Anonymous Referee #1

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Review of “Particulate-Phase Mercury Emissions during Biomass Burning and Impact on Resulting Deposition: a Modelling Assessment” by Francesco de Simone.

De Simone and co-authors have explored the sensitivity of an atmospheric mercury model (ECHMERIT) to assumptions about mercury emissions from biomass burning. The main focus of their sensitivity tests is the fraction of mercury that is emitted as Hg(p) vs. Hg(0), although they also test model sensitivity to emission time resolution and oxidants for Hg(0). They use several different plausible Hg(p) fractions (0 to 30%) and various way to apportion that fraction (constant or proportional to biomass burning CO, PM, or OC). The partitioning of emissions is an important issue, as the authors explain, because Hg(0) has a long atmospheric residence time and circulates globally while Hg(p) has a short residence time and deposits near the emission source. These are reasonable sensitivity tests and I expect that other mercury scientists and modelers will be interested in the results.

1) The main weakness of the paper is that it provides no comparison to observations, except for an unexplained and unused table in the Appendix. The paper therefore provides no insight into which, if any, of the many model configurations provide reasonable comparisons with observations. There are abundant surface and aircraft measurements of Hg(0), Hg(p), CO, OC, and PM that could be used for this purpose (GMOS, AMNET, CARIBIC, ARCTAS, INTEX-B). If the ECHMERIT model is run in a climate mode, so that it does not match the daily weather conditions at measurement sites, the simulated distributions and correlations between multiple species can still be compared with observations. Without comparison between model and observations, I do not think that this paper in its current form is suitable for publication in ACP.

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

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.

2) Another significant problem with the current version of the manuscript is that the methods do not contain enough detail to understand how the emissions were constructed. How are biomass burning emissions of Hg (=Hg(p)+Hg(0)) calculated from the biomass burning CO or DM provided by GFED? Please provide the relevant emission factors or emission ratios. In simulations where Hg(p) fraction depends on OC, PM, or FMC the manuscript needs to clearly explain how the Hg(p) fraction is calculated from OC, PM, or FMC. Do the emission factors (e.g. CO/DM, OC/DM) vary geographically with biome type? A simulation with 100% Hg(p) from biomass burning is discussed in Sect. 3.3 but not described in the methods. Regardless of how Hg is calculated in the emission inventory, please report the Hg/CO ratio because this would enable comparison to many observations that are reported this way.

Biomass Burning emissions of Hg(0), in all cases, are calculated from CO emissions of GFED (or the relevant inventory) by an uniform global enhancement ratio (ER) of 1.96 x 10^-7 as given by Friedli et. al 2009, calculated averaging the ERs obtained by measurement for different biome and areas.

The text has been modified appropriately in the revised manuscript.

\ce{Hg} emissions from BB were included in the model by mapping them to CO emissions using the global averaged Enhancement Ratio of 1.96×10^{-7} as obtained by \citet{Friedli2009} averaging field measurements from biome and areas globally distributed, including in plume measurements from CARIBIC project \citep{Ebinghaus2007}. Other previous modeling studies included different ERs \citep{DeSimone2015, Holmes2010}, however all these values are well within the uncertainties ($0.3-6.0\times10^{-7}$, see \citet{Wang2015}).

The Hg(p) emissions are calculated from CO, OC and PM GFED emissions, based on the respective scenario investigated. We have added a new appendix to describe in detail the methods used to calculate the different emission fields used in this study.

In the revised text we modified the relevant sections to clarify all these details.

“The ways how the different \ce{Hg} BB emission fields are calculated are detailed in the Appendix \ref{app:B}.”

\section{How Hg emission fields are calculated} %% Appendix A

\subsection{Mapping to CO}

When mapped to \ce{CO}, the emissions of \ce{Hg^{0}} were calculated from those of \ce{CO} using a global averaged ER ($1.96\times10^{-7} mol/mol$). These were unchanged in the run assuming \ce{Hg} emissions from BB to be 100% \ce{Hg^{0}}, whereas were opportunely fractioned between \ce{Hg^{0}} and \ce{Hg^{P}} species to be in the ratio $96:4$, $85:15$, and $70:30$, in mass, in the runs considering the respective constant fractions of \ce{Hg^{P}}. Consequently, the geographical and temporal distributions of \ce{Hg^{0}} and \ce{Hg^{P}} BB emissions follow those of \ce{CO}. For all cases, the GFEDv4 inventory was used based, except for those sensitivity runs performed to test the impact of different inventories (i.e. the FINNv1.5 and the GFAS1.4), which used the respective inventories.

\subsection{Mapping to OC}

When mapped to \ce{OC}, geographical and temporal distributions of \ce{Hg^{0}} BB emissions, as well as the total \ce{Hg} emitted, were calculated in the same way as described in Appendix \ref{app:subMCO}. The fractioning of \ce{Hg} emissions, in mass, between \ce{Hg^{0}} and \ce{Hg^{P}} species were assumed to be in the ratio $85:15$. The \ce{Hg^{P}} emissions so calculated were then geographically and temporally mapped to those of \ce{OC} from GFEDv4 inventory.

\subsection{Mapping to PM}

This mapping method is similar to one described in Appendix \ref{app:subMOC}, except for the fact the \ce{Hg^{P}} temporal and geographical distributions follow those of \ce{PM} from GFEDv4 inventory.

\subsection{Emissions speciation determination by FMC}

When using this procedure for determining the BB emissions speciation between \ce{Hg^{0}} and \ce{Hg^{P}} species, the geographical and temporal distributions of \ce{Hg^{0}} and \ce{Hg^{P}} BB emissions, as well as the total \ce{Hg} emitted, were calculated in the same way as described in Appendix \ref{app:subMCO}. The main difference is in that the fractioning of \ce{Hg} emissions, in mass, between \ce{Hg^{0}} and \ce{Hg^{P}} species were calculated dynamically using the piece wise linear relationship between Fuel Moisture Content empirically determined by relative figure in \citet{Obrist2007}.

As a proxy for FMC, we used the monthly averaged vegetation water content (VWC) derived from passive microwave remote sensing data (Advanced Microwave Scanning Radiometer 2 (ASMR2)), and employing the Land Parameter Retrieval Model (LPRM) available at (\url{http://gcmd.nasa.gov/search/Metadata.do?Entry=C1235316240-GES_DISC\#metadata}).

Regarding the CO/DM, OC/DM and PM/DM emissions factors, we use the biome based EF provided with the GFED4 script based on Akagy et al., 2011, as partially explained in Section 2.2.

We have modified the text:

A script is provided to derive gaseous and particle emissions from DM fields making use of bioma based emissions factors based on \citet{Akagi2011} and \citet{vanderWerf2010}.

Other issues:

3) Is there chemical reduction in the model? If so, is Hg(p) affected by it?

Atmospheric reduction of Hg reactive species 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 optimise the comparison with observations. However a number of reduction mechanisms have been proposed and some of them are unlikely to occur under most atmospheric conditions. Due to this uncertainty, we preferred to not include the reduction in this study.

We included this explanation in the revised paper:

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.

4) The total Hg emissions from biomass burning in this work are 400 Mg/yr. A previous analysis by the same authors reported much higher mean emissions of 675 Mg/yr (Pirrone et al., 2010). What is the reason for such a large change?

Naturally, Biomass Burning activity and associated emissions are subject to a strong year to year variability. More particularly the methods by which the activity retrieved is analyzed and the emissions of the different chemicals are estimated are subject to large uncertainties regarding both the DM and Carbon emissions and EFs being used. Moreover these are often revised due to new field measurements available and to technical advances in retrieval algorithms.

Just to give some details, looking at the historical GFED4 yearly estimated DM and C emissions, the ratio between maximum and minimum over the period 1997-2015 is about 1.7. For gases and particles, the BB emissions also depends on (the revision of) EFs used, so the differences can be greater. For example, regarding the CO GFED4 BB emissions estimates, from which Hg emissions are calculated, this ratio over the same period is greater than a factor 2.

Regarding the comparison with the annual averaged Hg emissions from BB reported in Pirrone et al 2010, it refers to the estimation calculated from version 2 of the GFED (Friedly et al. 2009). As reported in Van der werf et al., 2010, yearly estimated CO emissions of the revision 3 of GFED were found to be lower on average by 13%, and in some years by more than 50%.

We modified opportunely the text to explain this difference:

The total \ce{Hg} emitted in 2013 based on the GFED inventory is roughly 400\,Mg, at the lowest end of the initial estimates (675 ± 240\,Mg) \citep{Friedli2009}, but reasonable considering the natural variation of BB activity and the trend in diminishing the \ce{CO} emissions estimates of the latest inventory revisions (up to 50\% for some years) \citep{vanderWerf2010}.

5) None of the figures show the spatial map of Hg(p)/Hg ratio (or Hg(p)/Hg(0) ratio), which is the central focus of the paper. In addition, all 4 panels of Figure 2 are visually indistinguishable (and indistinguishable from Fig 1, except for magnitude). I think this space would be better used to show the Hg(p)/Hg emission ratios under the various schemes based on CO, PM, and OC.

In the revised text we have added a new figure (Figure 3) showing the ratio between Hg(p) and Hg(0) emissions for all relevant cases. Moreover we added panel (c) in the new Figure 4 to show the latitudinal distribution of this ratio for all relevant cases.

Compared to the cases where \ce{Hg^{P}} emissions are mapped to \ce{CO} and \ce{PM} (Figs. \ref{fig:EM_RM}(a-b) and (e-f)), mapping \ce{Hg^{P}} to \ce{OC} and using the FMC to determine the speciation (Figs. \ref{fig:EM_RM}(c-d) and (g-h)) result in enhanced \ce{Hg^{P}} emissions,above $60\degree$N, and over some areas of Amazonia, Central Africa and East Asia as is evident in Fig. \ref{fig:RATIO_EM}, potentially impacting the timing and location of deposition to these areas, particularly to the Arctic.

6) Some additional observational studies of Hg in biomass burning plumes should be discussed: Ebinghaus et al., 2007; Holmes et al., 2010.

The results of in plume measurements collected during the CARIBIC aircraft experiment reported in Ebinghaus et al., 2007 are included in of Friedly et al 2009. The ER of 1.0x10^{-7} included in the modeling study of Holmes et al., 2010 is based on limited aircraft measurements in a specific region and is not representing of the biome characteristics at a global scale.

However we quickly report these reference for the completeness of the review.

\ce{Hg} emissions from BB were included in the model by mapping them to CO emissions using the global averaged Enhancement Ratio of 1.96×10^{-7} as obtained by \citet{Friedli2009} averaging field measurements from different biomes and regions, including in plume measurements from the CARIBIC project \citep{Ebinghaus2007}. Other previous modeling studies included different ERs \citep{DeSimone2015, Holmes2010}, however all these values are well within the estimated uncertainty ($0.3-6.0\times10^{-7}$, see \citet{Wang2015}).

Minor

- Page 1 Line 3 (P1L3): Add that the Hg which is not Hg(p) is assumed to be Hg(0).

We have rewritten the sentence to be more clear.

The greatest fraction of \ce{Hg} from BB is released in the form of elemental Hg (\ce{Hg^{0}_{(g)}}). However, little is known about the fraction of \ce{Hg} bound to particulate matter (\ce{Hg^{P}}) released from BB

- P1L13: 71% to 62% of what?

We have rewritten the sentence to be more clear.

This reduces the fraction of \ce{Hg} from BB which deposits to the world's oceans from 71\% to 62\%.

- P1L15: Statement about mercury in water-stressed and warming forests is speculation that is not supported in the paper.

We have rewritten the sentence to be more clear

Under the on-going climatic changes this effect could potentially be exacerbated in the future.

- P1L19: Statement exaggerates the magnitude of biomass burning emissions relative to other anthropogenic emissions; it is certainly less than 1/2 of anthropogenic Hg emissions. First, it is widely acknowledged that a very large portion of biomass burning is anthropogenic, even though emission inventories are not labelled this way. Second, the Muntean et al., 2014 paper does not include mercury emissions from small-scale gold mining, so anthropogenic emissions are much larger than they estimated.

We agree with the referee regarding the anthropogenic to Biomass Burning emission ratio. However Hg emissions from wildfires are not included in anthropogenic emission inventories. More particularly, the reported ratio of the comparison regards the gridded inventories. However we agree to modify the statement to be more conservative.

Although the \ce{Hg} released by BB varies from year to year, it can amount to up to roughly one third of the anthropogenic emission estimates \citep{AMAP/UNEP2013,Friedli2009,DeSimone2015}

Conversely we don't agree with the referee about ASGM, since EDGARv4 contains Hg emissions from Artisanal and small scale gold mining, in fact his is stated in the Abstract of Muntean et al., 2014.

- P3L2: particle emissions are presumably also calculated.

Corrected.

- P4L2: "of" great importance

Corrected.

- P4L9: Define FMC

It is defined at its first appearance in Section 1: Introduction

- P4L23: Is the total Hg emission the same in all simulations? How is it calculated from the GFED DM or CO?

We modified the section to be clearer and we modified the Table 1 to include the total Hg emissions from BB for each run. See above for details.

The exact amount of \ce{Hg} emitted by BB injected in the model for the different runs is detailed in Table \ref{tab:simulations}

- P4L23. “Considering” should begin a new sentence.

Corrected.

- P5L14: How are the data in the figures normalized?

Data are normalized by division by the maximum value. We modified opportunely the caption of the respective figure to explain this..

- P5L16: It seems very unlikely that the fairly smooth zonal-mean distribution would be altered by finer spatial resolution.

We have rewritten the sentence.

Figure \ref{fig:Lat_DEP}(a) demonstrates the very limited impact of the time resolution used for BB emissions, probably due to the coarse horizontal resolution of the model.

- P6L23: What does “passive tracer” mean? In atmospheric modeling, “passive” usually means that a tracer does not alter the model’s transport or physics. (i.e. it is passively transported.) I would therefore expect that all of the Hg species in all of the simulations are passive in this sense.

We used the term passive tracer to indicate a tracer that is not involved in any chemical transformation. In the revised paper we use the term inert to better describe this property.

- P6L29: Not quite correct. Oxidant choice still has a big effect on the deposition pattern.

We reworded the sentence to be more clear.

Some of the model assumptions and parametrisations, in particular regarding emissions injection into the model layers, made little difference to the eventual deposition fields in the case where emissions from BB were considered to be 100\% \ce{Hg^{0}_{(g)} \citep{DeSimone2015}**.**

- P7L1: Statement says that vertical profile of emissions doesn’t matter, but I expect that the vertical profile would be quite important for scenarios with high Hg(p) emission fraction. Like other aerosols and reactive gases, Hg(p) emitted into the free troposphere should disperse much farther than Hg(p) emitted into the boundary layer.

This is actually due to the small differences between the two main height distributions used. Differences are evident for the sensitivity runs using other height injection assumptions. However these are a little speculative, so we don’t include most of them in the final analysis.

We reworded the sentences to be more clear.

However the choice of the two main vertical profile of the BB emissions used for this study, also when combined with the temporal resolution of the emissions actually have no influence on the final Hg total deposition fields, probably due to the limited differences between them. Other cases of emitting all of the emissions into a single model layer do have an impact. However these are a little speculative, and therefore they are not included in the final analysis.

- P7L6: 66% of what?

It refers to the Hg deposited. We fixed it.

- Fig 7c: Panel title says "Hg(p) fraction =30%" but one of the plotted quantities is "100% Hg(p)". Only one can be correct.

We modified both the caption and legend to be more clear.

- Table 2: How are the correlations calculated? Are they the spatial correlation of the annual mean? Is temporal variability considered in the correlations? What does "Ensemble" mean here?

We modified the caption to be more clear.

- Table 3: Title should say "from biomass burning"

We corrected the title.

- Table 4: Title says "Mercury deposition (Mg)" but only some rows have units of Mg.

We fixed it.

- Table 5: Terms "BASE Full" and "Br Full" are not defined.

We modified the nomenclature of runs to be more clear.

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009), Atmos. Chem. Phys., 10, 11707-11735, doi:10.5194/acp-10-11707-2010, 2010.

Wang, X., Zhang, H., Lin, C.-J., Fu, X., Zhang, Y., and Feng, X.: Transboundary transport and deposition of Hg emission from springtime biomass burning in the Indo-China Peninsula, J. Geophys. Res.: Atmospheres, 120, 9758–9771, 2015.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039–4072, 2011.