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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Use of criteria pollutants, active and passive mercury sampling, and receptor modeling to understand the chemical forms of gaseous oxidized mercury in Florida" *by* J. Huang et al.

Anonymous Referee #2

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The manuscript presents the measurement data of speciated mercury and a number of criteria pollutant (ozone, nitrogen oxides, PM, CO, and sulphur dioxide, etc.) in the Outlying Landing Field, northwest Florida over a period of approximately 2 years. Multiple samplers of different natures (Tekran speciation instrumentation and passive samplers) were deployed for the GOM measurement. Dry deposition of GOM was estimated using the Aerohead sampler and resistance modelling with modified Tekran GOM data. This is a major undertaking of field campaign and it appears that a large field data set has been collected. With that said, this is a manuscript that is somewhat difficult to

review because of a lack of a focused objective, large data uncertainties, somewhat arbitrary assignments in resistance modelling approach and product identification, and general data analysis (averaging the data over a long measurement period). These shortfalls impair the readability of the manuscript and weaken the primary conclusions of the study. Given the useful datasets obtained during the field study and the relevance to the scope of ACP, the manuscript should be considered for publication after revision. Below are a number of points that may help improve the quality of the manuscript.

1. The title of the manuscript is to "Use of criteria pollutants, active and passive mercury sampling, and receptor modeling to understand the chemical forms of gaseous oxidized mercury in Florida," but the conclusions of the study do not seem to provide conclusive remarks to demonstrate that the chemical forms of GOM in Florida have been understood. The use of criteria pollutant and the receptor modelling part of the manuscript do not seem to have much related to understanding the chemical forms of GOM, either. The authors should consider revising the title to better reflect the content and conclusions of the study presented in the manuscript.

2. Introduction. The text generally describes the measurement uncertainty of GOM and the state of measurement of atmospheric mercury in Florida without bringing out the primary scientific questions to be answered in this work. What is the primary objective of this study? If the primary focus of the study is to elucidate the source-receptor relationship, it would be much more deterministic to use those reliable datasets (GEM and criterion pollutants) to understand the sources and air transport. It will be also useful to look into the behaviours of specific pollution events in greater details. On the other hand, if the primary focus is to inter-compare different GOM measurement techniques and dry deposition estimates, it is necessary to establish well-defined quality standards and then look into the data difference in a more robust fashion. At its current form, the manuscript achieves a little bit of both but misses an excellent opportunity to extract the technical merits of such a unique field effort.

3. P12076, L20-25. Typically an MDL is a fixed value from the measurements of a

selected number of samples (for example, three times of the standard deviation of 7 sample measurements). Are the provided ranges referring to certain confidence intervals? Some quality indication of the criteria pollutants should also be mentioned.

4. P12077, Section 2.4. First, there are many parameters incorporated in the resistance model of Zhang (2013). At a minimum, how those parameter values were selected and how the model was "modified" (as described in the manuscript) should be clearly presented (perhaps in SI?). Second, the "adjusted GOM ambient concentration measured by the Tekran system" was applied for dry deposition calculation. The adjusted values for different GOM compounds are different as described here. But the Introduction states that the Tekran GOM concentration is adjusted by a factor of 3. Which one is correct? Also, using such adjustments seems arbitrary and might not provide a better estimate for a number of reasons: (1) the measurement uncertainty is also magnified by the adjustment factors, (2) the assignment of GOM products for ambient samples has yet to be verified under the given atmospheric condition (more on Comment #8), and (3) there is no indication of direct correspondence of Hg compounds between the Tekran denuder and the passive samplers, not to mention that there are also substantial difference between the two membrane materials. Some discussion alone this line should be given to ensure appropriate interpretation of the data.

5. It is suggested that the ratio of mixing ratios be used for representing the GEM/CO ratios.

6. Figure 2. The average of 2-year data dilutes valuable signals of the temporal dynamics. This is reflected in the magnitude of the error bar (much greater than the mean). It is unclear what specific information is given in these plots other than the GOM/PBM concentration is clearly enhanced during daytime. The discussion relating to this graph on P12080 is more on the criteria pollutants without linking the discussion to atmospheric mercury. Because plus/minus standard deviation is used for representing the error bars, the tails of many lower error bar limits extend into the negative range. Perhaps box plot is a better visualization method for these data.

7. Figure 3. The only use of the figure in the manuscript is to suggest the elevated pollution event and the general feature shown in the plots are not elaborated. Other than showing the magnitude and variability of the measurements, what are the observed correlations among those measurements? Another interesting feature is that there is a large disparity among the GOM data measured by the three methods and the value reported by the Tekran speciation instrumentation is not necessarily the lowest as suggested earlier in the manuscript. This brings about an interesting question: how much does Tekran instrumentation underestimate GOM under this atmospheric condition and what are the reasons for the occasional, large difference between the GOM concentrations measured by the two membrane samplers?

8. Figure 5. Using temperature breakthrough profile for product identification is risky and pre-mature for a number of reasons. First, temperature breakthrough profile is NOT product identification. Second, given that other pollutants are also present and that it is not clear how the deployed membranes interact with other trace gases (SO2, NOx, HNO3, HCl and H2SO4) and find particulates (sulphate, nitrate and chloride). The reported GOM species may be a result of chemical processes on the membranes rather than what is present in the ambient air EVEN IF the temperature breakthrough profile IS representative of respective chemical species. Third, can GOM species be "understood" (as indicated by the title) by only four samples with partial thermal desorption profiles? Forth, can the data rule out the interactions between Hg compounds with other trace gases that may or may not be collected by the membranes? The present discussion for Figure 5 in the manuscript sounds overly deterministic and might mislead the technical community (even with the precaution remark in Section 3.4). It is recommended that the authors revise the tone of the discussion.

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