Anonymous Referee #3

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De Simone et al. (doi:10.5194/acp-2016-685) provide a very detailed model sensitivity study on the influence of partitioning of particulate mercury from biomass burning on its deposition patterns. Such partitioning effect has not been incorporated into most mercury chemical transport models, but it is worthy of attention in the mercury community. The topic of this study is well within the scope of ACP. However, I think the authors should address the following general and specific comments before its consideration of publication.

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

General comments:

(1) A major weakness of this manuscript is lack of model observation comparison. The authors point out several significant differences of the deposition fluxes in different model scenarios. Do the available observations provide constraints on the parameterizations of mercury BB emissions?

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) It has been suggested that the partitioning of mercury in the atmosphere depends on temperature and aerosol concentrations (for example, Amos et al., 2012). What is the treatment in this study and what is its scientific basis?

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 sources or BB, and it is subject to transport and deposition processes only. However some studies (Steffen et al., 2014, Amos et al, 2012) have suggested that a partitioning of reactive Hg (i.e., Hg(II)) between gas and particle might occur. In particular it has been suggested that this process 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 portioning, to assess the impact of considering a fraction of Hg from BB as Hg(p) under this assumption.

We modified the text opportunely

\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 by \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}}.

(3) More details of the model parameterizations should be provided. A key process is the photo-reduction of oxidized mercury in the atmosphere. Does the model allow such process in this study? Would this process affect the major conclusion of this study?

We extended sections 2.2 and 2.3 to describe better the parameterizations included in the model, both in the base configuration or in the variants considered.

In particular, the 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 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, see Know and Selin 2016 for a recent review. Due to these large uncertainties, we preferred not to include the reduction in this study.

We included this explanation in the revised paper:

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. The \ce{Hg^{P}} log-normal particle size distribution is subdivided into a fixed number of size intervals. Details can be found in \citep{Jung2009}. Beyond this standard configuration a number of alternative processes and chemical mechanism has been considered for this study, as explained in \ref{subsec:sim_and_scopes}.

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.

Specific comments:

(1) Title: I suggest changing “during” to “from”.

We thank the referee for this suggestion.

(2) Page 2, line 31: What is the global average enhancement ratio? Does it fit in the observed range (for example, Slemr et al., 2014)?

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 Fried et. al

2009, calculated averaging the ERs obtained by measurement for different biome and areas. It is well within the overall observed range, as recently reviewed also by Wang et al., 2015.

The revised text reads:

\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}).

(3) Page 3, lines 15-20: I do not quite understand why these two schemes of vertical profiles are equal less than 4 km. Could more explanations be given here?

We thank the referee for pointing out this error within the text. The two schemes actually are equal when the PBL height is greater than 4km. This threshold value is purely arbitrary, but it is the standard configuration in ECHAM6-HAM2.

We corrected the error in the revised text:

The HAM-Profile is equal to PBL-Profile when the PBL height is greater than 4000 m, otherwise 75\% of the emissions are placed within the PBL, and the remainder in the two layers above the PBL (17 and 8\%). This threshold value is arbitrary, however is the standard configuration of ECHAM6-HAM2 \citep{Zhang2012ham,Veira2015}.

(4) Sect. 2.4: Are there any statistical relationships among OC, PM, and FMC? I am curious since they are all linked to the combustion characteristics.

In the revised text we included a new figure (the figure 3) showing the ratio between Hg(p) and Hg(0) annual BB emissions under the three scenarios PM, OC, and FMC. The distribution of the resulting ratio is different among the scenarios, but they agree on regions where the Hg(p) is relatively the highest, especially for OC and FMC, particularly in the NH. This could be related to the combustion characteristics in those areas where the FMC is the highest, generally yielding lower flame temperatures, smoldering-phase combustion, that in turn yields higher emissions of OC (Zhang et al., 2013).

In the revised text we add the following discussion:

Referring now to the panels of the Fig. \ref{fig:RATIO_EM}, it is evident how the geographical distributions of the ratio of the emissions between \ce{Hg^{P}} and \ce{Hg^{0}} are different among the assumption considered. However for \ce{OC} and FMC they generally agree on areas where the \ce{Hg^{P}} emissions are relatively the greatest, especially in the North Hemisphere, and particularly for areas above $60\degree$N. The agreement between \ce{OC} and FMC is not surprising and related to the combustion characteristics that enhance the \ce{OC} emissions, i.e. the lower temperatures and the dominant smoldering phase of combustion \cite{Zhang2013}, that are likely to occur where the FMC is the greatest.

(5) Page 4, line 29: Could more explanations be given about the differences of the emission (and also the deposition) patterns > 60-degree north in difference scenarios (mapping to OC vs FMC)?

As above, the relatively higher Hg(p) emissions in areas > 60 –degree north in both the OC and FMC scenarios are likely to be related to the existing linkage between combustion characteristics in areas with the highest FMC and the processes yielding to an increases of OC emissions.

We extend the discussion in the revised text.

As more evident in Fig. \ref{fig:Lat_EM}(c), the most notable differences among the different assumptions hypothesized, are above $60\degree$N, where both the \ce{OC} and the FMC cases agree on determining the greatest \ce{Hg^{P}} emissions probably due to the linkage between \ce{OC} emissions and combustion processes favored by FMC \citep{Zhang2013}, and between $30\degree$S and $45\degree$S, where only \ce{OC} agree, probably due to different processes.

(6) Figure 4: It seems that the influences of different parameterization of PBL-type vertical profiles and different temporal resolutions are insignificant. Could these be due to the gross spatial and temporal resolutions of the model used in this study?

These two assumption leads to very similar results. We agree with the reviewer that this could be due to the coarse spatial and temporal resolution of the model.

We underline this in the revised text:

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.

Editorial comments:

(1) Page 1, line 17: add brackets for “Hg”. (2) Page 1, line 23:

“asses” should be “assess”. (3) Page 2, line 6: add a comma before “however”. (4)

Page 2, line 27: wrong reference format. (5) Page 4, line 2: “is of great importance”.

(6) Page 4, line 28: “emissions”. (7) Page 5, line 11: “where” should be “were”. (8)

Page 6, line 28: remove comma. (9) Page 7, line 12, 15: wrong reference format. (10)

Page 8, line 14: remove “the”; full name of “TGM”.

We addressed all editorial comments in the revised text.

Kwon, S. Y. and Selin, N. E.: Uncertainties in Atmospheric Mercury Modeling for Policy Evaluation, Current Pollution Reports, 2, 103–114, 2016.

Wang, Y., Huang, J., Zananski, T. J., Hopke, P. K., and Holsen, T. M.: Impacts of the Canadian forest fires on atmospheric mercury and carbonaceous particles in northern New York, Environ. Sci. Technol., 44, 8435–8440, 2010.

Zhang, Y., Obrist, D., Zielinska, B., and Gertler, A.: Particulate emissions from different types of biomass burning, Atmos. Environ., 72, 27–35, 2013.