

Responses to Referee #1 comments

Referee #1 comment:

- The authors discuss how different assumptions affect the calculated deposition, however they do not discuss how the resulting simulations compare to observations. In particular they show MDN wet deposition observations in several figures, but fail to discuss them.

Author response:

The emphasis of this paper is not model performance, since all of the simulations are based on existing modeling databases that have been evaluated in past studies (for instance, the 2001 simulation in NAMMIS, Bullock et al., 2009). See also the discussion in response to referee #2 comments.

Referee #1 comment:

- I am not quite sure what is the value of adjusting the GEOS-Chem boundary conditions (section 3.2). The authors (and previous studies) have already established that the speciation of Hg at the boundaries influences wet/dry deposition. It seems obvious that changing the partitioning of Hg speciation in GEOS-Chem would affect deposition. I suggest eliminating section 3.2.

- Now that CMAQ exists on a hemispheric scale it seems that the exercise of using different global models for boundary/initial conditions for the regional CMAQ model is not very useful. Using the hemispheric CMAQ model directly would yield more self-consistent results in terms of having the same meteorology, chemistry, deposition schemes for both domains. The authors need to justify the value of using GEOS-Chem and GRAHM instead of CMAQ-hemispheric for boundary conditions.

Author response:

Readers should also refer to our responses to referee #2. The referees take opposite stances with respect to hemispheric CMAQ. Referee #1 says that hemispheric CMAQ should be used rather than other models in order to specify boundary concentrations for regional CMAQ. Referee #2 feels that hemispheric CMAQ is not established as a valid option and should not be included in this study. Currently, however, CMAQ users do not, in general, have hemispheric CMAQ results available to use for specifying boundary conditions. CMAQ users will most likely be forced to rely on some global model other than CMAQ for boundary concentrations. It is therefore useful for these users to have some sense of how the CMAQ hemispheric results might differ from the available options.

Referee #1 comment:

- Section 4 (page 10281). It is not surprising that different meteorology would yield different results. The authors simply note interannual variability. What would be more valuable is an analysis of why dry deposition is significantly larger with July 2005 meteorology compared to July 2001. Does it have to do with temperature? Vertical transport? Horizontal transport? etc...

Author response:

In our study, the point of including an alternate meteorology is not to determine whether or not results would differ, but whether the strong influence of upper level mercury would be present even with an alternate meteorology. In other words, is the strong influence of the upper levels due to the particular character of the 2001 meteorology? Including the 2005 results establishes that the influence of the upper level mercury is still present using the other meteorology. There, it is likely that CMAQ users must consider this strong upper level influence regardless of the year being simulated.

Minor comments

Referee #1 comment:

-Page 10275. The authors discuss removing the Hg-NO₃ pathway at length, but they don't really mention what are the main Hg oxidation/reduction reactions in the CMAQ model version that they use. Please correct that omission.

Author response:

Mercury oxidation reactions in CMAQ include reaction of Hg⁰ with ozone, peroxide and the OH radical in gas phase. In aqueous, reaction of Hg⁰ with ozone, chlorine, and OH are included. Various reduction reactions are included in the aqueous phase chemistry, including Hg⁺⁺ reaction with sulfite and with HO₂. More detailed documentation of the CMAQ mercury mechanism can be found in Bullock and Brehme (2002) and the technical support document for the Clean Air Mercury Rule (US EPA, 2005).

Referee #1 coment:

-Table 1. It would be useful to include the approximate altitude or pressure-altitude in this table.

Author response:

Approximate altitude will be added to this table.

References

Bullock Jr., O., Atkinson, D., Braverman, T., Civerolo, K., Dastoor, A., Davignon, D., Ku, J., Lohman, K., Myers, T., Park, R., Seigneur, C., Selin, N., Sistla, G., and Vija-yaraghavan, K.: The North American Mercury Model Intercomparison Study (NAMMIS): Study description and model-to-model comparisons, *J. Geophys. Res.*, 113, D17310, doi:10.1029/2008JD009803, 2008.

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Bullock, O. R., and K. A. Brehme (2002), Atmospheric mercury simulation using the CMAQ model: Formulation description and analysis of wet deposition results, *Atmos. Environ.*, 36, 2135–2146.

Pongprueksa, P., Lin, C. J., Lindberg, S. E., Jang, C., Braverman, T., Bullock, O. R., Ho, T. C., and Chu, H. W.: Scientific uncertainties in atmospheric mercury models III: Boundary and initial conditions, model grid resolution, and Hg(II) reduction mechanism, *Atmos. Environ.*, 42, 1828–1845, 2008.

US EPA (2005), Technical support document for the final Clean Air Mercury Rule: Air quality modeling, EPA Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. (Available at http://www.epa.gov/ttn/atw/utility/aqm_oar-2002-0056-6130.pdf)

Responses to Referee #2 comments.

Referee #2 comment:

Page 10276, lines 3-13: “The inclusion of this reaction mechanism in CMAQ 4.7 was found to overestimate the modeled wet deposition when compared to MDN observations (116% normalized mean bias in January and February 2002 simulations and 11% normalized mean bias (NMB) in July and August 2002 simulations) and found to result in ambient low, sub 1 ng m⁻³ GEM concentrations, in hemispheric CMAQ simulations. The removal of GEM oxidation by the NO₃ radical reduced the January and February wet deposition bias (31% NMB) and introduced a negative bias in the July and August 2002 simulations (23% NMB but decreased the normalized mean error by from 44% to 39%). CMAQ 4.7.1 with this change to the chemical mechanism was found to simulate wet deposition well when compared to MDN observations and CAMx simulations (Baker and Bash, 2012).”

There are several issues from the statements above. First of all, the reviewer thinks that poor model performance of the CMAQ model is not solely caused by the Hg-NO₃ reaction. It can be stemmed from model uncertainties such as natural emissions (re-emissions which are estimated to be about 2/3 of the global Hg emission) and/or inaccurate model assumptions [e.g. deposition of Hg(0) is in balance with re-emission].

In fact, low ambient Hg can be compensated by appropriate natural emission estimation.

By the way, lack of hemispheric CMAQ descriptions makes it very difficult for the reviewer to fully evaluate the model results. Secondly, the values of NMB from the CMAQ w/ Hg-NO₃ (116% and 11% for Jan-Feb and July-Aug, respectively) are comparable with the recent CMAQ model results w/o Hg-NO₃ [NMB 62% to 349% (Jan-Feb-Mar) and -49% to 111% (Jul-Aug-Sep)] from Baker and Bash (2012). Finally, the reviewer does not think that one can claim “well” model performance for those seasonal reported values. The reviewer believes that Baker and Bash (2012) claimed that their model performance is good for their annual evaluation and did not mean for the seasonal results.

Author response:

In comments that accompany the release version of CMAQ 4.7.1, it is noted that the inclusion of Hg—NO₃ reaction resulted in potentially low Hg⁰ concentrations and increases concentrations of oxidized mercury. Furthermore, the NO₃ oxidation of Hg reaction mechanism has no definitive experimental support and is thermodynamically unfavorable under ambient atmospheric conditions and degrades model performance. The single published rate for this reaction was based on an old understanding of the Hg⁰ thermochemistry and new experiments and insights in Hg⁰ thermochemistry make this reaction sufficiently endoergic to rule out a significant atmospheric Hg oxidation pathway even in polluted nighttime conditions (Hynes et al. 2009 and references therein). Balancing the gas phase oxidation with re-emissions is just a modeling exercise and should not be used to justify the inclusion of gas phase reactions that are not supported by chamber measurements or the current understanding of mercury atmospheric chemistry. We included this information about this reaction and its inclusion in CMAQ Versions 4.7 and 4.7.1 simply to document the model development and provide the reasoning for this choice. We also note that the Hg-NO₃ is included in neither the prior version of CMAQ (4.7) nor in the newest release of CMAQ (v5.0). Hence, including the Hg-NO₃ reaction in our study would make it a “one-off” study that would lead readers to wonder whether the results would be comparable to other versions of CMAQ.

Referee #2 comment:

Page 10279, lines 17-23: “Figure 2 demonstrates the substantially different estimates of mercury deposition that can result from the different boundary conditions. In particular,

dry deposition in some parts of California and Nevada drops from 4 g m⁻²

month⁻¹ using the GEOS-Chem boundary conditions to about 1.5 gm⁻² month⁻¹

using the GRAHM boundary conditions. Simulated wet deposition of mercury in some areas of Arizona is about $1.3 \text{ g m}^{-2} \text{ month}^{-1}$ using the GEOS-Chem boundary conditions but increases to $1.5 \text{ g m}^{-2} \text{ month}^{-1}$ using the GRAHM boundary conditions.”

What is the main message that the authors want to deliver? In general (from Fig. 1), GEOS-Chem seems to provide more Hg concentrations to the lateral CMAQ boundaries than GRAHM does for the most Hg species but HgP. However, it appeared (in Fig. 2) that CMAQ/GEOS-Chem simulated higher wet deposition but lower dry deposition when compared with CMAQ/GRAHM. Are those higher wet depositions from CMAQ/GRAHM caused by higher HgP concentrations coming out from the boundaries? It would be more informative if the authors add more discussions such as mercury species or mechanisms that responsible for differences in dry and wet depositions from using boundary conditions derived from the two global models.

Author response:

Figure 2 is included to show the strong influence of boundary concentrations on simulated deposition estimates. Although seeing the different contributions of particulate hg vs. rgm would be interesting, this investigation is looking the overall effect of changes in boundary conditions. Future work can investigate the role of different species.

Referee #2 comment:

Section 3.2: It is not clear why the boundary conditions of GEOS-Chem needed to be adjusted and why the authors chose a hemispheric CMAQ to downscale the GEOSChem data. Since the hemispheric model configurations and descriptions are not available to the public, the reviewer is skeptical about validity of the hemispheric model results.

First of all, note that this reviewer’s position is the opposite or referee 1’s position who stated that since hemispheric CMAQ is now available, comparisons of the use of boundary conditions based on other models is not useful. But, in fact, as referee 2 is aware, results of hemispheric CMAQ are not available to most CMAQ users. The goal of having a consistent global and regional CMAQ regional model is therefore not yet achieved. The CMAQ hemispheric model results that were available to the authors were used

here in order to get an indication of how the use of a consistent CMAQ hemispheric model might affect the mercury boundary concentrations for the regional model.

Author response:

The scaling of the GEOS-Chem boundary conditions was done to preserve the other modeled species and maintain a model atmosphere that had the same atmospheric concentrations of species that oxidize Hg in CMAQ. CMAQ hemispheric model profiles were used because they provided a complete set of feasible boundary conditions based on the CMAQ chemical mechanism. Furthermore, the mean values vertical profiles of these boundary conditions agreed reasonably well with the available aircraft observations in the Pacific Northwest (See figure 3).

Referee #2 comment:

Fig 4: The figures are poorly displayed. The sizes of the figures are different. The unit of the Hg(II) concentration is missing and the x-y axes are not labeled.

Author response:

The figure will be re-rendered and the units added to the color bar for the final version of the paper.

Referee #2 comment:

Section 4: Meteorological condition seems to pose a strong impact to Hg depositions (especially spatial distribution) which is not surprising. An interesting question would be “How does the model perform under different scenarios (which can be accessed by using various performance metrics)?” instead of “Will model results differ when use different meteorological conditions?” However, model evaluation is missing in this manuscript. The reviewer believes that adding some evaluations of measurement and simulation data can improve soundness of the manuscript.

Author response:

Model performance for the 2001 meteorology was evaluated in the NAMMIS (Bullock et al., 2009), although not for the month of July individually. Model performance for wet deposition was evaluated against the MDN measurements in the NAMMIS paper. For the summer season, simulated wet deposition was low on average by only 10% or less compared to observations when either the GRAHM or GEOS-Chem boundary concentrations were used. The use of the GRAHM boundary concentrations resulted in somewhat better agreement for the average wet deposition. The coefficient of determination for the summer season was about 0.25 for the CMAQ simulation using GEOS-Chem boundary concentrations and about 0.27 for the CMAQ simulation using the GRAHM boundary

concentrations. The reader is referred to the NAMMIS paper for more details on model performance. Model performance summaries for mercury are not available for the 2005 and 2002 simulations reported here.

Referee #2 comment:

Section 5: The zero-out technique used in this section produced some negative values (as high as 17.9%). These negative values cast a doubt over the robustness of the technique used and hence further discussion is required. The authors should also zero-out layers that below 5400 meters for a more complete analysis. It is quite strange that Hg concentrations at high-altitude (above cloud level) would have such a strong impact on wet deposition. In addition, a recent study by Lyman and Jaffe (2011) has estimated contribution of Hg(II) from the upper atmosphere to be only 4% of the Hg(II) deposition globally. Is it possible that Hg concentrations at lower altitude were diluted by the zero-out method? Did the Hg concentrations at the top layers remain zero at the end of the simulation period? Moreover, Hg concentration from ground-level should be shown in order to compare the results of zero-out method and the results of the inert tracer method shown in the latter sections (6&7).

Author response:

It is well known in numerical modeling that advection schemes can generate numerical waves in areas of steep concentration gradients. The areas where the negative calculated percentages occur are at the edges of steep gradients in deposition. Zeroing out the concentrations in particular layers introduces gradients in concentrations are the material mixes between layers in some areas more than others. It is therefore not surprising to see some calculated negative percentage values in limited areas. This does not mean the methodology is flawed or that the overall conclusion of large influence of the upper level boundary concentrations is incorrect. Nevertheless, the conclusion is important enough to warrant corroboration, which is the reason for the inclusion of tracer simulations that confirm that transport of material from the upper layers is consistent with a high availability of upper level mass for deposition at the surface. The results from this study apply to the CMAQ model applied with the inputs presented here, and these results may differ from other studies such as Lyman and Jaffe. The CMAQ model, and even the particular input data sets used in this study, is in wide use and it is important for the user community to be aware of the response of this particular model to inputs such as boundary concentrations.

Referee #2 comment:

Section 6&7: It is unclear why the authors used as many as 10 tracers for each Western and Northern boundaries and only 2 tracers for each Eastern and Southern as shown in Table 2. It would be more useful if the authors could tag individual Hg species just for two layers (1-12 & 13-14) instead of tagging total Hg.

Author response:

Again, investigating contributions of different species is an interesting topic and can be considered a topic for future work. The tracer definition is included for reference, but the analysis here concentrates on the relative contributions of the upper and lower parts of the boundaries. More detailed analysis using tracers (including, even, further analysis of the existing tracers) is certainly possible but is again left for future work.

Referee #2 comment:

Page 10285, lines 18-20: "The contribution from upper layers to wet and dry deposition of Hg is large regardless of global model used for boundary conditions."

The above statement for wet deposition may be true but the authors presented the results from one global model (GEOS-chem). Experiment with other global model can be very different. Besides, the contribution of upper layers Hg to dry deposition is not as large as wet deposition. The reviewer thinks that the statement should be modified.

Author response:

Reword as: The contribution from upper layers to wet and dry deposition is large based on sensitivity simulations using GEOS-Chem boundary concentrations. Tracer simulations imply that the high contribution from these upper layers is a result of the large amount of transport of material from the upper layers to the surface. It can therefore be expected that any boundary concentrations which include significant mass of divalent mercury in the upper layers will also result in a large influence of the upper layer boundary concentrations on mercury deposition.

Referee comment:

Page 10286, lines 13-17: "The influence of Hg concentrations on the dry deposition from the free troposphere in CMAQ is in agreement with the model and measurement

comparisons of Amos et al. (2012). These results may partially explain the recently documented discrepancies between modeled and observed speciated mercury concentrations

(Baker and Bash, 2012).”

Amos et al. (2012) compared between modeled and observed data in terms of wet deposition and speciated Hg concentrations in the air. They did not compare dry deposition.

The reviewer cannot make a connection between this work and the recent

work done by Amos et al. (2012). Moreover, the reviewer do not understand what specific

results may explain overestimated Hg species concentrations by Baker and Bash

(2012). Do the authors suggest that Hg species concentrations at the upper part of the

boundaries used in the work done by Baker and Bash (2012) were inaccurate (maybe

too high)?

Author response:

Rewrite paragraph quoted above as: “The influence of Hg concentrations on surface concentrations and subsequently dry deposition from Hg in the free troposphere in CMAQ is in agreement with the measurements of Lyman and Gustin (2009) and Weiss-Penzias et al. (2009) and with the modeling results of Amos et al (2012). If free tropospheric Hg(II) concentrations were too high in the boundary conditions, the entrainment of this air in the model may partially explain the recently documented discrepancies between modeled and observed speciated mercury concentrations at the surface (Baker and Bash, 2012).”

Without observations, it is difficult to come to the conclusion that the upper part of the boundary concentrations used by Baker and Bash were too high. However, this manuscript demonstrates that the modeled results in Baker and Bash (2012) were likely sensitive to the upper part of the boundary conditions used.

Dry deposition is related to the species in the air by the deposition velocity, $\text{dry deposition} = \text{deposition velocity} * \text{atmospheric concentration}$, for all mercury species in these simulations because the bidirectional exchange option was not used. The mercury concentrations at the surface in this study were sensitive to the free tropospheric concentrations. Thus surface speciated mercury concentrations are the most direct metric in evaluating the model dry deposition in the absence of flux measurements. The manuscript’s text will be edited to reflect this. Without observations, it is difficult to come to the conclusion that the boundary conditions in Baker and Bash (2012) were too high. However, this manuscript demonstrates that the modeled results in Baker and Bash (2012) were likely sensitive to concentrations in the free troposphere.

Minor concerns:

Referee #2 comment:

Page 10275, line 3: Pongprueska is misspelled. The correct name is Pongprueksa.

Author response:

Will be fixed.

Referee#2 comment:

Page 10275, line 27: Wrong reference is cited (Subir et al. 2012), the correct one is "Subir et al. 2011".

Author response:

Will fix.

Referee#2 comment:

Page 10276, line 10: Change "by from" to "from".

Author response:

Will fix.

Referee#2 comment:

Page 10277, line 16: GEOS-Chem data were generated from Harvard not MIT.

Author response:

Will fix.

Referee #2 comment:

Figures 2, 5, 6, 7: The scale of the color-bar is not linear and it is very difficult for the reviewer to interpret the data. Is there a particular reason to use such scale instead of using a simple linear scale? Moreover, the bubbles representing observed data embedded in those figures are not easy on the eyes. Those data would be more appropriate if put in a separate table which can also be served as model performance evaluation.

Author response:

The range in wet and dry deposition results was more than an order of magnitude in both the modeled and observed values. It is difficult to see the detail in the deposition using a linear scale due to a small number large values in the model results and observations. However, we will investigate a different set of scales to clarify the figures.

Referee #2 comment:

Figures 8, 9, 12: The color-bars are inconsistent. The reviewer suggests using a consistent color scheme for a better comparison.

Author response:

The colors in figures 9 & 12 will be revised.

References

Amos, H., Jacob, D., Holmes, C., Fisher, J., Wang, Q. Yantosca, R., Corbitt, E., Galarneau, E., Rutter, A., Gustin, M., Steffen, A., Schauer, J., Graydon, J., St. Louis, V., Talbot, R., Egerton, E., Zhang, Y., Sunderland, E.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition. *Atmos. Chem. Phys.* 12, 591-603, 2012

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