 62 square kilometers, and next to the site is a highway with moderate traffic. The total GEM emission within a 20 km cycle around the site was around 100kg/yr, indicating weak local human activities. The distance between the sampling site and coastal lines is about 50 km, making it capable of capturing the land-sea circulation. Its special geographical location (at the junction of Shanghai, Zhejiang and Jiangsu provinces) makes it possible to receive the air masses from all these populous regions. In addition, this site is located at the typical outflow path from East China to the Pacific Ocean. The red dots in Fig. 1 represent the amount of atmospheric Hg emitted by anthropogenic activities of each provinces in 2014 (Wu et al., 2016). The emission intensities of anthropogenic Hg in China were higher in the north and lower in the south. The atmospheric Hg emissions by province in 2014 are listed in Table S1.

2.2 Measurement of atmospheric mercury species

Atmospheric mercury species (GEM, GOM, and PBM) were collected and measured from June 2015 to May 2016 using the Tekran 2537B/1130/1135 system (Tekran Inc., Canada). The Tekran system has been widely used and the details have been described elsewhere (Landis and Keeler, 2002). In general, GEM, GOM, and PBM in the atmosphere were collected by dual gold cartridges, KCl-coated annular denuder, and regenerable quartz fiber filter, respectively. In this study, GEM was collected at an interval of 5 minutes with a flow rate of 1 L/min, while GOM and PBM were collected at an interval of 2 hours with a flow rate of 10L/min. After the collection, all mercury species were thermally decomposed to Hg^0 immediately and measured by cold vapor atomic fluorescence spectroscopy (CVAFS). GEM concentrations were expressed in ng/m^3, while GOM and PBM were in pg/m^3 at standard temperature of 273.14K and pressure of 1013 hPa.

A series of work need to be done to ensure the accuracy and validity of the measurement. The KCl-coated denuder, Teflon coated glass inlet, and impactor plate were replaced weekly and quartz filters were replaced monthly. Before sampling, denuders and quartz filters were prepared and cleaned according to the methods in Tekran technical notes. The Tekran 2537B analyzer was routinely calibrated using its internal permeation source every 47 hours, and was also cross-calibrated every 3 months against an external temperature controlled Hg vapor standard. Two-point calibrations (including zero calibration and span calibration) were performed separately for each

150 pure gold cartridge. Manual injections were performed to evaluate these automated calibrations

151 using the standard saturated mercury vapor.

152 Quality control on data were also performed during the data analysis. Some extremely high

153 concentrations (especially for GOM and PBM) were occasionally observed. If the values were

154 several times higher than the previous hour, those data were regarded as outliers and were excluded

155 in the data analysis.

156

2.3 Measurement of other air pollutants and meteorological parameters

158 Water-soluble inorganic anions (SO_4^{2-}, NO_3^-, Cl^-) and cations (K^+, Mg^{2+}, Ca^{2+}, NH_4^+) in $PM_{2.5}$

159 were simultaneously monitored by the Monitor for Aerosols and Gases in ambient Air (MARGA)

160 at the resolution of one hour. Ambient air was drawn into a sampling box at a flow rate of 16.7L/min.

161 After removing the water-soluble gases by an absorbing liquid, a supersaturation of water vapor

162 induced the particles in the airflow to grow into droplets, and then the droplets were collected and

163 transported into the analytical box which contains two ion chromatograph systems for the

164 determination of the water-soluble ions in $PM_{2.5}$.

165 Heavy metals (Pb, Fe, K, Ba, Cr, Se, Cd, Ag, Ca, Mn, Cu, As, Hg, Ni, Zn, V) in $PM_{2.5}$ were

166 measured hourly using the Xact-625 Ambient Metals Monitor (Cooper Environmental services,

167 Beaverton, OR, USA), which is a sampling and analyzing X-ray fluorescence spectrometer designed

168 for online measurements of particulate elements. In this study, ambient air was sampled at a flow

169 rate of 16.7L/min and the particles were collected onto a Teflon filter tape. Then the filter tape was

170 moved into the spectrometer, where it was illuminated with an X-ray tube under three excitation

171 conditions and the excited X-ray fluorescence was measured by a silicon drift detector. Daily

172 advanced quality assurance checks were performed during 30 minutes after midnight to monitor

173 shifts in the calibration.

174 The hourly meteorological data including air temperature, relative humidity (RH), wind

175 speed, and wind direction were simultaneously monitored at the observation site by the automatic

176 weather station (AWS). The data of the height of planetary boundary layer (PBL) were retrieved

177 from the U.S. National Oceanic and Atmospheric Administration

178 (https://ready.arl.noaa.gov/READYamet.php). Atmospheric ozone (O_3) concentration was

179 continuously measured using Thermo Fisher 49i, which operates on the principle that ozone

180   molecules absorb UV light at a wavelength of 254 nm. The ambient carbon monoxide (CO) and

181   PM$_{2.5}$ concentrations were measured by Thermo Fisher 48Itle and Thermo Fisher 1405F,

182   respectively. All data were averaged at the intervals of one hour.

183

184   **2.4 Potential source contribution function (PSCF)**

185   PSCF is a useful tool to diagnose the possible source areas with regard to the levels of air

186   pollutants when setting a contamination concentration threshold at the receptor site. Back trajectory

187   models are used to simulate the airflows. The principle of PSCF is to calculate the ratio of the total

188   number of back trajectory segment endpoints in a grid cell (i, j) which exceed the threshold

189   concentration (m_{ij}) to the total number of back trajectory segment endpoints in this grid cell (i, j)

190   during the whole sampling period (n_{ij}) as expressed by Equation (1) (Zhang et al., 2017;Cheng et

191   al., 2015).

$$\text{PSCF}_{ij} = \frac{m_{ij}}{n_{ij}} \qquad (1)$$

193   When a particular cell is associated with a small number of endpoint, weighting function (w_{ij})

194   is applied to reduce this uncertainty and the value of w_{ij} is shown in Equation (2) (Fu et al., 2011),

195   in which N_{avg} is the mean n_{ij} of all grid cells with n_{ij} greater than zero. PSCF$_{ij}$ is multiplied by w_{ij} to

196   derive the weighted PSCF values.

197

198
$$w_{ij} = \begin{cases} 1.0, & N_{ij} > 3N_{ave} \\ 0.7, & 3N_{ave} > N_{ij} > 1.5N_{ave} \\ 0.4, & 1.5N_{ave} > N_{ij} > N_{ave} \\ 0.2, & N_{ave} > N_{ij} \end{cases} \qquad (2)$$

199   In this study, we set the threshold concentration as the mean value of the whole sampling period.

200   The mean GEM, PBM, and GOM concentrations were 2.77 ng/m^3, 60.8 pg/m^3, and 82.1 pg/m^3,

201   respectively. The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is

202   applied for calculating air mass backward trajectories (Draxler and Rolph, 2012). The model was

203   run online at the NOAA ARL READY Website using the meteorological data archives of Air

204   Resource Laboratory (ARL). The meteorological input data used in the model was obtained from

205   NCEP (National Centers for Environmental Prediction)'s global data assimilation system (GDAS)

206   with a horizontal resolution of 0.5° × 0.5°. In this study, 72-hours back trajectories were calculated

207   at 500m AGL (above ground level) and the cell size was set as 0.5°×0.5°.

208

2.5 Positive matrix factorization (PMF)

The PMF model is widely used to quantitatively determine the source contributions of specific air pollutants (Gibson et al., 2015). The essential principle of PMF is that the concentration of each sample is determined by source profiles and different contributions. The equation of the PMF model is shown as Equation (3):

$$X_{ij} = \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij} \qquad (3)$$

Where X_{ij} is the concentration of the jth contamination at the receptor site in the ith sample. g_{ik} represent the contribution of the kth factor on the ith sample, f_{kj} is used to express the mass fraction of the jth contamination in the kth factor, P is the number of factors, which represent pollution sources, e_{ij} is the residual for each measurement or model error.

Before the model determines the optimal non-negative factor contributions and factor profiles, an objective function, which is the sum of the square difference between the measured and modeled concentrations weighted by the concentration uncertainties, has to be minimized (Cheng et al., 2015). The equation that determines the objective function is given by Equation (4):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} A_{ik} F_{kj}}{S_{ij}} \right)^2 \qquad (4)$$

where X_{ij} is the ambient concentration of the jth pollutant in the ith sample (m and n represent the total number pollutants and samples, respectively). A_{ik} is the contribution of the kth factor on the ith sample and F_{kj} is the mass fraction of the jth pollutant in the kth factor. S_{ij} is the uncertainty of the jth pollutant on the ith measurement, P is the number of factors, which imply the pollutant sources. 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.

237

3. Results and discussion

3.1. Characteristics of atmospheric mercury species

Fig. 2 displays the time series of atmospheric GEM, PBM, and GOM concentrations during 1 June, 2015 to 31 May, 2016 at DSL. 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. As shown in Table 1, the levels of GEM and PBM in this study were lower than some sites in China by a factor of 2-7, such as rural Miyun, suburban Xiamen, and urban Guiyang (Xu et al., 2015;Fu et al., 2011). However, compared to the studies conducted in urban and rural areas abroad such as New York (Choi et al., 2013), Chicago (Gratz et al., 2013), and Nova Scotia (Cheng et al., 2014), the concentrations of GEM and PBM in the suburbs of Shanghai were much higher by a factor of 1-3 and 3-8, respectively. Different from GEM and PBM, the GOM concentrations at DSL were higher than all the Chinese sites and other sites around the world listed in Table 1. The mean GOM concentration in this study (82.1 pg/m^3) was even higher than that in Guiyang (35.7 pg/m^3), where the emissions of GEM and GOM were quite intense due to the massive primary emission sources such as coal-fired power plants and cement plants (Fu et al., 2011). The abnormally high GOM concentrations observed in this study were likely dominated by strong primary emissions.

The monthly patterns of GEM, PBM, and GOM during the whole sampling period are shown in Fig. 3. The seasonal mean GEM concentrations were slightly higher in winter (2.88 ng/m^3) and summer (2.87 ng/m^3) than in spring (2.73 ng/m^3) and autumn (2.63 ng/m^3), with the highest monthly mean value of 3.19 ng/m^3 in June and the lowest of 2.39 ng/m^3 in March. Statistical test showed that no significant differences of the seasonal variations of GEM concentrations among spring, summer, and winter were observed (Table S2). This was different from many urban and remote sites in China, such as Guiyang, Xiamen, and Mt. Changbai, where GEM showed significantly high concentrations in cold seasons than those in warm seasons (Feng et al., 2004;Xu et al., 2015;Fu et al., 2012). The relatively high GEM concentrations during the cold season in China should be attributed to the increases of energy consumption (Fu et al., 2015). In this study, GEM concentration in summer was comparable to that in winter, which was likely attributed to the strong natural mercury emissions (e.g. soils, vegetations, and water) due to elevated temperature in summer (Liu et al., 2016). The seasonal mean PBM concentrations were the highest in winter (93.5 pg/m^3) while the lowest in summer (35.7 pg/m^3), and moderate in autumn (56.8 pg/m^3) and spring (51.6 pg/m^3), with the

268   highest monthly mean value of 109.4 pg/m^3 in January and the lowest of 28.9 pg/m^3 in September.

269   This seasonal pattern was consistent with other sites in China such as Beijing and Nanjing (Zhu et

270   al., 2014;Zhang et al., 2013). PBM concentrations at low altitude sites in the Northern Hemisphere

271   were commonly enhanced in winter, which was ascribed to intense emissions from residential

272   heating, the reduction of wet scavenging processes, enhanced gas-particle partitioning of

273   atmospheric mercury under low temperature, etc. (Rutter and Schauer, 2007). As for GOM, its

274   seasonal mean concentrations were the highest in winter (124.0 pg/m^3), followed by summer (77.3

275   pg/m^3), spring (68.1 pg/m^3), and autumn (61.0 pg/m^3). GOM concentrations in summer were much

276   lower than that in winter, which were largely due to the more favorable meteorological conditions.

277   However, GOM concentrations in summer were higher than spring and autumn, which should be

278   partly ascribed to the secondary transformation from GEM. More detailed analysis of the impact of

279   meteorological conditions on Hg species and the related formation mechanisms are presented in the

280   following sections.

281   Fig. 4 shows the diurnal variation of GEM, PBM, and GOM during the whole sampling period.

282   To ensure the time resolutions were consistent among all three mercury species, the temporal

283   resolution of measured GEM was converted from 5 minutes to a two-hour average. As shown in Fig.

284   4, GEM concentrations were higher during daytime with the maximum in the morning at around

285   10:00 and minimum in the midnight at around 02:00. The diurnal trends of GOM were as similar as

286   that of GEM, except that the minimum GOM occurred at around 20:00 in the evening. The diurnal

287   trends of PBM were different from those of GEM and GOM, exhibiting relatively higher

288   concentrations during nighttime. The PBM maximum occurred in the early morning at around 6:00

289   and the minimum was observed in the afternoon at 18:00. The diurnal trends of GEM, PBM, and

290   GOM were as similar as those in Nanjing (Zhu et al, 2012), but different from those in Guiyang,

291   Xiamen, and Guangzhou (Feng et al., 2004;Chen et al., 2013). Since DSL and Nanjing both belongs

292   to the Yangtze River Delta region, the similar meteorology and emission characteristics within the

293   Yangtze River Delta region may explain the similar diurnal patterns of Hg species between DSL

294   and Nanjing. The elevated GEM concentrations at DSL during daytime were likely related to the

295   stronger emissions from both human activities and natural releases. GOM and GEM showed similar

296   diurnal variations and both peaked at 10:00, probably suggesting that GOM and GEM were affected

297   by common sources (e.g. coal-fired power plants and industrial boilers). The high PBM

298 concentrations at night were likely derived from the adsorption of Hg species onto the preexisting

299 particles and the subsequent accumulation in the shallow nocturnal boundary layer. Fig. 4 shows

300 that wind speed was relatively low while high for relative humidity at night, which were conducive

301 to the adsorption of GOM onto the particles.

302

3.2. Relationship between Hg species and meteorological factors

304 Fig. 5 shows the relationship between wind direction/speed and atmospheric mercury species.

305 As shown in Fig. 5a, the prevailing wind at DSL during the study period came from the east,

306 accounting for approximately one-third of all the wind directions. Winds also prevailed from the

307 north with a fraction of 16%. Wind speed from all directions during the study period was mainly in

308 the range of 0-6 m/s, of which wind speed higher than 4 m/s mainly derived from the east. GEM as

309 a function of wind directions showed that the highest GEM concentrations were linked to the winds

310 from the south and southwest with the mean value of 3.92 ng/m^3, while the mean GEM

311 concentration from the other wind sectors was 2.71 ng/m^3 (Fig. 5b). GOM showed similar wind-

312 concentration patterns as GEM. While PBM showed high concentrations from the north/northwest

313 and south/southwest (Fig. 5c &5d). By referring to Fig. 1, the anthropogenic mercury emissions in

314 northern China were generally higher than southern China. Hence, the observation of high

315 atmospheric Hg concentrations from the north was expected. In this regard, the even higher

316 atmospheric Hg concentrations from the south and southeast than from the north cannot be simply

317 explained by anthropogenic emission sources, implying that there must be additional Hg emission

318 sources. (Feng et al., 2004) reported that the Hg concentrations in the surface soils of southern China

319 were generally higher than the northern China. A modeling study simulated that the mean annual

320 Hg air-soil flux in the southwest region of our sampling site (e.g. Zhejiang province) ranged from

321 8.75 to 15 ng m^{-2} h^{-1}, while that in the north/northwest region (e.g. Jiangsu province) ranged from

322 2.5 to 8.75 ng m^{-2} h^{-1} (Wang et al., 2016). Hence, emissions from natural sources, such as soils,

323 vegetations and water, should play an important role in the observed high atmospheric Hg

324 concentrations from the south and southeast.

325 In order to confirm this conjecture, the relationship between temperature and Hg concentrations

326 at DSL was investigated. Seasonal temperature in ascending order was divided into different groups

327 and the corresponding mean Hg concentrations were plotted in Fig. 6. In spring, the GEM

328   concentrations increased as the temperature increased. As for the other season, when the temperature

329   increased to a certain value, the trends of GEM variations were as similar as spring. This relationship

330   between GEM and temperature can be likely interpreted as the impact of surface emissions. It must

331   be noted that the height of PBL increased as the temperature increased, while at the same time, GEM

332   still showed a significant upward trend. This suggested that the atmospheric dilution effect caused

333   by the developing boundary layer was far from offsetting the increase of surface emissions caused

334   by increased temperature. The GOM concentration showed a clearly positive correlation with

335   temperature in summer. Higher temperature in summer in the Yangtze River Delta region is mostly

336   associated with ozone pollution days (Lu et al., 2018), thus implying higher GOM could be partially

337   related to the in situ oxidation of GEM in addition to its sources from direct emissions. In the other

338   seasons, no clear correlations between GOM and temperature were observed. As for PBM, it

339   appeared to have weakly negative correlations with the height of PBL, suggesting the atmospheric

340   diffusion conditions were influential on the concentrations of PBM.

341

342   **3.3. Tracing sources of Hg species**

343   **3.3.1. Potential source regions of Hg species**

344   PSCF was applied to identify the potential source regions of the three Hg species. As for GEM,

345   the major source areas were located in Anhui, Jiangxi, and Zhejiang provinces, and there were also

346   signals from Shandong province (Fig. 7a). As for the seasonal pattern (Fig. S1), the potential source

347   regions of GEM in spring were mainly from Jiangsu and Zhejiang provinces. In summer, the PSCF

348   hotspots were identified in Anhui and Jiangxi provinces. Jiangsu province was likely to become the

349   main potential source region of GEM in autumn. In winter, Anhui and Zhejiang provinces showed

350   relatively high PSCF values. In addition, there were also signals from Henan and Shandong

351   provinces, suggesting the importance of long-range transport in wintertime. There existed

352   substantial high PSCF signals in the southern areas, even stronger than those in the north. However,

353   as shown in Fig. 1, southern provinces such as Zhejiang and Jiangxi were estimated to release 25

354   tons/yr atmospheric Hg from anthropogenic activities, being far less than the northern provinces

355   such as Jiangsu and Shandong (77 tons/yr) (Wu et al., 2016). If only the anthropogenic emissions

356   of GEM were considered, the occurrence of stronger PSCF signals in southern provinces seemed

357   unreasonable. Based on the mean annual Hg air-soil flux of 8.75 to 15 ng m^{-2} h^{-1} in the southwest

region of our sampling site (Wang et al., 2016), it was estimated 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 province in 2014, it was approximately 15tons/yr (Wu et al., 2016). Thus, the magnitude of mercury from natural surfaces was comparable to that from anthropogenic sources. In this regard, the re-emission of GEM from natural surfaces in southern areas should be an important source, corroborating the discussion in Section 3.2. In addition, the East China Sea (including the offshore areas and open ocean) showed sporadic high PSCF signals of GEM in all four seasons (Fig. S1), indicating possible influences from shipping activities. The detailed estimation of variable sources would be discussed in Section 3.3.3.

The PSCF pattern of PBM was quite different from that of GEM (Fig. 7b). The potential source regions of all year round PBM were mainly from the north of Jiangsu and Anhui provinces, and from northeastern China, including Shandong and Hebei provinces. These provinces were regarded as the main Hg sources areas in China and accounted for approximately 25.2% of the Chinese anthropogenic atmospheric Hg emissions (Wu et al., 2016). As for the seasonal PSCF patterns of PBM (Fig. S2), its potential source regions in spring, autumn, and winter shared certain commonalities that exhibited the consistent PSCF patterns as the annual pattern. The exception was found for summer, which showed high PSCF values mainly in the southern areas of Shanghai. This might be attributed to that the prevailing winds in summer were from the south, southeast, and southwest where Zhejiang and Jiangxi provinces were important mercury source regions.

The potential source regions of all year round GOM were mainly located in Anhui and Zhejiang provinces and the coastal areas along Jiangsu province (Fig. 7c). The PSCF pattern of GOM was as similar as that of GEM but different from that of PBM. The potential source regions of GOM were more from southern China rather than from northern China, which might be due to the higher atmospheric oxidant levels in the southern regions. Especially in summer, the potential sources regions of GOM concentrated in Zhejiang and Jiangxi provinces (Fig. S3). In the other seasons, there were somewhat different PSCF patterns observed. In detail, while significant PSCF signals from the inland areas were found, moderate PSCF signals over the East China Sea and Yellow Sea also observed in spring. In autumn, the high PSCF values mainly occurred in Zhejiang province and there were also moderate signals over the Yellow Sea. In winter, the high PSCF values spread from the coastal areas of Jiangsu to a vast ocean of the Yellow Sea. One previous study suggested that the

marine boundary layer could provide considerable amounts of oxidants such as chlorine and bromine, which were beneficial for the production of GOM by oxidizing GEM (Auzmendi-Murua et al., 2014) and this may explain the substantial PSCF signals over the ocean.

The results of the PSCF analysis suggested the significant influences of adjacent areas of Shanghai on contributing to all the atmospheric mercury species. It was also illustrated that the long-range and regional transport via both land transport and sea breeze were important.

3.3.2. Comparison between the impact of quasi-local sources and regional/long-range transport on atmospheric mercury

According to the relationship between wind direction and Hg species as well as the PSCF analysis discussed above, the elevated GEM, GOM, and PBM concentrations at the observation site were generally related to the wind sectors from the southwest and north. In order to reveal the relative importance of local sources and regional transport, the ratio of GOM/PBM was applied as an indicator based on the fact that the residence time of GOM is generally considered to be shorter than that of PBM. If regional/long-range transport was evident, the ratio of GOM/PBM should be lower due to that GOM was more quickly scavenged than PBM during the transport, and vice versa when local sources dominated. In this regard, the ratios of GOM/PBM during the whole study period were grouped into four categories, i.e. 0-1, 1-2, 2-3, and higher than 3. The corresponding frequency of wind direction in each category was compared in Fig. 8. It was clear that the higher GOM/PBM ratios were associated with more frequent winds from the east and southeast. The frequency of these two wind sectors increased significantly from 27% under the GOM/PBM ratios less than 1 to 52% under the GOM/PBM ratios higher than 3. Winds from the east and southeast were typically characterized of relatively clean air masses, suggesting the local sources around the observational site should dominate. In contrast, the lower GOM/PBM ratios were associated with more frequent winds clockwise from the west to the north and the frequency of these wind sectors decreased significantly from 44% under the GOM/PBM ratios less than 1 to 21% under the GOM/PBM ratios higher than 3. These winds were indicative of the long-range/regional transport from northern China and were associated with the relatively low GOM/PBM ratios. According to the PSCF results above, the potential source areas of Hg species (GEM, GOM and PBM) derived mostly from the south and southwest of the sampling site. As shown in Fig. 8, the frequency of south, southwest, west, and

northeast winds showed no clear trend as the GOM/PBM ratios increased. This suggested the emissions of Hg in these directions of the sampling site were complicated, and the phenomenon above can not be simply explained by the impact of local sources or regional transport. In general, the GOM/PBM ratio can be used as a qualitative tracer for identifying the relative importance of long-range transport vs. local sources. However, when the influences from long-range transport and local emission were close, the result could be ambiguous based on this method and this may require further efforts such as chemical transport modeling.

The relationships among GEM, CO, secondary inorganic aerosols (SNA) and GOM/PBM ratios were further investigated. Fig. 9 displays the concentrations of GEM as a function of GOM/PBM ratios colored by CO. The sizes of the circles represented the corresponding concentrations of SNA in $PM_{2.5}$. CO was commonly used as a tracer of fuel combustion and SNA were derived from secondary particle formation via the gas-to-particle conversion. CO and SNA were collectively used as proxies of the extent of anthropogenic air pollutants and especially for evaluating the extent of regional/long-range transport. As shown in Fig. 9, GEM showed an overall increasing trend as the GOM/PBM ratios increased. In addition, it could be clearly seen that the lower GOM/PBM ratios were associated with higher CO and SNA concentrations and vice versa. 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.

In the GOM/PBM ratio bins of less than 2.5, GEM fluctuated with the mean values less than 2.6 ng/m^3. The mean GEM concentration increased from 2.61 ng/m^3 in the GOM/PBM ratio bin of 2.5-3.0 to 2.8 ng/m^3 in the bin of 3.0-3.5, and then remain relatively stable when the GOM/PBM ratio bins higher than 3.0. Generally, GEM showed an increasing trend as the GOM/PBM ratios increased while both SNA and CO decreased. The elevation of GEM concentrations tended to be associated with the impact of quasi-local sources. In contrast, under the high SNA and CO conditions when GOM/PBM ratios were lower, GEM showed relatively low concentrations. This suggested the regional/long-range transport didn't favor the elevation of GEM concentrations. It has been recognized that the common regional/long-range transport pathways on contributing to the particulate pollution events of Shanghai were from the north and northwest originating mostly from the North China Plain. The relatively lower GEM concentrations under the regional/long-range transport conditions corroborated the PSCF analysis that only moderate probabilities of GEM source

448   regions from northern China were found (Fig. 7a).

449

3.3.3. Source apportionment by combined PMF and PCA

451   PMF modeling has been widely used to apportion the sources of atmospheric pollutants. In this

452   study, GEM together with heavy metals and soluble ions, measured online synchronously, were

453   introduced into the EPA PMF5.0 model to apportion the major anthropogenic sources of GEM. A

454   six-factor solution was selected based on the results of multiple model runs, which can well explain

455   the measured concentrations of the introduced species. The profiles of six identified PMF factors

456   and contributions of major anthropogenic sources to GEM are shown in Fig. 10. It has to be noted

457   that since no tracers for the natural emissions (e.g. soils, vegetations, and ocean) were available in

458   this study, the identification of natural mercury sources was not possible based on the PMF modeling.

459   Factor 1 had high loadings for Se, As, Pb, NO_3^-, SO_4^{2-}, and NH_4^+. Se, As, and Pb were typical

460   tracers of coal combustion. SO_4^{2-} and NO_3^- were also formed from the gaseous pollutants emitted

461   from coal burning. Hence, this factor was defined as coal combustion sources and accounted for

462   12.3% of the anthropogenic GEM. Fig. S4 plotted wind roses of specific aerosol species. Of which,

463   SO_4^{2-} and As shared similar patterns with high concentrations mainly from the southwest. Since

464   combustion was an important source of GEM, this confirmed that the major sources of GEM were

465   located in the southwest region.

466   Factor 2 displayed particularly high loadings for Ni and V. The major sources of Ni in the

467   atmosphere can be derived from coal and oil combustions (Tian et al., 2012), and oil combustion

468   accounted for 85% of anthropogenic V emissions in the atmosphere (Duan and Tan, 2013). In

469   general, Ni and V have been considered as good tracers of heavy oil combustion, which has been

470   commonly used in marine vessels (Viana et al., 2009). Thus, this factor was identified as shipping

471   emissions. The sampling site is adjacent to the East China Sea and is located in Shanghai which has

472   the largest port in the world. Fig. S4 showed similar patterns of Ni and V with high concentrations

473   mainly from the northeast, east, and southeast. To further validate this factor, the time-series of GEM

474   concentrations from the shipping factor based on the PMF modeling were extracted and digested

475   into the PSCF modeling (Fig. S5), showed that the potential sources regions were mainly located

476   over the East China Sea and coastal regions. This indicated factor 2 from PMF should be

477   representative of the shipping sector as well as oil combustion in motor vehicles and inland shipping

478 activities. Overall, this factor accounted for 19.6% of anthropogenic GEM and ranked as the second

479 largest emission sector, highlighting the urgent need of controlling the marine vessel emissions.

480 Factor 3 showed high loadings for Ca and moderate loadings for Ba and Fe. Ca and Fe are rich

481 elements in crust that can be used for cement production. As mercury could be released during

482 industrial processes of cement production, Factor 3 was assigned as cement production and

483 accounted for a minor fraction of 6.3 % of the anthropogenic GEM.

484 Factor 4 was characterized by high loadings of Cr and moderate loadings of Mn, Fe, Ni, and

485 Cu. These species together served as markers of metals smelting. Metals smelting were known to

486 be large sources of Hg emitted to the atmosphere (Pirrone et al., 2010), especially in the YRD, one

487 of the most developed and industrialized areas in China. This factor accounted for 7.6% of the

488 anthropogenic GEM.

489 Factor 5 had high loadings of Cl$^-$. Waste incineration is an important source of enriched

490 chloride over land. Factor 5 was identified to be waste incineration, which contributed 6.4% of the

491 anthropogenic GEM.

492 Factor 6 was characterized by high loadings of Cd, Ag, K$^+$, and Na$^+$. The major sources of Cd

493 in China were iron and steel smelting industries (Duan and Tan, 2013). Ag was mainly used in

494 industrial applications, including electronic appliances and photographic materials. K$^+$ was a typical

495 tracer of biomass burning, which often stemmed from agriculture waste burning over the Yangtze

496 River Delta and the North China Plain. In this regard, Factor 6 was considered as a combined source

497 of the industrial and biomass burning emission sectors. It was estimated to contribute 47.8% of the

498 anthropogenic GEM.

499 As discussed in the above sections, surface emissions were likely to be important sources of

500 the observed atmospheric mercury. As PMF modeling didn't resolve the natural sources of mercury,

501 the PCA (Principal Component Analysis) was applied for further source apportionment by

502 introducing the temperature parameter. Four factors are resolved, which totally explained 75.32%

503 of the variance as shown in Table 2. Factor 1 accounted for 34.15% of the total variance with high

504 loadings for SO$_2$, SO$_4^{2-}$, NH$_4^+$, K$^+$, Pb, Se, and As, which was explained as coal combustion mixed

505 with biomass burning. Factor 2 accounted for 14.85% of the total variance with high loadings for

506 temperature, O$_3$, and NH$_3$, which was explained as surface emissions. Factor 3 explained 13.43%

507 of the total variance and showed high loadings for Ni and V, which indicated the contribution of

508 ship emissions. Factor 4 explained 12.89% of the total variance and showed high loading for Fe and
509 Ca, indicating the contribution of cement production.

510

511

512 **3.4. Factors affecting the formation and transformation of mercury species**

513 **3.4.1. Factors affecting the formation of GOM**

514   A typical case from July 24 to July 27, 2015 was chosen to investigate the possible formation

515 process of GOM. As shown in Fig. 11, the shaded episodes represented nighttime from 18:00 to

516 6:00 the next day. Both GEM and GOM exhibited rising trends during nighttime (Fig. 11a), which

517 was ascribed to nighttime accumulation effect due to the very shallow boundary layer (Fig. 11c).

518 Starting from 6:00 in the morning, GEM concentrations began to gradually decline as the boundary

519 layer developed. In contrast, the concentrations of GOM continued to rise from 6:00 until it reached

520 the peak value at around 10:00. During this period, the levels of ozone and temperature also kept

521 rising until surpassed 200 $\mu g/m^3$ and 34°C, respectively. Accordingly, as an anthropogenic emitting

522 tracer, the concentration of carbon monoxide was basically stable and even showing a downward

523 trend, which suggested some other factors accounted for the increase of GOM in addition to the

524 anthropogenic emissions. This phenomenon clearly revealed the acceleration of the conversion

525 process of GEM to GOM under favorable atmospheric conditions of higher O_3 concentration and

526 ambient temperature. In the case of atmosphere dilution by the rise of PBL, the fact that GOM was

527 not falling but rising suggested the great influence of this process on ambient GOM concentrations.

528 Similar observation has been found at the high-altitude Pic du Midi observatory in southern France

529 (Fu et al., 2016), which was almost impervious to anthropogenic emission sources. The important

530 role of GEM oxidation in our sampling site, which located in one of the most developed industrial

531 areas in China, was most likely due to the presence of sufficient oxidants in this area. Severe ozone

532 pollution frequently occurred in the YRD due to strong anthropogenic emission intensities (Lu et

533 al., 2018). Previous studies suggested that the primary oxidants in the terrestrial environment were

534 O_3 and OH radicals (Shon et al., 2005), while Br was an important oxidant in the subtropical marine

535 boundary layer (Obrist et al., 2011). It was possible that, in addition to O_3 and OH radicals, Br might

536 also be an important inducing species to the oxidation of GEM as the DSL site is adjacent to the

537 East China Sea.

538   Fig. 12 statistically analyzed the relationship among GOM, O_3, and temperature. Temperature

539   was plotted against a range of GOM/PBM bins colored by O_3 and the size of the circles represented

540   the concentrations of GOM. In general, as temperature and O_3 increased, the concentrations of GOM

541   were subject to substantial enhancement. For instance, when temperature (O_3) was below 12°C (65.7

542    $\mu g/m^3$), GOM averaged 37.8 pg/m^3. While temperature (O_3) increased to above 20°C (91.5 $\mu g/m^3$),

543   GOM rose to 168.8 pg/m^3, yielding a factor of 1- 5 GOM increases. This further confirmed the case

544   study above that the levels of oxidants under favorable environmental conditions were crucial for

545   the formation of GOM. Fig. 12 also suggested that the lower ratios of GOM/PBM were associated

546   with lower temperature and O_3 concentrations, indicating relatively weak photochemistry during

547   the cold seasons. On the contrary, the higher ratios of GOM/PBM were associated with higher

548   temperature and O_3 concentrations, indicating relatively strong photochemistry during the warm

549   seasons. This suggested that the formation of GOM was more favored by local atmospheric

550   processing rather than the transport. This study demonstrated the abnormally high GOM

551   concentrations observed at DSL were largely ascribed to local oxidation reactions. However, the

552   explicit formation mechanism of GOM need to be investigated by measuring more detailed

553   components of GOM and atmospheric oxidants.

554

555   **3.4.2. Factors affecting the transformation of PBM**

556   Previous studies have shown that PBM can be emitted directly from various anthropogenic

557   sources such as coal-fired power plants and industries (Liu et al., 2018;Wu et al., 2016).   In

558   addition, gas-particle partitioning was considered to be an important pathway for the formation of

559   PBM (Shon et al., 2005;Amos et al., 2012). Since most of the areas in the YRD belong to non-

560   attainment areas in regard of particulate pollution and the concentrations of GOM were particularly

561   high at DSL as discussed above, the role of gas-particle partitioning in the formation of PBM should

562   be investigated. Previous studies reported that the concentrations of $PM_{2.5}$ in eastern and northern

563   China are highest in the world (Auzmendi-Murua et al., 2014), elevated atmospheric particulate

564   matter probably facilitates the formation of PBM in the atmosphere in China (Fu et al., 2015). Fig.

565   13 shows the statistical pattern of the variation of PBM and GOM in the ascending bins of $PM_{2.5}$.

566   The concentrations of PBM increased with the concentrations of $PM_{2.5}$, which was due to both

567   primary emissions and the subsequent process of Hg species adsorbed on particulate matters. The

568 trend of GOM was somehow different from that of PBM. When $PM_{2.5}$ concentrations were at

569 relatively low levels under 75 μg/m³, GOM concentrations increased with $PM_{2.5}$. However, when

570 $PM_{2.5}$ concentrations increased to 75-105 μg/m³, GOM exhibited a clear decreasing trend as $PM_{2.5}$

571 increased. It seemed that when the concentration of $PM_{2.5}$ reached a certain value, the formation of

572 GOM was inhibited to some extent, which was likely due to the adsorption of GOM onto the

573 particles. When $PM_{2.5}$ concentrations exceeded 105 μg/m³, GOM exhibited a slightly increasing

574 trend as $PM_{2.5}$ increased. High $PM_{2.5}$ concentrations in China always related to severe anthropogenic

575 emissions (Auzmendi-Murua et al., 2014), so the moderate increasing trend of GOM in these bins

576 should be attributed to the impact of strong primary emissions.

577   A short episode from December 30, 2015 to January 1, 2016 was chosen to further investigate

578 this phenomenon. As shown in Fig. 14, in Stage 1, the concentrations of $PM_{2.5}$ were below 100

579 μg/m³, PBM and GOM shared the similar temporal variation as $PM_{2.5}$. In Stage 2, as $PM_{2.5}$ kept

580 climbing, GOM began to show somewhat negative correlation with $PM_{2.5}$, but not significant. The

581 reason might be that the relatively high temperature and low humidity during this period were not

582 conducive to the transfer of GOM to particle matters. In Stage 3, GOM decreased as $PM_{2.5}$ continued

583 to increase, showing a clear anti-correlation. During this period, PBM showed a consistent trend

584 with $PM_{2.5}$ and CO. Temperature was relatively low but with relatively high humidity. This

585 phenomenon clearly demonstrated the process of gas-particle partitioning of PBM formation. In

586 stage 4, GOM and PBM showed similar decreasing trend with $PM_{2.5}$ and CO. The low GOM

587 concentrations, low humidity, and high temperature resulted in no significant signs of GOM

588 adsorption to $PM_{2.5}$ in this stage. In general, under high $PM_{2.5}$ and GOM concentrations, high

589 humidity and low temperature conditions in our sampling site, clear processes of gas-particle

590 partitioning were observed .

591

592 **4. Conclusions**

593   In this study, a year-long observation of three atmospheric Hg species was conducted at the

594 Dianshan Lake (DSL) Observatory, located on the typical transport routes from mainland China to

595 the East China Sea. During the whole measurement period, the mean GEM, PBM, and GOM

596 concentrations were 2.77 ng/m³, 60.8 pg/m³, and 82.1 pg/m³, respectively.

597   Different from many sites in China, GEM at DSL exhibited high concentrations in winter,

summer, and spring, which was due to the strong re-emission fluxes from natural surfaces in summer and enhanced coal combustion for residential heating over northern China in winter. The relatively high GOM concentrations in summer indicated that the formation of GOM from GEM oxidation was likely crucial. PBM exhibited high concentrations in winter, indicating the impact from long-range transport. The diurnal patterns of GEM and GOM were similar with relatively high levels during daytime. For GEM, this was likely attributed to both human activities and re-emission from natural surfaces during daytime. For GOM, in addition to direct emissions, high concentrations during daytime were partially ascribed to photochemical oxidation of GEM. The PBM concentrations were higher during nighttime, which was ascribed to the accumulation effect within the shallow nocturnal boundary layer.

The relationship between meteorological factors and atmospheric Hg species showed that the high Hg concentrations were generally related to the winds from the south, southwest, and north and positively correlated with temperature. Both anthropogenic sources and natural sources contributed to the atmospheric mercury pollution at DSL. Higher GOM/PBM ratios corresponded to lower CO and SNA concentrations and vice versa. The ratio of GOM/PBM can be used as a tracer for distinguishing local sources and regional/long-range transport based on the fact that the residence time of GOM was shorter than that of PBM. GEM as a function of the GOM/PBM ratios indicated that when the quasi-local sources dominated, GEM concentrations were relatively higher than those events under the regional/long-range transport conditions. According to the PMF source apportionment results, six sources of anthropogenic GEM and their contributions were identified, i.e. industrial and biomass burning (47.8%), shipping emission (19.6%), coal combustion (12.3%), iron and steel production (7.6%), incineration (6.4%), and cement production (6.3%). The significant contribution of shipping emission suggested that in coastal areas mercury emitted from marine vessels can be significant. In addition, a considerable natural source of GEM was identified by digesting temperature into the principle component analysis.

The formation processes of GOM and PBM based on episodic studies were also investigated. The high GOM concentrations were partially attributed to strong local photochemical reactions under the conditions of high O_3 and temperature. Under high $PM_{2.5}$ concentrations, high humidity and low temperature conditions, the gas-particle partitioning processes were observed at DSL, which might be an important pathway for the formation of PBM.

628

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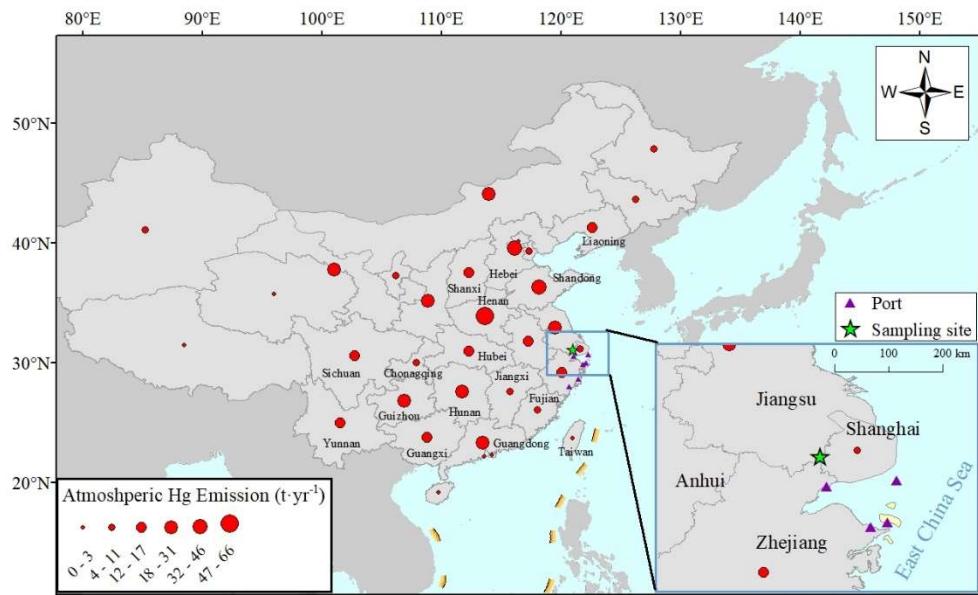
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802   Figure 1. The location of the Dianshan Lake (DSL) site in Shanghai, China. The red dots in the
803   map represent the anthropogenic atmospheric Hg emissions by each province in 2014 (Wu et al.,
804   2016).
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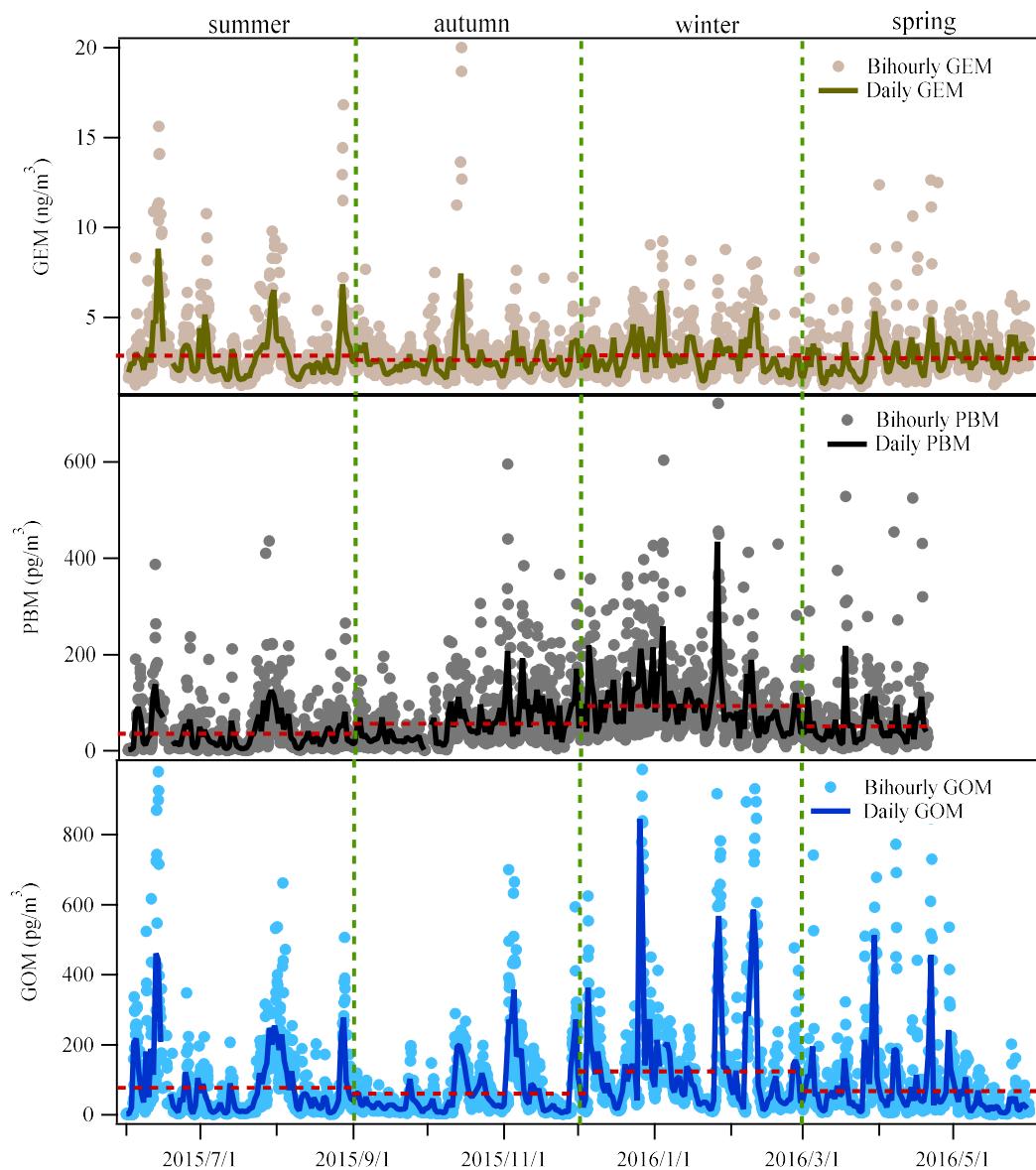
Figure 2. Time series of atmospheric Hg (GEM, PBM and GOM) concentrations during the whole
study period at DSL. The red-dashed lines represent the mean concentrations of Hg species in
each season.

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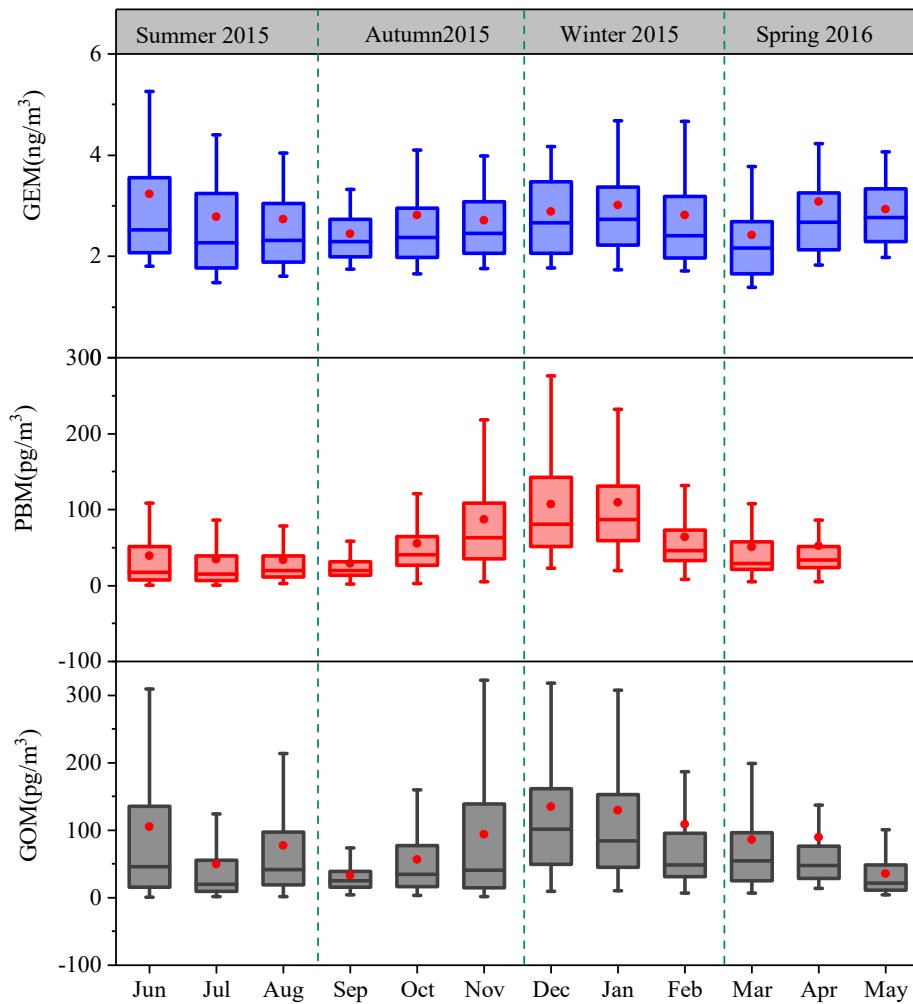
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816 Figure 3. Monthly variation of GEM, PBM, and GOM concentrations. The 10th,25th, median, 75th

817 and 90th percentile values are indicated in the box plots. The red dots represent the mean values.

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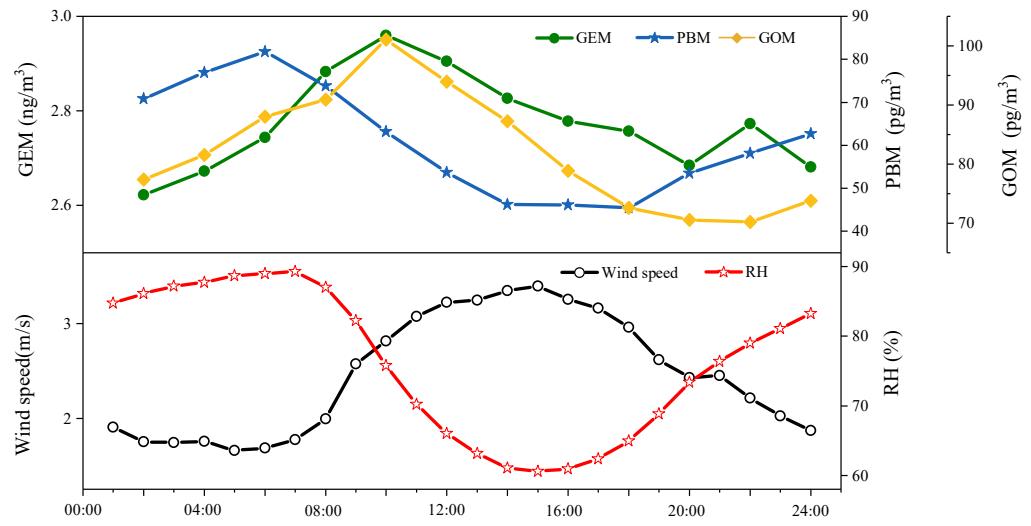
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821 Figure 4. Annual mean diurnal variation of GEM, PBM, and GOM concentrations.
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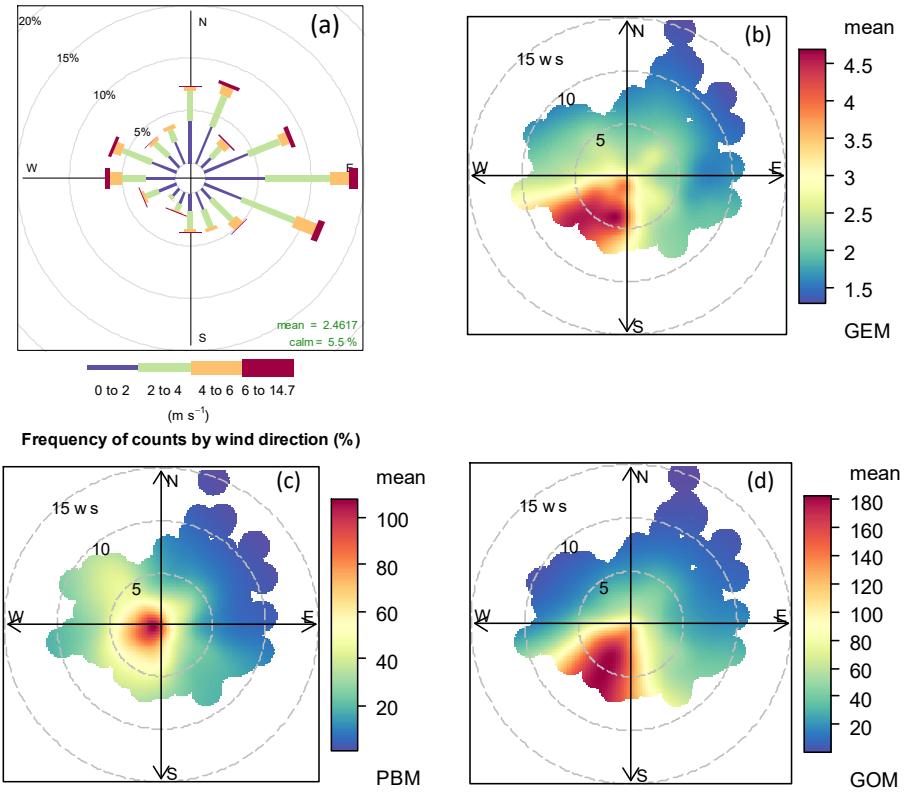
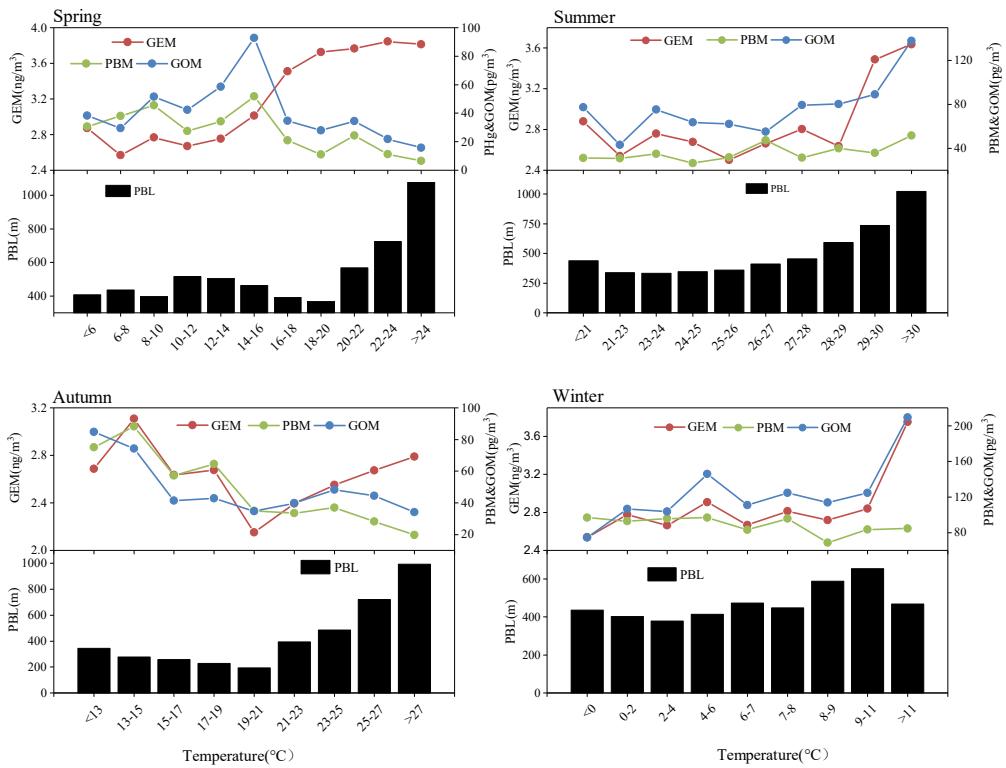


Figure 5. (a) Wind rose plot during the study period. Mean concentrations of (b) GEM, (c) PBM, and (d) GOM as a function of wind speed and wind directions. The radii of the circle in Figure 5 (a) represent the frequency of wind directions and the radii of the circle in Figure 5 (b), (c), and (d) represent the value of wind speed.

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830   Figure 6. The variation of atmospheric Hg (GEM, PBM, and GOM) and PBL as a function of

831   temperature in all four seasons.

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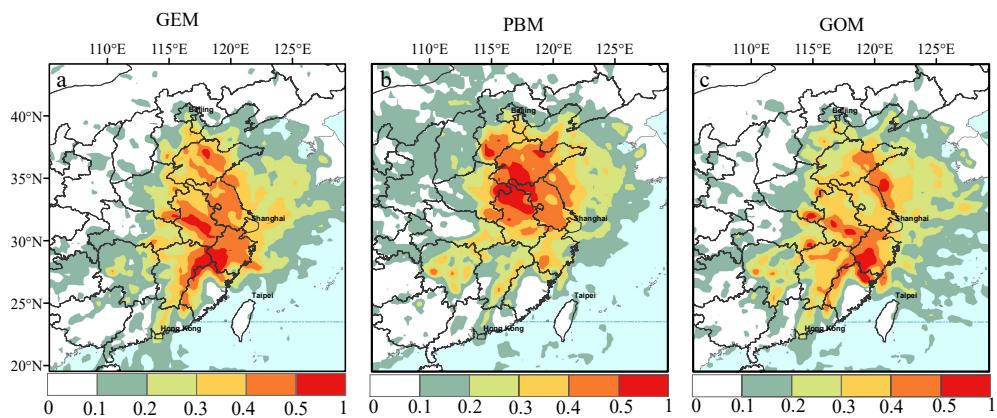
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834 Figure 7. Potential source regions of atmospheric Hg (GEM, PBM, and GOM) at the observational

835 site according to PSCF analysis.

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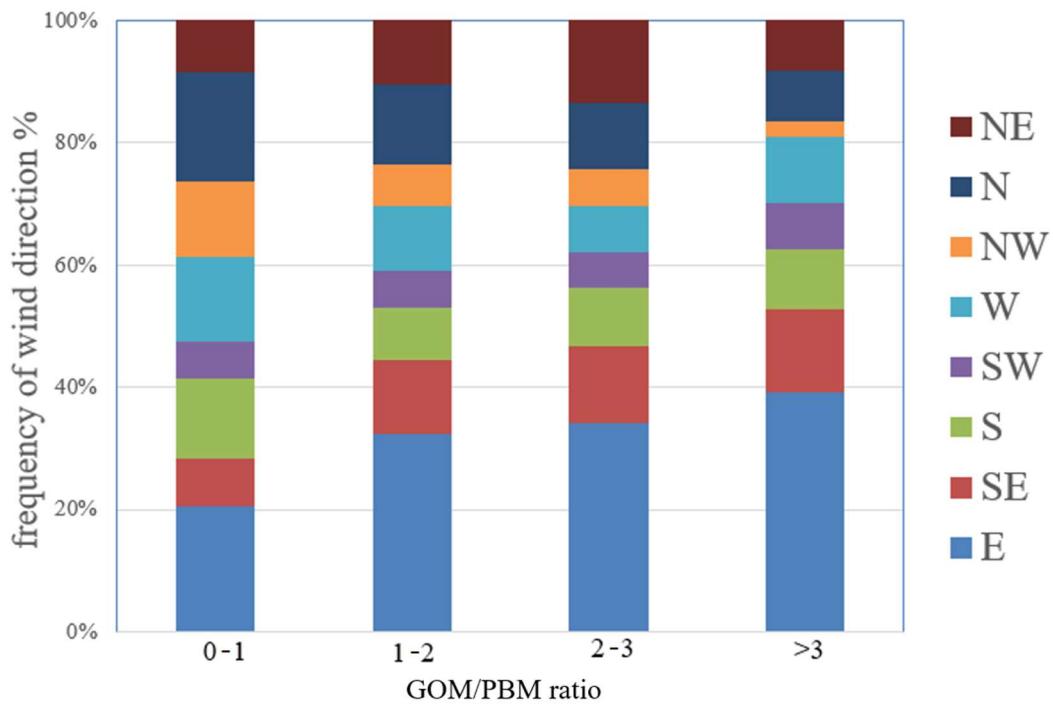
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838   Figure 8. Frequency of wind directions under different ranges of GOM/PBM ratios.

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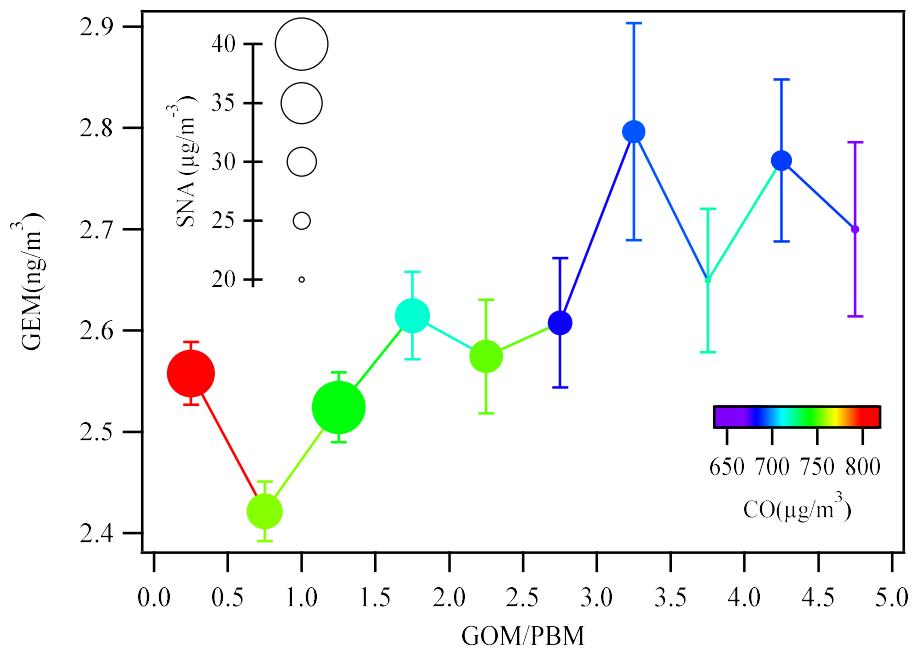
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841 Figure 9. The GEM concentrations as a function of the GOM/PBM ratios in each bin of 0.5. The

842 dots are colored by the concentrations of CO and the sizes of the dots represent the concentrations

843 of SNA in PM$_{2.5}$. The bars represent one standard error of GEM concentration in each bin.

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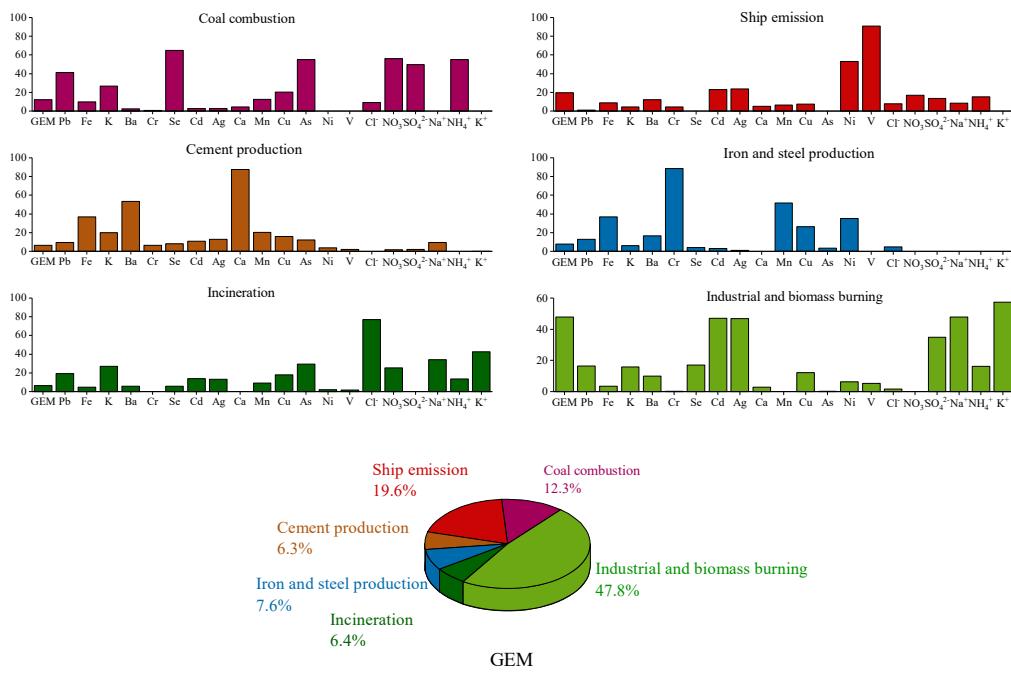
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846   Figure 10. A six factor source apportionment for anthropogenic GEM based on PMF analysis.

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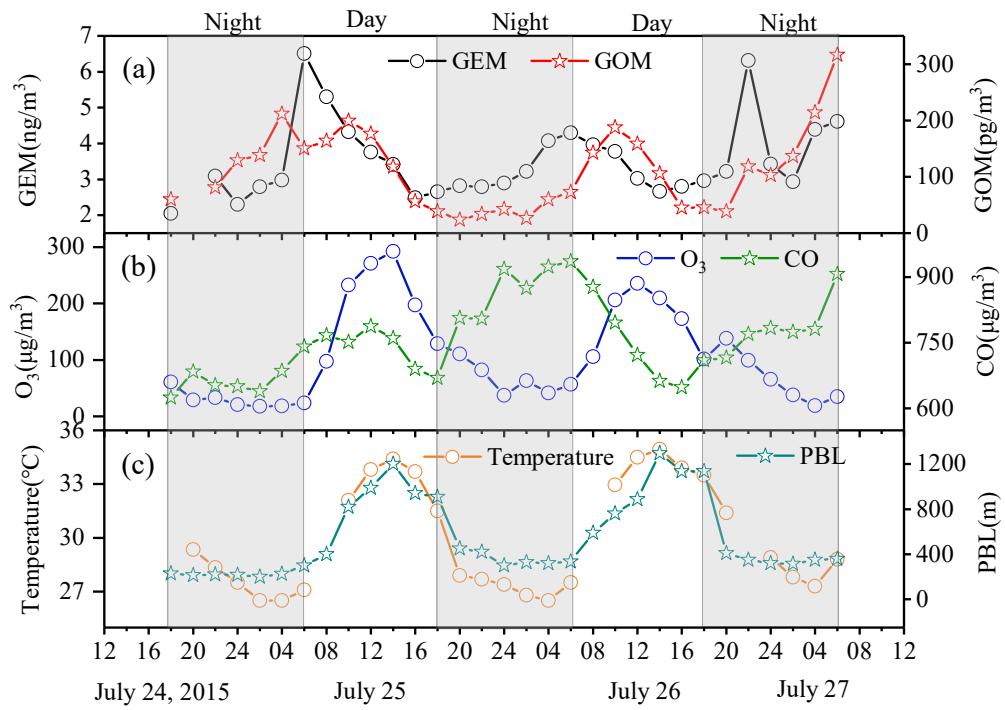
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849 Figure 11. A case study of GEM oxidation from July 24 to 27, 2015. The time-series of GEM, GOM,

850 O_3, CO, temperature, and PBL are plotted. The shaded parts represent nighttime.

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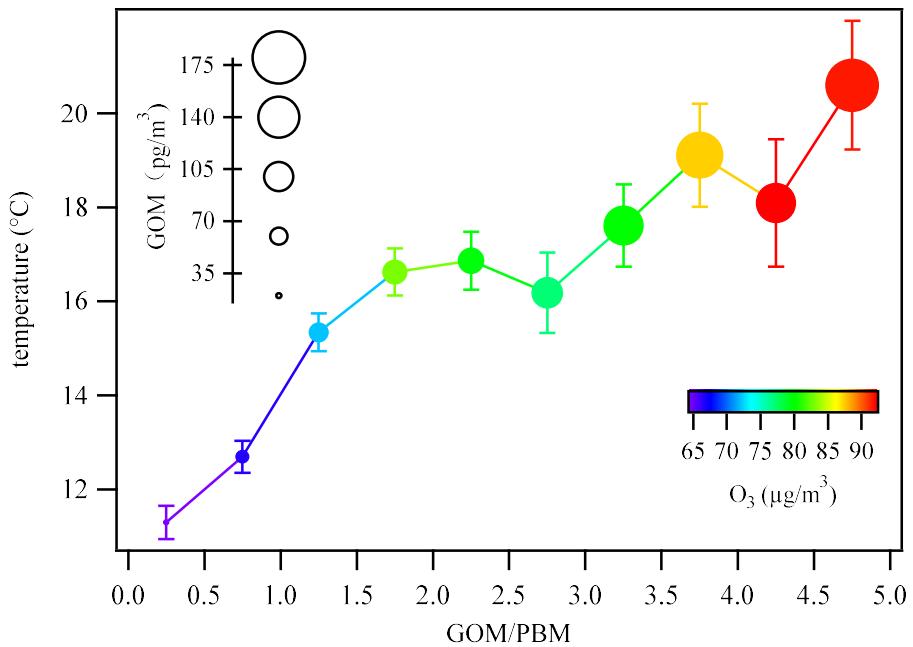
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853 Figure 12. Temperature variations in each bin of the GOM/PBM ratios. The dots are colored by the

854 concentrations of O_3 and the sizes of the dots represent the concentrations of GOM. The bars

855 represent one standard error of temperature in each bin.

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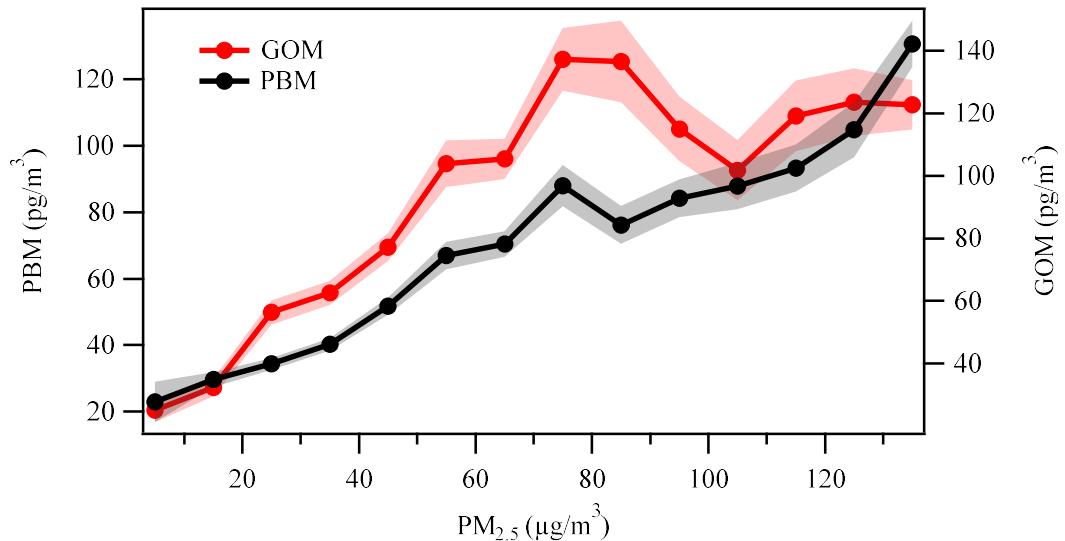
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859   Figure 13. The variations of PBM and GOM as a function of PM$_{2.5}$ in each bin of 10 μg/m^3. The

860   shaded areas represent one standard error of GOM and PBM concentrations.

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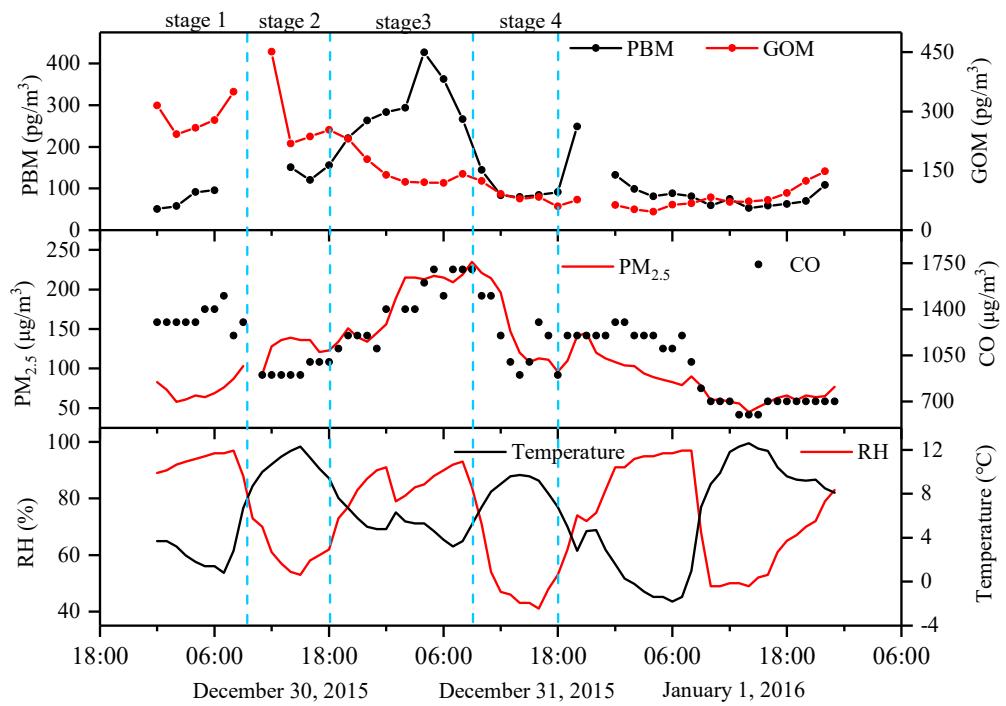
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863 Figure 14. A case study of gas-particle portioning between GOM and PBM from December 30, 2015

864 to January 1, 2016, which was divided into different stages. The time-series of PBM, GOM, PM$_{2.5}$,

865 CO, temperature, and RH are plotted.

Table 1. The concentrations of speciated atmospheric mercury in this study and other sites around the world.

Location	Remarks	Year	GEM (ng/m^3)	PHg (pg/m^3)	RGM (pg/m^3)	Reference
Dianshan Lake Shanghai, China	Suburban	2015-2016	2.77±1.36	60.8±67.4	82.13±115.5	This study
Chongming Shanghai, China	Suburban	2009-2012	2.65±1.73	21.5±25.4	8.0±8.8	Zhang et al. (2017)
Xiamen, China	Suburban	2012-2013	3.5	174.41	61.05	Xu et al. (2015)
Guiyang, China	Urban	2009	9.72±10.2	368±676	35.7±43.9	Fu et al. (2011)
Miyun, China	Rural	2008-2009	3.23	98.2	10.1	Zhang et al. (2013)
Mt.Waliguan, China	Remote	2007-2008	1.98±0.98	19.4±18.1	7.4±4.8	Wan et al. (2009)
Seoul, Korea	Urban	2005-2006	3.22±2.10	23.9±19.6	27.2±19.3	Kim et al. (2009)
Nova Scotia, Canada	Rural	2010-2011	1.38±0.2	0.4±1.0	3.5±4.5	Cheng et al. (2014)
Elora,Ontario, Canada	Rural	2006-2007	1.17	16.40	15.1	Baya and Van Heyst (2010)
Chicago, USA	Urban	2007	2.5±1.5	9±20	17±87	Gratz et al. (2013)
Reno,USA	Suburban	2007-2009	2.0±0.7	7±7	18±22	Lyman and Gustin (2009)
Rochester, NY, USA	Urban	2008-2009	1.49	6.57	4.08	Huang et al. (2010)

Table 2. PCA (Principal Component Analysis) analysis 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