#### Anonymous Referee #1

Received and published: 23 August 2016

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<sup>-7</sup> 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.

 $\label{eq:generalized_states} $$ \eqref{Hg} emissions from BB were included in the model by mapping them to CO emissions using the global averaged Enhancement Ratio of $1.96\times10^{-7}$ 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  $\eq Hg^{P}$  temporal and geographical distributions follow those of  $\eq PM$  from GFEDv4 inventory.

#### \subsection{Emissions speciation determination by FMC}

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

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 \pm 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  $1.0 \times 10^{-7}$  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.

 $\label{eq:Hg} emissions from BB were included in the model by mapping them to CO emissions using the global averaged Enhancement Ratio of $1.96\times10^{-7}$ 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 ( $ce{Hg^{0}}$ ). However, little is known about the fraction of  $ce{Hg}$  bound to particulate matter ( $ce{Hg^{0}}$ ) 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.

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Received and published: 22 September 2016

Review of "Particulate-Phase Mercury Emissions during Biomass Burning and Impact on Resulting Deposition: a Modelling Assessment" by Francisco De Simone et al.

#### General Comments:

De Simone et al. present a detailed assessment of the impact of mercury emissions from biomass burning on resulting atmospheric mercury deposition. The assessment is completed through utilization of an updated emissions database and an updated global mercury chemical transport model. Within this framework, the authors investigate a variety of model parameterizations and the role of other uncertainties on resulting magnitudes and spatial distributions of mercury deposition. Overall, this work represents a sizable effort and further informs the scientific community regarding speciation of mercury emissions, chemical oxidation mechanisms, and spatial and temporal variations, all within the specific context of biomass burning and with relevance to the implementation of mercury policy.

This manuscript represents a substantial contribution to the field, and is very much with the scope of ACP. However, there are several items that could be addressed by the authors and incorporated into revisions that would likely strengthen the manuscript overall.

#### We thanks the referee for his positive general comments and for his feedback that helped us to improve the general quality of the manuscript.

#### Specific Comments:

1. Much of the manuscript focuses on the potential impact of Hg P emissions. However, the issue of particle size is not discussed in the paper. Certainly, there have been assumptions made within the model regarding particle size, with direct implications to the potential transport distance prior to Hg P removal from the atmosphere (via either dry or wet processes). The manuscript would benefit from added discussion specific to particle size.

As discussed in the paper, although there is of experimental evidence that some significant fraction of Hg emitted from BB is bound to particulate, until now in models, Hg emissions from BB were considered only as Hg(0). This is the first modeling study that considers a fraction of Hg from BB to be bound to particulate. Within this scope, the main objective of the paper is to investigate how such speciation impacts the fate of Hg. We consider this study a substantial advance in Hg modeling scientific literature.

Undoubtedly, the particle size distribution will have an impact on the final fate of Hg(p) emitted. However there are large uncertainties regarding the size distribution of particles emitted, and how it evolves during the different phases of BB (see Janhäll and Pöschl, 2010 and the reference therein). Moreover in this first study we prefer to focus mostly on the mechanism related to the emission speciation and on the uncertainty related to some of the processes Hg(p) undergoes in the atmosphere, such as temperature dependent gas-particle partitioning.

*In the revised 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.

2. Table 5 presents summary statistics regarding comparison of model output with available observations from measurement networks. However, there is little text in the body of the manuscript in support of the inclusion of Table 5. The manuscript would benefit from added discussion to characterize and specify how well the model performed in comparison to observations.

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<sup>p</sup> 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<sup>0</sup> to Hg<sup>p</sup> in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg<sup>p</sup> 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<sup>p</sup> 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.

3. No explanation or justification is provided on the selection of 2013 as the model time period. This rationale should be provided in the revisions, along with some indication of the representativeness of 2013 compared to other recent 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 rationale 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).

4. Figures 1, 2, 5, & 9 seem to be very instructive. However, they are not easily legible. The size/resolution of these figures should be improved for the benefit of the reader.

We thanks the referee for this useful feedback. We will enlarge the figure at the maximum allowed resolution.

Technical/Editorial Comments:

The units reported in Table 3 need additional clarification (Mg and %).

Page 1 - line 13, "71% to 62%"...of total deposition? Seems this sentence is missing

some needed context.

Page 2 - line 7, should be "fraction of Hg emitted" (add "of").

Page 2 – line 24, period needed after "(Randerson et al., 2012)".

Page 3 – line 8, "equal to the 15%" (remove "the").

Page 4 – line 2, "Hg emissions is of great importance" (add "of").

Page 5 – line 18, "first model level level leads to" (remove "level").

Page 5 – line 19, "approx" should be "approximately".

Page 7 – line 1, instead of "have no influence", perhaps "have little influence"?

Page 8 – line 14, "between the the measurement" (remove "the").

#### In the revised paper we have fixed the editorial issues identified by the referee.

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.

#### Anonymous Referee #3

Received and published: 20 September 2016

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<sup>p</sup> 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<sup>0</sup> to Hg<sup>p</sup> in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg<sup>p</sup> 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<sup>p</sup> 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  $ce{Hg^{0}_{0}}$ , 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  $c\{Hg^{0}_{(g)}\}$  oxidation of in  $c\{Hg^{II}_{(g/aq)}\}$  oxidation by  $ce\{O_{3}\}/ce\{OH\}$  in the gas and aqueous phases. OH and  $O_{3}^{s}$  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  $1.96 \times 10^{-7}$  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:

 $\ensuremath{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\times10^{-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.

M. Cohen (Referee)

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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 photoreduction 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:

 $\label{eq:echMERIT, in the base configuration, includes the \ce{Hg^{0}_{(g)}} oxidation of in \ce{Hg^{II}_{(g/aq)}} oxidation by \ce{O_{3}} \ce{OH} in the gas and aqueous phases. OH and O_3$ 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  $ce{Hg^{0}_{0}}$ , 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<sup>p</sup> 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<sup>0</sup> to Hg<sup>p</sup> in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg<sup>p</sup> 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<sup>p</sup> 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 nearfield 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  $\ensuremath{\cells}$  deposition model cells obtained considering only BB emissions and assuming 0\%, 15\% and 30\% to be  $\ensuremath{\cells}$  under both the oxidation mechanisms considered,  $\ensuremath{\cells}$  (a) and  $\ensuremath{\cells}$  (b).

The maps show the areas where deposition is greater than  $\max$ .

. . .

Agreement maps, under three different speciation scenarios: 0% (a), 15% (b), and 30% (c)  $\eq Hg^{P}$ , of high  $\eq Hg$ } deposition model cells obtained considering only BB and using the  $\eq O_3\$ ,  $\eq OH$ , and the  $\eq Br$  oxidation mechanisms, and a sensitivity run where all  $\eq Hg$ } BB emissions were considered inert (i.e. all  $\eq Hg^{P}$ ). 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  $\medsilon \$ .

#### 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<sup>p</sup> 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<sup>0</sup> to Hg<sup>p</sup> in almost all sensitivity runs causes very little perturbation to the TGM and wet deposition results. Conversely the Hg<sup>p</sup> 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<sup>p</sup> 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.

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#### LIST OF CHANGES

Following Authors has been added due to the authorship of Hg measurements collected at sites used in the revised manuscript

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Old Appendix A regarding comparison with measurements has been deleted and a new section 3.4 focusing on the comparison with Hg measurements in air and wet deposition samples, has been added.

A new appendix A, focusing on the methods the emissions fields were constructed has been added.

New figures have been added (Figs 3, 9 10, 11 and 12), and text and other figures have been modified to accommodate reviewers' suggestions.

#### Particulate-Phase Mercury Emissions during from Biomass Burning and Impact on Resulting Deposition: a Modelling Assessment

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Abstract. Mercury (Hg) emissions from Biomass Burning (BB) are an important source of atmospheric Hg and is a major factor driving the inter-annual variation of Hg concentrations in the troposphere. Little The greatest fraction of Hg from BB is released in the form of elemental Hg (Hg<sup>0</sup><sub>(g)</sub>). However, little is known about the fraction of Hg bound to particulate matter (Hg<sup>P</sup>) released from BB, and the factors controlling this fraction are also uncertain. In light of the aims of the Minamata

- 5 Convention to reduce intentional Hg use and emissions from anthropogenic activities, the relative importance of Hg emissions from BB will have an increasing impact on Hg deposition fluxes. Hg speciation is one of the most important factors determining the redistribution of Hg in the atmosphere and the geographical distribution of Hg deposition. Using the latest version of the Global Fire Emissions Database (GFEDv4.1s) and the global Hg chemistry transport model, ECHMERIT, the impact of Hg speciation in BB emissions, and the factors which influence speciation, on Hg deposition have been investigated for the year
- 10 2013. The role of other uncertainties related to physical and chemical atmospheric processes involving Hg, and the influence of model parametrisations were also investigated, since their interactions with Hg speciation are complex. The <u>comparison with</u> atmospheric Hg<sup>P</sup> concentrations observed at two remote sites, Amsterdam Island (AMD) and Manaus (MAN) in the Amazon showed a significant improvement, when considering a fraction of Hg<sup>P</sup> from BB. The set of sensitivity runs also showed how the quantity and geographical distribution of Hg<sup>P</sup> emitted from BB has a limited impact on a global scale, although the
- 15 inclusion of increasing fractions  $Hg^P$  does limit  $Hg^0_{(g)}$  availability to the global atmospheric pool. This reduces the fraction of Hg deposition from BB from BB which deposits to the world's oceans from 71% to 62%. The impact locally is however significant, northern boreal and tropical forests where fires are frequent and uncontrolled leads to notable Hg inputs to local ecosystems. Under water-stressed conditions in tropical forests and warming temperatures in northern forests this effect may In the light of on-going climatic changes this effect could be potentially be exacerbated in the future.

#### 1 Introduction

Emissions from biomass burning (BB) are an important source of mercury (Hg) to the atmosphere (De Simone et al., 2015; Friedli et al., 2009), and a major factor in determining the inter-annual variations of its tropospheric concentration (Slemr et al., 2016). Although the Hg released by BB varies from year to year, it can amount to up to half of the most recent roughly one third

- 5 of the anthropogenic emission estimates (AMAP/UNEP, 2013; Friedli et al., 2009; De Simone et al., 2015). With the eventual implementation of the Minamata Convention (http://www.mercuryconvention.org/) and future curbs on industrial emission, as a by-product of industrial emission abatement measures, its relative importance will increase in the coming years. A previous modelling study (De Simone et al., 2015), used the global Hg chemistry model, ECHMERIT, and three BB inventories to asses assess the distribution of Hg deposition resulting from BB. A large part of the Hg released from BB deposits over oceans,
- 10 where its re-emission is driven by sea surface temperature among other factors (Carbone et al., 2016; Andersson et al., 2011), or where it can be converted to the toxic toxic methyl mercury (MeHg) compounds, with important implications for the food web, and through fish consumption, also for human health (see Chen et al. (2016) and references therein). The deposition flux of Hg from BB has been shown to be more sensitive to certain factors, in particular the chemical mechanism employed in the model and the choice of emission inventory, than to others such as the vertical profiles of emissions (De Simone et al., 2015).
- 15 In this previous study all Hg emitted from BB was considered to be Hg<sup>0</sup>(g). There is, however, evidence that the fraction of Hg emitted bound to particulates (Hg<sup>P</sup>) may be sizeable, up to 30%, especially when the Fuel Moisture Content (FMC) is high (Obrist et al., 2007; Finley et al., 2009; Friedli et al., 2009; Wang et al., 2010). These levels however remain uncertain since different methodologies have led to different conclusions (Zhang et al., 2013; Obrist et al., 2007). Little is known about the mechanisms that control the speciation of Hg in BB emissions, which leads to uncertainties in the Hg deposition patterns, since
- 20 the atmospheric lifetime of  $Hg^P$ , is significantly shorter than  $Hg^0_{(g)}$ , leading to greater local deposition. Local Hg deposition due to BB could have important repercussions in regions such as the South-East Asia where there is intensive rice cultivation, and which is subject to major BB events, especially during El Niño periods. Hg deposited to rice paddies can be readily converted to the toxic MeHg that can accumulate in the grains (Wang et al., 2015; Feng et al., 2008; Meng et al., 2014; Zhang et al., 2010). Moreover it has been reported that Hg<sup>P</sup> from BB deposited to foliage has the ability to enhance MeHg formation (Witt et al.,
- 25 2009). The aim of this study is to investigate the effects on simulated deposition fluxes of Hg resulting from BB, with changing when variations in Hg<sup>P</sup> fractions fraction and production processes are considered. Hence the The most recent version of the GFED BB emission inventory (van der Werf et 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. 2013 and to quantify the influence of variations in model inputs, assumptions and parametrisations.

#### 2 Methods

#### 2.1 The Biomass Burning Inventory

The reference BB inventory in this study, Global Fire Emissions Database version 4 (GFED4.1s), is based on an updated version of the inventory of van der Werf et al. (2010) with burned area from Giglio et al. (2013), and with the addition of small

- 5 fire burned area (Randerson et al., 2012). The standard temporal resolution of the emissions files is monthly, however data are provided to distribute these daily, and a diurnal cycle based on Mu et al. (2011) is providedalso available. Daily BB emissions from two other global inventories, GFASv1.2 (Kaiser et al., 2012, 2015) and FINNv1.5 (Wiedinmyer et al., 2011), were also included in the model for control runs, see sensitivity runs. These three inventories are all compiled using the imagery obtained from the MODIS instruments. However, the way in which the data are filtered or processed yield substantial differences
- 10 <u>between the final products, see</u> Andela et al. (2013) and references therein for a <u>detailed</u> description of the differences <del>between</del> among the inventories.

#### 2.2 Experimental Set-Up

The global Hg chemical transport model ECHMERIT (Jung et al., 2009; De Simone et al., 2014) uses T42 horizontal resolution (roughly 2.8° by 2.8° at the equator) and 19 vertical levels up to 10 hPa. Hg emissions from BB were included in the model

- 15 by mapping them to CO emissions using a global average Enhancement Ratio the global averaged Enhancement Ratio (ER) of  $1.96 \times 10^{-7}$  as obtained by Friedli et al. (2009) averaging field measurements from different biomes in various regions around the globe, including in plume measurements from the CARIBIC project (Ebinghaus et al., 2007). Previous modelling studies have used different ERs (De Simone et al., 2015; Holmes et al., 2010), however all these values were well within the range of uncertainty  $(0.3 6.0 \times 10^{-7})$ , see Wang et al. (2015)). ECHMERIT, in the base configuration, includes the oxidation of
- 20  $Hg^{0}_{(g)}$  to in  $Hg^{II}_{(g/aq)}$  oxidation by O<sub>3</sub>/OH in the gas and aqueous phases. OH and O<sub>3</sub> concentration fields were imported from MOZART (Model for Ozone and Related chemical Tracers) (Emmons et al., 2010).  $Hg^{P}$  is assumed to be inert, whether it is emitted from anthropogenic activities or BB, and it is subject to transport and deposition processes but is not involved in any chemical reactions. Mechanisms and parametrisations used for calculating the dry and the wet deposition of the different Hg species are the same as described in Jung et al. (2009). Beyond this standard configuration a number of alternative processes and
- 25 chemical mechanisms have been considered for this study, as explained in 2.3. Atmospheric reduction of  $Hg^{II}_{(g/aq)}$  to  $Hg^{0}_{(g)}$  has been included in many models to regulate the residence time of  $Hg^{0}_{(g)}$  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 Kwon and Selin (2016) for a recent review. Due to this uncertainty, reduction was not included in this study. No further  $Hg^{P}$  particulate matter (PM) dimension distributions other than the standard log-normal particle size distribution,
- 30 as described in detail in (Jung et al., 2009), were considered in this study due to large uncertainties regarding the dynamic size range of PM emitted during BB, see Janhall et al. (2010) and references therein. GFED4.1s provides monthly burned area, fire carbon (C) and dry matter (DM) emissions (http://www.falw.vu/~gwerf/GFED/GFED4/). A script is provided to derive gaseous and PM emissions from DM fields making use of emissions biome based emission factors based on Akagi et al. (2011)

and van der Werf et al. (2010). The resulting emission fields were then interpolated on to the ECHMERIT T42 grid using the mass conserving remapping function included in the Climate Data Operators (https://code.zmaw.de/projects/cdo). Where not explicitly declared, all simulations include only the emissions from BB.

#### 2.3 Simulations and their Scope

- 5 The "Base" simulation used as the reference case in this study includes daily BB emissions from GFEDv4.1s, in which a global uniform fraction of Hg<sup>P</sup>, equal to the 15% of the total Hg emissions emission is assumed. This value is within the range of observations (Obrist et al., 2007; Finley et al., 2009), however. However, since there are uncertainties in speciation the proportion of Hg<sup>P</sup> emitted from BB (Zhang et al., 2013), further simulations were carried out with varying fractions of Hg<sup>P</sup> (0%, 4% and 30%). Simulations were also conducted mapping the 15% of the total Hg emitted as Hg<sup>P</sup> to the geographical distribution of different proxy chemical species (see Section 2.4). The shorter lifetime of Hg<sup>P</sup> with respect to Hg<sup>0</sup><sub>(g)</sub> potentially means that the vertical profile of the emissions could have an impact on the distribution of Hg deposition, as is the case for other speciated Hg emission sources (De Simone et al., 2016). Therefore two vertical profile used (PBL-Profile) maps the Hg emissions uniformly within the Planetary Boundary Layer (PBL), whereas in the second, the HAM-Profile the-vertical
- 15 profile of the standard version of the ECHAM-HAM model was used (HAM-Profile) (Zhang et al., 2012). The HAM-Profile is equal to PBL-Profile when the PBL height is less greater than 4000 *m*, but in cases of very strong convection 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 it is the standard configuration of ECHAM6-HAM2 (Zhang et al., 2012; Veira et al., 2015). Biomass burning emissions from GFASv1.2 (Kaiser et al., 2012, 2015) and FINNv1.5 (Wiedinmyer et al., 2011), were also used in the study to
- assess uncertainty related to the satellite imagery processing and inventory compilation. These simulations primarily employ a  $O_3/OH Hg^0_{(g)}$  oxidation mechanism, however. However, since the precise atmospheric Hg oxidation mechanism remains unclear (Hynes et al., 2009; Subir et al., 2011, 2012; Gustin and Jaffe, 2010; Gustin et al., 2015; Ariya et al., 2015), a number of runs were performed using a Brbased\_based oxidation mechanism. Some studies (Steffen et al., 2014; Amos et al., 2012) suggest that the partitioning of reactive Hg species the between gas and particulate phases might be driven by air temperature
- and on the surface are of the aerosol present in the atmosphere. Therefore, two other simulations weer conducted including the temperature dependent gas particle partitioning described in Amos et al. (2012), one assuming BB Hg emissions to be only  $Hg^{0}_{(g)}$ , and another assuming a 15% of BB Hg emissions to be  $Hg^{P}$ . To estimate the ratio of Hg deposition from BB compared to anthropogenic sources, six further simulations were conducted including only anthropogenic emissions using the EDGAR (Muntean et al., 2014), AMAP2010 (AMAP/UNEP, 2013) and STREETS (Corbitt et al., 2011) inventories, employing the
- 30 O<sub>3</sub>/OH and Br oxidation mechanisms. This study covers a single year, 2013, chosen due to the availability of measurements from GMOS network (Sprovieri et al., 2016a, b; D'Amore et al., 2015). All simulations were performed for the year2013 a full year, without the rapid re-emission mechanism (Selin et al., 2008), and were continued without further emissions for another 12 months to allow most of the 2013 Hg emissions to be deposited. Finallytwo simulations were conducted, a selection of simulations were re-run including Hg emissions from all sourcesand including, BB, anthropogenic emissions from AMAP2010

(AMAP/UNEP, 2013), dynamic ocean emissions, terrestrial emissions and re-emissions as described in De Simone et al. (2014), to evaluate model performance against measurements see Appendix A and to evaluate the assumptions made in this study. Sources. A summary of the simulations performed can be found in Table 1.

#### 2.4 BB Emission Speciation

- 5 The release of Hg from BB occurs prevalently as  $Hg_{(g)}^{0}$ . However, as mentioned previously a measurable fraction may be emitted as  $Hg^{P}$  (Obrist et al., 2007; Friedli et al., 2009; Finley et al., 2009; Wang et al., 2010). No significant amounts of gaseous oxidised Hg ( $Hg_{(g)}^{II}$ ) have <u>so far</u> been detected in BB emissions (Obrist et al. (2007) and references therein). The speciation of Hg emissions is <u>of</u> great importance, since it largely determines the atmospheric lifetime and hence the distance <u>it emitted</u> Hg is transported in the atmosphere before deposition, as seen for other speciated <u>Hg</u>-Hg sources (Bieser et al., 2014). The fraction
- 10 of Hg<sup>P</sup> released by BB determined in field and laboratory studies ranges from fractions of a few percent to over 30% (Obrist et al., 2007). The factors determining speciation, and whether Hg<sup>P</sup> is directly emitted or if it is the product of the oxidation of Hg<sup>0</sup><sub>(g)</sub> within the plume (Obrist et al., 2007; Webster et al., 2016) are not known. However, foliage, moisture content, fuel type, plant species and combustion proprieties certainly play a role. Hg<sup>P</sup> emissions were found to be well correlated with particulate matter (PM) and Organic Carbon (OC) emissions (Obrist et al., 2007). Obrist et al. (2007) found that Hg<sup>0</sup><sub>(g)</sub> is the dominant
- 15 species in dry fuel combustion, whereas the fraction of  $Hg^P$  becomes appreciable when FMC reaches roughly 30%, above which  $Hg^P$  release appears to increase linearly with FMC. In the inventory used for the "Base" case both  $Hg^0_{(g)}$  and  $Hg^P$  follow the spatial distribution of the CO emissions from BB, and 15% of the emitted Hg is considered to be  $Hg^P$ , see Figs. 1(a) and 2(a). Hg emissions emission fields were also compiled in which the Hg<sup>P</sup> fraction of the total Hg emitted was mapped to OC and PM emissions, see Figs. 2(b and c). A further emission field was compiled in which the ratio of  $Hg^0_{(g)}$  to  $Hg^P$  is determined by
- 20 the FMC, Figs. 1(b) and 2(d). The ratio was determined using 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 (). A relationship was found to exist between Hg<sup>P</sup> emissions and the fire burn duration and severity, and combustion conditions (Obrist et al., 2007; Webster et al., 2016). In particular high Hg<sup>P</sup> fractions were observed during smouldering phases, whereas very low or undetectable Hg<sup>P</sup> levels were found during flaming
- 25 combustion. These potential parametrisations were not investigated here due to the difficulty in finding a suitable proxy data set. Appendix A contains a more detailed description of the methods used to calculate the different Hg BB emission fields.

#### **3** Results

#### 3.1 Emissions

The total Hg emitted in 2013 based on the GFED inventory is roughly 400 Mg, considering at the lower end of the initial
estimates (675 ± 240 Mg) (Friedli et al., 2009), but reasonable considering the natural variation of BB activity and the diminishing trend of the CO emission estimates in the latest inventory revisions (up to 50% for some years) (van der Werf et al., 2010).

Considering 15% of the emissions to be Hg<sup>P</sup>, in the BASE run this corresponds to approximately 340 Mg Hg<sup>0</sup><sub>(g)</sub> and 60 Mg Hg<sup>P</sup>. Interestingly the emissions of Hg<sup>P</sup> amount to 58 Mg when relating the Hg<sup>P</sup> fraction to FMC. The exact amount of Hg emitted by BB in the different model runs is detailed in Table 1. The spatial distribution and the vertical profile of the emission injection height, considering the PBL-profile for Hg<sup>0</sup><sub>(g)</sub> and Hg<sup>P</sup> in the different cases considered are shown in Figs. 1 and 2.

- 5 Both the geographical and vertical distributions of the emissions of the Hg species reveal notable differences depending on the methodology used, particularly for Hg<sup>P</sup>. Compared to the cases where Hg<sup>P</sup> emmissions emissions are mapped to CO and PM (Figs. 2(a-b) and (e-f)), mapping Hg<sup>P</sup> to OC and using the FMC to determine the speciation (Figs. 2(c-d) and (g-h)) result in enhanced Hg<sup>P</sup> emissions, above 60°N , potentially impacting the and over some areas the Amazon. Central Africa and East Asia as evident in Fig. 3. The timing and location of the enhanced Hg<sup>P</sup> emission at northerly latitudes could be particularly
- 10 relevant for Hg deposition to the Arctic. From Fig. 3, it is evident how the geographical distribution of the Hg<sup>P</sup> to Hg<sup>0</sup><sub>g</sub> emission ratio differs with the assumptions considered. However for OC and FMC there is general agreement on the areas where the Hg<sup>P</sup> emissions are relatively higher especially in the North Hemisphere, and particularly for areas above 60°N. The agreement between OC and FMC is not surprising and is related to the combustion characteristics that enhance OC emissions, i.e. lower combustion temperatures and the dominance of the smouldering phase of combustion Zhang et al. (2013), that are likely to
- 15 occur where FMC is greatest.

#### 3.2 Emission latitudinal profiles

The latitudinal profiles of  $Hg^0_{(g)}$  and  $Hg^P$  emissions, using the different approaches (Sect. 2.4) are shown in Figs. 4(a) and 4(b). For those emissions mapped to CO, only the  $\frac{85:15:85}{15:85}$  ( $\frac{1}{2}$ Hg<sup>P</sup>:Hg<sup>0</sup><sub>(g)</sub>) speciation is reported for clarity. The differences in the latitudinal profiles of the  $Hg^{0}_{(g)}$  emissions (Fig. 4(a)) are sizeable only for the peaks north of  $45^{\circ}N$ , where the FMC based speciation has an  $Hg_{(g)}^0$  fraction below 85%. The latitudinal profiles of  $Hg^P$  emissions mapped to PM and CO look very similar 20 over the entire domain (Figure Fig. 4(b)), apart from a peak a few degrees north of the equator. The Hg<sup>P</sup> emissions mapped to OC and FMC differ from the PM and CO profiles, but are similar to each other between roughly 30°S and 60°N. South of 30°S Hg<sup>P</sup> emissions mapped to OC are higher, while peak Hg<sup>P</sup> emissions derived from FMC at  $65^{\circ}N$  (1.5 g km<sup>-2</sup> y<sup>-1</sup>) are nearly 30% greater than those derived from OC and roughly double those mapped to CO and PM. Moreover, in this the FMC scenario the peak in Hg<sup>P</sup> emissions at 65°N are greater than the peak seen at 15°S (1.5 vs 1.4 g km<sup>-2</sup> y<sup>-1</sup>). As is particularly evident 25 in Fig. 4(c), the most notable differences among the different assumptions hypothesised, are above  $60^{\circ}$ N, where both the OC and the FMC cases agree on the location of the greatest Hg<sup>P</sup> emissions probably due to the linkage between OC emissions and combustion processes favoured by FMC (Zhang et al., 2013), and between  $30^{\circ}$ S and  $45^{\circ}$ S, where only OC and PM are greater than "Base". A previous modelling study focusing on the fate of Hg from BB, where all emissions where were considered as  $Hg^{0}_{(g)}$ , showed that the long atmospheric life of the elemental Hg smoothed the deposition latitudinal profiles compared 30 to the emission profiles (De Simone et al., 2015). Here the presence of shorter lived in the emissions may lead to greater

differences in the deposition fields. The four panels in Figure Fig. 5 compare the normalised latitudinal deposition profiles obtained for the "Base" simulation with those obtained from the alternative Hg<sup>P</sup> emission scenarios by category. Figure Fig. 5(a) demonstrates the very limited impact of the time resolution used for BB emissions. This outcome may well be different

if simulations are performed using finer spatial resolutions, most likely due to the coarse horizontal resolution of the model. The two vertical emission profiles (Figure Fig. 5(b)) give deposition fields that are to all effects indistinguishable, even when considering different temporal resolutions varying temporal resolution of the BB emissions, whereas assuming all emissions to be in the first model level level (with an average height of approximately 35 meters) leads to enhanced deposition near emission

5 peaks. In this instance, the maximum deposition coincides with peak emission, at approx approximately 15°S, whereas in all other cases maximum deposition is shifted towards the equator. This last vertical distribution scenarios are unrealistic, however the differences obtained here contrast with the findings of and are due to the fraction of included in this study.

The similarities in the latitudinal profiles of  $Hg^{P}$  emissions when mapped to CO and PM are reflected in their deposition profiles (Fig. 5(c)). The relatively greater deposition north of  $60^{\circ}N$  seen in Fig. 5(c) obtained when  $Hg^{P}$  emissions are mapped

- to OC and when driven by and FMC, reflect the peak in Hg<sup>P</sup> emissions at this latitude. The greatest differences in the latitudinal deposition profiles, using the GFED inventory, are seen when varying the percentage of Hg<sup>P</sup> in the emissions (Fig. 5(d)). Considering emissions to be solely Hg<sup>0</sup><sub>(g)</sub> yields a relatively smooth profile extending from pole to pole, increasing Hg<sup>P</sup> causes enhanced deposition near BB hot-spots. The emission peak at around 50°N remains relatively distinct in also in the deposition for all the simulations (although it seen as a shoulder in the 100% Hg<sup>0</sup><sub>(g)</sub> profile). The peak north of 60°N is more dependent
- 15 on emission speciation, supporting the previous finding that the location of Hg deposition depends on complex interactions between emission location , and the time of year and atmospheric which influences both atmospheric transport patterns and oxidant concentration fields (De Simone et al., 2015).

#### 3.3 Geographical Distribution of Hg Deposition

Due to the uncertainty in the atmospheric oxidation pathway of Hg, simulations were performed using both O<sub>3</sub>/OH and Br
oxidation mechanisms to investigate their impact on Hg deposition fields. Figure 6(a-d) compares the geographical distribution of the modelled Hg deposition field using emission fields with 0% and of 15% Hg<sup>P</sup>, for each of the oxidation mechanisms. Using the The O<sub>3</sub>/OH mechanism leads to enhanced deposition in the tropics, whereas the Br mechanism leads to relatively higher deposition over the South Atlantic and Indian oceans. Assuming a fraction of Hg<sup>P</sup> in the emissions subtracts some Hg<sup>0</sup><sub>(g)</sub> from the global pool, and this fraction is deposited nearer to emission sources in Central Africa, South-East Asia, the Amazon, and near the wildfires which occur in North America and in North Asia in the northern hemisphere summer. From Fig.6, it

- appears that assuming a fraction of the BB emissions to be  $Hg^P$  causes the deposition field simulated using the Br oxidation mechanism to more closely resemble those that using the O<sub>3</sub>/OH mechanism. 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 similarities and differences in the distribution of high-deposition
- 30 ( $\ge \mu + 1\sigma$ , the average plus 1 standard deviation) model cells in the different simulations as described in (De Simone et al., 2014). Figs. 7(a) and 7(b) show the agreement maps of the deposition for three different Hg<sup>P</sup> fractions using the two oxidation mechanisms. Using the O<sub>3</sub>/OH mechanism, the <u>number of</u> model cells in which the model predicts high deposition in all three emission speciation scenarios is higher than when using the Br mechanism (631 *vs.* 248). This is due to the combination of high emissions and high oxidant concentrations in the Tropics when using the O<sub>3</sub>/OH mechanism, constraining Hg deposition

to a relatively narrow latitude band. Using the Br mechanism, Hg has a greater possibility of being transported to mid and high latitudes before being oxidised and deposited. In both the oxidation scenarios the greatest higher deposition over the remote areas of North America and North Asia occurs only when the fraction of Hg<sup>P</sup> in the emissions is greater than zero. High local contributions to Hg deposition from BB using the Br mechanism occur more frequently when the fraction of Hg<sup>P</sup> is non-zero,

5 purple in Fig. 7(b), unlike the O<sub>3</sub>/OH simulations. Figure 8 confronts contrasts the results from the two oxidation mechanisms with varying percentages of Hg<sup>P</sup>, and a simulation in which the Hg<sup>P</sup> fraction was assumed to be 100%, so that it behaves as a passive an inert tracer. The agreement maps show clearly that the similarity in the deposition fields increases with increasing Hg<sup>P</sup> fraction, reflected in the number of cells where all three simulations agree (grey in the figure) and the decrease in the number of cells where only one simulation predicts deposition higher than  $\mu + \sigma$ , (red, blue and yellow).

#### 10 3.4 Constraints from Global Measurements networks

The output from the simulations including all emissions (as indicated in Table 1) for the year 2013 were compared to measurement data available from GMOS and other monitoring networks. The sites are the same as those used in Travnikov et al. (2016), the measurements from which have been reviewed Sprovieri et al. (2016a) and Sprovieri et al. (2016b). Table 6 summarises a selection of metrics from the comparison for Total Gaseous Mercury  $(Hg^0_{(g)} + Hg^0_{(g)})$  and for Hg in wet deposition.

- 15 The results are in line with those obtained from previous studies (De Simone et al., 2015, 2016) focusing on a different time period, and indicate a generally good agreement between measured and simulated TGM, especially for the run with the Br driven oxidation mechanism. For the Hg wet deposition fluxes, the results show poorer performance, due to the difficulties for coarse resolution global models to simulate precipitation events correctly (De Simone et al., 2014; Roeckner et al., 2003). Since the different sensitivity runs considering Hg<sup>P</sup> from BB differ by a only a small perturbation in the speciation of total Hg
- 20 emitted from the BASE (or the relevant reference) case, the results are actually indistinguishable from BASE (or the relevant reference) case. Therefore the table reports the comparison only from runs which yield different results. Also, this means that neither wet deposition nor TGM are the most appropriate variables to assess the validity of any of the assumptions concerning Hg<sup>P</sup> emitted during BB. During 2013, within the GMOS and other Hg monitoring initiatives, a number of measurement sites collected samples of atmospheric Hg<sup>P</sup>. These stations and their precise locations are reported in the Table 2. The result of the
- 25 comparison with the measurements from these sites is summarised in Fig. 9. Panel 9(a) shows the annually averaged surface concentrations of Hg<sup>P</sup> as simulated by the BASE run for 2013. As is evident, surface Hg<sup>P</sup> hots spot are close to the industrial areas of Eastern Europe, India, East Asia and South Africa, and to areas characterised by significant BB activity, including Indonesia, Central Africa and boreal areas of Canada and Asia.

A first analysis to find those areas where the model run assuming a fraction  $Hg^{P}$  from BB (i.e. BASE) gives results that are statistically distinguishable from the model run assuming Hg from BB to be only  $Hg^{0}_{(g)}$ , was performed to identify the measurements sites best suited for further analysis.

The geographical distribution of these differences is reported in panel(b) of Fig. 9. The areas were the anthropogenic input is the greatest differ little between the simulations (based on a student t-test at 95% level of confidence), as indicated by dot points in the panel. Most of the stations, depicted by the blue solid points in the same panel, are within these regions, and therefore

unsuitable for the analysis. Only three stations are in areas where the model results are significantly different. These, short names of which are reported in the panel, are Amsterdam Island (AMD), Manaus (MAN) and Muana Loa (MAU). However MAU and Mt. Waliguan (MWA) are high altitude sites and affected by processes other than BB. For both the remaining stations (AMD and MAN), the fraction of  $Hg^P$  that is assumed to be emitted by anthropogenic activities, as estimated by AMAP2010

- 5 inventory (AMAP/UNEP, 2013), is not sufficient alone to explain the averaged Hg<sup>P</sup> concentrations collected over the year, as is evident from Fig. 9(c). The inclusion of 30% Hg<sup>P</sup> from BB emissions at MAN and AMD, and also the inclusion of 15% Hg<sup>P</sup> from BB as using the FINN inventory at MAN, significantly improve the model performances, in terms of the annual average Hg<sup>P</sup> concentrations. The result of the comparison between the Hg<sup>P</sup> concentrations collected at these two stations with the same modelled at the same points by a selection of sensitivity runs at an finer temporal resolution (daily averages)
- 10 is reported in the two panels of Fig. 10. The same comparisons for all the stations, among with the box and whisker plot of distributions of the Hg<sup>P</sup> concentrations measured and modelled, are reported in Fig. 11. Although the measurement coverage of the year at MAN is sporadic, it is an important station because it is situated in a remote area where the local Hg emissions are due only to ASGM (only Hg<sup>0</sup><sub>(g)</sub>) and BB (Sprovieri et al., 2016b). The consistent reduction of the error between measured and modelled Hg<sup>P</sup> concentrations when consider a fraction of particulate bound Hg emitted from BB (NRMSE from 48% to
- 15 34% and 27% for 30% Hg<sup>P</sup> and FINN, respectively) clearly indicate the role of BB on the observed Hg<sup>P</sup> values. At AMD (Fig. 10 (b)), the inclusion of the fraction of Hg<sup>P</sup> from BB results only in a slightly better agreement with the measurements (NRMSE from 16% to 14%). However, the Hg<sup>P</sup> event matching grows from 25% to 32%, especially in the last part of the year, that a previous study have been associated with BB events in the central Africa (Angot et al., 2014). Peaks was evaluated using the "findpeak" function in MATLAB, available from https://it.mathworks.com/help/signal/ref/findpeaks.html. To summarise,
- 20 it seems that the emissions of a fraction  $Hg^{P}$  from BB is plausible and supported by the measures of atmospheric  $Hg^{P}$ , at least for the period investigated and for the location of the two remote stations AMD and MAN. However, it has to be noted that the uncertainties related to the precise nature of atmospheric  $Hg^{P}$  and to the processes it undergoes in the atmosphere could have an appreciable impact on the model results. For example, the assumption of a temperature dependent gas-particle  $Hg^{II}$  partitioning proposed by Amos et al. (2012) (i.e. the "Partitioning" and "Partitioning ref" runs) yield overall better model
- 25 agreement with annually average Hg<sup>P</sup> concentrations (stars in Fig. 9(c)). However, comparing the modelled daily average time series with measurements results in clearly poorer performance at both the AMD and MAN stations, see Fig. 12(b) and (c). More importantly, this assumption tends to render statistically indistinguishable (student t-test at 95% level of confidence) the contribution of any eventual Hg<sup>P</sup> from BB, as evident from Fig. 12(a).

#### 3.5 Uncertainty and Biomass Burning versus Anthropogenic Impact

Besides the uncertainty related to the atmospheric Hg oxidation mechanism (Hynes et al., 2009; Subir et al., 2011, 2012; Gustin et al., 2015; Ariya et al., 2015) there are a number - of other factors that lead to uncertainty in ascertaining the fate of Hg released by BB. Most Some of the model assumptions and parametrisations, in particular emission height made little difference to the eventual deposition fields in the case where emissions from BB were considered to be 100% Hg<sup>0</sup><sub>(g)</sub> (De Simone et al., 2015). However Other sensitivity studies of the speciation of anthropogenic emissions reveals that varying the fractions of  $Hg^{II}_{(g)}$  and  $Hg^{P}$  can result in quite different Hg deposition patterns, due to their shorter residence time compared to  $Hg^{0}_{(g)}$  (De Simone et al., 2016; Bieser et al., 2014).

The temporal resolution and However the choice of the two main vertical profile of the BB emissions actually have no used in this study, also when combined with the temporal resolution of the emissions actually have little influence on the final Hg total

- 5 deposition fields, if the unrealistic case of emitting all the emissions into the first model level is not considered deposition fields. Emitting all, or part, of the Hg in to a single model layer does have an impact. However these cases are a little speculative, and therefore not included in the final analysis. The factor which has the greatest influence on the Hg deposition pattern is the choice of emission inventory, whereas within the same for a given inventory the most important factors are the fraction of Hg<sup>P</sup> and the oxidation mechanism. Although, although as seen in Sect. 3.3 the impact of the oxidation mechanism decreases
- 10 with increasing Hg<sup>P</sup> fraction. The method of calculating the Hg<sup>P</sup> fraction has a limited impact on deposition on a global scale, with 66% of Hg deposited over the oceans, but the regional impact does change. Using FMC to determine the Hg<sup>P</sup> fraction increases deposition to the Arctic by 16 and 13% (O<sub>3</sub>/OH and Br, and to the Antaretie Southern Ocean by 30 and 25% (O<sub>3</sub>/OH and Br), see Table 4. Apart from the Polar oceans the oceanic basins most influenced by the fraction of Hg<sup>P</sup> in the BB emissions are the North and South Pacific and the Indian ocean. The total deposition to individual basins from the
- 15 limiting 0 and 30% Hg<sup>P</sup> cases are included in Table 4. The horizontal pattern correlation method (Santer et al., 1995, 1996) and the non-parametric Kolmogorov-Smirnov two-sample test were used to assess the differences in the deposition fields obtained from the simulations summarised summarized in Table 1as in , as in De Simone et al. (2015). The results of the comparison of the simulations with the "Base" run are presented in Table 3. The results of the Kolmogorov-Smirnov two-sample test were exploited to construct an inspected ensemble, following the approach of Solazzo and Galmarini (2015), and previously
- 20 employed in De Simone et al. (2015). The ensemble includes only those simulations with realistic assumptions and deposition fields with little or no probability of belonging to the same distribution. Hg deposition from the resulting ensemble is shown in Figure Fig. 13(a). The figure shows how the inclusion of Hg<sup>P</sup> in the BB emissions causes greater deposition near the hot spots of central Africa, Brazil, South-East Asia, North America and North Asia. Nonetheless approximately 70% of Hg deposition occurs over the oceans, with the Tropical Atlantic, Tropical Pacific and Indian Oceans most impacted (see Table 5). Figure
- 25 13(b) compares the BB ensemble results with an ensemble constructed using only anthropogenic emissions, using the EDGAR (Muntean et al., 2014), AMAP2010 (AMAP/UNEP, 2013) and STREETS (Corbitt et al., 2011) inventories, (considering both oxidation mechanisms (see Table 1). It can be seen that the contribution of BB to Hg deposition is close to or greater than that from anthropogenic activities in the areas near the locations of wildfires, central Africa, the Amazon, part of the Southern Atlantic and North Asia. The contribution to Hg deposition from BB relative to anthropogenic emissions is greater than 25%
- 30 everywhere in the Southern Hemisphere, and exceeds 30% in the South Pacific and South Atlantic, table 5. As anthropogenic Hg emissions decline the relative impact of BB Hg will rise, as shown in Figure Fig. 14, where the Hg deposition due to BB is compared with Hg deposition from anthropogenic sources in three different emission scenarios for 2035, see Pacyna et al. (2016) for details of the emission scenarios.

#### 4 Conclusions

#### A previous study-

5

That a fraction of Hg<sup>P</sup> is present in BB Hg emissions has been confirmed by several field measurements (Obrist et al., 2007; Finley et al., 2009), and this fact has bee suggested as an explanation of high Hg<sup>P</sup> observations at a remote site (Angot et al., 2014), but this is the first time it has been included in a model study to assess its effects on a global scale.

A previous modelling study assuming emissions from BB to be 100% Hg<sup>0</sup><sub>(g)</sub> (De Simone et al., 2015) suggested that as much as 75% of the Hg emitted by BB was deposited to ocean basins, with global implications for food webs and human health, however in that study emissions were assumed to be 100. Including a fraction of Hg<sup>P</sup> in the BB Hg emissions has an impact on the geographical distribution of the deposition fluxes for the year analysed, reducing input to the global oceans and some

- 10 high latitude regions, while enhancing potentially negative effects on ecosystems close to areas where significant BB occurs. The presence of Hg<sup>P</sup> in the emissions decreases the differences seen in Hg deposition patterns produced by employing different oxidation mechanisms, and in . In the remote areas of North Asia and North America, BB has a strong local impact if the Hg<sup>P</sup> fraction is non-zero. This latter result is independent of the atmospheric oxidation pathway. In simulations with 30% Hg<sup>P</sup> in the BB emissions, deposition over the Arctic increases by 11% with respect to 0% Hg<sup>P</sup> (30% in the Br simulations),
- 15 and by 16% when the Hg<sup>P</sup> fraction is determined by FMC (37% in the Br simulation). The fraction of Hg<sup>P</sup> released from BB while having an impact on the land-sea distribution of global Hg deposition, has a more significant impact in particular regions including the Polar regions, the South Atlantic and Pacific and Indian Oceans. Field studies in these areasThese results apply for the investigated year (2013) and may differ for other years, due to the complex interaction of the numerous factors determining the final fate of Hg. However few alternatives of analysis period exist due the limited time coverage of
- 20 global measurement network(s). Indeed the year selected for the analysis, allowed for the hypotheses tested in this study to be supported by observations at a number of sites from GMOS which has extended the observational network in the Tropics and the Southern Hemisphere (Sprovieri et al., 2016a, b). The eventual emissions of a fraction of Hg<sup>P</sup> from BB cannot be evaluated by comparison with observed atmospheric Hg concentrations or Hg in wet precipitation samples, due to the very small impact of Hg<sup>P</sup> from BB on both the atmospheric burden and wet deposition relative to all other emissions sources ( $\approx$
- 25 1-2%). Conversely, its contribution to atmospheric Hg<sup>P</sup> is comparable to that of anthropogenic activities and therefore may be investigated. The inclusion in the model run of a fraction of Hg<sup>P</sup> from BB contributes to better model performances at two remote sites, Manaus, and Amsterdam Island. However results are not definitive, due to the large uncertainty related to Hg<sup>P</sup> emissions and transformation processes. Further modelling, and more measurement sites, particularly in remote areas, would help reduce some of the uncertainties associated with Hg emissions from BB, and to constrain these processes. Biomass burn-
- 30 ing has and will continue to play a significant role in the cycling of legacy Hg, and its relative importance is likely to increase as anthropogenic emissions are reduced and global temperatures rise.

#### Appendix A: Comparison with Measurements How Hg emission fields are calculated

The results from those simulations which included all emission sources were compared to available measurement data, for gas phase concentration and

#### A1 Mapping to CO

When mapped to CO, the emissions of  $Hg_g^0$  were calculated from those of CO using a global averaged ER ( $1.96 \times 10^{-7}$ ). These

- 5 were unchanged in the run assuming Hg wet deposition flux. A statistical comparison is reported in Table 6. The comparison between the the measurement and emissions from BB to be 100% Hg<sup>0</sup><sub>g</sub>, and divided between Hg<sup>P</sup> and Hg<sup>0</sup><sub>g</sub> species, with ratios 4:96, 15:85, and 30:70, in mass, in the runs considering the respective constant fractions of Hg<sup>P</sup>. Consequently, the geographical and temporal distributions of Hg<sup>0</sup><sub>g</sub> and Hg<sup>P</sup> BB emissions follow those of CO. For all cases, the model results yield to reasonable results for both TGM and GFEDv4 inventory was used based, except for those sensitivity runs performed
  10 to test the impact of different inventories, FINNv1.5 and GFAS1.4.

#### A2 Mapping to OC

When mapped to OC, geographical and temporal distributions of  $Hg_g^0$  BB emissions, as well as the total Hg wet deposition flux, emitted, were calculated as described in Appendix A1. The fractioning of Hg emissions, in mass, between Hg<sup>P</sup> and is in line with previous comparisons.

15  $Hg_g^0$  species were assumed to be in the ratio 15:85. The  $Hg^P$  emissions so calculated were then geographically and temporally mapped to those of OC from the GFEDv4 inventory.

#### A3 Mapping to PM

This mapping method is similar to the one described in Appendix A2, except for the fact the Hg<sup>P</sup> temporal and geographical distributions follow those of PM from the GFEDv4 inventory.

#### 20 A4 Emissions speciation determination by FMC

When using this procedure for determining the BB emission speciation between  $Hg_g^0$  and  $Hg^P$ , the geographical and temporal distributions of  $Hg_g^0$  and  $Hg^P$  BB emissions, as well as the total Hg emitted, were calculated in the same way as described in Appendix A1. The main difference is in that the fractioning of Hg emissions, in mass, between  $Hg_g^0$  and  $Hg^P$  species were calculated dynamically using the piece wise linear relationship between Fuel Moisture Content empirically determined by relative figure in Obrist et al. (2007). As a proxy for FMC, we used the monthly averaged vegetation water content

25 by relative figure in Obrist et al. (2007). 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 (http://gcmd.nasa.gov/search/Metadata.do?Entry= C1235316240-GES\_DISC#metadata).

Acknowledgements. We are grateful to Sebastian Rast and colleagues at the Max Planck Institute for Meteorology in Hamburg, Germany 30 for the distribution of their software ECHAM5 and for providing the access to the processed ERA-INTERIM data. We are grateful to Xin Yang for providing the Br/BrO fields from p-Tomcat. The research was performed in the framework of the EU project GMOS (FP7–265113). The authors would also like to thank the referees whose helpful suggestions and comments contributed much to improving the original manuscript.

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**Figure 1.** Geographical distribution (a-b)) and PBL-type vertical profiles (c-d) of the  $Hg^0_{(g)}$  emissions, when mapped to CO (a,c) and when speciation is determined by FMC (b,d). For the emissions mapped to CO, only the speciation ( $85:15:85 Hg^P:Hg^0_{(g)}$ ) is shown for clarity.



**Figure 2.** Geographical distribution (a-d)) and PBL-type vertical profiles (e-h) of the Hg<sup>P</sup> emissions as injected in the model, when mapped to CO (a,e), PM(b,f) and OC(c,g), and when speciation is determined by FMC (d,h). For the emissions mapped to CO, only the speciation (85:15:85, Hg<sup>P</sup>:Hg<sup>0</sup><sub>(g)</sub>) is shown for clarity.



**Figure 3.** Geographical distribution of the  $Hg^{P}$ :  $Hg^{0}_{(g)}$  emissions ratio, when mapped to PM(a) and OC(b), and when speciation is determined by FMC (c). In the color bar are indicated the levels corresponding to the constant speciations (4:96, 15:85 and 30:70  $Hg^{P}$ :  $Hg^{0}_{(g)}$ ) used for the emissions mapped to CO.



**Figure 4.** Latitudinal profiles of (a)  $Hg^0_{(g)}$  emissions when mapped to CO and when speciation is determined by FMC; (b)  $Hg^P$  emissions when mapped to CO, PM, OC, and when speciation is driven by FMC, respectively . The latitudinal profiles of both and emissions are reported in fig. 4(a) and of (bc) , respectively the relevant ratio  $Hg^P$  :  $Hg^0_{(g)}$  . For both  $Hg^0_{(g)}$  and  $Hg^P$  emissions mapped to CO, only the speciation ( $\$5:15:\$5:Hg^P:Hg^0_{(g)}$ ) is reported for clarity ; whereas in panel (c) all the speciations are reported



**Figure 5.** Latitudinal profiles of the normalised Hg total deposition from the model "Base" run, compared with a selection of sensitivity of sensitivity runs, assuming: (a-b) different emission time resolution and vertical profile, and a combination of both, (c) different Hg<sup>P</sup> emission geographical distributions, and different Hg<sup>0</sup><sub>(g)</sub>:Hg<sup>P</sup> ratios. The normalisation was done by maximum.



**Figure 6.** Geographical distribution of the Hg total deposition from model runs including only BB emission sources and assuming two different Hg<sup>P</sup> emission fractions, 15% (a,c) and 0% (b,d), for the two oxidation mechanisms considered,  $O_3/OH$  (a-b) and Br (c-d).



**Figure 7.** Agreement maps of the high Hg deposition fields model cells obtained considering only BB emissions and assuming 0%, 15% and 30% to be Hg<sup>P</sup> for under both the oxidation mechanisms considered, O<sub>3</sub>/OH (a) and Br (b). The maps show the areas where deposition is greater than  $\mu + \sigma$ .



**Figure 8.** Agreement maps, <u>under three different speciation scenarios: 0% (a), 15% (b), and 30% (c) Hg<sup>P</sup>, of high Hg deposition fields model cells obtained considering only BB and using the O<sub>3</sub>/OH, and the Br oxidation mechanisms, and a <u>control sensitivity</u> run in which where all Hg BB emissions were considered to be 100 inert (i.e. all Hg<sup>P</sup>,). The deposition field from for this "inert" run was retained under the three different speciation scenarios: 0(a), 15(b), and 30(c). The maps show the areas where deposition is greater than  $\mu + \sigma$ .</u>



**Figure 9.** (a) Annual averaged surface  $Hg^{P}$  concentrations as simulated by BASE run including all emission sources. (b) Differences in annual averaged surface  $Hg^{P}$  concentrations as simulated by BASE and by NO  $Hg^{P}$  runs, both including emissions from all sources. Black dots indicate that differences are not significant based on a student-t-test at a 95 % confidence interval. Blue bigger points indicate the locations of measurements sites reported in Table 2. Short names are depicted for sites where the differences between BASE and NO  $Hg^{P}$  runs are significant. (c) Scatter plot of annual averaged  $Hg^{P}$  concentrations measured at sites of Table 2, compared with those obtained by different sensitivity runs. The circles in the figure indicate values relative to the sites further investigated at an higher temporal resolution, see Fig. 10.



Figure 10. Temporal evolution of daily averaged surface  $Hg^{P}$  concentrations measured at Manaus (MAN) and Amserdam Island (AMD) for the entire 2013, compared with a selection of sensitivity runs.

#### Table 1. Simulations performed

Name	Inventory (BB emiss Mg)	Full Version	Emiss. Time Res.	Fraction Hg <sup>P</sup>	Map Hg <sup>P</sup>	Chem.Mech.	Vertical Profile	Scope
BASE	GFED4.1s (390)	Yes	daily	15	CO	O <sub>3</sub> /OH	PBL	Reference
3-hourly	GFED4.1s (390)		3-h	15	CO	O <sub>3</sub> /OH	PBL	Emiss. Time resol.
Monthly	GFED4.1s (390)		monthly	15	CO	O <sub>3</sub> /OH	PBL	Emiss. Time resol.
HAM-Profile	GFED4.1s (390)		daily	15	CO	O <sub>3</sub> /OH	HAM	Vertical Profile
Only 1st lv	GFED4.1s (390)		daily	15	CO	O <sub>3</sub> /OH	1st	Vertical Profile
Only PBL Lev	GFED4.1s (390)		daily	15	CO	O <sub>3</sub> /OH	lev of PBL	Vertical Profile
3h+HAM-prof	GFED4.1s (390)		daily	15	CO	O <sub>3</sub> /OH	HAM	V. Pr. & E. T. res.
Hg <sup>P</sup> to PM	GFED4.1s (390)	Yes	daily	15	PM	O <sub>3</sub> /OH	PBL	Hg <sup>P</sup> Mapping
Hg <sup>P</sup> to OC	GFED4.1s (390)	Yes	daily	15	OC	O <sub>3</sub> /OH	PBL	Hg <sup>P</sup> Mapping
HgP to FMC	GFED4.1s (390)	Yes	daily	variable	CO	O <sub>3</sub> /OH	PBL	Hg <sup>P</sup> Mapping
NO Hg <sup>P</sup>	GFED4.1s (390)	Yes	daily	0	NA	O <sub>3</sub> /OH	PBL	Fraction $Hg^{P}$
4% Hg <sup>P</sup>	GFED4.1s (390)		daily	4	СО	O <sub>3</sub> /OH	PBL	Fraction $Hg^{P}$
30% Hg <sup>P</sup>	GFED4.1s (390)	Yes	daily	30	СО	O <sub>3</sub> /OH	PBL	Fraction $Hg^{P}$
100% Hg <sup>P</sup>	GFED4.1s (390)		daily	100	СО	None	PBL	Transport Hg <sup>P</sup>
Partitioning	GFED4.1s (390)	Yes	daily	15	СО	O <sub>3</sub> /OH	PBL	Partitioning Hg <sup>P/II</sup>
Partitioning Ref.	GFED4.1s (390)	Yes	daily	0	CO	O <sub>3</sub> /OH	PBL	Partitioning Hg <sup>P/II</sup>
Reduction	GFED4.1s (390)	Yes	daily	15	CO	O <sub>3</sub> /OH +Red.	PBL	Chemistry
Br	GFED4.1s (390)	Yes	daily	15	СО	Br	PBL	Chemistry
Br No Hg <sup>P</sup>	GFED4.1s (390)		daily	0	NA	Br	PBL	Chemistry
Br 30% Hg <sup>P</sup>	GFED4.1s (390)		daily	30	СО	Br	PBL	Chemistry
Br Hg <sup>P</sup> to OC	GFED4.1s (390)		daily	15	OC	Br	PBL	Chemistry
Br Hg P to FMC	GFED4.1s (390)		daily	variable	СО	Br	PBL	Chemistry
GFAS	GFASv1.2 (150)		daily	15	СО	O <sub>3</sub> /OH	PBL	Inventory
GFAS Br	GFASv1.2 (150)		daily	15	СО	Br	PBL	Chemistry
FINN	FINNv1.5 (550)	yes	daily	15	СО	O <sub>3</sub> /OH	PBL	Inventory
FINN Br	FINNv1.5 (550)		daily	15	CO	Br	PBL	Chemistry
AMAPOH	AMAP2010		NA	NA	NA	O <sub>3</sub> /OH	NA	Ratio to Anth. Emiss.
AMAPBr	AMAP2010		NA	NA	NA	Br	NA	Ratio to Anth. Emiss.
EDGAROH	EDGAR2008		NA	NA	NA	O <sub>3</sub> /OH	NA	Ratio to Anth. Emiss.
EDGARBr	EDGAR2008		NA	NA	NA	Br	NA	Ratio to Anth. Emiss.
STREETSOH	STREETS2005		NA	NA	NA	O <sub>3</sub> /OH	NA	Ratio to Anth. Emiss.
STREETSBr	STREETS2005		NA	NA	NA	Br	NA	Ratio to Anth. Emiss.

	Short name	Lat	Lon	Elev. (m)
Amsterdam Island	AMD	-37.8	77.58	<u>70</u>
Cape Hedo	CHE	26.86	128.25	<u>60</u>
Longobucco		39.39	16.61	1379
Manaus	MAN	-2.89	-59.97	110
Mauna Loa	MAU	19.54	-155.58	3399
Mt. Changbai	MCH	42.4	128.11	741
Mt. Waliguan	MWA	36.29	100.9	3816
Rao	RAO	57.39	<u>11.91</u>	5_

Table 2. Characteristics of ground-based sites measuring Hg<sup>P</sup>

Table 3. Correlations-Horizontal pattern correlation (R) and Probabilities that the Hg deposition fields of the different runs belong to the same distribution as the "Base" run ( $P_{KS}$ ). The tick in the Ensemble column indicates the inclusion of the respective run in the Ensemble in Fig. 13

	Sim.	R	$P_{KS}$	Ensemble
Time resolution	3-hourly	1	1	
&	Monthly	1	0.99	
Vertical profile	HAM-Profile	1	1	
	3h+HAM-Profile	1	1	
Hg <sup>P</sup> mapping	Hg <sup>P</sup> to PM	1	1	
	Hg <sup>P</sup> to OC	1	0.42	$\checkmark$
	Hg <sup>P</sup> to FMC	0.99	0.45	$\checkmark$
Hg <sup>P</sup> fraction	NO Hg <sup>P</sup>	0.94	0.38	$\checkmark$
	4% Hg <sup>P</sup>	0.97	0.72	$\checkmark$
	30% Hg <sup>P</sup>	0.97	0.5	$\checkmark$
Inventory	GFAS	0.98	0	$\checkmark$
	FINN	0.96	0	$\checkmark$
Oxidation Mech	Br	0.96	0	$\checkmark$
&	Br No Hg <sup>P</sup>	0.81	0	$\checkmark$
Combination	Br 30% Hg <sup>P</sup>	0.91	0	$\checkmark$
	Br Hg <sup>P</sup> to OC	0.95	0	$\checkmark$
	Br Hg <sup>P</sup> to FMC	0.94	0	$\checkmark$
	GFAS Br	0.94	0	$\checkmark$
	FINN Br	0.92	0	$\checkmark$

Total Deposition / Mg										%	
Run	N. Atlantic	S. Atlantic	N. Pacific	S. Pacific	Indian Ocean	Med. Sea	Arctic	S. Ocean	SEA	LAND	
BASE	31.7	32.5	75.3	67.4	45.9	1.1	5.0	2.3	66	34	
NO Hg <sup>P</sup>	32.1	32.4	82.0	74.4	48.9	1.2	4.7	2.6	71	29	
30% Hg <sup>P</sup>	31.3	32.5	69.3	61.0	43.2	1.0	5.2	2.0	62	38	
$Hg^{P}$ to FMC	31.4	32.1	74.3	66.6	44.7	1.1	5.8	2.3	66	34	
Br No Hg <sup>P</sup>	26.6	39.4	75.8	83.0	55.3	1.1	3.7	7.6	74	26	
Br 30% Hg <sup>P</sup>	28.0	36.4	61.7	61.1	44.9	0.9	4.8	4.6	62	38	
Br Hg <sup>P</sup> to FMC	27.3	36.8	66.6	68.8	47.1	1.0	5.6	5.8	66	34	

 Table 4. 2013 Mercury Hg deposition (Mg) coming from BB to the oceans as obtained by the different runs for the 2013. Last two columns reports the percentage of the total Hg that deposits over seas and lands, respectively.

**Table 5.** Mercury deposition (Mg) to the oceans for 2013 <u>due to from</u> BB and comparison (<u>ratio</u>) with deposition <u>due to from</u> anthropogenic activities for both oxidation mechanisms.

O <sub>3</sub> /OH	N. Atlantic	S. Atlantic	N. Pacific	S. Pacific	Indian Ocean	Med. Sea	Arctic	S. Ocean
Only BB	29.8	29.9	72.1	63.0	43.0	1.1	4.7	2.1
Only Anthropogenic	144.0	80.0	417.7	206.7	151.3	10.0	34.3	11.0
Ratio	0.21	0.37	0.17	0.31	0.28	0.11	0.14	0.19
Br	N. Atlantic	S. Atlantic	N. Pacific	S. Pacific	Indian Ocean	Med. Sea	Arctic	S. Ocean
Only BB	25.7	34.7	65.1	66.2	46.2	0.9	4.2	5.1
Only BB Only Anthropogenic	25.7 153	34.7 85.33	65.1 457.3	66.2 188.3	46.2 140	0.9 12.33	4.2 34	5.1 27.3

 Table 6. Comparison of the results of BASE Full and Br Full simulation results simulations including all emissions sources with observations from measurement networks for 2013.

	Te	otal Gase	ous Mer	cury	Wet Deposition			
	Regression		Stats		Regression		Stats	
	Intercept	ntercept Slope r NMRSE		NMRSE %	Intercept Slope		r	NMRSE %
<b>/</b> BASE	0.36	0.62	0.72	10.54	5.84	0.04	0.12	6.89
Partitioning	0.34	$\underbrace{0.7}_{\sim\sim\sim}$	0.73	11.9	3.71	0.03	$\underbrace{0.14}_{\sim\sim\sim\sim}$	4.76
Br	-0.08	0.96	0.74	15.68	7.1	0.08	0.18	9.12



**Figure 11.** (Left column) Temporal evolution of the daily averaged surface  $Hg^{P}$  concentrations measured at all sites from Table 2 for the entire 2013, compared with the modeled values as simulated by BASE and by NO  $Hg^{P}$  runs, including emissions from all sources. (Right column) Box plots of the distribution of the of the daily averaged surface  $Hg^{P}$  concentrations, for the entire 2013, as measured and simulated by the different sensitivity runs. Note the logarithmic for both MAU and MWA subplot



**Figure 12.** (a) Differences in annual averaged surface  $Hg^{P}$  concentrations as simulated by *Partitioning* and by *Partitioningref*. runs, both including emissions from all sources and the temperature dependent  $Hg^{II}$  gas-particle partitioning as implemented in Amos et al. (2012). Black dots indicate that differences are not significant based on a student-t-test at a 95 % confidence interval. Blue bigger points indicate the locations of measurements sites reported in Table 2 Temporal evolution of daily averaged surface  $Hg^{P}$  concentrations measured at Manaus (MAN) and Amserdam Island (AMD) for the entire 2013, compared with the modeled values from the same sensitivity runs.



**Figure 13.** Geographical distribution of the total Hg deposition from BB emissions obtained from an ensemble of simulations for the year 2013 (a) in terms of the average ( $\mu$ ) and standard deviation  $\sigma$  of the ensemble. The comparison of the BB simulation with an ensemble of runs including only anthropogenic emissions (De Simone et al., 2016) shows (b) the geographic distribution of the fraction of the BB contribution to the Hg deposition from the anthropogenic sources.



**Figure 14.** Ratio of the Hg deposition due to biomass burning with respect to Hg deposition due to anthropogenic emissions for three anthropogenic emissions scenarios for 2035. (a) CP, Current Policy; (b) NP, New Policy; (c) MFR, Maximum Feasible Reduction.