

Interactive comment on “Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition” by H. M. Amos et al.

Anonymous Referee #2

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This manuscript is well written and is an important addition to the scant scientific literature on the topic of gas-particle partitioning of oxidized mercury. However, it needs more quantitative analysis of model performance, and it makes several unjustified assumptions that need to be corrected. Specific comments are as follows:

Page 29446 lines 10-11: It's not clear to me from the papers cited how "surrogate methods suggest that the annular denuders do not have 100% collection efficiency." Please explain this.

Page 29448 lines 1-9: I am troubled by this paragraph. First, Rutter and Schauer, who are co-authors of this manuscript, showed in a previous paper (Rutter et al., 2008, JAWMA 58, 377-383) that their filter based method for particulate and gaseous oxidized mercury analysis in general worked well and compared well against Tekran mea-

surements, except that their particle measurements were higher than those from the Tekran. I'm surprised to see their method entirely discounted in this manuscript! I have some comments in defense of their filter method, though it seems strange that I am the one doing the defending:

1) Talbot et al. (2011, Atmosphere 2, 1-20; also a co-author of this manuscript) recently provided strong evidence that Tekran particulate mercury measurements are in fact too low, just as Rutter et al. (2008) found.

2) The KCl-coated filters used by Lyman et al. (2009) were surrogate surfaces deployed passively for days, and their poor collection efficiency has little bearing on the usefulness of Rutter's filter based method. Rutter and Schauer published several papers based on their filter method, including a direct comparison with KCl denuders, and these papers provide many indications that their method works. It would be inappropriate to simply throw out all that evidence just because it yielded results that were different from the Tekran data used in this manuscript.

3) Rutter and Schauer (2007b) were right to point out that heating the inlet, denuder, and particulate filter on the Tekran 1130/1135 system to 50°C is likely to cause a low bias in particle-bound mercury and a high bias in gas-phase oxidized mercury. I am surprised to see this manuscript discount the evidence for such a bias as "speculative", when the manuscript accepts as fact that gas-particle partitioning of oxidized mercury is temperature-dependent! It is worth noting that the maximum temperature difference between the Tekran 1130/1135 and ambient air in Figure 3 is more than 70°C. It is hard to imagine that this temperature change would not disrupt the ambient gas-particle partitioning of sampled oxidized mercury.

I suggest that the authors deal with these issues more completely, and that they include in the revised manuscript a discussion of how accounting for a likely temperature-induced bias in the Tekran measurements might change their results.

Page 29449 lines 1-12: Is there such a thing as "chemically inert Hg"? I'm not sure

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there is a mercury-containing molecule that could be classified as "inert."

The authors state, "it is not clear that heating to 800°C in the Tekran instrument would be sufficient to desorb such mercury from the collection filter." This statement is extremely speculative. The Milestone direct mercury analyzer uses thermal decomposition to analyze mercury in solid samples, and is an EPA approved method: (<http://milestonesci.com/index.php/product-menu/mercury/dma80-overview/resources.html>). I have not seen any indication in the peer-reviewed literature that the Milestone or any other thermal desorption-based analyzer "misses" refractory mercury that is too "inert" to be reduced and volatilized by heating to 800°C. If the authors are aware of any such information in the peer-reviewed literature they should provide it in the revised manuscript. If not they should remove this speculation from the manuscript and rework the analysis as necessary. It is reasonable that some refractory mercury emitted directly from sources doesn't volatilize. HgO and HgS would be expected to stay in the particle phase at ambient temperatures because of their extremely low vapor pressures. But in the absence of experimental evidence it is not reasonable to assume that the Tekran is unable to detect this mercury even when heating particulate samples to 800°C.

Page 29449 lines 13-29: I agree with the first reviewer that the choice of mercury speciation ratio in power plant emissions appears not to be based on the best available scientific information, but instead is designed to "tune" the model to get the best results. This is misleading and needs to be corrected, as described in detail by the first reviewer.

Page 29451 lines 20-24: Please provide evidence from peer-reviewed articles outside of your own research group that it is "standard practice" to "adjust parameters within their uncertainty to fit ... observations." What is the range of uncertainty for atmospheric in-cloud reduction? You reduced it by 50%. Where do the new and old in-cloud reduction rates fit in relative to the range of uncertainty?

Page 29452 line 7: What is "reasonable consistency"? A simple R2 value would be

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much more useful than qualitative statements like this one. The entire results and discussion section would be much improved by replacing qualitative descriptions and comparisons with statistical and numerical ones.

Page 29454 lines 1-3: As before, the assumption that primary mercury emissions are not measured by the Tekran is extremely speculative, and should not be included unless you have experimental evidence to support it.

Page 29455 line 6: Please replace "the model version presented here shows an improved ability..." with quantitative evidence of the ability of the model to simulate wet deposition.

Page 29455 lines 8-14: The statement about how the "improved" model vindicates mercury oxidation by bromine is an over-reach. Can you show quantitatively that the current model with a bromine oxidation mechanism simulates wet deposition better than the current model with OH and ozone oxidation? If not, it isn't appropriate to say any improvements in simulation of wet deposition show that mercury oxidation by bromine is the "correct" oxidation mechanism. As it stands now, the "improvements" could be due to something entirely separate from the oxidation mechanism.

To me Figure 6 looks very similar to Holmes et al. (2010). The "improved" model is still strongly underestimating wet deposition in Florida, and it would almost certainly underestimate the extremely high wet deposition measurements that have been made by USGS in Puerto Rico (mentioned in Engle et al., 2010, JGR 115, D18306).

Also, I'm not sure why the model used in this study doesn't incorporate mercury oxidation by bromine AND ozone and OH radical. Kinetics studies show that both oxidation mechanisms are possible. There is every reason to believe that many oxidation mechanisms operate simultaneously in the real world.

Page 29456 lines 24-28: As discussed above, I'm not sure this opinion has enough evidence behind it to be included in the manuscript.

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Page 29457 lines 10-19: As discussed above, I don't think this is the correct conclusion to draw.

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