Atmos. Chem. Phys. Discuss., 15, C4313–C4318, 2015
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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.

L. Zhang (Editor)

leiming.zhang@ec.gc.ca

Received and published: 3 July 2015

The following comments are from anonymous reviewers 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.

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 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.

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...". 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

ACPD
15, C4313–C4318, 2015

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.

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.

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? 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).

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.

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.

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 ex-

ACPD
15, C4313–C4318, 2015

ample, 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?

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%) 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.

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.

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 relative 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

ACPD
15, C4313–C4318, 2015

collection efficiency)? This interpretation needs to be revised.

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?

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?

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.

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

ACPD
15, C4313–C4318, 2015

dry deposition model parameters, its value cannot be used directly to differentiate Vd 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.

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