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Atmospheric
Chemistry
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Discussions

Interactive comment on "Evaluation of discrepancy between measured and modeled oxidized mercury species" *by* G. Kos et al.

Anonymous Referee #2

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Recent atmospheric monitoring of elemental mercury, Hg0, divalent gaseous mercury, Hg2+, and particulate mercury, Hgp, have elucidated a gap between the modeled and measured values of these Hg species at the surface. Closing this gap will likely require a re-evaluation of model atmospheric chemical mechanisms, emissions inventories, or both. This paper attempts to address this gap in modeled and measured values by evaluating the uncertainties in the observations and model estimates. However, the evaluation of the measurement uncertainties is brief and does not address potential spatial differences in the uncertainties due to sampling location or the presence of oxidants. The modeling uncertainty analysis is focused on finding emissions and reaction rates that can best replicate the wet deposition and ambient Hg observations rather than evaluating which mechanisms are likely under ambient conditions and what may be missing from current model chemical mechanisms that could potentially close this

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gap.

General comments

1.The authors suggest that the inclusion of in-plume reduction of Hg2+ improves the model results. However, they acknowledge that there is little current laboratory nor field data to support this process. The "in-plume" reduction sensitivities are performed by simply reducing the ratio of Hg2+ and Hgp emitted. This presents a problem, because (1) no in-plume mechanism is proposed nor evaluated, (2) no justification is presented as to why Hgp would be included in this mechanism, and (3) this part of the manuscript appears to be an emissions sensitivity re-branded as a sensitivity to in-plume processes.

2.The gas phase model sensitivities do not seem to be driven by the uncertainties in the chemical mechanism or reaction rates. This part of the study appears to be more of a model tuning exercise. The authors clearly state which model configuration compares best to the observations but they do not convince me that this was achieved by using the most feasible chemical mechanisms.

Specific comments

1.Abstract lines 7-8: "..., in addition to ... speciation of mercury near emissions sources..." This sentence is confusing. Are you quantitatively exploring the models speciation near sources as well as the uncertainties in the measurements?

2.Page 17248 Lines 3-6: In the abstract, the authors suggest that including in plume chemistry improved model results, but the language here indicates that there is no recent laboratory nor field experiments to justify this mechanism. Perhaps the authors should recast this model sensitivity as an emissions sensitivity given the uncertainties in the emissions and our ability to make accurate speciated Hg measurements.

3.Page 17248: Are the authors suggesting that modeled wet deposition results agree well with measurements because the driving meteorological models capture the ob-

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served precipitation well and that the measurements do not consider speciation? If so, this seems like a speculative claim.

4.Page 17248 Line 24: Please explicitly specify the MDL for Hg2+ and Hgp here so the reader does not have to flip between the table and this text.

5.Page 17248 Line 25: Assuming an ambient Hg0 concentration of 1.5 ng m-3 and examining the values on Table 4, a more reasonable fraction of Hg as Hg2+ and Hgp should be less than 1%.

6.Page 17249 Line 1: "These data ..." Which data? Ny Alesund and Rochester or AMNet? Given the large variability in the species concentration that the authors specified in the previous sentence, a measure of the variability, e.g. standard deviation or 5th and 95th quantile, in these measurements should be given.

7.Page 17251 Paragraph beginning with "Figure 1": The present and past tenses of verbs are used. The authors should pick a consistent tense.

8.Page 17252 Line 6: The Bullock and Brehme 2002 citation is not the primary source for the OH reaction rate used in CMAQ.

9.Page 17252 Line 9: Why were the halogen reactions only considered in the marine boundary layer?

10.Page 17252 Line 9: "Rate constants are from..." For which reactions? If this has been changed from previous GRAHM studies this needs to be specified.

11.Page 17252 Line 11: The Hg2+ reduction by the hydroperoxyl radical has been shown to be unlikely under normal atmospheric conditions (see Gardfeldt and Jonsson, J. Phys. Chem. A, 107, 2003) and the uncertainty of the aqueous phase reduction was not considered in this paper. Both the wet deposition and ambient Hg2+ concentrations are sensitive to the aqueous phase reduction mechanism (see Pongprueksa et al., Atmospheric Environment, 42, 2008) and the lack of an evaluation appears to be a gap in the analysis performed in this study.

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12. Page 17252 lines 18-19: "subsequent reactions in the plume, seems to be among the most important parameters .." What makes this seem so? On Page 17248 Lines 3-6 the authors suggested that observational and experimental evidence does not confirm this reaction mechanism.

13. Page 17252 line 26: What was the vertical resolution of the model?

14. Page 17262 line 11: "established OH/O3 processes" The OH/O3 mechanism may be established and widely used in atmospheric models but recent experimental and thermodynamic studies (See Hynes et al. MERCURY FATE AND TRANSPORT IN THE GLOBAL ATMOSPHERE 2009, 427-457, DOI: 10.1007/978-0-387-93958-2_14) indicate that these reactions are not likely to produce gas phase products.

15.Section 3.10 should be expanded and the cumulative uncertainties should be better explained.

16.Page 17264 lines 12-14: Does "no emissions" means no Hg2+ emissions in the U.S., North America, or globally? What is the uncertainty in the global emissions?

17.Page 17264 line 21: Are you sure this is the fault of chemical mechanism? What is the vertical resolution of the layers? Too course of a vertical structure could artificially increases surface concentrations by mixing too much of the stack emissions in the lowest model layer. Are similar biases seen in CO or black carbon emissions? Has the boundary layer height been evaluated against observations?

18.Page 17265 line 22: "produced the best results" This is true if the objective is replicating the observations. I am not convinced that this particular model configuration is using the best combination of gas phase chemical reaction rates, mechanism and emissions.

19.Page 17265 line 23: "spread in the bias" Perhaps the mean error or RMS error would be a more quantitative way of describing this change in the model results.

20.Page 17265 line 24: "no significant change" By what metric?

21.Page 17266 lines 22-23: What qualifies the results as noticeably high or markedly improved?

22.Page 17267 lines 10: "Hg2+ should be higher ..." I do not think that higher surface concentrations are needed to capture the wet deposition fluxes. It may be possible to capture the wet deposition fluxes with a slower or different aqueous phase Hg2+ reduction mechanism without having to increase surface level Hg2+ concentrations as shown in the model sensitives in Pongprueksa et al., (Atmospheric Environment, 42, 2008).

23.Page 17267 lines 14: "Bullock, 2009" is not the correct reference for uncertainties in wet deposition observations. Prestbo and Gay Atmospheric Environment, 43, 2009 is a better source for uncertainties in MDN wet deposition.

24.Page 17268 line 5: It is not clear to me how the factor of 8 uncertainty was derived.

25.Page 17268 lines 18-19: What are the units of the biases being discussed?

26.Figures: The labels on scale bars and axes are generally too small to be legible.

27.Figure 5: It is not clear to me that the bias decreases with distance from the emissions source. This plot appears to show that the bias increases with increased concentrations. No information regarding the locations or type of the Hg emission sources were given.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 17245, 2012.

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