Atmospheric
Chemistry
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Discussions

EGU

Interactive comment on "Characteristics of atmospheric mercury in East China: implication on sources and formation of mercury species over a regional transport intersection zone" *by* Xiaofei Qin et al.

Anonymous Referee #2

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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 under-

standing 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.

Specific comments: Line 26: what is meant by quasi-local? Please explain what local sources were affecting this site. 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. 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." Line 76: The treaty name is Minamata Convention on Mercury. 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? 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? 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. 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? Line 167: Please describe how the back trajectories were calculated and the relevant model inputs and parameters. 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? Lines 192-193: Please include the standard deviation for the concentrations. 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? 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.

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. 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)? 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/m3. Since wind speed and wind direction data were used, the sources are likely local which narrows down the area of investigation. 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.? 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. 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. 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? 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. 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. 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

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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? 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. 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. 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? 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. 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/m3 at times) as shown in the time-series plots are very concerning, and I would look further into what is the cause of this. 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

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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. 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.