



Particulate-Phase Mercury Emissions during 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 is known about the fraction of Hg bound to particulate matter (Hg^P) released from BB, and the factors controlling this fraction are also uncertain. In light of the aims of the Minamata Convention to reduce intentional Hg use and emissions from anthropogenic activities, the relative

- 5 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 2013. The role of other uncertainties related to physical and chemical atmospheric processes
- 10 involving Hg, and the influence of model parametrisations were also investigated, since their interactions with Hg speciation are complex. The quantity and geographical distribution of Hg^P emitted from BB has a limited impact on a global scale, although the inclusion of increasing fractions Hg^P does limit Hg⁰_(g) availability to the global atmospheric pool. This reduces Hg deposition from BB 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
- 15 conditions in tropical forests and warming temperatures in northern forests this effect may be exacerbated in the future.

1 Introduction

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Although the Hg released by BB varies from year to year, it can amount to up to half of the most recent anthropogenic emission estimates (Muntean et al., 2014; 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 the distribution of Hg deposition. A large part of

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).





the Hg released from BB deposits over oceans, 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 MeHg, 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 5 et al., 2015). In this previous study all Hg emitted from BB was considered to be $Hg^{0}(g)$. There is however, evidence that the fraction Hg emitted bound to particulates (Hg^P) 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 10 the atmospheric lifetime of Hg^P, is significantly shorter than Hg⁰_(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^P from BB deposited to foliage has the ability to enhance MeHg formation (Witt 15 et al., 2009). The aim of this study is to investigate the effects on simulated deposition fluxes of Hg resulting from BB, with changing Hg^P fractions and production processes are considered. Hence 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.

2 Methods 20

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 inventory of van der Werf et al. (2010) with burned area from Giglio et al. (2013), and with the addition of small fire burned area (Randerson et al., 2012) The standard temporal resolution of the emissions files is monthly, however data are

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provided to distribute these daily, and a diurnal cycle based on Mu et al. (2011) is provided. 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 (Andela et al.) and references therein for a description of the differences between 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 by 30 mapping them to CO emissions using a global average Enhancement Ratio (Friedli et al., 2009). GFED4.1s provides monthly





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burned area, fire carbon (C) and dry matter (DM) emissions (http://www.falw.vu/~gwerf/GFED/GFED4/). A script is provided to derive gaseous emissions from DM fields making use of emissions 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 Hg emissions from BB .

2.3 Simulations and their Scope

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^P, equal to the 15% of the total Hg emissions is assumed. 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 with varying fractions of Hg^P (0%, 4% and 30%). Simulations were also conducted mapping the 15% of the total Hg emitted as Hg^P to the geographical distribution of different proxy chemical species (see Section 2.4). The shorter lifetime of Hg^P with respect to Hg⁰_(g) 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 parametrisations, and different emission injection time resolutions, were also included in the

- 15 study. The principal vertical profile used (PBL-Profile) maps Hg emissions uniformly within the Planetary Boundary Layer (PBL), whereas in the second, the HAM-Profile the vertical profile of the standard version of the ECHAM-HAM model was used (Zhang et al., 2012). The HAM-Profile is equal to PBL-Profile when the PBL height is less than 4000 *m*, but in cases of very strong convection (Zhang et al., 2012), 75% of the emissions are placed within the PBL, and the remainder in the two layers above the PBL (17 and 8%) (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 employ a $O_3/OH Hg^0_{(g)}$ 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 et al., 2015), a number of runs were performed using a Br based oxidation mechanism. To estimate the ratio of Hg deposition from BB compared to anthropogenic sources, six further simulations were conducted including only anthropogenic
- 25 emissions using the EDGAR (Muntean et al., 2014), AMAP2010 (AMAP/UNEP, 2013) and STREETS (Corbitt et al., 2011) inventories, employing the O₃/OH and Br oxidation mechanisms. All simulations were performed for the year 2013, 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. Finally two simulations were conducted including Hg emissions from all sources and including re-emissions, to evaluate model performance against measurements see Appendix A. A summary of
- 30 the simulations performed can be found in Table 1.

2.4 BB Emission Speciation

The release of Hg from BB occurs prevalently as $Hg^{0}_{(g)}$. However, as mentioned previously a measurable fraction may be emitted as Hg^{P} (Obrist et al., 2007; Friedli et al., 2009; Wang et al., 2010; Finley et al., 2009). No significant amounts of





gaseous oxidised Hg (Hg $_{(g)}^{II}$) have been detected in BB emissions (Obrist et al. (2007) and references therein). The speciation of Hg emissions is great importance, since it largely determines the atmospheric lifetime and hence the distance it is transported in the atmosphere before deposition, as seen for other speciated Hg sources (Bieser et al., 2014). The fraction of Hg^P released by BB determined in field and laboratory studies ranges from fractions of a few percent to over 30% (Obrist et al., 2007). The

- 5 factors determining speciation, and whether Hg^{P} is directly emitted or if it is the product of the oxidation of $Hg_{(g)}^{0}$ 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^{P} 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 $Hg_{(g)}^{0}$ is the dominant species in dry fuel combustion, whereas the fraction of Hg^{P} becomes appreciable when FMC reaches roughly 30%, above which Hg^{P}
- 10 release appears to increase linearly with FMC. In the inventory used for the "Base" case both $Hg_{(g)}^{0}$ and Hg^{P} follow the spatial distribution of the CO emissions, and 15% of the emitted Hg is considered to be Hg^P, see Figs. 1(a) and 2(a). Hg emissions fields were also compiled in which the Hg^P 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 Hg⁰ to Hg^P is determined by 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
- 15 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). A relationship was found to exist between Hg^P emissions and the fire burn duration and severity, and combustion conditions (Obrist et al., 2007; Webster et al., 2016). In particular high Hg^P fractions were observed during smouldering phases, whereas very low or undetectable Hg^P levels were found during flaming combustion. These potential parametrisations were not investigated here

20 due to the difficulty in finding a suitable proxy data set.

3 Results

3.1 Emissions

The total Hg emitted in 2013 based on the GFED inventory is roughly 400 Mg, considering 15% of the emissions to be Hg^P, this corresponds to approximately 340 Mg Hg⁰_(g) and 60 Mg Hg^P. Interestingly the emissions of Hg^P amount to 58 Mg when relating the Hg^P fraction to FMC. The spatial distribution and the vertical profile of the emission injection height, considering the PBL-profile for Hg⁰_(g) and Hg^P in the different cases considered are shown in Figs. 1 and 2. Both the geographical and vertical distributions of the emissions of the Hg species reveal notable differences depending on the methodology used, particularly for Hg^P. Compared to the cases where Hg^P emmissions are mapped to CO and PM (Figs. 2(a-b) and (e-f)), mapping Hg^P to OC and using the FMC to determine the speciation (Figs. 2(c-d) and (g-h)) result in enhanced Hg^P emissions, above 60°N,

30 potentially impacting the timing and location of deposition to the Arctic.





3.2 Emission latitudinal profiles

The latitudinal profiles of Hg⁰_(g) and Hg^P emissions, using the different approaches (Sect. 2.4) are shown in Figs. 3(a) and 3(b). For those emissions mapped to CO, only the 85:15 (Hg⁰_(g):Hg^P) speciation is reported for clarity. The differences in the latitudinal profiles of the Hg⁰_(g) emissions (Fig. 3(a)) are sizeable only for the peaks north of 45°N, where the FMC based
speciation has an Hg⁰_(g) fraction below 85%. The latitudinal profiles of Hg^P emissions mapped to PM and CO look very similar over the entire domain (Figure 3(b)), apart from a peak a few degrees north of the equator. The Hg^P 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^P emissions mapped to OC are higher, while peak Hg^P emissions derived from FMC at 65°N (1.5 g km⁻² y⁻¹) are nearly 30% greater than those derived from OC and roughly double those mapped to CO and PM. Moreover, in this scenario the peak in Hg^P emissions at 65°N are greater than the peak seen at 15°S (1.5 vs 1.4 g km⁻² y⁻¹). A previous modelling study focusing on the fate of Hg from BB, where all emissions where considered as Hg⁰_(g), showed that the long atmospheric life of

- focusing on the fate of Hg from BB, where all emissions where considered as $Hg_{(g)}^{0}$, showed that the long atmospheric life of the elemental Hg smoothed the deposition latitudinal profiles compared to the emission profiles (De Simone et al., 2015). Here the presence of shorter lived Hg^P in the emissions may lead to greater differences in the deposition fields. The four panels in Figure 4 compare the normalised latitudinal deposition profiles obtained for the "Base" simulation with those obtained from the
- 15 alternative Hg^P emission scenarios by category. Figure 4(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. The two vertical emission profiles (Figure 4(b)) give deposition fields that are to all effects indistinguishable, even when considering different temporal resolutions of the BB emissions, whereas assuming all emissions to be in the first model level level leads to enhanced deposition near emission peaks. In this instance, the maximum deposition coincides with peak emission, at approx
- 20 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 De Simone et al. (2015) and are due to the fraction of Hg^P 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. 4(c)). The relatively greater deposition north of $60^{\circ}N$ seen in Fig. 4(c) obtained when Hg^{P} emissions are mapped

- to OC and when driven by and FMC, reflect the peak Hg^P emissions at this latitude. The greatest differences in the latitudinal deposition profiles, using the GFED inventory, are seen when varying the percentage of Hg^P in the emissions (Fig. 4(d)). Considering emissions to be solely $Hg_{(g)}^0$ yields a relatively smooth profile extending from pole to pole, increasing Hg^P causes enhanced deposition near BB hot-spots. The emission peak at around 50°N remains relatively distinct in all the simulations (although it seen as a shoulder in the 100% $Hg_{(g)}^0$ profile). The peak north of 60°N is more dependent on emission speciation,
- 30 supporting the previous finding that the location of Hg deposition depends on complex interactions between emission location, time of year and atmospheric oxidant concentration fields (De Simone et al., 2015).





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3.3 Geographical Distribution of Hg Deposition

Due to the uncertainty in the atmospheric oxidation pathway of Hg, simulations were performed using both O_3/OH and Br oxidation mechanisms to investigate their impact on Hg deposition fields. Figure 5(a-d) compares the geographical distribution of the modelled Hg deposition field using emission fields with 0% and of 15% Hg^P, for each of the oxidation mechanisms. Using the O_3/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^P in the emissions subtracts some Hg⁰_(g) 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.5, it appears

assuming a fraction of the BB emissions to be Hg^P causes the deposition using the Br oxidation to more closely resemble

- 10 those using the O_3/OH . 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 ($\ge \mu + 1\sigma$, the average plus 1 standard deviation) (De Simone et al., 2014). Figs. 6(a) and 6(b) show the agreement maps of the deposition for three different Hg^P fractions using the two oxidation mechanisms. Using the O₃/OH mechanism, the model cells in which the model predicts high deposition in all three emission speciation scenarios is higher than when
- 15 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_3/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 deposition over the remote areas of North America and North Asia occurs only when the fraction of Hg^P 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^P is non-zero, purple in Fig. 6(b), unlike the O₃/OH simulations. Figure 7 confronts the results from the two oxidation mechanisms with varying percentages of Hg^P, and a simulation in which the Hg^P fraction was assumed to be 100%, so that it behaves as a passive tracer. The agreement maps show clearly that the similarity in the deposition fields increases with increasing Hg^P 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
- 25 higher than $\mu + \sigma$, (red, blue and yellow).

3.4 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) there are a number, of other factors that lead to uncertainty in ascertaining the fate of Hg released by BB. Most of the model assumptions and parametrisations made little difference to the eventual deposition fields in the case

30 where emissions from BB were considered to be 100% $Hg^0_{(g)}$ (De Simone et al., 2015). However studies of the speciation of anthropogenic emissions reveals 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 $Hg^0_{(g)}$.





The temporal resolution and the choice of the vertical profile of the BB emissions actually have no influence on the final Hg total deposition fields, if the unrealistic case of emitting all the emissions into the first model level is not considered. The factor which has the greatest influence on the Hg deposition pattern is the choice of emission inventory, whereas within the same inventory the most important factors are the fraction of Hg^P and the oxidation mechanism. Although as seen in Sect. 3.3 the

- 5 impact of the oxidation mechanism decreases with increasing Hg^P fraction. The method of calculating the Hg^P fraction has a limited impact on deposition on a global scale, with 66% deposited over the oceans, but the regional impact does change. Using FMC to determine the Hg^P fraction increases deposition to the Arctic by 16 and 13% (O₃/OH and Br, and to the Antarctic by 30 and 25% (O₃/OH and Br), see Table 3. Apart from the Polar oceans the oceanic basins most influenced by the fraction of Hg^P in the BB emissions are the North and South Pacific and the Indian ocean. The total deposition to individual basins from the
- 10 limiting 0 and 30% Hg^P cases are included in Table 3. 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 in Table 1 as in (De Simone et al., 2015). The results of the comparison of the simulations with the "Base" run are presented in Table 2. The results of Kolmogorov-Smirnov two-sample test were exploited to construct an inspected ensemble, following the approach of Solazzo and Galmarini (2015), and previously employed in (De Simone
- 15 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 8(a). The figure shows how the inclusion of Hg^P 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 4). Figure 8(b) compares the BB
- 20 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 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% everywhere in the Southern
- 25 Hemisphere, and exceeds 30% in the South Pacific and South Atlantic, table 4. As anthropogenic Hg emissions decline the relative impact of BB Hg will rise, as shown in Figure 9, 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

30 A previous study suggested that as much as 75% of the Hg emitted by BB was deposited to ocean basins, with implications for food webs and human health, however in that study emissions were assumed to be 100% $Hg^{0}_{(g)}$ (De Simone et al., 2015). Including a fraction of Hg^P in the BB Hg emissions has an impact on the geographical distribution of the deposition fluxes, reducing input to the global oceans and some high latitude regions, while enhancing potentially negative effects on ecosys-





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tems close to areas where significant BB occurs. The presence of Hg^P in the emissions decreases the differences seen in Hg deposition patterns produced by employing different oxidation mechanisms, and in the remote areas of North Asia and North America, BB has a strong local impact if the Hg^P fraction is non-zero. This latter result is independent of the atmospheric oxidation pathway. In simulations with 30% Hg^P in the BB emissions deposition over the Arctic increases by 11% with respect to 0% Hg^P (30% in the Br simulations), and by 16% when the Hg^P fraction is determined by FMC (37% in the Br simulation). The fraction of Hg^P 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 areas would help reduce some of the uncertainties associated with Hg emissions from BB. Biomass burning 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

The results from those simulations which included all emission sources were compared to available measurement data, for gas phase Hg concentration and Hg wet deposition flux. A statistical comparison is reported in Table 5. The comparison between the the measurement and the model results yield to reasonable results for both TGM and Hg wet deposition flux, and is in line with previous comparisons (De Simone et al., 2015, 2016).

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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 $Hg^0_{(g)}$:Hg^P) is shown for clarity.







Figure 2. Geographical distribution (a-d)) and PBL-type vertical profiles (e-h) of the Hg^P 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 Hg⁰_(g):Hg^P) is shown for clarity.







Figure 3. 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 $Hg^0_{(g)}$ and Hg^P emissions are reported in fig. 3(a) and (b), respectively. For both $Hg^0_{(g)}$ and Hg^P emissions mapped to CO, only the speciation (85:15 $Hg^0_{(g)}$:Hg^P) is reported for clarity.







Figure 4. Latitudinal profiles of the normalised Hg total deposition from the model "Base" run, compared with a selection of sensitivity runs, assuming: (a-b) different emission time resolution and vertical profile, and a combination of both, (c) different Hg^P emission geographical distributions, and different Hg⁰_(g):Hg^P ratios.







Figure 5. Geographical distribution of the Hg total deposition from model runs including only BB emission sources and assuming two different Hg^P 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 6. Agreement maps of the Hg deposition fields obtained considering only BB emissions and assuming 0%, 15% and 30% to be Hg^P for both the oxidation mechanisms considered, O₃/OH (a) and Br (b). The maps show the areas where deposition is greater than $\mu + \sigma$.







Figure 7. Agreement maps of Hg deposition fields obtained considering only BB and using the O₃/OH, and the Br oxidation mechanisms and a control run in which emissions were considered to be 100% Hg^P, under three different speciation scenarios: 0% (a), 15% (b), and 30% (c) Hg^P. The maps show the areas where deposition is greater than $\mu + \sigma$.







Figure 8. 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 (μ) and standard deviation σ 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 9. 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.





Table 1. Simulations performed

Name	Inventory	Emiss. Time Res.	Fraction Hg ^P	Map Hg ^P	Chem.Mech.	Vertical Profile	Scope
BASE	GFED4.1s	daily	15	СО	O ₃ /OH	PBL	Reference
3-hourly	GFED4.1s	3-h	15	СО	O ₃ /OH	PBL	Emiss. Time resol.
Monthly	GFED4.1s	monthly	15	СО	O ₃ /OH	PBL	Emiss. Time resol.
HAM-Profile	GFED4.1s	daily	15	CO	O ₃ /OH	HAM	Vertical Profile
Only 1st lv	GFED4.1s	daily	15	СО	O ₃ /OH	1st	Vertical Profile
Only PBL Lev	GFED4.1s	daily	15	CO	O ₃ /OH	lev of PBL	Vertical Profile
3h+HAM-prof	GFED4.1s	daily	15	CO	O ₃ /OH	HAM	V. Pr. & E. T. res.
Hg ^P to PM	GFED4.1s	daily	15	PM	O ₃ /OH	PBL	Hg ^P Mapping
Hg ^P to OC	GFED4.1s	daily	15	OC	O ₃ /OH	PBL	Hg ^P Mapping
Hg ^P to FMC	GFED4.1s	daily	variable	CO	O ₃ /OH	PBL	Hg ^P Mapping
NO Hg^{P}	GFED4.1s	daily	0	NA	O ₃ /OH	PBL	Fraction Hg ^P
4% Hg ^P	GFED4.1s	daily	4	СО	O ₃ /OH	PBL	Fraction Hg ^P
30% Hg ^P	GFED4.1s	daily	30	СО	O ₃ /OH	PBL	Fraction Hg ^P
100% Hg ^P	GFED4.1s	daily	100	СО	None	PBL	Transport Hg ^P
Br	GFED4.1s	daily	15	СО	Br	PBL	Chemistry
Br No Hg ^P	GFED4.1s	daily	0	NA	Br	PBL	Chemistry
Br 30% Hg ^P	GFED4.1s	daily	30	CO	Br	PBL	Chemistry
Br Hg ^P to OC	GFED4.1s	daily	15	OC	Br	PBL	Chemistry
Br Hg ^P to FMC	GFED4.1s	daily	variable	CO	Br	PBL	Chemistry
GFAS	GFASv1.2	daily	15	CO	O ₃ /OH	PBL	Inventory
GFAS Br	GFASv1.2	daily	15	СО	Br	PBL	Chemistry
FINN	FINNv1.5	daily	15	СО	O ₃ /OH	PBL	Inventory
FINN Br	FINNv1.5	daily	15	CO	Br	PBL	Chemistry
AMAPOH	AMAP2010	NA	NA	NA	O ₃ /OH	NA	Ratio to Anth. Emiss.
AMAPBr	AMAP2010	NA	NA	NA	Br	NA	Ratio to Anth. Emiss.
EDGAROH	EDGAR2008	NA	NA	NA	O ₃ /OH	NA	Ratio to Anth. Emiss.
EDGARBr	EDGAR2008	NA	NA	NA	Br	NA	Ratio to Anth. Emiss.
STREETSOH	STREETS2005	NA	NA	NA	O ₃ /OH	NA	Ratio to Anth. Emiss.
STREETSBr	STREETS2005	NA	NA	NA	Br	NA	Ratio to Anth. Emiss.
BASE Full	GFED4.1s + all sources	daily	15	СО	O ₃ /OH	PBL	Model Validation
Br Full	GFED4.1s + all sources	daily	15	CO	Br	PBL	Model Validation





	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 ^P mapping	Hg ^P to PM	1	1	
	Hg ^P to OC	1	0.42	\checkmark
	Hg^{P} to FMC	0.99	0.45	\checkmark
Hg ^P fraction	NO Hg ^P	0.94	0.38	\checkmark
	4% Hg ^P	0.97	0.72	\checkmark
	30% Hg ^P	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 ^P	0.81	0	\checkmark
Combination	Br 30% Hg ^P	0.91	0	\checkmark
	Br Hg $^{\rm P}$ to OC	0.95	0	\checkmark
	Br Hg $^{\rm P}$ to FMC	0.94	0	\checkmark
	GFAS Br	0.94	0	\checkmark
	FINN Br	0.92	0	\checkmark

Table 2. Correlations and Probabilities that the Hg deposition fields of the different runs belong to the same distribution as the "Base" run

Table 3. 2013 Mercury deposition (Mg) to the oceans as obtained by the different runs.

				Total Danas	ition / Ma					0%
				Total Depos	luon / Mg					-70
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 ^P	32.1	32.4	82.0	74.4	48.9	1.2	4.7	2.6	71	29
30% Hg ^P	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 ^P	26.6	39.4	75.8	83.0	55.3	1.1	3.7	7.6	74	26
Br 30% Hg ^P	28.0	36.4	61.7	61.1	44.9	0.9	4.8	4.6	62	38
Br Hg ^P to FMC	27.3	36.8	66.6	68.8	47.1	1.0	5.6	5.8	66	34





Table 4. Mercury deposition (Mg) to the oceans for 2013 due to BB and comparison with deposition due to anthropogenic activities for both oxidation mechanisms.

O ₃ /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
Br Only BB	N. Atlantic 25.7	S. Atlantic 34.7	N. Pacific 65.1	S. Pacific 66.2	Indian Ocean 46.2	Med. Sea	Arctic 4.2	S. Ocean 5.1
Br Only BB Only Anthropogenic	N. Atlantic 25.7 153	S. Atlantic 34.7 85.33	N. Pacific 65.1 457.3	S. Pacific 66.2 188.3	Indian Ocean 46.2 140	Med. Sea 0.9 12.33	Arctic 4.2 34	S. Ocean 5.1 27.3

Table 5. Comparison of the BASE Full and Br Full simulation results with observations from measurement networks for 2013.

	To	cury	Wet Deposition						
	Regression		Stats		Regres	sion	Stats		
	Intercept	Slope	r	NMRSE %	Intercept	Slope	r	NMRSE %	
O ₃ /OH	0.36	0.62	0.72	10.54	5.84	0.04	0.12	6.89	
Br	-0.08	0.96	0.74	15.68	7.1	0.08	0.18	9.12	