M. Cohen (Referee)

mark.cohen@noaa.gov

Received and published: 3 September 2016

Review of "Particulate-Phase Mercury Emissions during Biomass Burning and Impact

on Resulting Deposition: a Modelling Assessment", by De Simone et al., Atmos. Chem.

Phys. Discuss.

GENERAL COMMENTS

De Simone et al. present a model-based study of mercury emissions and deposition arising from global biomass burning (BB), examining a range of different model inputs and assumptions, with particular emphasis on the fraction of mercury emitted from BB as particulate mercury [HgP]. Overall, this seems to be an excellent investigation, although as noted below, there are some areas that might need some additional explanation and/or justification.

We thank the referee for his positive general comments and also for his specific comments and feedback that helped us to improve the general quality of the manuscript.

SPECIFIC COMMENTS

1. The model year 2013 was selected. How does 2013 compare with other years in terms of BB emissions? Should note that conclusions from this work apply to 2013 and will likely be at least somewhat different for different years.

The authors have already investigated many uncertainties related to Hg emissions from BB in De Simone et al., 2015, including the year-to-year Hg BB emission variability for a decade. As explained above, this study focusses on the speciation of Hg emissions from BB, and on the effects on the resulting deposition, and it is investigated for the first time in a CTM. Results for other years could be somewhat different . However we decided to choose 2013 because it was one of the years best covered by measurements within the GMOS project. This allows us to have feedbacks from the comparison with measurements collected at a global scale.

We modified the text to include the reason for the choice:

This study cover a single year, the 2013, which has been chosen due the large availability of measurements from GMOS network \citep{Sprovieri2016_conc, Sprovieri2016_wet,Damore2015}.

These results apply for the investigated year (2013) and could be to some extent different considering other years, due to the complex interaction of the numerous actors determining the final fate of \ce{Hg}. However few alternatives of analysis period exist due the limited time coverage of global measurement network(s).

2. (P2.L27). Would be helpful if you could say something about the differences in the inventories. E.g., a few sentences at least regarding the essential differences in how they were constructed, and of course, what the different emissions were in each inventory.

The inventories used for this study, GFAS, GFED and FINN, and the differences about the way they are compiled, are fully detailed in Andela et al. 2013, and also partially in De Simone et al., 2015. However, in the revised text we added some details and a column in the Table 1 reporting the total amount of Hg emissions from BB included in each run/inventory.

These three inventories are all compiled using the imagery obtained from the MODIS instruments. However, the way by which the data are filtered or processed yields to substantial differences among the final product, see \citet{Andela2013} and references therein for a detailed description of the differences among the inventories.

3. Section 2.2 Experimental Setup. Would be helpful if you included here (or elsewhere) additional details about the model. Here are some details, for example, that might be helpful:

We extended the relevant sections to describe better the parameterizations included in the model, either in the base configuration or in the variants considered.

* Is HgP created from Hg(0) oxidation in the model, and if so, what fraction of the oxidation products are assumed to be HgP with different reactions, etc.?

* Once HgP is emitted into the model (and/or created within the model), can it be transformed to any other form of mercury, i.e., can HgP be converted to Hg0 or Hg2 in the model?

* Is there any conversion or partitioning of Hg2 to HgP in the model? If so, how is this estimated, and is it reversible?

In the base configuration of the model Hg(p) is assumed to be inert, it is not considered a product of Hg(0) oxidation. It is emitted from either anthropogenic or BB (if any) sources, and it is subject to transport and deposition processes only. However some studies (Steffen et al., 2014, Amos et al, 2012) have been suggested that a partitioning of reactive Hg (i.e., Hg(II)) between gas and particle might exist. In particular has been suggested that it could be driven by air temperature and availability of aerosol particles (Amos et al, 2012). Therefore, two other simulations were conducted including this temperature dependent gas-particle partitioning, to assess the impact of considering a fraction of Hg from BB as Hg(p) under this assumption.

The atmospheric reduction of Hg(2) to Hg(0) has been included in different modeling studies, including De Simone et al, 2014 , to regulate the atmospheric residence time of elemental Hg and to finally best match the observations. The mechanisms that have been proposed are many, including the photo-reduction of the oxidized Hg. However some of them are unlikely to occur under most atmospheric condition. Due to these uncertainties, we preferred to not include reduction in this study.

We modified the text opportunely:

ECHMERIT, in the base configuration, includes the \ce{Hg^{0}_{(g)}} oxidation of in \ce{Hg^{II}_{(g/aq)}} oxidation by \ce{O_{3}}/\ce{OH} in the gas and aqueous phases. OH and O$_3$ concentration fields were imported from MOZART (Model for Ozone and Related chemical Tracers) \citep{Emmons2010}.

\ce{Hg^{P}} is assumed to be inert, whenever it is emitted from anthropogenic or BB activities, is subject to transport and deposition processes and it is not involved in any chemical reactions.

…

Some studies \citep{Steffen2014,Amos2012} suggested that the partitioning of reactive specie between gas and particle might be driven by air temperature and on availability of aerosol particles. Therefore, two other simulations were conducted including the temperature dependent gas particle partioning described \citet{Amos2012}, one assuming BB \ce{Hg} emissions to be only \ce{Hg^{0}_{(g)}}, and another assuming a 15\% of BB \ce{Hg} emissions as \ce{Hg^{P}}.

Atmospheric reduction of \ce{Hg^{II}_{(g/aq)}} to \ce{Hg^{0}_{(g)}} has been included in many models to regulate the residence time of \ce{Hg^{0}_{(g)}} in the atmosphere. However, a number of the proposed mechanisms are unlikely to occur under most atmospheric conditions, or are based on empirical rates to better match the observations, see \citet{Kwon2016} for a recent review. Due to this uncertainty, reduction was not included in this study.

* What particle size(s) are assumed for HgP? What information exists on the particle size distribution of HgP in the BB plumes? This would seem to be a very important factor, considering particulate deposition is critically influenced by particle size. This could be noted as a relatively uncertain aspect of the simulation that is not being addressed in the present study.

The particle size distribution has undoubtedly an impact on the final fate of Hg(p) emitted by different sources. However there are large uncertainties regarding the size distribution of particles emitted, and how it evolves during the different phases of BB (see for example, Janhäll and Pöschl, 2010 and the reference therein).

In the revision paper we included the following text:

No further \ce{Hg^{p}} particle dimension distributions other than the standard log-normal particle size distribution, as described in detail in \citep{Jung2009}, were considered in this study due to large uncertainties regarding the dynamic size range of particle emitted during BB, see \citet{Janhall2010} and the references therein.

* How is particulate dry deposition handled in the model? Is gravitational settling velocity factored in? If so, what are the size(s), shape factor(s), and density(s) of HgP-carrying particles?

* How is particulate wet deposition handled in the model? In my modeling work, I have found the parameterisations used in HgP wet deposition to have a very big impact on the fate/transport of HgP.

Dry deposition velocities are calculated considering both dry deposition and gravitational settling, following Slinn and Slinn (1980), and similar to the implementation within the CAMx model (CAMx, 2006). The assumed log-normal particle size distribution is divided into a fixed number of size intervals, then the deposition velocity is calculated for each interval and finally these are aggregated in a weighted mean.

Regarding the wet deposition of different species, both below-cloud and in-cloud scavenging are considered. Wet scavenging of dry particles only occurs below precipitating clouds and it is proportional to the mixing ratios of air pollutants. The scavenging rate, depends on scavenging efficiency, total rainfall intensity, a mean cloud or rain droplet radius and rain droplet falling velocity, following the approach of Seinfeld and Pandis (1998), and similar to the implementation within the CAMx model (CAMx, 2006).

All these mechanism remain unchanged in the model since Jung et al., 2009, where they are described in detail. Therefore we prefer not to include too much detail in this study, and to refer to Jung et al., 2009.

In the revision paper we included the following text:

Mechanisms and parameterizations used for calculating the dry and the wet deposition of the different \ce{Hg} species are the same as described by \citet{Jung2009}.

* Has the model been evaluated by comparison against HgP measurements? If so, what were the results?

In the revised text we have included a new subsection within section 3 dedicated to the comparison with Hg measurements from the GMOS network for 2013, to validate the model, and to assess any feedbacks/constraints related to the different assumptions considered about the Hg^p emissions from BB. More particularly, when considering the Hg emissions from all other sources, the very small perturbation produced by moving a fraction of Hg BB emissions from Hg^0 to Hg^p in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg^p in air concentration samples collected in a number of sites from GMOS networks for the year 2013 enabled us to assess the impact of Hg^p emissions from BB and to distinguish between the different assumptions. In particularly at two remote sites the model runs including a fraction of Hg(p) from fires resulted in a better agreement with measurements.

We included the new Section 3.4 "Constraints from Global Measurements networks" see page 7 of the revised paper.

4. The model is being run with a relatively coarse grid (e.g., on the order of 2.8 x 2.8 degrees at the equator), and so, as with any model of this type, sub-grid phenomena could be adding uncertainty to the results. Especially, for example, for emissions from BB, the height of emissions could significantly impact the near-field deposition. In real world BB situations, the emissions will not be uniformly distributed throughout the PBL, and deposition from the real vertical distribution could be much different than that with the assumed uniform-PBL assumption. In some cases, the near-field deposition could be much greater, to the extent that the emissions are emitted nearer to the ground. Along these same lines, the authors do carry out a simulation with emissions confined to the first layer of the PBL. While the height of this layer does not appear to be specified in the paper, I'm not sure it should be considered such an unrealistic simulation, as is done in the analysis. The fact that it seems to give relatively different results could be seen as evidence that emission height really does make a difference. While I am not that familiar with the literature, I believe there have been numerous studies published regarding the height of BB emissions under different conditions. As a related point, the manuscript notes that "In particular high HgP fractions were observed during smouldering phases, whereas very low or undetectable HgP levels were found during flaming combustion." [P4.L18-19]. This could mean that the highest HgP emissions might occur with relatively low injection heights, i.e., if the injection heights under smouldering conditions are lower than the heights under more intense combustion conditions.

We thank the referee for this comment. The average height of the first level is approximately 35 meters. Therefore we agree with Mark that considering the emission release within the first level only is not completely unrealistic. We modified the term unrealistic with speculative.

This comment also gave us the idea to do another sensitivity run in which the all the Hg(p) from BB is released in the first layer, whereas the Hg(0) continued to be emitted uniformly in the PBL. Unfortunately, this run did not give any further contribution to the discussion, so we have not included it in the analysis.

5. Figures 6 and 7 are a really interesting way to present the results! However, it took a little time to get my head around what they were saying at first. Perhaps a little more explanation could be added in the caption for these figures?

We added a more detailed explanation to the figures

Agreement maps of high \ce{Hg} deposition model cells obtained considering only BB emissions and assuming 0\%, 15\% and 30\% to be \ce{Hg^{P}} under both the oxidation mechanisms considered, \ce{O_3}/\ce{OH} (a) and \ce{Br} (b).

The maps show the areas where deposition is greater than $\mu+\sigma$.

…

Agreement maps, under three different speciation scenarios: 0\% (a), 15\% (b), and 30\% (c) \ce{Hg^{P}}, of high \ce{Hg} deposition model cells obtained considering only BB and using the \ce{O_3}/\ce{OH}, and the \ce{Br} oxidation mechanisms, and a sensitivity run where all \ce{Hg} BB emissions were considered inert (i.e. all \ce{Hg^{P}}). The deposition field from for this ``inert`` run was retained under the three different speciation scenarios. The maps show the areas where deposition is greater than $\mu+\sigma$.

Technical corrections and/or suggestions

(...Note that in the following, if a wording change or other correction is being suggested, I have simply included the final wording being suggested, rather than any sort of "track changes" notation. Apologies if this leads to any lack of clarity.)

- P1.L22. "Its relative importance may increase in the coming years, e.g., if the Minimata Convention and/or other efforts lead to reductions in anthropogenic emissions."

We prefer to maintain the original sentence.

- P2.L16-17. "...resulting from BB, when variations in HgP fractions and production processes are considered."

We implemented the suggestion.

- P2.L17-19. "The most recent version of the GFED BB emission inventory (van der Werfet al., 2010; Randerson et al., 2012; Mu et al., 2011), has been included in the global online Hg chemical transport model ECHMERIT, to simulate Hg deposition from BB for the year 2013 and to quantify the influences of variations in model inputs, assumptions and parameterisations."

We implemented the suggestion.

- P2.L23. "... version of the inventory..."

We corrected it.

- P2.L24. Need period at end of sentence.

We corrected it.

- P2.L27. Wouldn’t these be considered "sensitivity" runs, rather than "control" runs?

We implemented the suggestion.

- P2.L27. "... see Andela et al. (2013) (and references therein) for a description..."

We modified the sentence.

- P3.L4. "Unless explicitly stated,..."

We removed this sentence.

- P3.L9. "This value is within the range of observations (Obrist et al., 2007; Finley et al., 2009). However, since there are uncertainties in Hg speciation from BB (Zhang et al., 2013), further simulations were carried out with varying fractions of HgP (0%, 4% and 30%)."

We implemented the suggestion.

- P3.L15-17. "The principal vertical profile used (PBL-Profile) maps Hg emissions uniformly within the Planetary Boundary Layer (PBL), whereas in the second, the vertical profile of the standard version of the ECHAM-HAM model was used (HAM-Profile)(Zhang et al., 2012)."

We implemented the suggestion.

- P3.L16. Could the "HAM" acronym be defined the first time it's used?

HAM refers to the complete aerosol module coupled to ECHAM6 in the ECHAM6-HAM model, but it seems to be Hamburg Aerosol Model, it was developed at the MPI-Hamburg, but we can't find this is any of the publications.

- P3.L21-23. "These simulations primarily employ a O3/OH Hg0(g) oxidation mechanism. However, since the precise atmospheric Hg oxidation mechanism remains unclear (Hynes et al., 2009; Subir et al., 2011, 2012; Gustin and Jaffe, 2010; Gustin etal., 2015), a number of runs were performed using a Br-based oxidation mechanism."

We implemented the suggestion.

- P3.L28-29. "Finally two simulations were conducted including Hg emissions from all sources and including re-emissions, to evaluate model performance against measurements (see Appendix A)."

We changed this section in the revised text.

- P3.L28-29. What additional emissions were used for these "all-source" simulations?

We modified the text to explain the Hg sources included:

- P3.L32. "The majority of Hg releases from BB is believed to occur as Hg0(g)."

We prefer to maintain the original sentence.

- P4.L7. "properties" is misspelled.

We corrected it.

- P4.L13-16. What equation(s) were used, with what parameters? That is, you say that the Hg0 to HgP ratio is determined by FMC, but what is the mathematical relationship used?

The partitioning were calculated dynamically using the piece wise linear relationship between Fuel Moisture Content empirically determined from the relative figure in Obrist et al., 2007.

- P4.L27. I cannot really see very many "notable differences" in Figures 1 and 2. Part of the issue is that the figures are very small and the color ramp does not have a lot of contrast. Could the figures be bigger?

We thank the referee for this useful feedback. We will upload the images at the maximum resolution allowed. Moreover in the revised text we included a new figure showing the ration between Hg(p) and Hg(0) emissions for all relevant cases where the differences are more evident.

- P5.L3. At a number of points in the document, it is stated that only the 85:15 emissions speciation results are shown "for clarity". Its not clear to me why showing the results for other speciation profiles would make things less clear. There would be more figures, but would clarity really suffer?

We reported only the 85:15 emissions speciation, since the ratio between two species remains constant over the entire space domain. However we have added a new Figure showing the geographical distribution of the ratio Hg(p):Hg(0) for all relevant cases, and the latitudinal profile in a new panel in the new Figure 4. This allows for a quick comparison for all emissions assumptions considered.

- P5.L14. How were the latitudinal deposition profiles normalized?

We normalized the latitudinal profiles by the maximum value. We include this detail in the revised text.

- P5.L18. What is the height of the first model level?

On average approximately 35 meters. We included this detail.

- P5.L20-22. A few comments about the following sentence: "This last vertical distribution scenarios are unrealistic, however the differences obtained here contrast with the findings of De Simone et al. (2015) and are due to the fraction of HgP included in this study."

- Not exactly sure what you are trying to say here in terms of comparison to findings of De Simone et al. (2015).

- As noted above in the Specific Comments, I'm not sure I agree that the vertical distribution being referenced is unrealistic.

- This sentence needs to be reworded somewhat for grammar and clarity.

We finally decided to delete this sentence from the revised text.

- P5.L28. Do you mean the "deposition peak"?

We reworded the sentence:

The emission peak at around 50$\degree$N remains relatively distinct also in the deposition for all the simulations

- P6.L1. Maybe would be clearer if the section was called something like this: "Impact of atmospheric oxidation pathway and speciation profiles on geographic distribution of deposition".

We thank the referee, however we prefer to maintain the original title of the section.

- P6.L10-12. This sentence is a little confusing, particularly with the use of "all" towards the end. This "all" confused me before I realized you didn't really mean "all".

We corrected it.

- "To better understand the combined effect of Hg speciation and oxidation pathway on the deposition distribution, agreement maps were created, to highlight the model cells where different simulations all predict significant deposition..." Maybe better to say something like this: "To better understand the combined effect of Hg speciation and oxidation pathway on the deposition distribution, agreement maps were created, to highlight the similarities and differences in the distribution of high-deposition model cells in different simulations..."

We implemented the suggestion.

- P6.L12. What statistical distribution is the "standard deviation" calculated for, e.g., is it the combined data set of cell-by-cell deposition for all cells in all relevant simulations?

It is exact: it is calculated for all cells in all relevant simulations.

- P6.L14. "Using the O3/OH mechanism, the number of model cells in which the model predicts high deposition..."

We implemented the suggestion.

- P6.L21. maybe "contrasts" (or simply "presents") rather than "confronts"

We implemented the suggestion.

- P6.L22. Not sure what you mean by "passive tracer" in this context. It still deposits, right? In other simulations, how are HgP emissions not like a "passive tracer" in the same context? I guess you are implying here that there is no chemical reactions in which Hg0 is oxidized to HgP, and/or that there are no processes converting HgP to another form of Hg. And so, there should be no impact of the oxidation mechanism chosen. But, as noted above in the specific comments above, you could add some additional detail to the text regarding these and other issues to make things clearer.

We corrected the term passive with the more exact inert.

- P6.L26. Seems like maybe this section could be divided into two. One called "Uncertainty" and one called "Biomass Burning versus Anthropogenic Impact"

We thank the referee, however we prefer to maintain the original organization for the section.

- P7.L1. Could refer the reader to the figure or table that shows the point you are making. Also, instead of "actually have no influence", could say something like "have little influence". And as noted above, you haven't convinced me that the emissions into the first model level – or at least emissions into something less than the full PBL – are really "unrealistic".

We corrected it.

- P7.L7. I don't see the Antarctic in the tabular results, but you give results here?

We refer to the Southern Ocean. We corrected it.

- P7.L12. "... as in De Simone et al. (2015)." (and same correction a few lines later)

We corrected it.

- P7.L13-16. What is an "inspected ensemble"? How was the eventual ensemble created – medians of values for each cell, or mean values for each cell, or some other method?

An inspected ensemble is an ensemble constructed excluding redundant information, i.e. excluding the runs that give very similar results. The ensemble is created by the mean values for each cell.

- P7.L24. "just about everywhere" (seems like there are a few locations less than 25%?)

We agree with the referee, but we want to underline the higher relative contribute in the SH.

- Table 1. Model Evaluation (not Model Validation)

We modified the structure of the table

- Table 2. Would be helpful to explain the "R" and "P-KS" parameters a little either in the Table or in the text. At least to me, it seems a little too cryptic.

We included the description in the table.

- Table 3 and Table 4. Maybe could make these into some sort of graphic, either instead of or in addition to?

We thank the referee, however we prefer to maintain the tables. There are a lot of figure in the text.

- Table 5. What measurement sites? How many sites? What networks? What averaging time for "r" and for "NMRSE%"? Need some more detail here. What about comparison against HgP measurements? This would seem to be important for this paper!

In the revised text we have included a new subsection within section 3 dedicated to the comparison with Hg measurements from the GMOS network for 2013, to validate the model, and to assess any feedbacks/constraints related to the different assumptions considered about the Hg^p emissions from BB. More particularly, when considering the Hg emissions from all other sources, the very small perturbation produced by moving a fraction of Hg BB emissions from Hg^0 to Hg^p in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg^p in air concentration samples collected in a number of sites from GMOS networks for the year 2013 enabled us to assess the impact of Hg^p emissions from BB and to distinguish between the different assumptions. In particularly at two remote sites the model runs including a fraction of Hg(p) from fires resulted in a better agreement with measurements.

We included the new Section 3.4 "Constraints from Global Measurements networks" see page 7 of the revised paper.

- Figure 3, and in fact, most figures: Why so small? For Figure 3, could make it much wider and I think would be much clearer. Difficult to see data when lines overlap so much. Maybe consider some sort of differential dotted/dashed line(s) so that they might be able to be distinguished even when congruent?

We thanks the referee for this useful feedback. See above. We thank the referee for the suggestion, however we believe that using different style for the lines will be more confusing.

Andela, N., Kaiser, J., Heil, A., van Leeuwen, T., van der Werf, G., Wooster, M., Remy, S., and Schultz, M.: Assessment of the Global Fire Assimilation System (GFASv1), MACC-II (Monitoring Atmospheric Composition and Climate) project, 2013; http://juser.fz-juelich.de/record/186645.

Jung, G., Hedgecock, I., and Pirrone, N.: ECHMERIT V1. 0–a new global fully coupled mercury-chemistry and transport model, Geosci. Model Dev., 2, 175–195, 2009.

CAMx: CAMx, user's guide, version 4.40, Environ International Corporation, California, 2006.

Slinn, S. A. and Slinn, W. G. N.: Prediction for particle deposition of natural waters, Atmos. Environ., 14, 1013–1016, 1980.

Seinfeld, C. P. and Pandis, S. N.: Atmospheric Chemistry and Physics, From Air Pollution to Climate Change, 1998.

Janhäll, S., Andreae, M. O., and Pöschl, U.: Biomass burning aerosol emissions from vegetation fires: particle number and mass emission factors and size distributions, Atmos. Chem. Phys., 10, 1427-1439, doi:10.5194/acp-10-1427-2010, 2010.

Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., Corbitt, E. S., Galarneau, E., Rutter, A. P., Gustin, M. S., Steffen, A., Schauer, J. J., Graydon, J. A., Louis, V. L. S., Talbot, R. W., Edgerton, E. S., Zhang, Y., and Sunderland, E. M.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition, Atmospheric Chemistry and Physics, 12, 591–603, 2012.

Steffen, A., Bottenheim, J., Cole, A., Ebinghaus, R., Lawson, G., and Leaitch, W.: Atmospheric mercury speciation and mercury in snow over time at Alert, Canada, Atmospheric Chemistry and Physics, 14, 2219–2231, 2014.