

## ***Interactive comment on “Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level: a critical review” by M. Sexauer Gustin et al.***

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Interactive comment on “Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level: a critical review” by M. Sexauer Gustin et al. Anonymous Referee #2 Received and published: 9 March 2015

This paper is a review of the state of atmospheric mercury measurements and the associated modeling, and the current challenges associated with both. The paper provides an initial review of the methods that have been used for measurements and then discusses some results that cast doubt on the validity of the results from the

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automated Tekran instrument which is the most widely used instrument for measuring Hg speciation in air. The review bases much of the discussion on recent papers by Gustin, Huang et al and I feel that the review pushes the point of view of the authors and maybe there could be more general discussion of the literature that is available.

Response: We thank this reviewer for his/her comments. Unfortunately there are few people working on this issue. This makes it difficult to cite additional literature. It has taken diligent work doing experiments and collecting field observations to come to this stage of our understanding; in addition, we have worked very hard to consistently publish our results in high quality peer review journals and highly scrutinized by reviewers.

More specific comments: 1) I concur with many of the comments posted by Slemr in his review.

Response: We have addressed the many constructive comments provided by Dr.Slemr.

2) One area I think could be better presented is a review of the historical literature on the measurements of Hg speciation in air, and perhaps some additional references could be included. There are a number of papers that could be referenced or talked about especially for surrogate surfaces. For example, there is no mention of the use of a water surrogate surface sampler - papers by Sakata and others - and other papers on surrogate surfaces are not mentioned - Caldwell et al 2006, some earlier papers by the Holsen and Keeler groups, the Marsik et al paper from the Everglades etc. This review paper has a very North American flavor and I think it would be good to focus as well on studies done in Asia and elsewhere.

Response: As pointed out in the review by Slemr this paper focuses on measurement of atmospheric Hg not the passive samplers. We refer to the Huang et al. paper that is a review paper and contains many references to the passive sampling systems. Studies done outside of the United States are included in this review. It is a good practice to refer to a review paper it reduces the number of references.

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3) The writing could be improved and the paper shortened as a result. There are numerous places where the writing is cumbersome, or there are minor errors. Some examples include: pg 3783, ln 15 "...been used to as a means to remove..."; equation R1 - kJ not kj; pg 3791, 7 "...provided a start for better understanding of..."; ln 22 "...different compounds containing GOM in air"; pg 3792, ln 2 "...biased low through spikes of GOM.."; pg 3800, ln 17 "Gom and PBM due to their solubility.." not all PBM is soluble.

Response: pg 3783, ln 15 "...been used to as a means to remove..." has been changed to "...been used to remove..."

"equation R1 - kJ not kj" has been corrected.

pg 3791, 7 "...provided a start for better understanding of..." has been changed to "started providing a better understanding of..."

ln 22 "...different compounds containing GOM in air" has been changed to "different GOM compounds in air"

pg 3792, ln 2 "...biased low through spikes of GOM.." We prefer to leave this as is.

4) A more detailed explanation early in the paper of the typical speciation in air would help the reader understand the paper better. There could also be some discussion, based on either measurements or modeling about the likely forms of GOM in the air. This is relevant to the results of the suitability of the various surfaces proposed for GOM collection. Also I do not like the use of RM for designating both GOM and PBM. The inherent assumption is that the PBM is reactive and soluble in deposition and we know this is not the case. Another term is needed besides RM.

Response: The following sentence has been added to the paper. Previously it was thought that GEM was 95-99% of Hg in the atmosphere. Recent work is pointing to GOM being 25% of that in the planetary boundary layer see the discussion below. Work in snowpack suggests PBM is soluble and reactive upon deposition (Steffen et al.

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2015). We clarify throughout the text that RM is recommended in place of interpreting PBM measurements alone because you have breakthrough and collection of GOM on the particulate unit and other surfaces. Steffen, A., Lehnher, I., Cole, A., Ariya, P., Dastoor, A., Durnford, D., Kirk, J., Pilote, M. Atmospheric mercury measurements in the Canadian Arctic Part 1: A review of recent field measurements, *Science of the Total Environment*, 509-510 3-15, 2015.

5) pg 3781, ln 26. A bit more explanation of the statement of the controversy about "whether the 2537 measured TGM or GEM" would be useful here. Furthermore, more detail on the Univ of Houston system should be included in the body of the paper as this is not well explained. This is also so for the discussion about the DOHGS - line 25, pg 3783.

Response: Section 3.1 'Are we measuring TGM or GEM?' has been revised. The UHMERC system was described in Gustin et al. (2013) Data from the complete system has not been described in other papers that we are aware of. The discussion about the DOHGS instrument has been revised for clarity.

6) Section 3.1. there is a lack of references to the statements in this section. What does "uncovered lines" mean? There are no references associated with the discussion of Maryland data and other numbers included in this section. Other papers besides Steffen could be referred to concerning depletion events. There are also speciation papers related to the Arctic that I do see mentioned in this paper. The sentence at the end about the requirement of a pyrolyzer is not explained or any reason given.

Response: "Covered lines" has been clarified on line 303,

"Limited work in dry air with uncovered lines (i.e., exposed to sunlight) indicated that the Tekran<sup>®</sup> 2537 measures TGM (see SI)."

We have clarified the reference for the Maryland data.

A reference to a review paper on atmospheric Arctic measurements has been added.

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The sentence about the pyrolyzer has been expanded for clarity.

"To measure total mercury (TM) requires the use of a pyrolyzer at the inlet to the sampling line to convert RM to GEM."

7) Section 3.2 would be improved with a better discussion of historical literature not just the recent papers. The comment that "evidence is coalescing.... vary seasonally and spatially" is not true. We have known about this variability for a long time. This is overstating the recent advances.

Response: We respectfully disagree with this reviewer. We do not think a discussion of the historical literature is needed. This is in other papers and we refer to them now in the text. We also do not think anyone has demonstrated that GOM compounds vary over space and time and evidence is coalescing to demonstrate that they vary across space and time. This is included at the end of section 3.2.2

8) pg 3789, ln 23 "denuders loaded with HgCl<sub>2</sub>..." is this correct? More explanation is needed. Response: The word loaded has been added. Section 3.2.1 on O<sub>3</sub> and OH has been rewritten for clarity.

9) pg 3790, lines 20 onwards. There is no details of how the experiments were done, what the air concentrations were and were they realistic, and how the collection efficiency was determined. More details are required here.

Response: The reader is referred to the original publication for details,

"Figure 1 and Table 2 show the correlation between specific GOM compounds concentrations measured by the nylon and cation exchange membranes versus the KCl-coated denuder in the Tekran<sup>®</sup> system (see Huang et al. (2013) for detail on the experimental setup)."

10) It would be good to include some discussion and contrast the results of the lab studies and those of RAMIX (pg 3792). Also some explanation of the thermal desorption

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approach would help.

Response: We added the comment that RAMIX results were similar to those observed for laboratory tests. Detail about the thermal desorption method may be found in Huang et al. (2013) no reason to repeat it here.

11) As noted above, a better discussion of surrogate surfaces that have been used is needed (pg 3793).

Response: The discussion of surrogate surfaces in Section 2.4 has been revised and several references have been added.

12) The potential explanation for the Cheeka Peak data (Section 4) is that the ocean boundary layer has more Hg<sub>0</sub> because of ocean evasion. Additionally, I think that the detailed discussion, with lots of assumption and speculation in this section is totally unwarranted and not supported. I suggest removing this section. There is no validity for deriving an equation from one location and thinking this could be applicable elsewhere. I also think that the idea of trying to come up with a way to convert Tekran data into what may be obtained by another methods is foolhardy based on current understanding. I do not agree this is possible given all the variability and differences in sources. I think the recommendations that refer to this are not sufficiently supported to be included in the manuscript. They should be removed.

Response: GEM was higher in marine boundary when winds were slow – you'd expect the opposite if evasion played an important role.

13) The section on the MBL doesn't even reference any of the papers that have made measurements that the models were based on and this is not right. Include references to the data that Holmes et al and Hedgcock et al etc used for their modeling.

Response: Laurier and Mason (2007), Laurier et al. (2003), and Sprovier et al. (2003) have been added.

14) The last paragraph on pg 3800 and the discussion on the next page should be

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shortened - it is repetitive and somewhat obvious.

Response: The paragraph has been condensed and obvious statements removed.

15) I do not agree with recommendations 2 and 5 (pg 3803) and think they should not be included in the paper.

Response: Section 6 has been heavily revised based on Franz Slemr's comments. Recommendation 2 has moved to be recommendation 1. Recommendation 5 has been revised.

1 6) More minor comments: i) pg 3779, ln 4 - generally I thought it was now agreed that the residence time was <1 yr; Response: The sentence has been revised,

“Although the atmosphere is a relatively minor reservoir of Hg compared to the ocean or soils, it is an important pathway by which Hg is distributed globally over short timescales (on the order of 1 year).”

ii) ln 23 - I think there are good potential explanations, such as that put forward in Soerensen et al 2012 about the importance of evasion from the ocean - this could also explain the Cheeko Peak data as noted above;

Response: see above response. iii) remove comment about "a small city" (pg 3784, ln 12. Response: Removed.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 3777, 2015.