

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.

J. Huang et al.

mgustin@cabnr.unr.edu

Received and published: 15 July 2015

The authors thank the reviewers and editor for his/her comments.

Response to Anonymous Referee #2

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

C4891

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.

Response: This reviewer is correct that we do not definitively know the chemical forms. The title was long. We have changed it to the following: “Work towards Understanding Dry Deposition and the Chemical Forms of Gaseous Oxidized Mercury in Florida” We added some of the words deleted to the key words.

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.

C4892

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.

Response: The following sentence has been moved from the beginning of the conclusions to the introduction and some additional information added. We hope this makes the objectives of this work clearer. "Active and passive membrane samplers data were applied along with Tekran[®] Hg and criteria air pollutant measurements to understand GOM chemistry and dry deposition at OLF. A detailed investigation was done for specific events, Principle Component Analyses (PCA), correlation analyses, and HYSPLIT analyses were used to understand sources. Evidence is presented for different potential GOM compounds being present during specific time periods. Although the valid data size for the latter is small, a detailed dry deposition inter-comparison was done."

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.

Response: We have added the following sentence to clarify what we did. "The MDL was calculated for each period of sampling due to the fact this can vary based on treatment of the membranes when preparing samples for deployment, treatment at the field site, and handling once returned to the laboratory. The membranes may also vary by lot."

C4893

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?).

Response: The parameters that were modified are explained in the text. This text has been adjusted as follows: "In previous studies, most scientists used scaling factors similar to HNO₃ ($\alpha=\beta=10$) to calculate oxidized Hg dry deposition velocity (Marsik et al., 2007; Castro et al., 2012); however, Lyman et al. (2007) used the effective Henry's Law constant, and half-redox reactions in neutral solutions of HgCl₂, and indicated HONO might better represent the chemical properties of oxidized Hg rather than HNO₃. In Huang et al. (2015a), results indicated that due to the limitation of understanding of oxidized Hg chemical properties, no single value can be used to calculate oxidized Hg dry deposition, because α and β would change with different GOM compounds. After potential GOM compounds in ambient air at OLF were identified (using nylon membranes with thermal desorption), dry deposition rates associated with the specific compounds (determined using the surrogate surface) were then applied in a multiple-resistance model modified from Zhang et al. (Zhang et al., 2003) by Lyman et al. (2007) to calculate Hg dry deposition velocities. Modeled Hg dry deposition fluxes were determined using calculated dry deposition velocities and adjusted GOM ambient concentrations measured by the Tekran[®] system multiplied by 3 similar to Huang and Gustin (2015a). GOM ambient concentrations from Tekran[®] measurements were also adjusted using each compound's corresponding correction factor, derived in the laboratory through comparison of cation-exchange membrane measured concentrations versus those measured using the KCl-denuder (average: 3. HgBr₂: 1.6, HgCl₂:2.4, HgSO₄: 2.3, HgO: 3.7, and Hg(NO₃)₂: 12.6) (Gustin et al., 2015).

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

C4894

GOM concentration is adjusted by a factor of 3. Which one is correct?

Response: The best way would be to apply the corresponding corrected factors for different GOM compounds. However, we do not understand GOM chemical/physical properties in enough detail enough to do an accurate GOM dry deposition estimation. This is the best we can do.

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 along this line should be given to ensure appropriate interpretation of the data.

Response: The adjustment is not arbitrary, and currently, is the best we can do because of the different uptake by the denuder of specific compounds, and influence of relative humidity and ozone. Please see the response above. Our group is focused on trying to understand the different GOM compounds present in air. A new project to explore this more fully would take three years and more funding resources. At this point, we have done our best. Detailed information is explained in the discussion of the active and passive sampler results, and in our other work. We have added the following to the text: "The three-fold correction must be used with caution since the correction factors above were determined in charcoal scrubbed air, we do not know the exact chemical compounds being permeated, and denuder and membrane recoveries are influenced by ozone and relative humidity (Gustin et al., 2015; Huang and Gustin, 2015)."

5. It is suggested that the ratio of mixing ratios be used for representing the GEM/CO ratios. Response: These are used except in one case where we are comparing data normalized similarly.

C4895

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.

Response: We have generated a box plot.

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?

Response: A table has been added to the SI showing the correlation of Hg forms and other pollutant data where they overlapped n=20 2-week periods and the following discussion has been added to the text: "Table SI2 indicates all GOM, PBM and RM measurements were highly correlated over 20 two-week periods, and linked to ozone and CO concentrations, but not SO₂ or nitrogen species. This implies RM sources maybe from chemical processes rather than fossil fuel combustion. Despite the long sampling time, the negative correlation with temperature and relative humidity for the Tekran measurement illustrates that 1) GOM is associated with input of cooler air, and 2) drier air, both of which are indicative of free tropospheric input, and the latter would facilitate GOM collection by the KCl-denuder."

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

C4896

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?

Response: The following discussion has been added to the text. In general, GOM measured by the ICE450 was significantly higher than the nylon membrane and Tekran GOM (Figure 3-note difference in scale). Tekran GOM was highly variable. GOM data were not collected using the ICE 450 3 weeks or was below the MDL (10 weeks) Data were collected by the nylon membrane 28 weeks. Capture of GOM by the nylon membrane and denuder are influenced by relative humidity whereas condensation on the cation exchange membrane can enhance uptake (Huang and Gustin, 2015). These limitations of the GOM collection measurements need to be considered.

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, NO_x, HNO₃, HCl and H₂SO₄) and fine 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? Fourth, 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.

Response: We have added the following sentence.” Although data are limited, because we get similar thermal desorption compounds in air with different chemistry (i.e. Huang et al, 2013 and Heidecorn et al., in progress for this Special Issue) we believe we are

C4897

collecting different chemical forms, and that the compounds are not being generated on the membranes; however, this needs to be tested.”

Response to an anonymous reviewer who communicated with the editor directly.

The manuscript: 1) covers too many topics on a superficial level, sweeping aside alternative explanations to fit their conclusions, 2) has a lot of hand-waving and fudge factors needed before statistical analysis and 3) perpetuates the concept that there are a handful of different GOM species in the atmosphere, but the evidence is not at all convincing.

Response: We agree this is a complex paper. We have attempted to explain alternate scenarios. We have addressed our major research hypothesis using various methods; together they provide evidence that there are various GOM compounds in the atmosphere and these could come from different sources. We agree some measurements still have high uncertainties, such as nylon membranes and passive samplers, and the atmospheric influences on membranes measurements are still unclear. More research groups are also demonstrating the difference of GOM measurements using cation-exchange membranes and KCl-coated denuder s(ICMGP 2015 at South Korea). Principal Component Analysis is a useful tool to understand the factors influencing ambient air concentrations, and it is a very solid method applied by air quality scientists to identify the pollutant sources and/or behaviors. Although in this study, it is useful for discerning determining that halogens reactions are not important for generating GOM during the day at this site and not much Hg comes directly from mobile sources. All analyses are based on statistical analyses. These data analysis methods, sampling methods and analytical methods have been published in peer-reviewed journals and have been supported by other atmospheric Hg research groups in ICMGP 2015 at South Korea.

There are too many concepts presented and thus there is nothing that has significant weight and substance. The analysis is scattered and frequently asks the reader to

C4898

accept dubious leaps in logic to reach conclusions that are not well supported, or often have simple and plausible alternative explanations. The working hypothesis presented by the author in the introduction (page 12074, lines 19-21) is not all supported by direct evidence, since there is no time resolved direct measurements of individual GOM compounds that can be attributed to emissions of the same GOM species from specific sources or processes.

Response: The reviewer is correct there are currently no highly time resolved methods for measuring GOM or the chemical forms in the air. It is noteworthy that Parisa Aryia's group just published paper on measurement of two forms of Hg in Montreal air. We have added this reference to the paper. Deeds DA, Ghoshdastidar A, Raofie F, Guerette EA, Tessier A, Ariya PA. Development of a Particle-Trap Preconcentration-Soft Ionization Mass Spectrometric Technique for the Quantification of Mercury Halides in Air. *Analytical Chemistry* 2015; 87: 5109-5116. We respectfully disagree with the reviewer and feel that the working hypothesis is supported by direct evidence.

There are too many assumptions that are not validated by supporting data. Here are just some examples:

The paper depends on Huang et al. (2013) as justification for the nylon membranes being able to accurately collect and preserve GOM mercury species over long time periods for species identification in the laboratory by thermal desorption. The paper discusses how mercury sample collection on nylon membranes are biased by changing relative humidity and points to a future paper, Gustin and Huang (2015). There is no evidence presented in this paper or Huang et al. (2013) disputing the alternative explanation that during field sample conditions, "GOM [species] could be formed or reduced on the membrane through reactions...".

Response: The paper identified has been published in EST. Huang, J. and Gustin, M.S. 2015 Effect of relative humidity on KCl denuders and membranes used to collect gaseous oxidized mercury, *Environmental Science and Technology* 49: 6102-6108.

C4899

DOI: 10.1021/acs.est.5b00098. In addition, tests need to be done to determine if specific Hg compounds may be lost from the nylon membrane after addition, and what happens during transport. This has been added to the paper. Actually, Huang and Gustin 2015 ES&T has demonstrated nylon membranes could be influenced by ozone concentrations; however, other tests are needed.

In this paper and the important supporting paper, Huang et al. (2013), the impact of particulate matter on GOM collection, preservation and potential for measurement bias on the nylon membranes is given short shrift. The authors must realize that particulate matter, with or without mercury, that comes from different sources (i.e., Interstate I-10 at 1 km distance) and changing meteorological conditions, will have a variable and unknown influence on the GOM sampling, surface chemistry, preservation and analysis of the nylon filters. Figure 5 is at best, inconclusive about the presences or absence of individual GOM compounds and potential unidentified species released from nylon membrane samples, since there is a lack of distinct peaks and large error bars. I do not think a reasonable scientist would conclude that the 5/21/13 nylon membrane shows the presence of Hg(NO₃)₂. Also, based on Figure 5, it is difficulty to have any confidence in table 3, which lists "tentative GOM compounds" identified that are used for the subsequent expanded analysis and interpretation of modeled and measured individual GOM species dry deposition rates. Without conclusive GOM species evidence presented, Table 3 and the subsequent interpretation should be scrapped. The results in the paper are not sufficient to support the conclusion that five GOM compounds were identified.

Response: We prefer to leave this in the manuscript. We have listed the compounds as tentative. Since we are the only people attempting this, eventually with highly resolved measurements other scientists will either support or dismiss our claims. We think our work is useful for moving atmospheric Hg science that has stagnated and is based on an inaccurate measurement method forward. We have added the following text to address this reviewers concern. "Cation exchange membranes have been

C4900

demonstrated to quantitatively measure specific compounds of GOM; however, may not measure all compounds. The active system is thought to primarily collect GOM; however, some fine aerosol may be collected. Nylon membranes do not retain GOM compounds quantitatively, and retention during transport needs to be tested.”

Comment on the PCA sections are listed below: I agree with Referee #2 that the PCA results (receptor modeling part) do not improve the understanding of the chemical forms of GOM unlike what is stated in the title of the paper. It seems PCA was used to identify potential sources of atmospheric mercury in Florida. The PCA sections in the paper need to be revised because some of the explanations don't seem to be related to the PCA factors. I also don't agree with some of the interpretations of the factors; thus more explanations are needed.

Response: We have addressed the comments of Referee 2 and changed the title. We believe the factor 1 and 2 are very straightforward, factor 3 and 4 represent diurnal and nocturnal patterns, in general temperature and solar radiation are highly correlated. At night, the boundary layer collapses, and GEM was concentrated, NO_x and O₃ will react with each other and form HNO₃ and GOM that can be removed removed by high humidity and condensation, respectively.

Section 2.3: “Hourly air concentrations and meteorological data were merged to Tekran sampling hour; data below MDL and missing data were replaced by half of MDL and mean”. Are there MDLs for meteorological parameters?

Response: These data were QAed by ARA and MDL limits are not typically reported for meteorological parameters.

How did you determine MDLs for GOM and PBM? Please explain the purpose of determining the factor scores and what the positive and negative factor scores indicate (referring to Fig. SI 2).

Response: Calculation of MDLs and other information are presented in Peterson et al.

C4901

(2012). We prefer not to add more information to this paper that is already long. The following has been added to the methods section. “Negative values indicate there is a negative or inverse relationship while positive values indicate a positive relationship.”

Section 3.2: The factor loadings for variables that are significantly correlated are not shown in bold in Table 2. Please mention what SR stands for.

Response: We have clarified they are in red or in bold. We have explained that SR is solar radiation.

The factor numbers in Table 2 should be labeled with the sources inferred for convenience, similar to the description in the caption for Table SI 1.

Response: The following has been added to table 2 caption “Factor 1= mobile sources, factor 2 - oxidation with compounds, factor 3= meteorological influence, and factor 4= trapping in the nocturnal boundary layer.

P12082 L4-8: Since PCA was performed on the data sets with and without mercury, more discussion should be included comparing the two sets of PCA results. For example, in the mobile factor (P12082 L16), you could mention that this factor was not associated with any Hg forms similar to the PCA results without Hg data in Table SI

1. Were the PCA factors derived from the dataset with Hg similar/different than those without Hg? Response: The following sentence has been added to the factor analyses section: “It is important to note that factor 1=1, factor 2=2, and factor 3 and 4 = factor 3 with and without Hg, respectively. “

P12083 L3-4: This sentence is not very logical, “humidity enhances GOM and PBM atmospheric removal processes; therefore, the highest GOM concentrations were found at noon.” Should it be, “. . .the lowest GOM concentrations were found at nighttime.”, since the previous part talks about removal processes? Also, I'm not sure if there is strong evidence that humidity enhances GOM and PBM atmospheric removal. What is the potential mechanism? It's possible that relative humidity may be high (60-70%)

C4902

but there may not be precipitation to scavenge the air pollutants. It's also important to mention that PCA indicates there's a correlation between humidity and GOM and PBM, and not necessarily a cause and effect relationship.

Response: The reviewer has a good point and this sentence has been changed. High humidity has high chance of dew and fog formation during the nighttime, which would enhance scavenging processes.

P12083 L4-11: This discussion doesn't tie in with the PCA results very well. The first point suggests the transport from the free troposphere enhances GOM, but this shouldn't increase SO₂ concentrations (unless there is a free troposphere source of SO₂) since both pollutants are present in this PCA factor. In the second point, you mentioned some instances of an anti-correlation between GOM and O₃ and SO₂, which is not consistent with the PCA factor with positive loadings on GOM, O₃ and SO₂.

Response: PBM, GOM, SO₂, and O₃ are all related. We have SO₂, O₃, GOM and PBM correlated in factor 2, we have tried different analysis data sets to separate SO₂ and O₃ sources, however, none of them worked. We discussed this in the text "The second factor was fossil fuel combustion mixed with gas phase oxidation which correlated with O₃, SO₂, GOM, and PBM. Huang et al. (2010) clearly separated coal combustion (SO₂, GOM and PBM) and gas phase oxidation (O₃, GOM, and PBM) factors. However, in this study, SO₂ and O₃ peaked at different times (Figure 2), and since they are lumped in the same factor it is difficult to resolve the source."

Factor three (P12083 L11-13): You should discuss that other pollutants were not present in this factor because meteorological variation and boundary layer collapse would affect not only Hg, but other air pollutants as well. The factor loading for PBM in Table 2 is quite high; is this important and what could this indicate? "There is no Hg associated with this factor, and this could be due to it not being measured by the denuder due to high relative humidity." If Hg is not associated with this factor (but rela-

C4903

tive humidity is), how can there be a relationship between GOM and relative humidity as you alluded to in the last part of the sentence (high relative humidity reduces GOM collection efficiency)? This interpretation needs to be revised.

Response: For factor 3 and 4, please see the response above. We have added the reference to Huang and Gustin 2015 that demonstrates that collection of HgBr₂ by the denuder is affected by relative humidity.

P12083 L14: Remind me again of what factor 2 represented for this paragraph. Factor four (P12083 L19): I'm unsure about the interpretation of this factor. It's the same interpretation as factor 3. How is it different from factor 3? Would it be better to select 3 factors in the final PCA solution, instead of 4? Also, why does the collapse of the boundary layer affect GEM only, and not any other pollutants? The discussion from L20 onwards doesn't relate to the PCA results very well. Why did you discuss about Hg chemistry and relative humidity interferences on GOM collection here for factor 4?

Response: the other pollutants would react during the night and we hypothesize the form of GOM produced could be Hg(NO₃)₂ and this is not captured very well by the denuder. This reviewer needs to be reminded that this analysis was over a year.

P12083 L21-22: "GOM concentrations usually peaked at noon associated with gas phase oxidation; however, halogen related reactions do not appear to be involved based on the ozone diel pattern." I'm interested in knowing why the surface ozone peaked so early in the morning (7:00 local time in Fig. 2). I expected the largest peak to occur some time around noon or afternoon because it should coincide with the maximum solar radiation intensity and it takes time for the photochemical production of ozone. Also, "halogen related reactions do not appear to be involved based on the ozone diel pattern." Is it because the higher ozone during the daytime would react with halogens leading to lower halogen concentrations? But ozone generally peaks during daytime, does this mean halogens are never involved in GOM production at noon based on these diurnal patterns?

C4904

Response: Ozone peaks at noon and NO in the morning. We have changed the figure showing diel trends to box and whisker plots that are easier to interpret. This is not only based on the diurnal patterns we are seeing in this study, but also the findings of Engle et al., 2008. We cannot 100% rule out halogens; however, based on what we see, we believe halogens do not dominate the reactions at this site during the day. However they could be important during the night. There is evidence of HgCl₂ and HgBr₂ in the thermal desorption profiles.

The editor also has these comments: Lines 10-13 in the abstract: it is stated PBM uncertainties are larger. However, Gustin et al. (2015, ACP) stated that GOM uncertainties are much larger. Please clarify.

Response: The sentence has been changed to read as follows: "Only gaseous elemental Hg and GOM are discussed since the cation exchange membranes in the UNR active system are thought to primarily collect GOM. "

The second last statement in the conclusion and related dry deposition analysis in the paper: the approach of identifying different GOM species by comparing modeled and measured dry deposition is not scientifically sound. While the Henry's law constant has been used as one of the reference parameters proposing chemical-species dependent dry deposition model parameters, its value cannot be used directly to differentiate V_d in a quantitative measure because other parameters might dominate the dry deposition process (this is especially the case for reactive species like GOM). Besides, the measured dry deposition using surrogate surface does not necessarily represent the actual dry deposition, a good agreement does not mean you have identified the right chemical forms or right model parameters.

Response: We agree with this comment and nothing has been changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 12069, 2015.