

Anonymous Referee #2

We would like to thank the referee for their thoughtful and useful comments. We have provided our responses to the referee's comments below (in blue).

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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.

We have re-written the sentence for clarity,

“Previous work has suggested that there are artifacts associated with PBM collection (Lynam and Keeler, 2005; Malcolm and Keeler, 2007; Rutter et al., 2008a; Talbot et al., 2011) and interferences with the collection of RGM on KCl coated denuders (Lyman et al., 2010).”

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 measurements, 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:

Page 29448, lines 4-9 have been removed from the text.

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.

The authors acknowledged the work of Talbot et al. (2011) on page 29454 lines 11-12 of the ACPD paper,

“Comparison of Tekran and filter-based sampling methods suggests that the Tekran instrument underestimates the total aerosol concentration (Talbot et al., 2011).”

We now include Talbot et al. (2011) in the discussion of Tekran artifacts in Section 2,

“Previous work has suggested that there are artifacts associated with PBM collection (Lynam and Keeler, 2005; Malcolm and Keeler, 2007; Rutter et al., 2008a; Talbot et al., 2011) and interferences with the collection of RGM on KCl coated denuders (Lyman et al., 2010).”

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.

We have removed the text referring to Lyman et al. (2009). Please see response above.

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.

We have removed the phrase “speculative” and have added an estimate of the magnitude of the Tekran heating artifact to Section 2,

“Rutter and Schauer (2007b) hypothesized that the difference in partitioning between their filter-based method and the Tekran instrument could reflect a sampling artifact associated with internally heating the Tekran instrument to 50°C. Comparison of our regression with the filter-based regression of Rutter and Schauer (2007b) in Figure 3 would imply a ~30°C thermal bias, although the filter-based regression is based on very limited data. We will discuss the effect of the possible thermal bias in the GEOS-Chem simulation of Hg atmospheric concentrations and wet deposition fluxes.”

We have conducted a sensitivity simulation using the Hg(II) partitioning relationship derived from the filter-based methods of Rutter and Schauer (2007) to test how this artifact might affect the skill of GEOS-Chem at simulating RGM and PBM concentrations at the surface, and Hg wet deposition fluxes. In Sections 4-5, we have added quantitative statements about the performance of the model using the partitioning relationship derived in our work and the filter-based relationship from Rutter and Schauer

(2007b).

Page 29449 lines 1-12: Is there such a thing as "chemically inert Hg"? I'm not sure there is a mercury-containing molecule that could be classified as "inert."

We now treat Hg(P) as Hg(II) and make no claim about it being chemically 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.

The statement "it is not clear that heating to 800°C in the Tekran instrument would be sufficient to desorb such mercury from the collection filter" has been removed from the text and we have revised our hypothesis about Hg(p). In the absence of experimental evidence about the chemical or physical nature of Hg(p), we no longer assume Hg(p) to be chemically inert and now assume it to be a Hg(II) compound. In Section 4, we discuss the apparent inconsistencies that arise between simulated and measured PBM if Hg(p) is assumed to be chemically inert (as it was assumed to be in previous versions GEOS-Chem).

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.

Please see response to Referee #1 above.

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?

We have added references and quantified the impact of changing the rate of in-cloud reduction 50% relative to Holmes et al. (2010). The text has been modified to read,

“We discussed above the tentative evidence for fast reduction of Hg(II) in power plant plumes. No such constraints are available for Hg(II) reduction in the background atmosphere. In models, Hg(II) reduction is generally assumed to take place by aqueous-phase photochemistry in clouds but is virtually unconstrained, with laboratory data for reduction rate constants spanning several orders of magnitude (Subir et al., 2011 and references therein). Past GEOS-Chem model studies have used Hg(II) reduction as a tuning parameter to reconcile emissions (natural and anthropogenic) with atmospheric Hg(0) concentrations (Selin et al., 2007), and similar tuning has been used in other models as well (Seigneur et al., 2006; Pongprueksa et al., 2008). Here we use an in-cloud reduction rate constant decreased by 50% from that in Holmes et al. (2010), yielding a tropospheric Hg(II) lifetime of 2.4 months against reduction as compared to 1.7 months in Holmes et al. (2010).”

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

We have replaced “reasonable consistency” with quantitative statements of the model’s performance at simulating the annual mean of Hg(0), RGM, and PBM:

“Simulated annual mean Hg(0), RGM, and PBM concentrations are shown in Figure 1. The correlation coefficients between the model and observations are $r_{\text{Hg}(0)} = 0.75$, $r_{\text{RGM}} = 0.93$, $r_{\text{PBM}} = 0.75$, which suggests that the model has some skill in simulating the spatial distribution of Hg species. The normalized mean biases (NMB) of the model are -5%, 117%, and 18% for Hg(0), RGM, and PBM, respectively.”

We have included more quantitative statements about the model’s skill at matching the observations throughout the discussion section.

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.

We have removed the hypothesis that primary anthropogenic Hg(p) may not be quantified as PBM by a standard Tekran instrument.

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.

We have included a quantitative statement of the model’s ability to simulate annual wet

deposition as compared to MDN observations and have modified the text to clarify the improved performance of our simulation,

“Figure 6 compares model results to the MDN observed annual Hg wet deposition fluxes for 2007-2009. The NMB of the model is -11% and the correlation coefficient is $r = 0.71$. A sensitivity simulation using the filter-based Hg(II) gas-particle partitioning relationship from Rutter and Schauer (2007b) yields a NMB of 6.9% and $r = 0.62$. The model captures the observed regional maximum in the Southeast US though not the particularly high values along the Gulf Coast. Y. Zhang et al. (2011) show that a nested GEOS-Chem simulation with $1/2 \times 2/3$ horizontal resolution over North America has more skill at capturing these high values, perhaps due to better representation of deep convection. Our simulation improves over the previous GEOS-Chem version of Holmes et al. (2010) using Br as Hg(0) oxidant where the simulated eastern US maximum of Hg deposition was too far north. This largely reflects improvement of the washout algorithm (see Appendix and Wang et al. (2011)).”

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.

Please see previous response.

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).

We do much better at simulating the regional maximum in the Southeast US though we still underestimate the Gulf Coast and Florida. This is now clarified in the text. We also cite the recent nested GEOS-Chem simulation with $1/2 \times 2/3$ degrees resolution of Y. Zhang et al. (2011) as improving the representation of the Gulf Coast/Florida maximum. Please see response to comments above.

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.

We are using the atmospheric module developed by Holmes et al. (2010), which can either perform Br oxidation or OH/O₃ oxidation, but not Br and OH/O₃ oxidation simultaneously. We agree that many oxidation mechanisms are likely to operate simultaneously in the real world. However, it is not the goal of this manuscript to

constrain chemistry or arbitrate between oxidants, so we did not re-write the Hg chemical mechanisms in GEOS-Chem.

We have added the following text to the model description in Section 3,

“Oxidation of Hg(0) by OH/O₃ is an alternative to oxidation by Br in GEOS-Chem (Holmes et al., 2010), but we do not use the OH/O₃ reaction scheme (Hall, 1995; Sommar et al., 2001) here because of doubt in the associated kinetics (Calvert and Lindberg, 2005; Hynes et al., 2009; Subir et al., 2011).”

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.

We have replaced,

“There is ambiguity about the nature of Hg(p) included in current anthropogenic emission inventories. If it represents refractory mercury embedded in soot or fly ash particles then it might not be operationally measured as PBM. If it semi-volatile and behaves as Hg(II), then it is inconsequential beyond the immediate source area because most Hg(II) is of secondary origin.”

with,

“Little is known about the chemical or physical nature of primary Hg(p) included in current anthropogenic emission inventories. Here we assume that Hg(p) is emitted as Hg(II) and thus available for gas-particle partitioning. Previous versions of GEOS-Chem have assumed Hg(p) to be chemically inert but we find that this would cause an overestimate of PBM at North American sites.”

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

The text now states,

“Compared to the previous version of GEOS-Chem (Holmes et al., 2010), our model shows an improved ability to reproduce the observed spatial distribution of MDN annual Hg wet deposition fluxes over the US. Holmes et al. (2010) had found that implementing Br as an Hg(0) oxidant degraded the model’s skill at simulating the MDN data relative to the older model version (Selin et al., 2007; Selin and Jacob, 2008) with oxidation by OH and O₃. Our improved simulation of the MDN data (using Br as the Hg(0) oxidant) largely reflects improvements in the washout algorithm. We still underestimate MDN wet deposition in Florida.”