

Reply to comments by Referee #1

The authors are grateful to the reviewer for very thorough reading and for recommendations. Below there is an answer to particular comment (the original comment of the reviewer is in italic font).

This paper does require some English polishing and seems unfinished in places, the level is good and doesn't take away from the readability most of the time but there are a number of small errors which is surprising seeing as there are a number of English mother tongue co-authors.

A thorough language editing of the manuscript has been performed to remove the errors and misprints. All corrections suggested by the reviewer have been addressed in the revised manuscript.

Reply to comments by Referee #2

The authors are thankful to the reviewer for the critical comments and suggestions. They resulted in significant improvement of the manuscript. Below we present point-by-point answers to particular comments (original comments of the reviewer are in italic font).

1) The main issue is that the 4 models used are completely different (see paragraph 2.2) in terms of spatial resolution (1 to 2.8 degrees in lat. and log.), upper boundary domain (from 30 km to 80 km), primary and secondary emission parametrization, chemical scheme utilized. Under this heterogeneity of the models it is hard to find a process or a chemical scheme that is better than the other or useful to explain or to better understand how mercury is dispersed in the atmosphere.

We cannot completely agree with this statement. The models used in the study are significantly different but not completely as it is mentioned. Indeed, in terms of spatial resolution they differ from 1 to 2.8 degrees. This is a typical range of spatial resolution for global scale models used for this purpose. Significantly higher resolution (down to few kilometres) is commonly applied in regional models, whereas much lower resolution (tens of lat/lon degrees) is characteristic of global compartmental or box models. It means that in spite of quantitative difference in resolution the models relate to the same class of chemical transport models and should provide comparable results.

The difference in the upper boundary height (from 30 km to 80 km) is also mostly quantitative. Computational domains of all the models cover the entire troposphere (10-15 km) and, at least, significant part of the stratosphere (up to 50 km). It is enough to take into account the majority of processes governing mercury dispersion in the atmosphere.

The models utilize exactly the same inventory of primary anthropogenic emissions with somewhat different emission speciation in the base case. The parameterisation of natural/secondary emissions does differ considerably among the models. However, in many cases it is a part of a model set-up reflecting mercury cycling between the surface and the atmosphere, which cannot be easily modified without disturbing the entire model formulation.

Probably, the largest difference among the models is associated with the chemical schemes applied in the BASE case. However, other numerical experiments of the study (Table 2) were formulated in such a way to study particular processes when all the models used the same (to the extent possible) chemical mechanisms.

The aim of the study was to reveal similarities in simulation results of the models taking into account the mentioned above differences. Therefore, the results when the models agree either in reproduction of observed dependencies (e.g. spatial or temporal variation) or in failing to reproduce them appear to be particularly valuable.

The discussion on the model differences has been appropriately extended in Section 2.2 of the updated manuscript (page 5, lines 8-25).

2) Page 9, lines 12-19. In describing the comparison of model simulations and observations reported in figure 2, authors report: “models predict similar spatial pattern of the observed Hg with pronounced gradient between Southern and Northern Hemisphere”. It is correct that qualitatively all the models reproduce the north to south gradient, but the absolute values are completely different from model to model and also the spatial distribution. The question is: Which one is better? Would be interesting to explore the reasons of these differences between models and give the reasons that can be useful to other modeler. Moreover this will help to understand the process and

the chemistry important to predict mercury with models.

We agree with this critical comment. This part of the paper was completely rewritten including detailed analysis of the simulated patterns and comparison with observations (see the revised manuscript, Section 3.1, page 10, lines 9-35, page 11, lines 1-5). Besides, a new figure (Fig. S5) was added to the Supplement to support the analysis.

3) Page 9, lines 22-25: Authors report: “models demonstrate lower spatial variation of annual GEM concentrations than the measurements do. This can be partly explained by relatively low spatial resolution of the model grids (1-3 hundreds of kilometers) that can hardly allow them to reproduce local meteorological conditions at measurement sites”. First of all, if this poor spatial resolution of the model explain only partially the disagreement between model and observation spatial variation, explain the other reasons. On the other hand, from this sentence is evident that a model with high spatial resolution is required to explain the observations more quantitatively, otherwise with models we can have just a general picture.

This statement mostly relates to sites compactly located in North America and Europe. They are often affected by regional or local emission sources. Besides, even rural measurement sites in these regions are representative for limited surrounding area that can hardly exceed tens of kilometers in size. On the other hand, chemical transport models that applied on a global scale commonly relatively rough resolution (1-3 degrees). It is quite enough to characterise concentration levels over the globe and major physical and chemical processes governing dispersion in the environment. To characterize detailed concentration and deposition patterns over particular region or continent regional scale models are commonly applied. They have much finer spatial resolution (down to a few kilometers) but also require definition of boundary conditions.

Another reason of the lower variability can be associated with possible overestimation of GEM residence time in the atmosphere that leads to additional smoothing of the simulated concentration patterns. Current model estimates of the GEM residence time vary from 0.5 to 1 year. But recent studies show that it can be scaled down to a few months (Horowitz et al., 2017).

Appropriate changes has been done in the text of the revised manuscript (page 10, lines 1-8).

4) Page 10, lines 9-11: Authors report: “The models predict some decrease of concentration further northward, which is not evident from the observations. It can be connected with overestimation of the oxidation chemistry in the Arctic or with underestimation of Hg re-emission from snow and seawater”. This is really important to know: is it the oxidation scheme in the model or underestimation of the Hg re-emission from snow and seawater? Addressing this point is something that help to go further in our understand of mercury chemistry, and is mandatory to give some evidence of the process responsible for the model-measurement discrepancy, otherwise which is the added value of using 4 models?

It is mostly connected with underestimation of Hg re-emission. More detailed analysis of the modelling results in the polar regions and their comparison with measurements performed in the Arctic and Antarctica is given in the companion paper (Angot et al., 2016). In particular, it is shown that three of the four models successfully reproduced the stringtime minimum of GEM concentration caused by occurrence of the atmospheric mercury depletion events (AMDEs). However, the models tend to underestimate the summertime maximum that is determined by revolatilization from snowpack/meltwaters and evasion from the ocean.

This clarification and the reference has been added to the text (page 11, lines 14-20).

5) Page 10, lines 33-34 and page 11, lines 1-2: Authors report: “Simulations with different chemical mechanisms (BrCHEM1, BrCHEM2, O3CHEM, OHCHEM) do not lead to considerable changes of both spatial distribution and temporal variation of GEM concentration in the surface air. Somewhat better spatial correlation was obtained for the oxidation reactions with Br (BrCHEM1) and OH radical (OHCHEM) and worse for the reaction with ozone (O3CHEM)”. This conclusion are a bit confusing: if as reported at the beginning, different chemical mechanisms do not influence the models performance, this means that chemistry is not an issue. On the other hand if is correct that somewhat better spatial correlation between measurements and simulations can be achieved with Br and OH oxidation reactions and worse results with O3 oxidation, then it is this the direction to explore: why Br and OH chemistry improve the performance of the models and O3 chemistry does not?

Agree. Use of different chemical mechanisms do provide different spatial patterns of GEM concentration. The difference is not too large in terms of the comparison with measurements but still requires consideration. We have revised this section including additional analysis of the influence of chemical mechanisms on simulated GEM patterns (page 12, lines 4-15 of the revised manuscript).

6) Page 13, lines 16-18: Author report: “The deviations between the modelled and measured RM/GEM are again mostly within a factor of 5 and the model-to-model difference is probably resulted from application of somewhat different reaction constants”. If the differences are probably due to different reaction constants used by the models, this is another variable to take into account and this further issue does not help to understand the problem. What happen if all the models use the same reactions constants? This test could be useful to exclude one of the uncertainties of the model simulations.

The model experiments were originally formulated to use the models in their standard configurations (including particular parameterizations and rate constants). However, we agree that the use of different reaction constants by the models introduces additional uncertainty to the analysis. Therefore, results of the mentioned experiment (OHCHEM) have been recalculated by one of the models (GLEMOS) with the common reaction rate to harmonize conditions of the experiment. The new results demonstrate much better agreement between the models (Fig. 7 of the revised manuscript). All figures containing the OHCHEM results have been updated accordingly.

7) Page 14, lines 2-8 and figure 8: The simulations of RM/GEM is a disaster for the ECHMERIT model that show a maximum during summer with all the chemical schemes, whereas the observations show a maximum in March and a minimum during summer. Also the other models do not do a good job in reproducing the observation of RM/GEM, only GEOS-Chem is quit fine with the BRCHEM1 scheme. This is a big issue that need to be explored and the explanation can help to go further with our knowledge of the mercury chemistry.

An additional analysis has been performed to address this issue. High levels of oxidized Hg in spring are evidently caused by high Br concentrations in both the free troposphere and the boundary layer in the Northern Hemisphere. Only GEOS-Chem reproduces correctly the time of the maximum in March. Two other models move the highest RM/GEM ratio to April and May. This discrepancy can be explained by partitioning the GEM oxidation products. GEOS-Chem is the only model that uses dynamic gas-particle partitioning of RM. This means that oxidized Hg originated from GEM oxidation is dynamically fractionated between GOM and PBM. This equilibrium is sensitive to air temperature shifting to GOM under warmer conditions. On the other hand, GOM is more efficiently removed from the atmosphere than PBM by both precipitation and surface uptake. This phenomenon leads to higher deposition and lower RM concentrations in late spring (April and May). Two other models predict a fixed share of the products of GEM oxidation by Br, thus missing

changes in RM concentration during the season. The fourth model (ECHMERIT) predicts the highest ratios during late summer independently of the chemical mechanism used, a phenomenon that is determined by meteorological conditions and removal processes. In particular, the model simulates extremely low precipitation in late summer and early fall. This leads to significant underestimation of wet RM removal and ultimately to overestimation of oxidized Hg concentrations during this period.

Appropriate discussion has been added to the revised manuscript (page 15, lines 14-27).

8) Page 15, lines 7-12 and figure 10: It is not a good idea to exclude one model (ECHMERIT) results from the statistics only because excluding the results of this model improves the overall performance of the models simulation. This exclusion does not help to understand what is going on, and if one model is excluded only one time the results show in figure 10 are not comparable with those of the other figures since here the statistics includes 3 models and not 4. On the other hand, this exclusion of one model indirectly says that one model is worst the others: is this an indirect conclusion of Authors?

Agree. Results of the model have been returned back to Figs. 11-12 along with appropriate description (page 16, lines 29-34, page 17, lines 26-28, page 18, lines 7-10).

References

Angot, H., Dastoor, A., De Simone, F., Gårdfeldt, K., Gencarelli, C. N., Hedgecock, I. M., Langer, S., Magand, O., Mastromonaco, M. N., Nordstrøm, C., Pfaffhuber, K. A., Pirrone, N., Ryjkov, A., Selin, N. E., Skov, H., Song, S., Sprovieri, F., Steffen, A., Toyota, K., Travníkov, O., Yang, X., and Dommergue, A.: Chemical cycling and deposition of atmospheric mercury in polar regions: review of recent measurements and comparison with models, *Atmos. Chem. Phys.*, 16, 10735-10763, doi:10.5194/acp-16-10735-2016, 2016.

Horowitz, H. M., Jacob, D. J., Zhang, Y., Dibble, T. S., Slemr, F., Amos, H. M., Schmidt, J. A., Corbitt, E. S., Marais, E. A., and Sunderland, E. M.: A new mechanism for atmospheric mercury redox chemistry: Implications for the global mercury budget, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-1165, in review, 2017.

Multi-model study of mercury dispersion in the atmosphere: Atmospheric processes and model evaluation

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Abstract.

Current understanding of mercury (Hg) ~~behaviour~~behavior in the atmosphere contains significant gaps. Some key characteristics of Hg processes, including anthropogenic and geogenic emissions, atmospheric chemistry, and air-surface exchange, are still poorly known. This study provides a complex analysis of processes governing Hg fate in the atmosphere involving both ~~measurement~~measured data from ground-based sites and simulation results ~~of~~from chemical transport models. A variety of long-term measurements of gaseous elemental Hg (GEM) and reactive Hg (RM) concentration as well as Hg wet deposition flux ~~has~~have been compiled from different global and regional monitoring networks. Four contemporary global-scale trans-

port models for Hg were ~~applied-used~~, both in their state-of-the-art configurations and for a number of numerical experiments ~~aimed at evaluation of to evaluate~~ particular processes. Results of the model ~~simulation-simulations~~ were evaluated against measurements. As ~~it~~ follows from the analysis, the inter-hemispheric ~~gradient of GEM-GEM gradient~~ is largely formed by the ~~prevailing~~ spatial distribution of anthropogenic emissions ~~which prevail~~ in the Northern Hemisphere. ~~Contribution-The~~
5 ~~contributions~~ of natural and secondary emissions ~~enhances-enhance~~ the south-to-north gradient, but their effect is less significant. ~~The atmospheric chemistry does not affect considerably both-Atmospheric chemistry has a limited effect on the~~ spatial distribution and temporal variation of GEM concentration in ~~the~~ surface air. On the other hand, RM air concentration and wet deposition are largely defined by oxidation chemistry. The Br oxidation mechanism ~~allows successfully reproducing-can~~
10 ~~reproduce successfully the~~ observed seasonal variation of the RM/GEM ratio in the near-surface layer, ~~whereas it predicts~~
~~maximum in wet deposition-but it predicts a wet deposition maximum in spring, instead of~~ in ~~spring instead of~~ summer as observed at monitoring sites ~~located~~ in North America and Europe. Model runs with ~~the~~ OH chemistry correctly simulate both the periods of maximum and minimum values and the amplitude of observed seasonal variation ~~but lead to shifting-, but~~
15 ~~shift~~ the maximum RM/GEM ratios from spring to summer. ~~The O₃ chemistry does not provide-predict~~ significant seasonal variation of Hg oxidation. ~~Thus, Hence, the~~ performance of the ~~considered~~ Hg oxidation mechanisms ~~differs in reproduction of~~
~~different observed parametersthat can imply-under study differs in the extent to which they can reproduce the various observed~~
~~parameters. This variation implies~~ possibility of more complex chemistry and multiple ~~pathways of Hg oxidation-Hg oxidation~~
~~pathways~~ occurring concurrently in various parts of the atmosphere.

1 Introduction

Mercury (Hg) is widely ~~recognised-recognized~~ as a toxic pollutant ~~that is~~ capable of long-range transport, bioaccumulation in
20 ecosystems and biota ~~as well as-, and~~ adverse effects on human health and the environment. ~~In spite of being-Although it is~~ a natural element, its concentrations in the environment ~~has-have~~ been considerably enriched by human activities since ~~the~~ pre-industrial times (Fitzgerald et al., 1998; Mason and and Sheu, 2002; Krabbenhoft and Sunderland, 2013). Once emitted to the atmosphere, Hg can be dispersed globally, impacting remote regions through deposition to aquatic ecosystems, transformation to a potent neurotoxic form (methylmercury), and bioaccumulation in food chains (Mahaffey et al., 2004; Sunderland et al.,
25 2010; Mason et al., 2012). The character of Hg transport and fate in the atmosphere is largely determined by ~~the~~ properties of its ~~various~~ chemical forms. Mercury is emitted into the atmosphere from anthropogenic sources in ~~a-the~~ form of both gaseous elemental mercury (GEM) and ~~Hg oxidized-oxidized Hg~~ chemical compounds (Pirrone et al., 2010). The latter are typically divided into two operationally defined forms—: gaseous oxidized mercury (GOM) and ~~particle-bound-particle-bound~~ mercury (PBM). In addition, GEM can also originate from natural geogenic and secondary sources (Mason, 2009). Reactive mercury
30 (RM = GOM + PBM) can also be produced in the atmosphere from gas- and aqueous-phase oxidation of GEM (Lindberg and Stratton, 1998). Relatively stable and slightly soluble GEM can drift in the atmosphere for months, providing transport of Hg mass ~~over-around~~ the globe (Schroeder and Munthe, 1998). In contrast, RM is easily removed from the air by precipitation scavenging (wet deposition) or surface uptake (dry deposition) (Schroeder and Munthe, 1998; Gustin et al., 2012; Sather et al.,

2013; Wright et al., 2014). GEM can also contribute to Hg dry deposition through air-surface exchange with various terrestrial and aquatic compartments (Zhang et al., 2009; Wang et al., 2014, 2016). ~~On the other hand, previously deposited Hg may~~ Previously deposited Hg can also be reduced to ~~the~~ its elemental form and re-emitted back to the atmosphere (Gustin, 2012; Qureshi et al., 2012).

5 Atmospheric redox chemistry plays an important role in Hg long-range dispersion and deposition. However, the particular mechanisms of Hg oxidation in the atmosphere are not well understood (Lin et al., 2006; Subir et al., 2011, 2012; Gustin et al., 2015; Ariya et al., 2015). Gaseous reactive halogens, in particular atomic ~~Br~~ bromine (Br), are believed to play a major role in ~~the~~ atmospheric oxidation of GEM (Goodsite et al., 2004, 2012; Donohoue et al., 2006; Hynes et al., 2009). ~~There exists observational evidence that the~~ Observational evidence exists that Br-initiated chemistry is a dominant GEM oxidation pathway in some atmospheric environments, including the marine boundary layer, the polar regions, and the upper troposphere ~~and~~ lower stratosphere (Hedgecock and Pirrone, 2004; Holmes et al., 2009; Lyman and Jaffe, 2010; Obrist et al., 2011; Gratz et al., 2015). However, very limited data ~~exists~~ exist with respect to this mechanism in the global atmosphere (Kos et al., 2013). Nevertheless, ~~application~~ use of the Br chemistry as the only oxidation pathway in a chemical transport model ~~allows simulation of~~ enables simulation of the Hg atmospheric cycle and reproduction of available observations (Holmes et al., 2010; Soerensen et al., 2010; Amos et al., 2012; Shah et al., 2016). On the other hand, in spite of theoretical doubts ~~of~~ about the viability and significance of direct GEM oxidation by ~~ozone (O₃ and radical) and hydroxyl radical (OH)~~ ozone (O₃) and hydroxyl radical (OH) under atmospheric conditions (~~?Hynes et al., 2009~~) (Calvert and Lindberg, 2005; Hynes et al., 2009), numerous modelling ~~works applying studies using~~ these reactions as the main pathways of GEM oxidation GEM oxidation pathways in the free troposphere also demonstrate reasonable results ~~in terms of comparison compared~~ with observed GEM concentration and wet deposition flux (Christensen et al., 2004; Travnikov and Ilyin, 2009; Pan et al., 2010; Baker et al., 2012; Kos et al., 2013; Gencarelli et al., 2014; De Simone et al., 2015; Cohen et al., 2016). Besides, both theoretical and laboratory studies suggest that complex Hg oxidation mechanisms involving O₃ and OH can exist in the atmosphere in the presence of aerosol particles and secondary reactants (Snider et al., 2008; Cremer et al., 2008; Rutter et al., 2012; Subir et al., 2012; Ariya et al., 2015). ~~It is interesting to note that recent comparison studies showed~~ Note that recent comparative studies have shown that models with diverse ~~formulations of atmospheric chemistry~~ atmospheric chemistry formulations agree well when ~~simulated~~ used to simulate Hg transport on a global scale and the source attribution of Hg deposition (Travnikov et al., 2010; AMAP/UNEP, 2013a, 2015).

~~Application of chemical transport models complimented by extensive measurement~~ Chemical transport models complemented by extensive measured data can facilitate a better understanding of the principal mechanisms governing Hg dispersion and cycling in the atmosphere. ~~Effect~~ The effects of atmospheric redox chemistry as well as anthropogenic and natural emissions on the fate of atmospheric Hg were investigated systematically in a number of earlier modelling studies (Seigneur et al., 2006; Seigneur and Lohman, 2008; Lohman et al., 2008). In more recent work, Kos et al. (2013) performed a detailed analysis of the uncertainties associated with RM ~~measurements~~ measurement and modelling. A number of model sensitivity runs were carried out to evaluate different chemical mechanisms and speciation of anthropogenic ~~emissions of Hg~~ Hg emissions. In particular, they found evident ~~inconsistency~~ inconsistencies between the emission speciation in ~~the~~ existing emission inventories ~~with~~ and the measured RM concentration in ~~the~~ surface air. Weiss-Penzias et al. (2015) ~~applied~~ used a global-scale ~~model for Hg to~~

~~analyse Hg model to analyze~~ speciated atmospheric Hg measurements from five ~~high-high~~ and mid-elevation sites. The results of the study suggested the presence of different chemical regimes in different parts of the troposphere and ~~signals signalled~~ that there is not necessarily one single global oxidant. Shah et al. (2016) used the same chemical transport model to interpret aircraft measurements of RM and ~~to~~ place new constraints on Br-initiated chemistry in the free troposphere. They found that ~~the~~ standard model simulations significantly ~~underestimate-underestimated~~ observed RM and that modelling with tripled Br concentrations or a faster oxidation rate constant ~~can-improve-improved~~ agreement with observations. A detailed process-specific atmospheric lifetime analysis was carried out by Cohen et al. (2016) ~~providing-and provided~~ important insights into the fate and transport of atmospheric Hg as well as total Hg deposition to the Great Lakes. A global-scale chemical transport model ~~has-also-been-applied-was also used~~ by Song et al. (2015) for inverse modelling aimed at constraining present-day atmospheric Hg emissions and relevant physiochemical parameters.

~~In-the-current-study-we-apply-The current study uses~~ four contemporary global-scale Hg chemical transport models in combination with a variety of long-term ~~measurements-of~~ Hg concentration and wet deposition ~~measurements~~ from different monitoring networks to ~~analyse-analyze~~ processes governing Hg fate in the atmosphere. A number of numerical experiments ~~aimed at-evaluation-of-have tried to evaluate the~~ effect of anthropogenic and natural/secondary emissions as well as different chemical oxidation mechanisms on ~~the~~ levels and spatio-temporal variation of GEM and RM air ~~concentration-concentrations~~ and Hg wet deposition. ~~The-This~~ study was performed as part of the Mercury Modelling Task Force (MMTF), a scientific cooperative initiative under the ~~EU-funded-projectEU-funded project~~, "Global Mercury Observation System" (GMOS, www.gmos.eu).

2 Methods

2.1 Measurements

A variety of ~~measurement data was used for evaluation-of-measured data were used to evaluate~~ the model experiments. The ~~measurement dataset-is measured dataset was~~ based on the global GMOS monitoring network for Hg (Sprovieri et al., 2016a, b; GMOS, 2016) ~~complemented-with-complemented by~~ data from the ~~EMEP-European Monitoring and Evaluation Programme (EMEP)~~ regional network for Europe (Tørseth et al., 2012; EMEP, 2016) and ~~by~~ data from the ~~Mercury Deposition Network of the National Atmospheric Deposition Program (NADP/MDN(Prestbo and Gay, 2009; NADP/MDN, 2016), AMNet(Gay et al., 2013; AMN~~ ~~NAtChem (Cole et al., 2013; Steffen et al., 2015; NAtChem, 2016) networks-)~~ (Prestbo and Gay, 2009; NADP/MDN, 2016), ~~the Atmospheric Mercury Network (AMNet) (Gay et al., 2013; AMNet, 2016), and the Canadian National Atmospheric Chemistry Database (NAtChem) (Cole et al., 2013; Steffen et al., 2015; NAtChem, 2016)~~ for North America. ~~We compiled available-Available~~ measurements of GEM, GOM~~and PBM concentration in air~~, and ~~PBM concentrations in air were compiled~~, as well as wet deposition flux ~~measurements~~ performed at ground-based sites in 2013. At ~~the majority-most of the~~ sites of interest, the un-speciated measurements of atmospheric Hg ~~are-were~~ performed as GEM (Gay et al., 2013; Sprovieri et al., 2016a; Angot et al., 2016). However, ~~there is still no complete scientific evidence on-the scientific evidence is still incomplete as to~~ whether GEM or ~~TGM-total gaseous mercury (TGM)~~ concentration is measured at some particular sites ~~since-it-because this~~ largely depends on local ambient conditions and ~~the~~ configuration of the measurement setup (Gustin et al., 2015; Slemr et al., 2015).

Nevertheless, ~~as because~~ the difference between long-term observations of GEM and TGM commonly does not exceed a few ~~percents (Slemr et al., 2015) we interpret all the percentage points (Slemr et al., 2015), all~~ unspiciated Hg measurements ~~were~~ interpreted as GEM. Measured values of RM are used in the study instead of observations of individual species GOM and PBM. RM appears to be more valuable for the analysis ~~since because~~ measurements of the individual species are associated with higher uncertainties (Gustin et al., 2015; Weiss-Penzias et al., 2015). Therefore, only sites with co-located observations of GOM and PBM ~~are use were used~~ in the study.

The original ~~measurement measured~~ data with high temporal resolution were processed to ~~get obtain~~ monthly and yearly mean values. According to ~~the accepted criteriamonthly averages are accepted criteria, monthly averages were~~ used for the analysis if the original data ~~cover covered~~ at least 15 days of the month. Monthly averages ~~are used both for generation of~~ were used both to generate yearly mean values and ~~for characterizing to characterize~~ the seasonal variation of the observed parameter. In both cases, only sites with temporal coverage of at least ~~7 months are selected. Characteristics seven months were~~ selected. The characteristics of the selected sites measuring GEM, RM, and wet deposition are given respectively in Tables S1, S2, and S3 in the Supplement, ~~respectively. Geographical. The geographical~~ location of the whole collection of sites is shown in Fig. 1. In total, the dataset ~~includes included~~ 49 sites measuring GEM, 14 sites measuring RM, and 124 sites measuring wet deposition. ~~Observations of GEM GEM observations~~ are relatively uniformly ~~distribution distributed~~ over the globe, with somewhat higher density in the Northern Hemisphere. In contrast, RM is ~~mostly observed in the observed mostly in~~ northern temperate latitudes. ~~There are only, with only a~~ few sites located in the Tropics and further southward. ~~The majority of Most~~ wet deposition measurements are located in North America and Europe ~~limiting, limiting the~~ possibility of model evaluation in other regions.

2.2 Models

The model ensemble ~~of the used in this~~ study includes four chemical transport models simulating mercury on a global scale (Table ~~table:models1~~). The models differ considerably in their general formulation, spatial resolution, and ~~applied parameterizations of~~ physical and chemical ~~processes. Horizontal process parameterizations. The horizontal~~ spatial resolution of the models ranges from 1 to 2.8 degrees in latitude and longitude. The upper boundaries of the model domains vary from 10 hPa (~ 30 km) to 0.01 hPa (~ 80 km). Hence, the models cover the entire troposphere and at least a significant part of the stratosphere, which is enough to take into account most processes governing mercury dispersion in the atmosphere. Two of the models (GLEMOS, GEOS-Chem) ~~utilize off-line use offline~~ meteorological data prepared by an external pre-processor, whereas the ~~two others other two~~ (GEM-MACH-Hg and ECHMERIT) generate the meteorological fields along with ~~simulation of the the simulation of~~ pollutant transport. All the models used the same ~~dataset of~~ Hg anthropogenic emissions ~~(AMAP/UNEP, 2013a, b) dataset (AMAP/UNEP, 2013a, b),~~ with somewhat different ~~speciation speciations~~ of mercury forms ~~applied in the BASE in the base case. In contrast, parameterizations the other model experiments, the emissions speciation was~~ harmonized by assuming all emissions to be a form of GEM (Table 2). By contrast, total values of natural and secondary emissions ~~significantly differ differed significantly~~ among the models. Parameterization of these processes is an essential element of the model setup describing Hg cycling between the Earth's surface and the atmosphere, which cannot be easily changed or

~~removed without disturbing the entire model balance.~~ The major chemical mechanisms ~~applied~~ in the standard model configuration ~~that used in the BASE case are in the base case were~~ also essentially different. The base-case reactions of GLEMOS and ECHMERIT ~~include~~ Hg oxidation by ~~ozone and OH radical.~~ ~~The chemical scheme of GEM-MACH-Hg is base~~ O₃ ~~and OH.~~ ~~The GEM-MACH-Hg chemical scheme was based~~ on the reaction with ~~OH radical with application of the Br~~ chemistry in the Polar OH, ~~with Br chemistry applied in the polar~~ regions. GEOS-Chem ~~considers the~~ Br chemistry as the only ~~pathway of Hg oxidation~~ Hg oxidation pathway in the gas phase. ~~Besides~~ In addition, two of ~~the~~ four models (GLEMOS and ECHMERIT) also ~~include the~~ Hg redox chemistry in the aqueous phase in cloud water. ~~More~~ However, ~~it should be noted that the numerical experiments in this study (see Section 2.4) were formulated to investigate particular processes when all models used the same chemical mechanisms. Considering these differences, the results, whether the models~~ succeed or fail in reproducing the observed dependencies, appear to be particularly valuable. A more detailed description of the model ~~parameterisations is given below~~ parameterizations is given subsequently.

2.2.1 GLEMOS

GLEMOS (Global EMEP Multi-media Modelling System) is a multi-scale chemical transport model developed ~~for the simulation of to simulate~~ environmental dispersion and cycling of ~~different chemicals including mercury~~ various chemicals including Hg based on the older ~~hemispheric model MSCE-HM-Hem~~ MSCE-HM-Hem hemispheric model (Travnikov, 2005; Travnikov and Ilyin, 2009; Travnikov et al., 2009). The model simulates atmospheric transport, chemical ~~transformations~~ transformation, and deposition of three Hg species (GEM, GOM and PBM). ~~The atmospheric~~ Atmospheric transport of the tracers is driven by meteorological fields generated by the Weather Research and Forecast modelling system (WRF) (Skamarock et al., 2007) fed by ~~the~~ operational analysis data from the European Centre for Medium-Range Weather Forecasts (ECMWF) (ECMWF, 2016). In the base configuration, the model grid ~~has had~~ a horizontal resolution of 1° × 1°. Vertically, the model domain ~~reaches~~ reached 10 hPa and ~~consists~~ consisted of 20 irregular terrain-following sigma layers. The atmospheric chemical scheme ~~includes~~ included Hg oxidation and reduction chemical reactions in both the gaseous ~~phase~~ and aqueous phase of cloud water. The major chemical mechanisms in the gas phase ~~include~~ included Hg oxidation by ~~and OH radical with the rate constants of reactions~~ O₃ and OH radical, with the reaction rate constants from Hall (1995) and Sommar et al. (2001), respectively. The latter ~~mechanism~~ was scaled down by a factor of 0.1 in the cloud environment and below clouds to account for ~~reduction of reduced~~ photochemical activity (Seigneur et al., 2001). The ~~and OH concentration fields are~~ O₃ and OH concentration fields were imported from MOZART (Emmons et al., 2010). ~~A two-step~~ Two-step gas-phase oxidation of GEM by Br ~~is included optionally~~ was included as an option. Aqueous-phase reactions include oxidation by ~~ozone, chlorine and hydroxyl radical and reduction via decomposition of sulphite complexes~~ Van Loon et al. (2000) O₃, OH and Cl and reduction by decomposition of ~~sulfite complexes (Van Loon et al., 2000).~~ The model ~~distinguishes~~ distinguished between in-cloud and sub-cloud wet deposition of PBM and GOM based on empirical data. The dry deposition scheme ~~is~~ was based on the resistance analogy approach (Wesely and Hicks, 2000). Prescribed fluxes of Hg natural and secondary emissions from soil and seawater were generated depending on Hg ~~concentration in soil~~ soil concentration, soil temperature and solar radiation for emissions from land and ~~proportional to the~~ proportionally to primary production of organic carbon in seawater for emissions from the ocean (Travnikov

and Ilyin, 2009). In addition, an empirical parameterization of ~~the~~ prompt Hg re-emission from snow- and ice-covered surfaces ~~is applied based on the observational data~~ based on observed data was used.

2.2.2 GEOS-Chem

The GEOS-Chem global chemical transport model (v9-02; www.geos-chem.org) is driven by assimilated meteorological data
5 from the NASA GMAO Goddard Earth Observing System (Bey et al., 2001). ~~The~~ GEOS-FP and GEOS-5.2.0 data ~~are~~ were used
for the ~~simulation year of 2013~~ 2013 simulation year and the spin-up period, respectively (http://gmao.gsfc.nasa.gov/products/).
GEOS-Chem couples a 3-D atmosphere (Holmes et al., 2010), a 2-D mixed layer slab ocean (Soerensen et al., 2010), and a
2-D terrestrial reservoir (Selin et al., 2008) ~~in~~ at a horizontal resolution of $2^\circ \times 2.5^\circ$. Three ~~mercury~~ Hg tracers (GEM, GOM,
and PBM) ~~are~~ were tracked in the atmosphere (Amos et al., 2012). A two-step gaseous oxidation mechanism initialized by
10 Br atoms ~~is~~ was used. Br fields ~~are~~ were archived from a full-chemistry GEOS-Chem simulation (Parrella et al., 2012) ~~while~~
~~the rate constants of reactions are~~, and the reaction rate constants were obtained from Goodsite et al. (2012), Donohoue
et al. (2006), and Balabanov et al. (2005). The ~~surface fluxes of GEM include~~ GEM surface fluxes included anthropogenic
sources, biomass burning, ~~geogenic activities~~, and geogenic activities as well as ~~the~~ bidirectional fluxes in ~~the~~ atmosphere-
terrestrial and atmosphere-ocean exchanges (Song et al., 2015). Biomass burning emissions ~~are~~ were estimated using a global
15 CO ~~emission database and a volume ratio of~~ emissions database and an Hg/CO volume ratio of 1×10^{-7} . Geogenic activities
~~are~~ were spatially distributed based on the locations of ~~mercury~~ Hg mines. For atmosphere-terrestrial exchange, GEOS-Chem
~~treats the~~ treated evasion and dry deposition of GEM separately (Selin et al., 2008). Dry deposition ~~is~~ parameterized with
was parameterized by a resistance-in-series scheme (Wesely, 1989). ~~Besides~~, ~~an~~ In addition, effective GOM uptake by sea-
salt ~~aerosol~~ is aerosols was also included over the ocean (Holmes et al., 2010). GEM evasion ~~includes~~ included volatilization
20 from soil and rapid recycling of newly deposited Hg. The former ~~is~~ was estimated as a function of soil Hg content and solar
radiation. The latter ~~is~~ modeled was modelled by recycling a fraction of wet/dry deposited RM to the atmosphere as GEM
immediately after deposition (60% for snow covered land and 20% for all other land ~~uses~~ surfaces) (Selin et al., 2008). GEOS-
Chem ~~estimates the~~ estimated atmosphere-ocean ~~exchange of GEM~~ GEM exchange using a standard two-layer diffusion model.
~~The ocean mercury~~ Ocean Hg in the mixed layer ~~interacts~~ was assumed to interact, not only with the atmospheric boundary
25 layer, but also with ~~the~~ subsurface waters through entrainment ~~and~~ detrainment of the mixed layer and wind-driven Ekman
pumping (Soerensen et al., 2010).

2.2.3 GEM-MACH-Hg

GEM-MACH-Hg is a new chemical transport model for ~~mercury that is~~ Hg based on the GRAHM model developed by Environ-
ment and Climate Change Canada (~~Dastoor04, Dastoor08, Durnford10, Durnford12, Kos13, Dastoor15~~) (Dastoor and Larocque, 2004; Dastoor
30 GEM-MACH-Hg uses a newer version of the operational meteorological model of the Environment and Climate Change
Canada's ~~operational meteorological model~~. The horizontal resolution of the model is $1^\circ \times 1^\circ$. GEM is oxidized in the atmo-
sphere by ~~OH~~ the OH radical. The ~~rate constant of the reaction is~~ reaction rate constant was obtained from Sommar et al. (2001),
but was scaled down by a coefficient of 0.34 to ~~take into account possible dissociation~~ account for possible dissociation and re-

duction reactions (Tossell et al., 2003; Goodsite et al., 2004). ~~The gaseous oxidation of mercury by bromine is applied~~ Gaseous oxidation of Hg by Br was modelled in the polar regions using reaction rate constants from Donohoue et al. (2006), Dibble et al. (2012) and Goodsite et al. (2004). ~~The parameterization of AMDEs is based on Br~~ AMDE parameterization was based on Br production and chemistry, and snow re-emission of GEM (Dastoor et al., 2008). ~~OH fields are~~ OH fields were obtained from MOZART (Emmons et al., 2010) ~~while, and BrO is derived from 2007–2009~~ was derived from 2007–2009 satellite observations of BrO vertical columns. The associated ~~Br concentration is~~ Br concentration was then calculated from a photochemical steady state (Platt and Janssen, 1995). Dry deposition in GEM-MACH-Hg ~~is was~~ based on the resistance approach (Zhang, 2001; Zhang et al., 2003). In the wet deposition scheme, GEM and GOM ~~are were~~ partitioned between cloud droplets and air using a temperature-dependent Henry's law constant. Total global emissions from natural sources and re-emissions of previously deposited Hg (from land and oceans) in GEM-MACH-Hg ~~are based on the were based on~~ global Hg budgets by Gbor et al. (2007), Shetty et al. (2008) and Mason (2009) from (Gbor et al., 2007; Shetty et al., 2008; Mason, 2009). Land-based natural emissions ~~are were~~ spatially distributed according to the natural enrichment of Hg. Land re-emissions ~~are were~~ spatially distributed according to ~~the historic deposition of Hg~~ historic Hg deposition and land-use type and ~~depend were~~ dependent on solar radiation and the leaf area index. Oceanic emissions ~~depend depended~~ on the distributions of primary production and atmospheric deposition.

2.2.4 ECHMERIT

ECHMERIT is a global ~~on-line online~~ chemical transport model, ~~derived on~~ derived from the ECHAM5 global circulation model, with a highly flexible chemistry mechanism designed to facilitate the investigation of atmospheric ~~mercury-Hg~~ chemistry (Jung et al., 2009; De Simone et al., 2014, 2015, 2016). The model uses the same spectral grid ~~of as~~ ECHAM. The standard horizontal resolution of the model is T42 (approximately $2.8^\circ \times 2.8^\circ$), whereas in the vertical dimension the model is discretized with a hybrid-sigma pressure system with non-equidistant levels up to 10 hPa. The base chemical mechanism includes ~~the~~ GEM oxidation by OH and OH and O₃ in the gaseous and aqueous phases. Reaction rate constants ~~are were~~ obtained from Sommar et al. (2001), Hall (1995), and Munthe (1992), ~~respectively. OH and~~ OH and O₃ concentration fields were imported from MOZART (Emmons et al., 2010). ~~The~~ Hg oxidation by Br is Br was also optionally available by means of a two-step ~~gas phase gas phase~~ oxidation mechanism with reaction rates ~~as described in from~~ Goodsite et al. (2004), Goodsite et al. (2012) and Donohoue et al. (2006). ECHMERIT ~~applied parameterisation of~~ parameterized dynamic air-seawater exchange as a function of ambient parameters, but using a constant value of ~~mercury-Hg~~ concentration in seawater (De Simone et al., 2014). Emissions from soils and vegetation were calculated ~~off-line offline~~ and derived from the EDGAR/POET emission inventory (Granier et al., 2005; Peters and Olivier, 2003) ~~that includes, which included~~ biogenic emissions from the GEIA inventories (http://www.geiacenter.org), as described by Jung et al. (2009) in (Jung et al., 2009). Prompt re-emission of a fixed fraction (20%) of wet and dry deposited ~~mercury is applied in the model~~ Hg was included to account for reduction and evasion processes ~~which govern mercury that govern~~ short-term Hg cycling between the atmosphere and terrestrial reservoirs (Selin et al., 2008). This fraction ~~is was~~ increased to 60% for snow-covered land and ~~the ice covered ice covered~~ seas.

2.3 Emissions data

The ~~A~~ global inventory of Hg anthropogenic emissions for 2010 (AMAP/UNEP, 2013a, b) was used in the study. The original dataset ~~consists~~ consisted of gridded emission data with ~~spatial resolution~~ a spatial resolution of $0.5^\circ \times 0.5^\circ$ for three Hg species (GEM, GOM, and PBM). Total global ~~emissions of mercury~~ Hg emissions from anthropogenic sources ~~are~~ were estimated at 1875 tonnes per year, with the overall ~~share~~ shares of GEM, GOM, and PBM emissions equal to 81%, 15%, and 4%, respectively. As ~~it was mentioned above~~ mentioned earlier, some models modified the original speciation of anthropogenic emissions (Table 1) in the BASE case simulation. No information on temporal ~~variation of emissions~~ variability of emissions ~~was~~ available in the dataset. Geographically, significant Hg emissions ~~are~~ were predicted in industrial regions of East and South Asia, Central Europe, and the eastern part of North America (Fig. S1 in the Supplement). ~~Besides~~ In addition, high emission fluxes ~~are~~ characteristics of characterized some areas of Central and South America, Sub-Saharan Africa, and Southeast Asia due to ~~mercury releases from the~~ Hg releases from artisanal and small-scale gold mining. Almost no emissions ~~are~~ were predicted in the Arctic and Antarctic regions.

2.4 Model experiments

The study was organized ~~in a form of~~ as multiple model experiments ~~aimed at evaluation of~~ to evaluate particular processes and mechanisms of Hg atmospheric chemistry as well as anthropogenic and natural/secondary emissions. A summary of the model experiments is given in Table 2. All the models ~~performed~~ were used to perform the BASE case simulation representing the state-of-the-art model configuration ~~and is~~, which was used as a reference point for other model experiments. All the models ~~use~~ used the same anthropogenic emissions ~~but applying the~~, but with model specific speciation (~~see Section~~ Section 2.3). The NoANT run ~~is~~ was based on the same standard model configuration ~~but is carried out with the~~ turned off anthropogenic emissions. ~~Since~~, but with anthropogenic emissions turned off. Because Hg emissions from natural and secondary sources ~~are~~ were fully or partly represented in the models as bi-directional air-surface exchange ~~flux or as re-emission~~ fluxes or as re-emissions of previously deposited Hg (Table 1), simple exclusion of this emission type from ~~simulations~~ is the simulations ~~was~~ not feasible without ~~disturbance of~~ disturbing the whole Hg cycle in the model. On the other hand, assuming additivity of Hg processes in the atmosphere with respect to ~~contribution of different sources~~ contributions from different sources, the effect of natural ~~and~~ secondary emissions (NoNAT) ~~can~~ could be estimated by ~~subtraction of~~ subtracting the NoANT results from the BASE case. Four additional model experiments ~~are aimed at evaluation of~~ were intended to evaluate different chemical mechanisms of GEM oxidation in the atmosphere. To avoid ~~the~~ influence of direct anthropogenic emissions on simulated RM concentrations ~~all emissions are~~, all emissions were assumed to be ~~in~~ a form of GEM. The ~~model runs~~ BrCHEM1 and BrCHEM2 ~~include the only~~ model runs included a single mechanism of GEM oxidation by atomic Br ~~but utilizing~~, but using two different datasets of Br concentration in the atmosphere: ~~simulated by the~~ one simulated by GEOS-Chem (Parrella et al., 2012) and ~~the other by~~ p-TOMCAT (Yang et al., 2005, 2010) ~~models. Comparison of~~. A comparison of the spatial and temporal ~~variation of~~ variations in Br concentration from these two datasets is given in Figs. ~~S6 and S9~~ S7 and S10 in the Supplement. Two other experiments, O3CHEM and OHCHEM ~~are based on application of~~, were based on O₃- and OH-initiated

OH-initiated oxidation chemistry. The models utilized the same datasets of used the same O₃ and OH concentrations extracted from simulations results of the MOZART model (Emmons et al., 2010). Spatial OH concentration datasets extracted from MOZART model simulations results (Emmons et al., 2010). The spatial gradients and seasonal variation of the reactants are shown respectively in Figs. S7-S8 and S10-S11 S8-S9 and S11-S12 in the Supplement, respectively. It should be noticed. Note

5 that not all of the models performed the whole simulations program. Results of the study are presented below bases models were used to perform the whole simulation program. The results presented below are based on available simulations for each particular experiment.

2.5 Statistical analysis

Comparison of modelling results with observations are performed. Modelling results were compared with observations using the following statistical parameters. Both spatial and temporal correlation correlations of simulated and observed values is characterized were characterized by the Pearson correlation coefficient:

$$R_{corr} = \frac{\sum_i (M_i - \bar{M})(O_i - \bar{O})}{\sqrt{\sum_i (M_i - \bar{M})^2 \sum_i (O_i - \bar{O})^2}}, \quad (1)$$

where M_i and O_i are are monthly or annual mean simulated and observed values, respectively, respectively and \bar{M} and \bar{O} are average values. The averaging and summing are were performed over monthly values for calculation of temporal correlation at particular site to calculate temporal correlations at particular sites or over annual mean values of all the sites for calculation of the spatial correlation coefficient for all sites to calculate spatial correlation coefficients. An arithmetic mean of all temporal correlation coefficients for individual sites is was then used in the analysis. Discrepancy The discrepancy between simulated and observed values is was characterized by a symmetric relative bias:

$$RBIAS = 2 \frac{\bar{M} - \bar{O}}{\bar{M} + \bar{O}} 100\% \quad (2)$$

20 where RBIAS varies within the range $\pm 200\%$, and small deviations between model results and observations are characterized by values that are close to zero.

3 Results and discussion

3.1 Gaseous elemental mercury

Concentration of GEM The GEM concentration in air is a parameter representing the balance between Hg global emissions and sinks via by chemical transformation to other Hg forms or direct interaction with the surface. Given GEM the long residence time of GEM in the atmosphere, its spatio-temporal gradients likely characterize the distribution of global emission regions as well as long-range atmospheric dispersion and cycling in the atmosphere (Selin, 2009; Travnikov, 2012; Ariya et al., 2015). Figure 2 shows global distributions the global distribution of GEM concentration in the surface air surface air as simulated by four global models according to the BASE case, along with ground-based observations presented by coloured represented by

colored circles in the same colour-color palette. The models predict similar spatial patterns of Hg concentration with predicted spatial Hg concentration patterns with a pronounced gradient between the Southern Hemisphere (ca. 0.9-1.1 ng m⁻³) and the Northern Hemispheres Hemisphere (ca. 1.1-1.6 ng m⁻³) and elevated concentrations in the major industrial regions – in East and South Asia, Europe, and North America (above 1.4 ng m⁻³). Elevated concentrations are-were also predicted in tropical areas of South America, Central Africa, and Southeast Asia, where considerable Hg emissions from the-artisanal and small-scale gold mining are expected (AMAP/UNEP, 2013a). The models generally agree-agreed with ground-based observations, as shown in Fig. 2. The measurements also demonstrate-evidence-of-the-provided evidence of a statistically significant inter-hemispheric gradient and relatively high concentrations in industrial regions (Sprovieri et al., 2016a). More A more detailed comparison of the-modelling results with measurements is given in Fig. S2 in the Supplement. The model-measurement divergence does-not-commonly-commonly did not exceed ±30%. In general, the models demonstrate-lower spatial-variation-of-exhibited lower spatial variations in annual GEM concentration than did the measurements. This observation relates mostly to sites that are compactly located in North America and Europe. It can be explained by the measurements do. This can be partly explained-by-relatively low spatial resolution of the model grids (1-3-hundreds-of-kilometres)that can-hardly-allow-them-to-reproduce-local-1-2 hundreds of kilometers), which made it difficult for the models to reproduce the influence of local emission sources and specific meteorological conditions at measurement sites. Another reason can be associated with possible overestimation of GEM residence time in the atmosphere, leading to additional smoothing of the simulated concentration patterns. The possibility of a shorter GEM lifetime with respect to oxidation was recently proposed in (Horowitz et al., 2017), but this would require the existence of a fast atmospheric reduction process to match observations.

It should be noticed that the models predict similar global spatial patterns of GEM concentration in spite of significant deviations in applied parameterizations of-The model-to-model difference in simulated GEM concentrations did not exceed ±20% (see also Fig. S5 in the Supplement). Nevertheless, pronounced distinctions could be observed among the spatial patterns simulated by different models because of deviations in physical and chemical processes. As it was process parameterizations. As mentioned in Section 2.2the models in their base configurations apply-, the various models used quite different chemical mechanisms of GEM oxidation in the atmosphere. Besides, even-utilizing-in their base configurations. Moreover, even if they used the same anthropogenic emissions data they largely differ-, they differed in their estimates of natural and secondary emissions and Hg air-surface exchange. Higher oxidative capacity of the atmospheric chemistry leads to shorter residence time of GEM in-As shown in Fig. 2 and Fig. S5 in the Supplement, all four models were in relatively agreement when simulating GEM concentrations in regions affected by direct anthropogenic emissions (e.g., Eastern North America, Western and Central Europe, East Asia). However, the differences between the models became larger as the distance from emission regions increased. For instance, GLEMOS and ECHMERIT predicted lower GEM concentrations (below 1.3 ng m⁻³) over North America (mostly Canada) and Eastern Siberia (Figs. 2a and 2d). This phenomenon was caused by two factors: use of O₃ oxidation chemistry with elevated O₃ concentrations in the northern mid-latitudes (Fig. S8 in the Supplement), and use of relatively low levels of natural/secondary emissions over these regions. In particular, this led to some underestimation of observed GEM levels at North American sites. In contrast, GEM-MACH-Hg simulated higher GEM concentrations (above 1.4 ng m⁻³) than other models over the North Atlantic and Pacific Oceans due to relatively high Hg evasion from seawater in these aquatic regions and

use of the OH oxidation mechanism. The latter provided weak oxidative capacity in the temperate and high latitudes of both hemispheres due to the atmosphere and ultimately to larger deposition to the ground, which, pronounced meridional profile of OH concentrations, with high values in the Tropics (Fig. S9 in the Supplement). The elevated GEM concentrations over the Pacific generally agreed with observations at Mauna Loa site in Hawaii and at coastal sites in Europe (Fig. 2c). However, the former is a high-elevation site (3384 m a.s.l.), where conditions are more like those in the free troposphere. Besides, it can be affected by Hg emissions from the active Kilauea Volcano (Gay et al., 2013). Note that GLEMOS and ECHMERIT also used the OH mechanism in their base configurations. However, the effect described above diminished when used in combination with O₃ chemistry. Simultaneous use of these two oxidation mechanisms can probably lead to surplus GEM oxidation or imply the existence of an Hg reduction mechanism in its turn, can be compensated by more intensive natural or re-emission to the atmosphere. Thus, combination of these compensative factors allows simulation of realistic GEM concentration levels using different model approaches. Evaluation of particular processes governing Hg cycling in the atmosphere require more detailed analysis of its spatial and temporal variation.

Analysis of the inter-hemispheric gradient of GEM concentration is presented in. In particular, it can explain some underestimation of observed GEM concentrations over the oceans by ECHMERIT. The effect was less pronounced in the case of GLEMOS because it used a reduced rate constant for the reaction with OH (Table 1). Use of Br chemistry by GEOS-Chem provided reasonable agreement with most observations (Fig. 2b). Unlike GEM-MACH-Hg, it simulated lower GEM concentrations over the North Atlantic and Pacific Oceans, somewhat underestimating available observations in these regions. Note that the Br oxidation mechanism predicted strong GEM oxidation in the southern high latitudes due to high Br concentrations (Fig. 3S7 in the Supplement), which was compensated for by large re-emission fluxes from seawater, leading to intensive air-surface exchange in this region. All models tended to overpredict GEM concentrations in the northern part of South America as measured at two sites: Manaus (Brazil) and Nieuw Nickerie (Surinam). As mentioned earlier, the high simulated concentrations in this region were caused by large expected emissions from artisanal and small-scale gold mining, which were probably overestimated.

Figure 3 illustrates an analysis of the inter-hemispheric GEM concentration gradient. The figure shows the meridional distribution of both observed and model-predicted concentration in the model-predicted concentrations in surface air. The later is latter are split into two fractions contributed by anthropogenic and natural/secondary sources. As seen all four models reproduce the observed difference of GEM concentration. All four models reproduced the observed GEM concentration differences between the Southern and Northern Hemispheres. The lowest concentrations (below 1) are typical for ng m⁻³ were typical of the high and temperate latitudes of the Southern Hemisphere. There is was a weak maximum of zonal-mean zonal-mean GEM concentration (1.4-1.6 ng m⁻³) in the temperate latitudes of the Northern Hemisphere corresponding to location of the majority of, corresponding to the location of most anthropogenic emission sources. The models predict some decrease of concentration further northward, which is not evident from the observations. It can be connected with overestimation of the oxidation chemistry in the Arctic or with underestimation of Hg re-emission from snow and seawater. As seen the Hence, the inter-hemispheric gradient is largely formed by the contribution of direct anthropogenic emissions, which is larger in the Northern Hemisphere. Contribution The contribution of natural and secondary emissions also increases northward, but the gra-

dient is commonly smaller. The models predicted some decrease in concentrations further northward, which was not evident from the observations. This decrease was mostly connected with underestimation of Hg re-emissions from snow and seawater. More detailed analysis of the modelling results in the polar regions and a comparison with measurements performed in the Arctic and Antarctica is given in the companion paper (Angot et al., 2016). In particular, three of the four models successfully reproduced the springtime GEM concentration minimum caused by occurrence of atmospheric mercury depletion events (AMDEs). However, the models tended to underestimate the summertime maximum, which is determined by revolatilization from snowpack and meltwater and evasion from the ocean.

~~Statistics of the comparison of~~ Statistics for simulated and observed GEM ~~concentration concentrations~~ for different model experiments (see Table 2) ~~is shown~~ are illustrated in Fig. 4 in terms of ~~the~~ spatial and temporal correlation coefficients and ~~the~~ relative bias. Details of the ~~applied statistics is~~ statistics used are given in Section 2.5. In the BASE simulation ~~all the models produce concentration distributions, which well agree,~~ all models produced concentration distributions that agreed well with measurements (the spatial correlation coefficient ~~is was~~ about 0.7 and the bias ~~is around~~ approximately zero). On the other hand, the models ~~differ~~ differed in their ability to reproduce temporal ~~variation of GEM in the~~ GEM variations in surface air. The ~~coefficient of temporal correlation~~ temporal correlation coefficient between simulated and observed monthly mean values ~~varies~~ varied between -0.3 and 0.5. (Fig. 4**(b)**~~c~~). Sprovieri et al. (2016a) found a consistent seasonal cycle of ~~GEM concentration~~ observed-observed GEM concentration at most measurement sites ~~of in~~ both Northern and Southern Hemispheres, with higher concentrations during winter and spring and lower concentrations in summer and fall. However, it should be noted that ~~the~~ seasonal variation of monthly mean concentration ~~is was~~ not significant at temperate and low latitudes, where most of the sites ~~are located and commonly does~~ were located, and commonly did not exceed $\pm 20\%$. Therefore, reproduction of ~~the~~ GEM temporal variation is a challenging task for models ~~taking into account absent in the absence of~~ data on seasonal variation ~~of in the~~ anthropogenic emissions used in ~~the~~ this study (AMAP/UNEP, 2013b).

Switching off anthropogenic emissions (NoANT) ~~leads to decrease of~~ led to a decrease in GEM levels in the atmosphere (the bias ~~is was~~ -40%) and some decrease ~~of in the~~ spatial correlation with measurements. It is worth ~~to say that noting that~~ the spatial distribution of Hg ~~concentration concentrations~~ in this experiment ~~is was~~ largely determined by ~~model-specific~~ model-specific natural and secondary emissions and ~~, therefore, the change of spatial correlation considerably differs that~~ therefore the change in spatial correlation differed considerably among the models. Removing anthropogenic emissions from the model simulations ~~does did~~ not affect the temporal variation of the modelling ~~result results~~. In contrast, ~~the~~ results of the experiment with no natural and secondary emissions (NoNAT) ~~demonstrates significant improvement of~~ demonstrated significant improvement in temporal correlation with measurements for the models ~~showed poor correlation in the BASE~~ that showed poor correlations in the base run. Besides, the exclusion of natural and secondary emissions ~~leads led~~ to some decrease ~~of in~~ spatial correlation and a large negative bias (~~-100% \approx 100%~~). Simulations with different chemical mechanisms (BrCHEM1, BrCHEM2, O3CHEM, ~~OHCHEM~~) ~~do not lead to considerable changes of both spatial distribution and temporal variation of GEM concentration in the~~ and OHCHEM) provided somewhat different spatial GEM concentration patterns in surface air. ~~Somewhat better spatial correlation was~~ The model run with the first Br dataset (BrCHEM1) showed practically unbiased results, whereas the GEM concentrations from the BrCHEM2 run based on the second dataset were biased high

(Fig. 4(b)) due to the lower Br concentrations provided by this dataset compared to the first one (Fig. S7 in the Supplement). The O3CHEM and OHCHEM simulations also showed a positive bias, indicating the smaller oxidation capacities of these mechanisms. The spatial correlation coefficient varied among the model runs with different chemical mechanisms (0.61–0.73). Somewhat higher spatial correlations were obtained for the oxidation reactions with Br (BrCHEM1, 0.72 ± 0.01) and OH radical (OHCHEM) and worse for the reaction with ozone, 0.71 ± 0.02 , which better reproduced the meridional profile of GEM concentration. The reaction with O_3 (O3CHEM) provided poorer spatial correlation (0.65 ± 0.04) because it levelled the intercontinental GEM gradient. As mentioned earlier, O_3 concentrations are considerably higher in the northern mid-latitudes than in the Southern Hemisphere (Fig. S8 in the Supplement), leading to more intensive oxidation and decreased GEM levels in the Northern Hemisphere.

3.2 Reactive mercury

~~Oxidized~~ The oxidized Hg species composing RM originate in the atmosphere both from direct anthropogenic emissions and through oxidation of GEM in the gas phase, the aqueous phase of cloud water, and heterogeneously in a heterogeneous manner at various atmospheric interfaces (Ariya et al., 2015). Therefore, simulation of RM by simulating RM with contemporary models is a much more challenging task taking into account incomplete current knowledge on given the incomplete state of current knowledge of Hg atmospheric chemistry as well as lack the sparsity and uncertainty of measurement data (Gustin et al., 2015). Global measurements (Gustin et al., 2015). Fig. 5 shows the global distributions of RM concentration in the surface air surface air as simulated by the models for the BASE case is shown in Fig. 5. As seen the models predict. The models predicted considerably different spatial patterns of RM concentration. The concentration levels are RM concentration patterns. The concentrations were comparable in industrial regions, which are were affected by direct anthropogenic emissions, but differ differed significantly in remote regions where the influence of emissions weakens. Thus was weaker. Hence, the simulated patterns highly depend on applied depended strongly on the chemical mechanisms and parameterisations of removal processes removal process parameterizations used. Indeed, the models that apply ozone used O_3 and/or OH–OH oxidation chemistry in the BASE case (Figs. 5a, 5c, 5d) predict predicted elevated RM concentrations at low latitudes (the tropics and the equatorial Tropics and the Equatorial zone) due to high concentrations of these photo-oxidants (mainly ,OH the OH radical) in these regions (see Fig. S8–S9 in the Supplement). On the other hand, application of the use of Br-derived chemistry (Fig. 5b) leads to the led to a spatial pattern with elevated RM concentrations in the polar regions, particularly ,of in the Southern Hemisphere. It This observation is in agreement with the spatial distribution of Br in the atmosphere (Fig. S6–S7 in the Supplement). In addition, model parameterisation the model parameterization of dry deposition also considerably affects RM concentration in the affected RM concentrations in surface air. Application of the Inclusion of effective RM removal in the marine boundary layer by sea-salt aerosol aerosols in GEOS-Chem (Holmes et al., 2010) results resulted in lower RM concentrations over the oceans than those simulated by other models (Fig. 5b).

Scarce long-term observations of RM do not allow to reconstruct a The scarcity of long-term RM observations did not permit reconstruction of reliable spatial trends on a global scale. Annual mean RM observations for the considered year year under study are available only at 9 nine sites in North America, 2 two sites in Europe, 1 one site in the Arctic and 2, and two sites in the

Southern Hemisphere (Fig. 1). ~~Taking into account~~ Considering the short lifetime of RM in the atmosphere with respect to its deposition (Gustin et al., 2015; Ariya et al., 2015) this limited ~~observations dataset can hardly characterize spatial variation of RM over observational dataset cannot characterize spatial RM variation around~~ the globe. Nevertheless, the measurements can be used ~~for evaluation of the~~ to evaluate modelling results at particular locations. The models ~~vary in their performance when~~ showed variable performance in reproducing measured values. The scatter plots of the model-to-measurement comparison ~~shown~~ shown in Fig. S3 in the Supplement demonstrate significantly poorer model agreement with ~~observation~~ observations than in the case of GEM. From 30% to 90% of the simulated values ~~fall beyond the agreement range~~ fell outside the range of agreement within a factor of 3. ~~Besides, there is~~ In addition, there was a general tendency to overestimate ~~the~~ observed concentrations. The level of overestimation ~~varies among the~~ varied among sites and among ~~the~~ models and can be explained by a number of factors ~~including uncertainties of the measurements~~, including measurement uncertainties associated with losses due to interference of oxidants and incomplete capture of GOM (Lyman et al., 2010; Huang and Gustin, 2015; Gustin et al., 2015), incorrect emissions speciation (Zhang et al., 2012; Amos et al., 2012; Kos et al., 2013; Bieser et al., 2014), and the uncertainties of atmospheric chemistry (Weiss-Penzias et al., 2015; Ariya et al., 2015; Shah et al., 2016).

Figure 6 shows statistics ~~of for~~ of for model-to-measurement ~~comparison~~ comparisons of RM air concentration for different model experiments. As ~~it was mentioned above~~ mentioned earlier, the models considerably ~~overestimate~~ overestimated the observed values in the BASE case simulation. Similar overestimation was observed by Kos et al. (2013) when simulating Hg ~~oxidised~~ oxidized forms in a series of model sensitivity runs. ~~And it~~ This observation was attributed to a significant extent to incorrect speciation of anthropogenic emissions ~~with too high~~, with a too-high proportion of oxidized Hg forms. ~~It is~~ This was also confirmed by the NoANT experiment ~~of in~~ of in the current study ~~with zeroed out anthropogenic emissions that leads to the~~, where ~~zeroed out anthropogenic emissions led to a~~ significantly lower positive or even negative bias (Fig. 6a). To reduce the effect of this uncertainty in the current study ~~we use the~~, a modified speciation of emissions data was used for the model experiments focused on ~~comparison of the chemical mechanisms~~ comparing chemical mechanisms, with all Hg emissions treated as GEM (Section 2.4). The overprediction of observed RM concentrations by a factor of 2.5 was also found by Weiss-Penzias et al. (2015) for a number of high- and mid-elevation sites and ~~it was connected with~~ was found to be connected with the collection inefficiency of the KCl denuder used for the GOM measurements (Gustin et al., 2013). The models ~~differ~~ differed in their ability to reproduce ~~temporal variation of the~~ temporal variation in RM concentration (the correlation coefficient ~~varies within the range~~ varied from -0.5 ~~-0.6~~ to 0.6 in the BASE case) (Fig. 6b). ~~It is connected with both~~ This variation was connected both with the different chemical mechanisms ~~applied~~ used in the standard model configurations (Table 1) and with deviations in model treatment of the removal processes responsible for dry and wet deposition. Exclusion of anthropogenic and natural/secondary emissions (NoANT and NoNAT) only slightly ~~affect temporal correlation~~ affected the temporal correlations of the modelling results with observations. However, it should be pointed out once again that the emissions inventory used for ~~the this~~ study ((AMAP/UNEP, 2013b)) ~~does did~~ not resolve the intra-annual variability of anthropogenic emissions. ~~So~~ Hence, one can expect a stronger effect of anthropogenic emissions on RM temporal variation. Among the chemical mechanisms ~~the best correlation between modelled~~, the best correlations between modeled and observed values were obtained for reactions with Br (BrCHEM1 and BrCHEM2), followed by the ~~OH~~ OH oxidation mechanism (OHCHEM). ~~Application~~ Inclusion of the

reaction with O₃ ~~leads to~~ led to a negative correlation with observations. ~~Interesting to note that taken alone OH- and -initiated chemistry predicts somewhat stronger oxidation of GEM in comparison with the Br chemistry that results in a positive bias of simulated RM concentrations (Fig. 6a).~~

More ~~A more~~ detailed analysis of ~~the~~ chemical oxidation mechanisms is ~~presented~~ illustrated in Fig. 7 in terms of ~~comparison~~ of simulated and observed RM/GEM ratios. Indeed, atmospheric RM originates either from direct emissions from anthropogenic sources or as a product of GEM oxidation in the atmosphere (Selin, 2009; Travnikov, 2012; Kos et al., 2013; Ariya et al., 2015). ~~So~~ Hence, in the immediate vicinity of emission sources, the RM/GEM ratio reflects the speciation of Hg emissions, whereas in remote regions far away from any emissions, it largely quantifies ~~the~~ oxidative capability of the atmosphere. Given ~~short life time~~ the short lifetime of RM in the atmosphere with respect to deposition, the influence of direct emissions on the RM/GEM ratio should quickly weaken with ~~the~~ distance from sources. Following the methodology suggested by Kos et al. (2013) ~~we classified~~ the sites used for the following analysis ~~were classified~~ with respect to their remoteness from significant emission sources, based on the model sensitivity run with ~~the turned off~~ Hg atmospheric chemistry ~~turned off~~. The simulated RM concentrations ~~show~~ showed (Fig. S5-S6 in the Supplement) that all the selected sites (except one) ~~can~~ could be classified as ~~located~~ being far from sources (0-30 pg m⁻³). ~~It agrees with~~ This observation agrees with the characteristics of the North American sites ~~as~~ given by Lan et al. (2012). The only site that ~~is~~ was probably directly affected by anthropogenic emissions ~~is~~ was Waldhof, Germany (Weigelt et al., 2013). Nevertheless, ~~since both~~ because both the mean levels and ~~the~~ seasonal variation of RM concentrations measured at this site ~~does~~ did not differ significantly from ~~others~~ other sites, it was retained in the dataset. However, it should be noted that this analysis essentially ~~depends upon the applied emissions data and can translate their uncertainties to~~ depended upon the emissions data used and could translate any data uncertainties into the classification results.

Figure 7 shows ~~a~~ comparison of simulated and observed annual mean RM/GEM ratios for different chemical mechanisms. ~~Whiskers show~~ The whiskers show the standard deviation of monthly mean simulated and observed values. It should be ~~pointer~~ pointed out that the observed values of RM/GEM (1-10 pg ng⁻¹) correspond to ~~the~~ background conditions of the continental boundary layer and are considerably lower ~~than~~ those from mountain sites ~~analysed~~ analyzed by Weiss-Penzias et al. (2015) (10-100 pg ng⁻¹). Exceptions are the site ~~at~~ Alert, Canada, located in the ~~high~~ High Arctic (86 pg ng⁻¹) and the elevated site ~~at~~ Salt Lake City, ~~USA~~ United States (21 pg ng⁻¹). It is interesting to note that the other elevated site (Longobucco, Italy ~~does not show similar~~) ~~did not show similarly~~ increased RM/GEM values (9.5 pg ng⁻¹). As ~~seen from the figure the~~ shown in Figure 7, the best qualitative agreement between ~~the models and measurements is~~ model and measurements was found in the ~~experiment~~ BrCHEM1 ~~experiment~~ with the Br chemistry and one of the Br concentration datasets (Fig. 7a). Three of ~~four models demonstrate good performance~~ the four models demonstrated good performance in this experiment, reproducing observations at most ~~of the sites~~ sites with a deviation within a factor of 3. The fourth model (ECHMERIT) ~~shows significant overestimation of~~ significantly overestimated the observed values, which ~~is typical also for~~ was also typical of the other model experiments (except for O3CHEM). ~~Therefore, most probably it is not caused by the applied chemistry but~~ This overestimation was caused, not by other factors such as removal processes. ~~As it will be shown below the model tends to underestimate wet deposition of Hg that is mostly consists of scavenging of highly soluble RM. Application of the~~ chemistry

used, but by underestimation of wet scavenging as shown below. Use of Br chemistry with the other Br concentration dataset (BrCHEM2) leads led to less consistent results (Fig. 7b). Generally, the model-to-measurement deviations are within a factor of 5 except for the results of ECHMERIT discussed above. The RM/GEM ratios simulated by two other models vary the models varied from moderate underestimation to overestimation of the observed values. The inter-model difference can be differences could have been caused both by discrepancies in formulation of removal processes removal process formulation and by particular implementation implementations of the Br chemical mechanism (see Table 1). Somewhat similar results were obtained in the experiment with the OH chemistry (OHCHEM, Fig. 7d). The deviations between the modelled and measured RM/GEM are again were mostly within a factor of 5 and the model-to-model difference is probably resulted from application of somewhat different reaction constants (Table 1). In contrast, application of the, and the models tended to overestimate the observed values. Application of the O₃-initiated chemistry leads led to very consistent results (O3CHEM, Fig. 7c). The models predict some overestimation of also somewhat overestimated the measured RM/GEM ratios, with minimum scattering of the modelling results. On the other hand, the models tend to considerably underestimate tended to underestimate considerably the intra-annual variation of monthly values shown by, as shown by the whiskers. None of the chemical mechanisms allows to reproduce could reproduce the high annual RM/GEM ratios (above 80 pg ng⁻¹) observed at the Arctic site Alert, Canada (Fig. 7a-c). These high annual values are connected with intensive Hg oxidation during the springtime atmospheric mercury depletion events (AMDEs) springtime AMDEs. Analysis of specific processes typical for of the polar regions is beyond the scope of this paper. Discussion of results of the study A discussion of the results of studies focused on the polar regions can be found elsewhere (Angot et al., 2016).

More insight into the effect effects of different chemical mechanisms can be obtained from the analysis of by analyzing RM/GEM seasonal variation. Figure 8 shows both measured and simulated variation of in the monthly mean RM/GEM ratio averaged over selected sites. Since the Because seasonal variation of both RM and GEM differs in the Northern and Southern Hemispheres and majority of considered because most of the study sites are located in North America and Europe we selected for this purpose only sites situated northward the Equator. Besides, we excluded, two sites situated north of the Equator were selected for this purpose. In addition, the Arctic site (Alert) and two high-elevated the two high-elevation sites (Salt Lake City and Longobucco) to avoid were excluded to avoid the effects of specific conditions of in the polar regions and the free troposphere, respectively. Thus respectively. Hence, the collection of sites characterises characterizes the seasonality of Hg oxidation in the continental boundary layer of the in northern temperate latitudes. As seen the observed values demonstrate a The observed values demonstrated pronounced seasonal changes of in RM/GEM with, with a maximum in March and a minimum in September (Fig. 8). Similar seasonal variation of Hg oxidised variations of Hg oxidized forms at background sites were observed in previous studies (Poissant et al., 2005; Sigler et al., 2009; Nair et al., 2012; Weigelt et al., 2013). The chemical oxidation mechanisms differ differed in their ability to reproduce the observed seasonal variation. Application of the Use of Br chemistry with both Br concentration datasets (BrCHEM1 and BrCHEM2) provides provided the best agreement with measurements reproducing the. Three of the four models (GEOS-Chem, GEM-MACH-Hg, and GLEMOS) reproduced the maximum RM/GEM ratios during spring months by three of four models the spring months (Figs. 8a and 8b). High levels of oxidized Hg in spring are evidently caused by high Br concentrations in both the free troposphere and the boundary layer

in the Northern Hemisphere (Fig. S10 in the Supplement). However, only GEOS-Chem reproduced correctly the time of the maximum in March. Two other models moved the highest RM/GEM ratio to April and May. This discrepancy can be explained by partitioning the GEM oxidation products. GEOS-Chem is the only model that used dynamic gas-particle partitioning of RM (Table 1). This meant that oxidized Hg originated from GEM oxidation was dynamically fractionated between GOM and PBM. This equilibrium is sensitive to air temperature shifting to GOM under warmer conditions (Amos et al., 2012). On the other hand, GOM is more efficiently removed from the atmosphere than PBM by both precipitation and surface uptake. This phenomenon leads to higher deposition and lower RM concentrations in late spring (April and May). Two other models predicted a fixed share of the products of GEM oxidation by Br, thus missing changes in RM concentration during the season. The fourth model ~~predicts~~ (ECHMERIT) ~~predicted~~ the highest ratios during late summer independently of ~~applied chemical mechanism that is probably determined by other factors including the chemical mechanism used, a phenomenon that was determined by~~ meteorological conditions and removal processes. ~~The simulated maximum of RM/GEM in the spring months can be explained by high Br concentrations in both the free troposphere and the boundary layer of the Northern Hemisphere (Fig.S9 in the Supplement).~~ In particular, the model simulated extremely low precipitation in late summer and early fall (Figs. 12i and 12j). This led to significant underestimation of wet RM removal and ultimately to overestimation of oxidized Hg concentrations during this period.

Model simulations with OH chemistry (OHCHEM) ~~predict the predicted~~ maximum RM/GEM ratios during ~~the~~ summer months (Fig. 8d) in accordance with ~~the~~ seasonal variation of OH concentration ~~which is also the~~, ~~which was also~~ highest in summer (Fig. S11-S12 in the Supplement). Use of the O₃-initiated chemistry ~~does did~~ not lead to ~~any~~ significant variation of Hg oxidation during the year (Fig. 8c).

3.3 Wet deposition

Wet deposition is one of the major removal mechanisms responsible for ~~exchange of Hg~~ ~~Hg exchange~~ between the atmosphere and the Earth's surface (Travnikov, 2012; Swartzendruber and Jaffe, 2012). It is largely determined by precipitation events ~~on one hand; on the one hand~~ and by availability of soluble Hg forms in the atmosphere ~~on the other~~. Given ~~the~~ poor solubility of GEM (Clever et al., 1985; Ariya et al., 2015), Hg wet deposition ~~mostly consists~~ ~~consists mostly~~ of scavenging of Hg oxidized forms (GOM and PBM). Therefore, Hg concentration in precipitation and ~~ultimately~~ ~~ultimately~~ wet deposition flux largely depends upon three factors ~~—~~: direct emissions of oxidized Hg from anthropogenic sources, Hg oxidation in the atmosphere, and precipitation amount. Figure 9 shows ~~the~~ spatial patterns of annual mean Hg wet deposition ~~as~~ simulated by the four models according to the BASE case. Available measurements are also shown in the same ~~colour~~ ~~color~~ palette. Generally, the simulated deposition maps have similar spatial distributions, reflecting the influence of ~~the global precipitation pattern~~ ~~global precipitation patterns~~ and major emission regions. High deposition fluxes are ~~characteristics~~ ~~characteristic~~ of Asia, Europe, and North America, where significant anthropogenic sources are located, as well as of regions with intensive precipitation (e.g. ~~the Inter-tropical~~, ~~the Inter-Tropical~~ Convergence Zone). The lowest wet deposition fluxes ~~are occurred~~ in dry regions (e.g. in Northern Africa, Greenland, and Antarctica). Divergences among the modelling results ~~are could be~~ mostly explained by ~~the~~ different chemical mechanisms ~~applied~~ ~~used~~ by the models in the BASE case. For instance, GEOS-Chem ~~predicts~~

~~predicted~~ elevated wet deposition in the high latitudes of the Southern Hemisphere, where high Br concentrations (Fig. ~~S6~~ ~~S7~~ in the Supplement) ~~excite intensive oxidation of GEM~~ caused intensive GEM oxidation in the atmosphere (Fig. 9b). On the other hand, significant deposition fluxes ~~are were~~ simulated in the ~~high~~ High Arctic by GEM-MACH-Hg (Fig. 9c) ~~due to application of parameterisations of~~ because parameterizations of physical and chemical processes occurring during AMDEs ~~were used~~. The models ~~relatively well agree~~ agreed relatively well with available long-term observations of Hg wet deposition. ~~The model-to-measurement deviations commonly do~~ Model-to-measurement deviations commonly did not exceed a factor of two (Fig. ~~S4~~ in the Supplement). However, it should be ~~noticed~~ noted that available observations of Hg wet deposition are still mostly restricted ~~by two regions~~ to two regions: North America and Europe. Only a few measurements are available in other regions ~~and, in particular, in~~ particularly in the Southern Hemisphere.

~~Statistics~~ Figure 10 shows statistics of the comparison of simulated and observed wet deposition fluxes ~~is given in Fig. 10~~. Results of the BASE case simulation are characterized by significant temporal correlation with ~~with~~ measurements (0.4 ~~0.6~~ 0.6) and some slight bias ($\pm 40\%$) ~~which is variable among the~~ that varies among models. Direct anthropogenic emissions of oxidized Hg ~~considerably contributes~~ contributed considerably to wet deposition ~~and so its~~ and hence their elimination (NoANT) ~~results in~~ resulted in a noticeable deposition decrease characterized by negative bias. In contrast to anthropogenic emissions, natural/secondary sources emit Hg mostly as GEM. Nevertheless, turning off natural/secondary emissions (NoNAT) also ~~leads to substantial decrease of wet deposition~~ led to a substantial decrease in wet deposition, indicating their indirect effect through GEM oxidation ~~to the on~~ soluble Hg forms, with subsequent scavenging by precipitation. ~~Temporal~~ The temporal correlation of wet deposition ~~is was~~ not sensitive to emission changes. ~~That is not wondering~~ This is not surprising because the anthropogenic emissions inventory used in ~~the study does not contains~~ this study did not contain information on temporal ~~variation of emissions~~. ~~The oxidation chemistry considerably affects both~~ emissions variation. Oxidation chemistry considerably affected both the general level and ~~the~~ temporal variation of Hg wet deposition. The Br oxidation mechanism ~~provides relatively good~~ provided a relatively high correlation with observations ~~but there is a large difference between results for two different~~ but the results for the two Br concentration datasets (BrCHEM1 and BrCHEM2) ~~differed widely~~ in terms of relative bias. The highest correlation ~~is obtained for the~~ was obtained for OH oxidation chemistry (OHCHEM). ~~It should be noticed that~~ differently from ~~Note that, unlike the~~ other models used for this study, ECHMERIT is based on the ECHAM climate model ~~that, which~~ which is expected to reproduce ~~the actual weather behaviour~~ actual weather behavior, in particular ~~precipitations~~ precipitation events, over a relatively longer temporal period and ~~wider areas, and a wider area than the other models, but~~ may diverge on shorter time scales and ~~over~~ smaller regional areas (see ~~for example~~ for example, Angálil et al. (2016)). ~~Since~~ Because simulated Hg wet deposition is largely driven by ~~the model generated precipitation~~ we prefer to not include model-generated precipitation, the results of the climate-based ECHMERIT model ~~in the following analysis to avoid biasing the statistics~~ can be significantly biased with regard to other wet deposition models and observations (Fig. 10).

~~Similar~~ Similarly to RM concentration ~~wet deposition of Hg is a parameter that is~~ Hg wet deposition is strongly determined by atmospheric oxidation chemistry (Selin and Jacob, 2008; Kos et al., 2013). Therefore, analysis of wet deposition can ~~be also applied for evaluation of~~ also be used to evaluate the chemical mechanisms of Hg oxidation in the atmosphere. Unlike ~~RM concentration levels measured at ground-based sites near the surface~~ near-surface RM observations, wet deposition mea-

measurements characterize processes occurring in the free troposphere ~~since the~~ because scavenging of soluble Hg takes place both in the cloud environment and below clouds along the whole ~~path of convective or large-scale precipitation~~. Comparison precipitation pathway. Figure 11 shows a comparison of simulated and observed wet deposition fluxes for different model experiments ~~is shown in Fig. 11~~. Both measured and simulated values are averaged over different groups of sites ~~including 7~~, including seven groups in North America following the latitudinal ranges suggested by Selin and Jacob (2008), ~~3~~ three groups in Europe (Southern Europe, Western Europe, and Northern Europe), and ~~4~~ one group per region in Asia, Australia, and the Indian Ocean (see Table S3 in the Supplement). ~~As seen from the figure~~ Note that the highest observed wet deposition values (30-45 ng m⁻² day⁻¹) are associated with the southern United States, whereas the lowest values (below 10 ng m⁻² day⁻¹) are characteristic of sites located in East Asia and in the Southern Hemisphere (see Fig. 9). As shown in Fig. 11, simulations with the Br oxidation mechanism and the first set of Br concentration data (BrCHEM1) satisfactorily ~~reproduces~~ reproduced observations (Fig. 11a). The models ~~relatively well agree~~ agreed relatively well with each other ~~and the model-to-measurement deviations mostly do~~, and the model-to-measurement deviations generally did not exceed a factor of 2. However, all ~~the models overpredict~~ models overpredicted low deposition fluxes (~~below 10~~) measured in Asia and in the Southern Hemisphere at Asian and southern sites. The overestimation of Hg wet deposition at two high-altitude Asian sites (Mt. Waliguan and Mt. Ailao) can be connected with the inability of the ~~global models with rough spatial resolution~~ coarse-spatial-resolution global models to reproduce complex meteorological conditions ~~of the in~~ mountain regions. ~~The overprediction at the~~ Overprediction at southern sites (Cape Grim and Amsterdam Island) ~~might can~~ be explained by the very high Br concentrations predicted by the first dataset at temperate latitudes ~~of in~~ the Southern Hemisphere (Fig. ~~S6-S7~~ in the Supplement). ~~Application~~ Use of the same mechanism with the other Br dataset ~~leads led~~ to considerably lower ~~levels of wet deposition~~ wet deposition levels (Fig. 11b) due to use of much ~~smaller~~ lower Br concentrations, particularly ~~in~~ the free troposphere (Fig. ~~S6-S7~~ in the Supplement). ~~Thus, uncertainties of~~ Hence, uncertainties in the available estimates of Br atmospheric concentration ~~largely affect simulation results of the~~ strongly affected simulation results for Hg cycling in the atmosphere. Model simulations with the O₃ and OH oxidation mechanisms (O3CHEM and OHCHEM) ~~also provide~~ provided reasonable agreement between ~~the~~ modelling results and measurements (Figs. 11c and 11d). ~~In both cases the simulated values well correlate with the observed ones and deviations are mostly within a factor of 2.~~ Two of the three models (GEM-MACH-Hg and GLEMOS) demonstrated fairly good correlations with observations, but again tended to overestimate lower observed values. The OH oxidation chemistry ~~provides~~ provided somewhat better agreement in terms of the slope of ~~regression line that is~~ the regression line, which was closer to the reference 1:1 line, indicating better reproduction of both low and high wet deposition fluxes. The third model (ECHMERIT) showed wider divergence of simulation results because of the uncertainties described above in its reproduction of precipitation events in some locations. In particular, these uncertainties led to significant underestimation of Hg wet deposition in the southern part of North America.

More information on the performance of different chemical mechanisms can be obtained ~~from the analysis of seasonal patterns of wet deposition~~. ~~Since the majority of~~ by analyzing seasonal wet deposition patterns. Because most available wet deposition measurements are ~~at sites located~~ obtained at sites in North America and Europe ~~we focus our further discussion~~, further discussion will focus on these two regions. Figure 12 shows ~~comparison of modelled~~ a comparison of modeled and

measured temporal variation of monthly mean wet deposition flux averaged over sites ~~located~~ in North America and Europe. The monthly fluxes were normalized by the annual average value to remove absolute differences among the models and reveal peculiarities of seasonal changes. ~~As seen the observations demonstrate well~~ The observations exhibit a pronounced seasonal cycle ~~with, with a~~ with a maximum in summer and a minimum during the cold season (winter and early spring). Similar seasonal variations ~~has have~~ have been reported in previous studies (Guentzel et al., 2001; Keeler et al., 2005; Choi et al., 2008; Prestbo and Gay, 2009; Sprovieri et al., 2016b). Sprovieri et al. (2016b) ~~attributes attributed~~ attributes these seasonal changes to ~~variation of variations~~ in meteorological conditions (~~mostly, mainly~~ precipitation amount), more effective Hg scavenging by rain compared to snow, and changes in availability of soluble Hg. As ~~seen from shown in~~ shown in Figs. 12i and 12j ~~precipitation amount, precipitation amounts~~ precipitation amounts measured in North America and Europe ~~, respectively, does not reveal do not reveal a~~ do not reveal a similar seasonality to explain the intra-annual variation of wet deposition. Seasonal variation of precipitation ~~amount amounts~~ amounts in North America ~~demonstrate similar pattern with exhibits a similar pattern, with a~~ exhibits a similar pattern, with a maximum in summer and a minimum in winter, but the amplitude of the variation is much ~~smaller less~~ less than that of wet deposition. Average precipitation ~~amount in Europe does not have amounts in Europe do not show an~~ amounts in Europe do not show an evident seasonal pattern. Note that one of the four models (ECHMERIT) failed to reproduce the seasonal cycle of precipitation amounts in North America and Europe for the reasons mentioned previously. Because precipitation variation directly affects seasonal variation of Hg wet deposition, the simulation results from this model were not used when analyzing the performance of chemical mechanisms. However, the results themselves are shown in Fig. 12 for completeness. Availability of soluble Hg in the free troposphere ~~highly depends on the depends strongly on~~ depends strongly on oxidation chemistry. Therefore, different chemical mechanisms should ~~differently affect affect the~~ affect the seasonality of wet deposition differently. Indeed, both model runs with the Br oxidation chemistry (BrCHEM1 and BrCHEM2) ~~predict predicted a~~ predicted a maximum in wet deposition during the spring months instead of in summer (Figs. 12a-da-12d) following the seasonal variation of Br concentration in the atmosphere (Fig. S9 S10 in the Supplement). Simulations with ~~the~~ the O₃-initiated chemistry (O3CHEM) ~~provide provided a~~ provided a much lower seasonality of deposition flux (Figs. 12e-fe-12f). In contrast, ~~application of the use of~~ application of the use of OH chemistry (OHCHEM) ~~well reproduces reproduced faithfully~~ reproduces reproduced faithfully the observed seasonal variation of wet deposition in both ~~considered study~~ study regions (Figs. 12g-hg-12h). Similar results were obtained by other ~~researches researchers~~ researchers. Selin and Jacob (2008) simulated Hg wet deposition over the United States ~~applying the using~~ using combined OH/O₃ oxidation chemistry and successfully reproduced the measured seasonal variation. They attributed the summer maximum in the Northeast to GEM photochemical oxidation and to inefficient scavenging by snow in winter. Holmes et al. (2010) compared the Br mechanism ~~vs. with~~ with the OH/O₃ mechanism for simulating the Hg global cycle. They found that the OH/O₃ chemistry ~~allows better simulating the southeast summer maximum in better simulated the southeast~~ allows better simulating the southeast summer maximum in better simulated the southeast Hg wet deposition ~~, where it reflects summer maximum. It was postulated that the maximum reflected~~ where it reflects summer maximum. It was postulated that the maximum reflected scavenging of GOM from the free troposphere by deep convection. Kos et al. (2013) also performed a number of sensitivity runs with different ~~parameterizations of chemical processes chemical process parameterizations~~ chemical process parameterizations and showed that using the OH oxidation chemistry ~~improves simulations improved simulation~~ improved simulation of the seasonal cycle of wet deposition in North America. ~~Taking into account~~ Considering that Hg wet deposition is largely defined by ~~oxidation of GEM (Selin and Jacob, 2008), we can expect GEM oxidation (Selin and Jacob, 2008), a~~ oxidation of GEM (Selin and Jacob, 2008), we can expect GEM oxidation (Selin and Jacob, 2008), a significant effect of ~~the~~ the OH-initiated chemistry on Hg oxidation in the free troposphere can be expected. On the other hand, when comparing this conclusion with the results presented in Section 3.2, where it was

shown that the seasonal dynamics of the RM/GEM ratio observed at ground-based sites is dominated by ~~the~~ Br oxidation chemistry, one can assume the possibility of different Hg oxidation mechanisms occurring concurrently in different parts of the atmosphere.

4 Conclusions

5 The ~~presented study~~ study presented here provides a complex analysis of the processes governing Hg cycling in the atmosphere ~~involving both measurement~~, involving both measured data from ground-based sites and application of chemical transport models. A variety of long-term ~~measurements of~~ GEM and RM concentration measurements as well as wet deposition flux ~~has readings have~~ been compiled from different global and regional monitoring networks. Four contemporary global-scale ~~transport models for Hg were applied~~ Hg transport models were used, both in their state-of-the-art configurations and for a
10 number of numerical experiments aimed at evaluation of particular processes. Results of the model ~~simulation~~ simulations were evaluated against measurements. The models ~~predict~~ predicted similar global spatial ~~patterns of GEM concentration in the GEM~~ concentration patterns in near-surface air ~~in spite of significant deviations in applied~~. The model-to-model difference in simulated GEM concentrations did not exceed $\pm 20\%$ and agreed with observed values within $\pm 30\%$. Nevertheless, there were pronounced distinctions among the spatial patterns simulated by different models, which resulted from deviations in the
15 parameterizations of physical and chemical processes. ~~The model-measurement divergence does not commonly exceed $\pm 30\%$.~~ All four models ~~reproduce the observed decrease of GEM concentration between the Northern and Southern Hemispheres. As it follows from the analysis the~~ reproduced the observed GEM concentration decrease from the Northern to the Southern Hemisphere. Analysis revealed that the inter-hemispheric gradient is largely formed by the spatial distribution of anthropogenic emissions ~~which prevail that prevails~~ in the Northern Hemisphere. ~~Contribution~~ The contributions of natural and secondary
20 emissions ~~enhances~~ enhanced the south-to-north gradient, but their effect ~~is~~ was less significant. ~~The oxidation chemistry does not affect considerably both spatial distribution and temporal variation of GEM concentration in the~~ Simulations with different chemical mechanisms provided somewhat different spatial GEM concentration patterns in surface air. Higher spatial correlations were obtained for the oxidation reactions with Br and OH radical, enabling better reproduction of the meridional GEM concentration profile. The reaction with O₃ provided poorer spatial correlation because it leveled the intercontinental
25 GEM gradient.

Model simulation of RM is a much more challenging task ~~taking into account because of~~ incomplete current knowledge ~~on~~ of Hg atmospheric chemistry ~~as well as lack and uncertainty of measurement and the scarcity and uncertainty of measured~~ data. The models ~~differ considerably in prediction~~ differed considerably in their predictions of spatial and temporal ~~patterns of RM concentration~~ RM concentration patterns. The simulated RM levels ~~are~~ were comparable in industrial regions, which are
30 affected by direct anthropogenic emissions, but ~~differ~~ differed significantly in remote regions where the influence of emissions ~~weakens. Thus is weaker. Hence,~~ the simulated patterns ~~highly depend on applied~~ depended strongly on the chemical mechanisms and ~~parameterisations of removal processes. The model-to-measurement comparison demonstrate~~ removal process parameterizations used. Model-to-measurement comparisons demonstrated significantly poorer model agreement with obser-

vations than in the case of GEM. From 30% to 90% of the simulated values ~~fall~~fell beyond the agreement range within a factor of 3. ~~Besides, there is~~In addition, there was a general tendency to overestimate ~~the~~ observed RM concentrations, which can be attributed to incorrect speciation of Hg emissions, the uncertainties of Hg atmospheric chemistry, and incomplete RM capture by measurements. Atmospheric chemistry ~~largely affects~~strongly affected the RM/GEM ratio in the atmosphere. ~~Application of the~~The Br chemistry ~~provides~~provided the best agreement with observations, reproducing both general levels and seasonal variation of the RM/GEM ratio in the near-surface layer. However, the global distribution of Br concentration is highly uncertain. Model simulations with the OH chemical mechanism ~~predict shifting the~~predicted a shift in maximum RM/GEM ratios from spring to summer, ~~whereas the~~but O₃-initiated chemistry ~~does not lead to significant seasonal variation of~~did not predict significant seasonal variations in Hg oxidation.

10 Wet deposition maps simulated by different models ~~have had~~similar spatial distributions, reflecting the influence of ~~the global precipitation pattern and situation~~global precipitation patterns and the location of major emission regions. High deposition fluxes are ~~characteristics~~characteristic of Asia, Europe, and North America~~where~~, where regions with significant anthropogenic sources ~~are located as well as of regions with intensive precipitation and intensive precipitation are located~~. The models ~~relatively well agree~~agreed relatively well with available long-term ~~observations of~~observations.
15 The model-to-measurement deviations commonly ~~do~~did not exceed a factor of 2. However, there ~~is~~was a tendency to over-predict low deposition fluxes measured in Asia and in the Southern Hemisphere. ~~Similar~~Similarly to RM concentrations, wet deposition of Hg in background regions is strongly determined by ~~the~~ atmospheric oxidation chemistry. Model runs with the ~~Br oxidation mechanism predict maximum in wet deposition~~Br oxidation mechanism predicted a wet deposition maximum in spring, instead of in spring instead of summer as observed at monitoring sites ~~located~~ in North America and Europe. ~~The~~ O₃
20 chemistry ~~does not provide~~did not predict significant seasonal changes of wet deposition flux in these regions. ~~Application of the~~Use of OH chemistry ~~allows reproducing~~enabled reproduction of both the periods of maximum and minimum values and the amplitude of observed seasonal ~~variation~~variations.

~~Thus, Hence, the~~ performance of the ~~considered~~ Hg oxidation mechanisms ~~differs in reproduction of different observed parametersthat can imply~~studied differed in the quality of their reproduction of the various observed parameters, which can
25 imply the possibility of more complex chemistry and multiple ~~pathways of Hg oxidation~~Hg oxidation pathways occurring concurrently in various parts of the atmosphere. More extensive measurements of ~~both RM atmospheric RM~~ (including identification of Hg chemical species) and wet deposition are needed in various ~~geographical~~geographic regions and under different climatic conditions ~~for to achieve~~ further improvement of Hg chemical transport models.

Author contributions. The names after the first author in the above list are in alphabetical order and all authors have made significant
30 contribution. In particular,
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References

- AMAP/UNEP, Technical Background Report for the Global Mercury Assessment 2013a. Arctic Monitoring and Assessment Programme, Oslo, Norway / UNEP Chemicals Branch, Geneva, Switzerland. vi + 263 pp., 2013, available at <http://www.unep.org/chemicalsandwaste/Mercury/ReportsandPublications/tabid/3593/Default.aspx>, access: 1 August 2016.
- 5 AMAP/UNEP, Geospatially distributed mercury emissions dataset 2010v1, 2013b, <http://www.amap.no/mercury-emissions>, access: 1 August 2016.
- AMAP/UNEP, Global Mercury Modelling: Update of Modelling Results in the Global Mercury Assessment 2013. Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch, Geneva, Switzerland. iv + 32 pp., 2015, available at <http://www.unep.org/chemicalsandwaste/Mercury/ReportsandPublications/tabid/3593/Default.aspx>, access: 1 August 2016.
- 10 AMNet: Atmospheric Mercury Network. <http://nadp.sws.uiuc.edu/amn/>, access: 1 August 2016.
- Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., Corbitt, E. S., Galarneau, E., Rutter, A. P., Gustin, M. S., Steffen, A., Schauer, J. J., Graydon, J. A., St Louis, V. L., Talbot, R. W., Edgerton, E. S., Zhang, Y., and Sunderland, E. M.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition, *Atmos. Chem. Phys.*, 12, 591-603, doi:10.5194/acp-12-591-2012, 2012.
- 15 Angálil, O., Perkins-Kirkpatrick, S., Alexander, L. V., Stone, D., Donat, M. G., Wehner, M., Shiogama, H., Ciavarella, A., Christidis, N.: Comparing regional precipitation and temperature extremes in climate model and reanalysis products, *Weather and Climate Extremes*, 13, 35-43, doi:10.1016/j.wace.2016.07.001, 2016.
- Angot, H., Dastoor, A., De Simone, F., Gårdfeldt, K., Gencarelli, C. N., Hedgecock, I. M., Langer, S., Magand, O., Mastromonaco, M. N., Nordstrøm, C., Pfaffhuber, K. A., Pirrone, N., Ryjkov, A., Selin, N. E., Skov, H., Song, S., Sprovieri, F., Steffen, A., Toyota, K.,
- 20 Travnikov, O., Yang, X., and Dommergue, A.: Chemical cycling and deposition of atmospheric mercury in polar regions: review of recent measurements and comparison with models, *Atmos. Chem. Phys.*, 16, 10735-10763, doi:10.5194/acp-16-10735-2016, 2016.
- Ariya, P. A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., Poulain, A., Ryjkov, A., Semeniuk, K., Subir, M., and Toyota, K.: Mercury Physicochemical and Biogeochemical Transformation in the Atmosphere and at Atmospheric Interfaces: A Review and Future Directions, *Chem. Rev.*, 15 (10), 3760-3802, doi: 10.1021/cr500667e, 2015.
- 25 Baker, K. R. and Bash, J. O.: Regional Scale Photochemical Model Evaluation of Total Mercury Wet Deposition and Speciated Ambient Mercury. *Atmos. Environ.*, 49, 151-162, 2012.
- Balabanov, N., Shepler, B., Peterson, K.: Accurate global potential energy surface and reaction dynamics for the ground state of HgBr₂. *J. Phys. Chem. A*, 109, 8765-8773, 2005.
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q., Liu, H. Y., Mickley, L. J., and Schultz, M. G.:
- 30 Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.-Atmos.*, 106, 23073-23095, doi:10.1029/2001jd000807, 2001.
- Bieser, J., De Simone, F., Gencarelli, C., Geyer, B., Hedgecock, I., Matthias, V., Travnikov, O., and Weigelt, A.: A diagnostic evaluation of modeled mercury wet depositions in Europe using atmospheric speciated high-resolution observations, *Environ. Sci. Pollut. Res.*, 21, 9995-10012, doi:10.1007/s11356-014-2863-2, 2014.
- 35 Calvert, J. G. and Lindberg, S. E.: Mechanisms of mercury removal by O₃ and OH in the atmosphere, *Atmos. Environ.*, 39, 3355-3367, doi:10.1016/j.atmosenv.2005.01.055, 2005.

- Cohen, M.D., Draxler, R.R., Artz, R.S., Gustin, M., Han, Y-J., Holsen, T.M., Jaffe, D., Kelley, P., Lei, H., Loughner, C., Luke, W., Lyman, S., Niemi, D. Pacyna, J.M., Pilote, M., Poissant, L., Ratte, D., Ren, X., Steenhuisen, F., Tordon, R., and Wilson, S.: Modeling the global atmospheric transport and deposition of mercury to the Great Lakes. *Elementa: Science of the Anthropocene*, 4, 000118, doi: 10.12952journal.elementa.999118, 2016.
- 5 Choi, H.-D., Sharac, T. J., and Holsen, T. M.: Mercury deposition in the Adirondacks: A comparison between precipitation and throughfall, *Atmospheric Environment*, 42, 1818-1827, 2008.
- Christensen, J., Brandt, J., Frohn, L., Skov, H.: Modelling of Mercury in the Arctic with the Danish Eulerian Hemispheric Model. *Atmos. Chem. Phys.*, 4, 2251-2257, 2004.
- Clever, H. L., Johnson, S. A., Derrick, M. E.: The solubility of mercury and some sparingly soluble mercury salts in water and aqueous
10 electrolyte solutions. *J. Phys. Chem. Ref. Data*, 14, 631-680, 1985.
- Cole, A. S., Steffen, A., Pfaffhuber, K. A., Berg, T., Pilote, M., Poissant, L., Tordon, R., and Hung, H.: Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude sites, *Atmos. Chem. Phys.*, 13, 1535-1545, doi:10.5194/acp-13-1535-2013, 2013.
- Cremer, D., Kraka, E., and Filatov, M.: Bonding in Mercury Molecules Described by the Normalized Elimination of the Small Component
15 and Coupled Cluster Theory, *Chem. Phys. Chem.*, 9, 2510-2521, doi:10.1002/cphc.200800510, 2008.
- Dastoor, A. P., and Larocque, Y.: Global circulation of atmospheric mercury: a modelling study, *Atmospheric Environment*, 38, 147-161, 2004.
- Dastoor, A. P., Davignon, D., Theys, N., Van Roozendael, M., Steffen, A., and Ariya, P. A.: Modeling dynamic exchange of gaseous elemental mercury at polar sunrise, *Environmental Science and Technology*, 42, 5183-5188, 2008.
- 20 Dastoor, A., Ryzhkov, A., Durnford, D., Lehnher, I., Steffen, A., and Morrison, H.: Atmospheric mercury in the Canadian Arctic. Part II: Insight from modeling, *Sci. Total Environ.*, 509-510, 16-27, doi: 10.1016/j.scitotenv.2014.10.112, 2015.
- De Simone, F., Gencarelli, C. N., Hedgecock, I. M., and Pirrone, N.: Global atmospheric cycle of mercury: a model study on the impact of oxidation mechanisms, *Environ. Sci. Ppollut. R.*, 21, 4110-4123, 2014.
- De Simone, F., Cinnirella, S., Gencarelli, C. N., Yang, X., Hedgecock, I. M., and Pirrone, N.: Model study of global mercury deposition from
25 biomass burning, *Environ. Sci. Technol.*, 49, 6712-6721, 2015.
- De Simone, F., Cinnirella, S., Gencarelli, C. N., Carbone, F., Hedgecock, I. M., and Pirrone, N.: Particulate-Phase Mercury Emissions during Biomass Burning and Impact on Resulting Deposition: a Modelling Assessment, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-685, in review, 2016.
- Dibble, T. S., Zelig, M. J., and Mao, H.: Thermodynamics of reactions of ClHg and BrHg radicals with atmospherically abundant free
30 radicals, *Atmos. Chem. Phys.*, 12, 10271-10279, 2012.
- Donohoue, D. L., Bauer, D., Cossairt, B., and Hynes, A. J.: Temperature and Pressure Dependent Rate Coefficients for the Reaction of Hg with Br and the Reaction of Br with Br: A Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence Study, *J. Phys. Chem. A*, 110, 6623-6632, doi: 10.1021/jp054688j, 2006.
- Durnford, D., Dastoor, A., Figueras-Nieto, D., and Ryjkov, A.: Long range transport of mercury to the Arctic and across Canada, *Atmospheric
35 Chemistry and Physics*, 10, 6063-6086, 2010.
- Durnford, D., Dastoor, A., Ryzhkov, A., Poissant, L., Pilote, M., and Figueras-Nieto, D.: How relevant is the deposition of mercury onto snowpacks? – Part 2: A modeling study, *Atmos. Chem. Phys.*, 12, 9251-9274, 10.5194/acp-12-9251-2012, 2012.
- ECMWF: European Centre for Medium-Range Weather Forecasts, <http://www.ecmwf.int/en/forecasts/dataset>, access: 1 August 2016.

- EMEP: The European Monitoring and Evaluation Programme, EBAS database, <http://ebas.nilu.no/Default.aspx>, access: 1 August 2016.
- Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J. F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, 3, 43-67, 10.5194/gmd-3-43-2010, 2010.
- 5 Fitzgerald, W. F., Engstrom, D. R., Mason, R. P., Nater, E. A.: The case for atmospheric mercury contamination in remote areas, *Environ. Sci. Technol.*, 32, 1-7, 1998.
- Gay, D., Schmeltz, D., Prestbo, E., Olson, M., Sharac, T., and Tordon, R.: The atmospheric mercury network: measurement and initial examination of an ongoing atmospheric mercury record across North America, *Atmospheric Chemistry and Physics*, 13, 10 521?10 546, 2013.
- 10 Gbor, P. K., Wen, D., Meng, F., Yang, F., Sloan, J. J.: Sloan Modeling of mercury emission, transport and deposition in North America. *Atmos. Environ.*, 41, 1135-49, 2007.
- Gencarelli, C. N., De Simone, F., Hedgecock, I. M., Sprovieri, F., Pirrone, N.: Development and Application of a Regional-Scale Atmospheric Mercury Model Based on WRF/Chem: A Mediterranean Area Investigation. *Environ. Sci. Pollut. Res.*, 21, 4095-4109. 2014.
- GMOS: Global Mercury Observation System, Spatial Data Infrastructure, <http://www.gmos.eu/sdi/>, access: 1 August 2016.
- 15 Goodsite, M. E., Plane, J. M. C., and Skov, H. A Theoretical Study of the Oxidation of Hg⁰ to HgBr₂ in the Troposphere. *Environ. Sci. Technol.*, 38, 1772-1776, 2004.
- Goodsite, M. E., Plane, J. M. C., and Skov, H.: Correction to A Theoretical Study of the Oxidation of Hg⁰ to HgBr₂ in the Troposphere, *Environ. Sci. Technol.*, 46, 5262, 2012.
- Granier, C., Lamarque, J., Mieville, A., Muller, J., Olivier, J., Orlando, J., Peters, J., Petron, G., Tyndall, G., Wallens, S.: POET, a database of
- 20 surface emissions of ozone precursors, available at <http://www.aero.jussieu.fr/projet/ACCENT/POET.php>, 2005, access: 1 August 2016.
- Gratz, L. E., Ambrose, J. L., Jaffe, D. A., Shah, V., Jaeglé, L., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Selin, N. E., Song, S., Zhou, X., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Campos, T. L., Apel, E., Hornbrook, R., Blake, N. J., Hall, S., Tyndall, G. S., Reeves, M., Stechman, D., Stell, M.: Oxidation of mercury by bromine in the subtropical Pacific free troposphere, *Geophys. Res. Lett.* 42(23), 10,494-10,502, 2015.
- 25 Guentzel, J. L., Landing, W. M., Gill, G. A., and Pollman, C. D.: Processes Influencing Rainfall Deposition of Mercury in Florida, *Environ. Sci. Technol.*, 35, 863-873, 2001.
- Gustin, M. S.: Exchange of Mercury between the Atmosphere and Terrestrial Ecosystems, in: Liu, G., Cai, Y. and N. O'Driscoll (Eds.), *Environmental Chemistry and Toxicology of Mercury*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 423-451, doi: 10.1002/9781118146644.ch13, 2012.
- 30 Gustin, M. S., Weiss-Penzias, P. S., and Peterson, C.: Investigating sources of gaseous oxidized mercury in dry deposition at three sites across Florida, USA, *Atmos. Chem. Phys.*, 12, 9201-9219, doi:10.5194/acp-12-9201-2012, 2012.
- Gustin, M. S., Huang, J., Miller, M. B., Finley, B. D., Call, K., Ambrose, J. L., Peterson, C., Lyman, S. N., Everhart, S., Bauer, D., Remeika, J., Hynes, A., Jaffe, D. A., and Lindberg, S. E.: RAMIX - a step towards understanding mercury atmospheric chemistry and Tekran[®] observations, *Environ. Sci. Technol.*, 47, 7295-7306, 2013.
- 35 Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn K.: Measuring and modeling mercury in the atmosphere: a critical review, *Atmos. Chem. Phys.*, 15, 5697-5713, doi:10.5194/acp-15-5697-2015, 2015.
- Hall, B.: The gas phase oxidation of mercury by ozone. *Water Air Soil Poll.*, 80, 301-315, 1995.

- Hedgecock, I. M. and Pirrone, N.: Chasing quicksilver: Modeling the atmospheric lifetime of Hg-(g)(0) in the marine boundary layer at various latitudes, *Environmental Science and Technology*, 38, 69-76, 2004.
- Holmes, C. D., Jacob D. J., Mason R. P., Jaffe D. A.: Sources and deposition of reactive gaseous mercury in the marine atmosphere, *Atmospheric Environment* 43(14), 2278-2285, 2009.
- 5 Holmes, C. D., Jacob, D. J., Corbitt, E. S., Mao, J., Yang, X., Talbot, R., and Slemr, F.: Global atmospheric model for mercury including oxidation by bromine atoms, *Atmos. Chem. Phys.*, 10, 12037-12057, 2010.
- [Horowitz, H. M., Jacob, D. J., Zhang, Y., Dibble, T. S., Slemr, F., Amos, H. M., Schmidt, J. A., Corbitt, E. S., Marais, E. A., and Sunderland, E. M.: A new mechanism for atmospheric mercury redox chemistry: Implications for the global mercury budget, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-1165, in review, 2017.](#)
- 10 Huang, J. and Gustin, M. S.: Impacts of relative humidity on GOM measurements, *Environ. Sci. Technol.*, 49, 6102-6108, doi:10.1021/acs.est.5b00098, 2015.
- Hynes, A. J., Donohoue, D. L., Goodsite, M. E., and Hedgecock, I. M.: Our current understanding of major chemical and physical processes affecting mercury dynamics in the atmosphere and at the air-water/terrestrial interfaces, in: *Mercury Fate and Transport in the Global Atmosphere*, edited by: Mason, R. and Pirrone, N., Springer, New York, 427-457, 2009.
- 15 Jung, G., Hedgecock, I. M., and Pirrone, N.: ECHMERIT V1.0 - a new global fully coupled mercury-chemistry and transport model, *Geosci. Model Dev.*, 2, 175-195, 10.5194/gmd-2-175-2009, 2009.
- Keeler, G., Gratz, L., and Al-wali, K.: Long-term Atmospheric Mercury Wet Deposition at Underhill, Vermont, *Ecotoxicology*, 14, 71-83, 2005.
- Kos, G., Ryzhkov, A., Dastoor, A., Narayan, J., Steffen, A., Ariya, P. A., and Zhang, L.: Evaluation of discrepancy between measured and
20 modelled oxidized mercury species, *Atmos. Chem. Phys.*, 13, 4839-4863, 2013.
- Krabbenhoft, D. P. and Sunderland, E. M.: Global change and mercury. *Science*, 341, 1457-1458, 2013.
- Lan, X., Talbot, R., Castro, M., Perry, K., and Luke, W.: Seasonal and diurnal variations of atmospheric mercury across the US determined from AMNet monitoring data, *Atmos. Chem. Phys.*, 12, 10569-10582, doi:10.5194/acp-12-10569-2012, 2012.
- Lin, C.-J., Pongprueksa, P., Lindberg, S. E., Pehkonen, S. O., Byun, D. and Jang, C.: Scientific uncertainties in atmospheric mercury models
25 I: Model science evaluation. *Atmospheric Environment* 40, 2911-2928, 2006.
- Lindberg, S. E. and Stratton, W. J.: Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air, *Environ. Sci. Technol.*, 32, 49-57, 1998.
- Lohman, K., Seigneur, C., Gustin, M., Lindberg, S.: Sensitivity of the global atmospheric cycle of mercury to emissions, *Applied Geochemistry*, 23, 454-466, 2008.
- 30 Lyman, S. N., Jaffe, D. A., and Gustin, M. S.: Release of mercury halides from KCl denuders in the presence of ozone, *Atmos. Chem. Phys.*, 10, 8197-8204, doi:10.5194/acp-10-8197-2010, 2010.
- Lyman, S. N. and Jaffe, D. A.: Formation and fate of oxidized mercury in the upper troposphere and lower stratosphere, *Nat. Geosci.*, 5, 114-117, 2011. Jaeglé
- Mahaffey, K.R., Clickner, R. P., and Bodurow, C. C.: Blood organic mercury and dietary mercury intake: National Health and Nutrition
35 Examination Survey, 1999 and 2000, *Environmental Health Perspectives*, 112(5), 562-670, 2004.
- Mason, R. P. and Sheu, G.R.: Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles*, 16(4), 1093, doi:10.1029/2001GB001440, 2002.

- Mason, R.: Mercury emissions from natural processes and their importance in the global mercury cycle, in: Mercury fate and transport in the global atmosphere, in: Pirrone, N. and Mason, R. P. (Eds.): Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements, and Models, Springer, pp. 173-191, 2009.
- Mason, R. P., Choi, A. L., Fitzgerald, W. F., Hammerschmidt, C. R., Lamborg, C. H., Soerensen, A. L., Sunderland, E. M.: Mercury biogeochemical cycling in the ocean and policy implications, *Environmental Research*, 119, 101-117, 2012.
- Munthe, J.: The aqueous oxidation of elemental mercury by ozone, *Atmos. Environ.*, 26, 1461-1468, 1992.
- Nair, U. S., Wu, Y., Walters, J., Jansen, J., Edgerton, E. S.: Diurnal and seasonal variation of mercury species at coastal suburban, urban, and rural sites in the southeastern United States. *Atmos. Environ.* 47, 499-508, 2012.
- NADP/MDN: National Atmospheric Deposition Program (NRSP-3), Mercury Deposition Network (MDN), NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820, <http://nadp.sws.uiuc.edu/MDN/>, access: 1 August 2016.
- NAtChem: The Canadian National Atmospheric Chemistry Database And Analysis System. <http://www.ec.gc.ca/natchem/>, access: 1 August 2016.
- Obrist, D., Tas, E., Peleg, M., Matveev, V., Faïn, X., Asaf, D., Luria, M.: Bromine-induced oxidation of mercury in the mid-latitude atmosphere. *Nature Geoscience* 4, 22-26, 2011.
- Pan, L., Lin, C.-J., Carmichael, G. R., Streets, D. G., Tang, Y., Woo, J.-H., Shetty, S. K., Chu, H.-W., Ho, T. C., Friedli, H. R.: Study of Atmospheric Mercury Budget in East Asia Using STEM-Hg Modeling System. *Sci. Total Environ.*, 408, 3277-3291, 2010.
- Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J., Yang, X., Pyle, J. A., Theys, N., and Van Roozendaal, M.: Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury, *Atmos. Chem. Phys.*, 12, 6723-6740, 2012.
- Peters, J.A.H.W. and Olivier, J.G.J.: EDGAR3/POET ENUSSUIBS; 1997 emissions and scenarios for 1995-2020; technical background information on global and regional sectoral emissions, Report no. 773301003, RIVM, Bilthoven, 2003.
- Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R. B., Friedli, H. R., Leaner, J., Mason, R., Mukherjee, A. B., Stracher, G. B., Streets, D. G., and Telmer, K.: Global mercury emissions to the atmosphere from anthropogenic and natural sources, *Atmos. Chem. Phys.*, 10, 5951-5964, doi:10.5194/acp-10-5951-2010, 2010.
- Platt, U. and Janssen, C.: Observation and role of the free radicals NO₃, ClO, BrO and IO in the troposphere, *Faraday Discuss.*, 100, 175-198, 1995.
- Poissant, L., Pilote, M., Beauvais, C., Constant, P., Zhang, H. H.: A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hgp) in southern Quebec, Canada, *Atmos. Environ.*, 39, 1275-1287, doi:10.1016/j.atmosenv.2004.11.007, 2005.
- Prestbo, E. M. and Gay, D. A.: Wet deposition of mercury in the U.S. and Canada, 1996-2005: Results and analysis of the NADP mercury deposition network (MDN), *Atmospheric Environment*, 43, 4223-4233, 2009.
- Qureshi, A., Macleod, M., Sunderland, E., Hungerbühler, K.: Exchange of elemental mercury between the oceans and the atmosphere, in: Liu, G., Cai, Y. and N. O'Driscoll (Eds.), *Environmental Chemistry and Toxicology of Mercury*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 389-421, doi: 10.1002/9781118146644.ch12, 2012.
- Rutter, A. P., Shakya, K. M., Lehr, R., Schauer, J. J., Griffin, R. J.: Oxidation of gaseous elemental mercury in the presence of secondary organic aerosols. *Atmospheric Environment* 59, 86-92, 2012.
- Sather, M. E., Mukerjee, S., Smith, L., Mathew, J., Jackson, C., Callison, R., Scrapper, L., Hathcoat, A., Adam, J., Keese, D., Ketcher, P., Brunette, R., Calstrom, J., and Van der Jagt, G.: Gaseous oxidized mercury dry deposition measurements in the Four Corners Area and Eastern Oklahoma, USA, *Atmos. Pollut. Res.*, 4, 168-180, 2013.

- Schroeder, W. H. and Munthe, J.: Atmospheric mercury – an overview, *Atmos. Environ.*, 32, 809–822, 1998.
- Seigneur, C., Karamchandani, P., Lohman, K., Vijayaraghavan, K., and Shia, R.-L.: Multiscale modeling of the atmospheric fate and transport of mercury, *J. Geophys. Res.*, 106, 27795-27809, 2001.
- Seigneur, C., Vijayaraghavan, K., and Lohman, K.: Atmospheric mercury chemistry: Sensitivity of global model simulations to chemical reactions, *J. Geophys. Res.*, 111, D22306, doi:10.1029/2005JD006780, 2006.
- Seigneur, C., and Lohman, K.: Effect of bromine chemistry on the atmospheric mercury cycle, *J. Geophys. Res.*, 113, D23309, doi:10.1029/2008JD010262, 2008.
- Selin, N. E. and Jacob, D. J.: Seasonal and spatial patterns of mercury wet deposition in the United States: Constraints on the contribution from North American anthropogenic sources, *Atmos. Environ.*, 42, 5193-5204, doi:10.1016/j.atmosenv.2008.02.069, 2008.
- 10 Selin, N. E., Jacob, D. J., Yantosca, R. M., Strode, S., Jaeglé, L., and Sunderland, E. M.: Global 3-D land-ocean-atmosphere model for mercury: present-day versus preindustrial cycles and anthropogenic enrichment factors for deposition, *Global biogeochemical cycles*, 22, doi:10.1029/2007GB003040, 2008
- Selin, N. E.: Global biogeochemical cycling of mercury: A review, *Annu. Rev. Environ. Resour.*, 34, 43-63, 2009.
- Shah, V., Jaeglé, L., Gratz, L. E., Ambrose, J. L., Jaffe, D. A., Selin, N. E., Song, S., Campos, T. L., Flocke, F. M., Reeves, M., Stechman, D., Stell, M., Festa, J., Stutz, J., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Tyndall, G. S., Apel, E. C., Hornbrook, R. S., Hills, A. J., Riemer, D. D., Blake, N. J., Cantrell, C. A., and Mauldin III, R. L.: Origin of oxidized mercury in the summertime free troposphere over the southeastern US. *Atmos. Chem. Phys.*, 16, 1511-1530, doi:10.5194/acp-16-1511-2016, 2016.
- Shetty, S. K., Lin, C.-J., Streets, D. G., Jang, C.: Model estimate of mercury emission from natural sources in East Asia, *Atmos. Environ.*, 42, 8674-8685, 2008.
- 20 Sigler, J. M., Mao, H., and Talbot, R.: Gaseous elemental and reactive mercury in Southern New Hampshire, *Atmos. Chem. Phys.*, 9, 1929-1942, doi:10.5194/acp-9-1929-2009, 2009.
- Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O., Barker, D. M., Wang, W., Powers, J. G.: A description of the Advanced Research WRF Version 2. NCAR/TN-468+STR.. NCAR Technical Note. Boulder, CO, USA, 2007.
- Slemr, F., Angot, H., Dommergue, A., Magand, O., Barret, M., Weigelt, A., Ebinghaus, R., Brunke, E.-G., Pfaffhuber, K., Edwards, G., Howard D., Powell J., Keywood, M., and Wang, F.: Comparison of mercury concentrations measured at several sites in the Southern Hemisphere, *Atmospheric Chemistry and Physics*, 15, 3125–3133, doi:10.5194/acp-15-3125-2015, 2015.
- 25 Snider, G., Raofie, F., and Ariya, P. A. A.: Effects of relative humidity and CO(g) on the O₃-initiated oxidation reaction of Hg⁰(g): Kinetic & product studies, *Phys. Chem. Chem. Phys.*, 10, 5616-5623, doi:10.1039/B801226A, 2008.
- Soerensen, A. L., Sunderland, E. M., Holmes, C. D., Jacob, D. J., Yantosca, R. M., Skov, H., Christensen, J. H., Strode, S. A., and Mason, R. P.: An improved global model for air-sea exchange of mercury: high concentrations over the north atlantic, *Environmental Science and Technology*, 44, 8574-8580, 2010.
- 30 Sommar, J., Gårdfeldt, K., Strömberg, D., and Feng, X.: A kinetic study of the gas-phase reaction between the hydroxyl radical and atomic mercury, *Atmos. Environ.*, 35, 3049-3054, 2001.
- Song, S., Selin, N. E., Soerensen, A. L., Angot, H., Artz, R., Brooks, S., Brunke, E.-G., Conley, G., Dommergue, A., Ebinghaus, R., Holsen, T. M., Jaffe, D. A., Kang, D., Kelley, P., Luke, W. T., Magand, O., Marumoto, K., Pfaffhuber, K. A., Ren, X., Sheu, G.-R., Slemr, F., Warneke, T., Weigelt, A., Weiss-Penzias, P., Wip, D. C., and Zhang, Q.: Top-down constraints on atmospheric mercury emissions and implications for global biogeochemical cycling, *Atmos. Chem. Phys.*, 15, 7103-7125, 2015.
- 35

- Sprovieri, F., Pirrone, N., Bencardino, M., D'Amore, F., Carbone, F., Cinnirella, S., Mannarino, V., Landis, M., Ebinghaus, R., Weigelt, A., Brunke, E.-G., Labuschagne, C., Martin, L., Munthe, J., Wängberg, I., Artaxo, P., Morais, F., Cairns, W., Barbante, C., Diéguez, M. C., Garcia, P. E., Dommergue, A., Angot, H., Magand, O., Skov, H., Horvat, M., Kotnik, J., Read, K. A., Neves, L. M., Gawlik, B. M., Sena, F., Mashyanov, N., Obolkin, V. A., Wip, D., Feng, X., Zhang, H., Fu, X., Ramachandran, R., Cossa, D., Knoery, J., Maruszczak, N., Nerentorp, M., and Norström, C.: Atmospheric Mercury Concentrations observed at ground-based monitoring sites globally distributed in the framework of the GMOS network, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-466, 2016.
- Sprovieri, F., Pirrone, N., Bencardino, M., D'Amore, F., Angot, H., Barbante, C., Brunke, E.-G., Arcega-Cabrera, F., Cairns, W., Comero, S., Diéguez, M. D. C., Dommergue, A., Ebinghaus, R., Feng, X. B., Fu, X., Garcia, P. E., Gawlik, B. M., Hageström, U., Hansson, K., Horvat, M., Kotnik, J., Labuschagne, C., Magand, O., Martin, L., Mashyanov, N., Mkololo, T., Munthe, J., Obolkin, V., Islas, M. R., Sena, F., Somerset, V., Spandow, P., Vardè, M., Walters, C., Wängberg, I., Weigelt, A., Yang, X., and Zhang, H.: Five-year records of Total Mercury Deposition flux at GMOS sites in the Northern and Southern Hemispheres, *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-517, in review, 2016.
- Steffen A., Lehnerr I., Cole A., Ariya P., Dastoor A., Durnford D., Kirk J., Pilote M.: Atmospheric mercury in the Canadian Arctic. Part I: A review of recent field measurements, *Science of the Total Environment* 509-510, 3-15, doi:10.1016/j.scitotenv.2014.10.109, 2015.
- Subir, M., Ariya, P. A. and Dastoor, A. P.: A review of uncertainties in atmospheric modeling of mercury chemistry I. Uncertainties in existing kinetic parameters – Fundamental limitations and the importance of heterogeneous chemistry. *Atmospheric Environment* 45, 5664-5676, 2011.
- Subir, M., Ariya, P. A., and Dastoor, A. P.: A review of the sources of uncertainties in atmospheric mercury modeling II. Mercury surface and heterogeneous chemistry – A missing link. *Atmospheric Environment* 46, 1-10, 2012.
- Sunderland, E., Corbitt, E., Cossa, D., Evers, D., Friedli, H., Krabbenhoft, D., Levin, L., Pirrone, N., Rice, G.: Impacts of Intercontinental Mercury Transport on Human & Ecological Health, in: Pirrone, N. and T. Keating, *Hemispheric Transport of Air Pollution 2010, Part B: Mercury*, Air Pollution Studies No. 16. United Nations, 97-144, 2010.
- Swartzendruber, P. and Jaffe, D.: Sources and Transport: A Global Issue, in: Bank M. S. (Ed.) *Mercury in the environment*, University of California Press, Berkeley and Los Angeles, California, 2012.
- Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009, *Atmos. Chem. Phys.*, 12, 5447-5481, doi:10.5194/acp-12-5447-2012, 2012.
- Tossell, J. A.: Calculation of the energetics for oxidation of gas-phase elemental Hg by Br and BrO, *J. Phys. Chem. A*, 107, 7804-7808, 2003.
- Travnikov, O.: Contribution of the intercontinental atmospheric transport to mercury pollution in the Northern Hemisphere. *Atmos. Environ.* 39, 7541-7548, 2005.
- Travnikov, O. and Ilyin, I.: The EMEP/MSCE Mercury Modeling System, in: Pirrone, N. and Mason, R. P. (Eds.): *Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements, and Models*, Springer, pp. 571-587, 2009.
- Travnikov, O., Jonson, J. E., Andersen, A. S., Gauss, M., Gusev, A., Rozovskaya O., Simpson D., Sokovyh V., Valiyaveetil, S., and Wind, P.: Development of the EMEP global modelling framework: Progress report. EMEP/MSCE Technical Report 7/2009, Meteorological Synthesizing Centre - East of EMEP, Moscow, 44 pp., available: <http://www.msceast.org/index.php/publications/reports>, 2009.
- Travnikov, O., Lin C. J., Dastoor, A., Bullock, O. R., Hedgecock, I., Holmes, C., Ilyin, I., Jaegle, L., Jung, G., Pan, L., Pongprueksa, P., Ryzhkov, A., Seigneur, C., and Skov, H.: Global and Regional Modeling, in: Pirrone, N. and T. Keating, *Hemispheric Transport of Air Pollution 2010, Part B: Mercury*, Air Pollution Studies No. 16. United Nations, 97-144, 2010.

- Travnikov, O.: Atmospheric transport of mercury, in: Liu, G., Cai, Y. and N. O'Driscoll (Eds.), Environmental Chemistry and Toxicology of Mercury, John Wiley & Sons, Inc., Hoboken, NJ, USA, 331-365, doi: 10.1002/9781118146644.ch10, 2012.
- Van Loon, L., Mader, E., Scott, S. L.: Reduction of the aqueous mercuric ion by sulfite: UV spectrum of HgSO₃ and its intramolecular redox reaction. *J. Phys. Chem. A*, 104, 1621-1626, 2000.
- 5 Wang, X., Lin, C.-J., Feng, X.: Sensitivity analysis of an updated bidirectional air-surface exchange model for mercury vapor, *Atmos. Chem. Phys.*, 14, 6273-6287, 2014.
- Wang, X., Lin, C.-J., Yuan, W., Sommar, J., Zhu, W., and Feng, X.: Emission-dominated gas exchange of elemental mercury vapor over natural surfaces in China, *Atmos. Chem. Phys.*, 16, 11125-11143, doi:10.5194/acp-16-11125-2016, 2016.
- Weigelt, A., Temme, C., Bieber, E., Schwerin, A., Schuetze, M., Ebinghaus, R., and Kock H. H.: Measurements of atmospheric mercury species at a German rural background site from 2009 to 2011 - methods and results, *Environ. Chem.*, 10, 102-110, doi:/10.1071/EN12107, 2013.
- 10 Weiss-Penzias, P., Amos, H. M., Selin, N. E., Gustin, M. S., Jaffe, D. A., Obrist, D., Sheu, G.-R., and Giang, A.: Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites, *Atmos. Chem. Phys.*, 15, 1161-1173, doi:10.5194/acp-15-1161-2015, 2015.
- 15 Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, 23, 1293-1304, doi:10.1016/0004-6981(89)90153-4, 1989.
- Wesely, M. L. and Hicks, B.B.: A review of the current status of knowledge on dry deposition. *Atmos. Environ.* 34, 2261-22, 2000.
- Wright, G., Miller, M. B., Weiss-Penzias, P., and Gustin, M.: Investigation of mercury deposition and potential sources at six sites from the Pacific Coast to the Great Basin, USA, *Sci. Total Environ.*, 470-471C, 1099-1113, doi:10.1016/j.scitotenv.2013.10.071, 2014.
- 20 Yang, X., Cox, R., Warwick, N., Pyle, J., Carver, G., O'Connor, F., Savage, N.: Tropospheric bromine chemistry and its impacts on ozone: A model study, *J. Geophys. Res.*, 110, D23311, 2005.
- Yang, X., Pyle, J. A., Cox, R. A., Theys, N., and Van Roozendaal, M.: Snow-sourced bromine and its implications for polar tropospheric ozone, *Atmos. Chem. Phys.*, 10, 7763-7773, doi:10.5194/acp-10-7763-2010, 2010.
- Zhang, L.: A size-segregated particle dry deposition scheme for an atmospheric aerosol module, *Atmos. Environ.*, 35, 549-560, doi:10.1016/S1352-2310(00)00326-5, 2001.
- 25 Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air quality models, *Atmos. Chem. Phys.*, 3, 1777-1804, doi:10.5194/acpd-3-1777-2003, 2003.
- Zhang, L., Wright, L. P., Blanchard, P. A: Review of Current Knowledge Concerning Dry Deposition of Atmospheric Mercury, *Atmos. Environ.*, 43, 5853-5864, 2009.
- 30 Zhang, Y., Jaeglé L., van Donkelaar, A., Martin, R. V., Holmes, C. D., Amos, H. M., Wang, Q., Jacob, D. J., Talbot, R., Artz, R., Holson, T. M., Felton, D., Miller, E. K., Perry, K. D., Schmeltz, D., Steffen, A., and Tordon, R.: Nested-grid simulation of mercury over North America, *Atmos. Chem. Phys.*, 6095-6111, doi:10.5194/acp-12-6095-2012, 2012.

~~Spatial correlation coefficient (a), relative bias (b) and temporal correlation coefficient (c) of simulated and observed GEM air concentration for different model experiments.~~

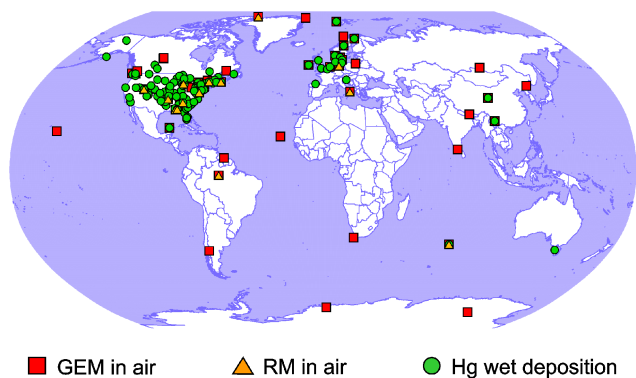


Figure 1. Location of measurement sites used in the study

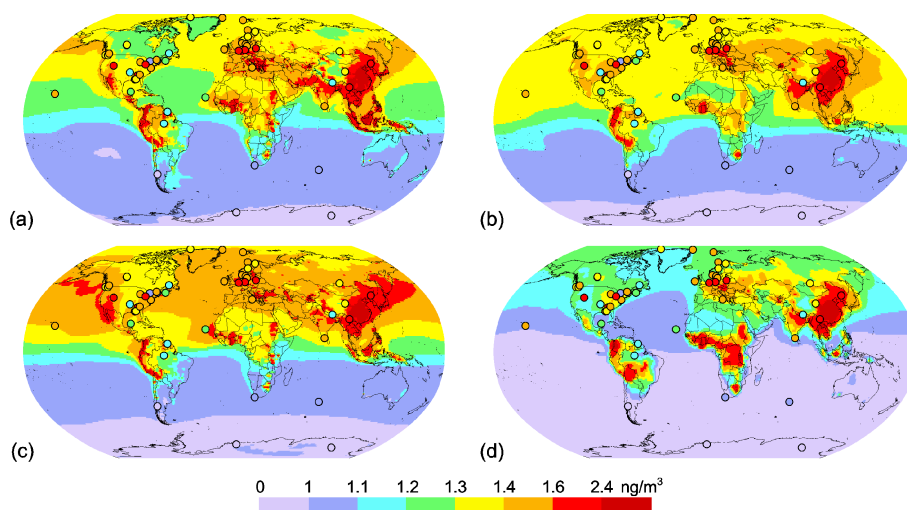


Figure 2. Spatial distribution of GEM air concentration in 2013 simulated according to the BASE case by four global models: (a) – GLEMOS; (b) – GEOS-Chem; (c) – GEM-MACH-Hg; (d) – ECHMERIT. Circles show observed values in the same colour scale.

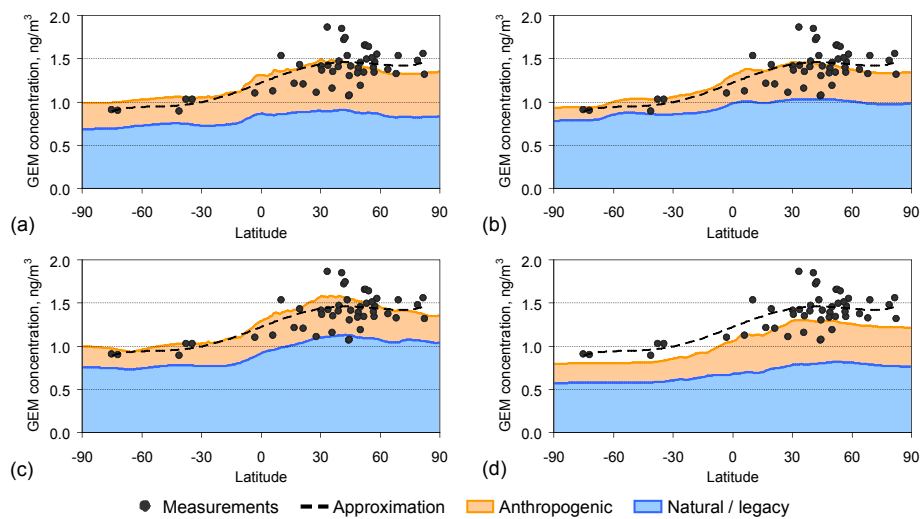


Figure 3. Global zonal-mean distribution of GEM air concentration in 2013 simulated by four models: (a) – GLEMOS; (b) – GEOS-Chem; (c) – GEM-MACH-Hg; (d) – ECHMERIT. Black dots are the same observations as in Fig. 2 and dotted line is a polynomial approximation

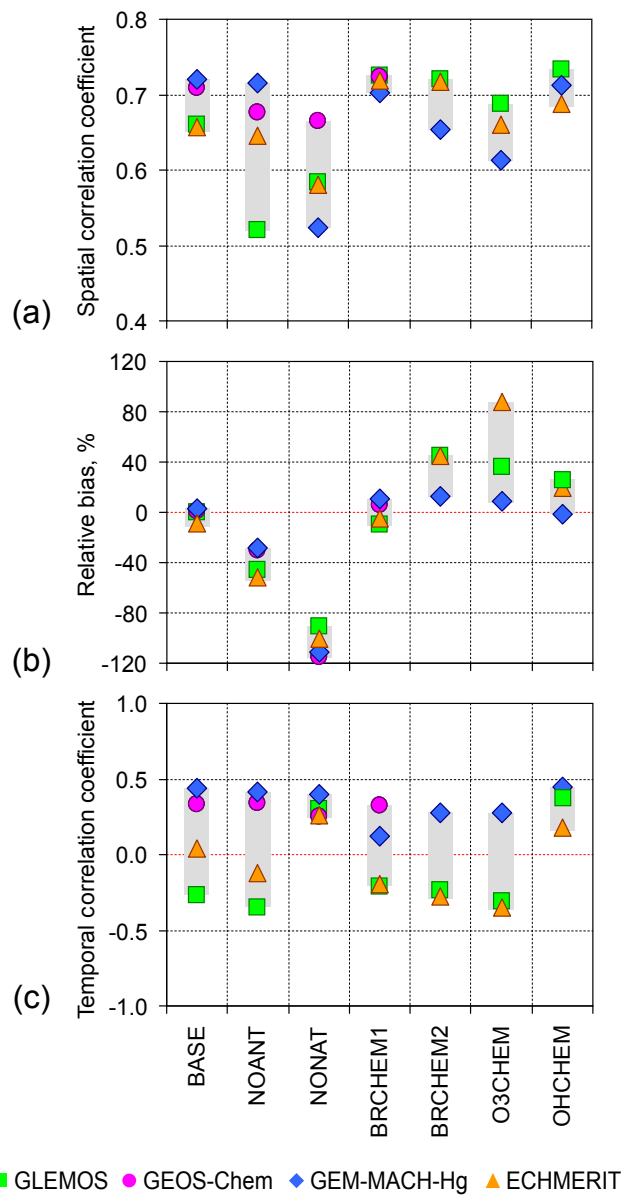


Figure 4. Spatial correlation coefficient (a), relative bias (b) and temporal correlation coefficient (c) of simulated and observed GEM air concentration for different model experiments.

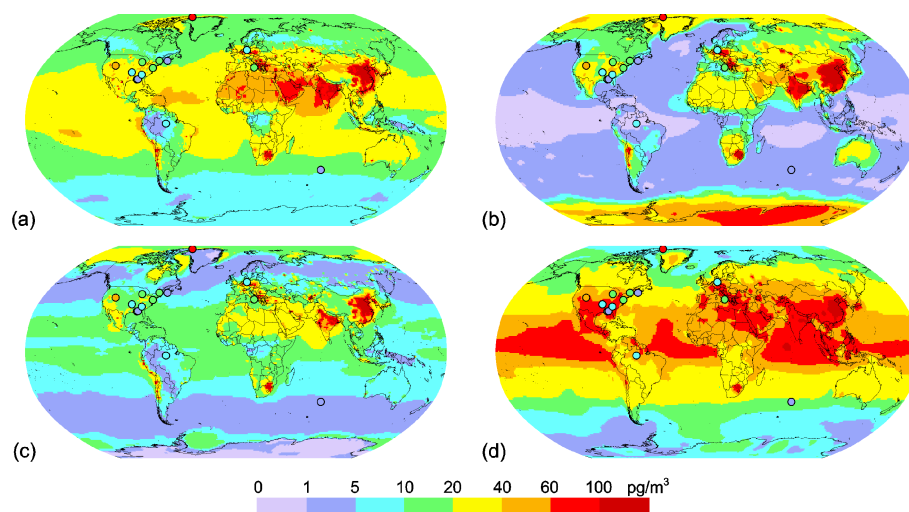


Figure 5. Spatial distribution of annual mean RM air concentration in 2013 simulated according to the BASE case by four global models: (a) – GLEMOS; (b) – GEOS-Chem; (c) – GEM-MACH-Hg; (d) – ECHMERIT. Circles show observed values in the same colour scale.

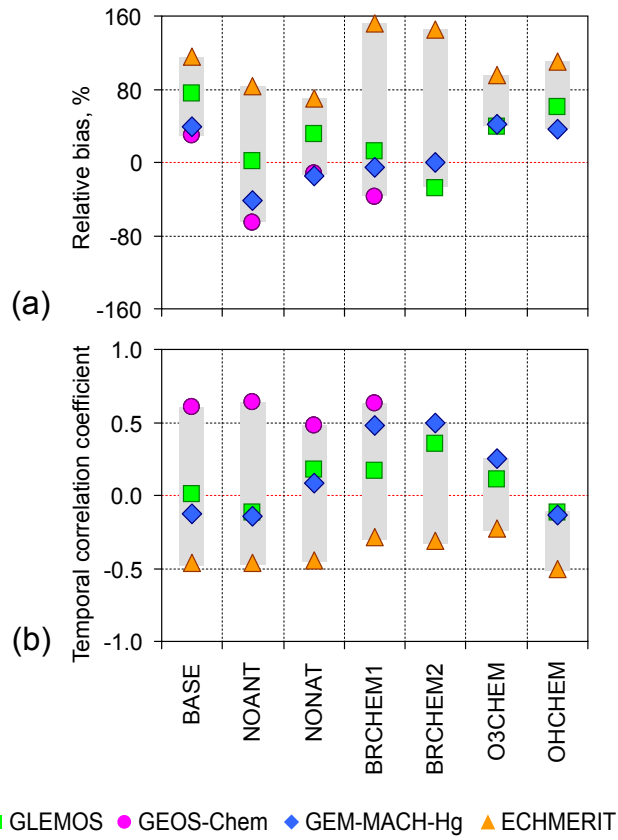


Figure 6. Relative bias (a) and spatial correlation coefficient (b) of simulated and observed annual mean RM air concentration for different model experiments.

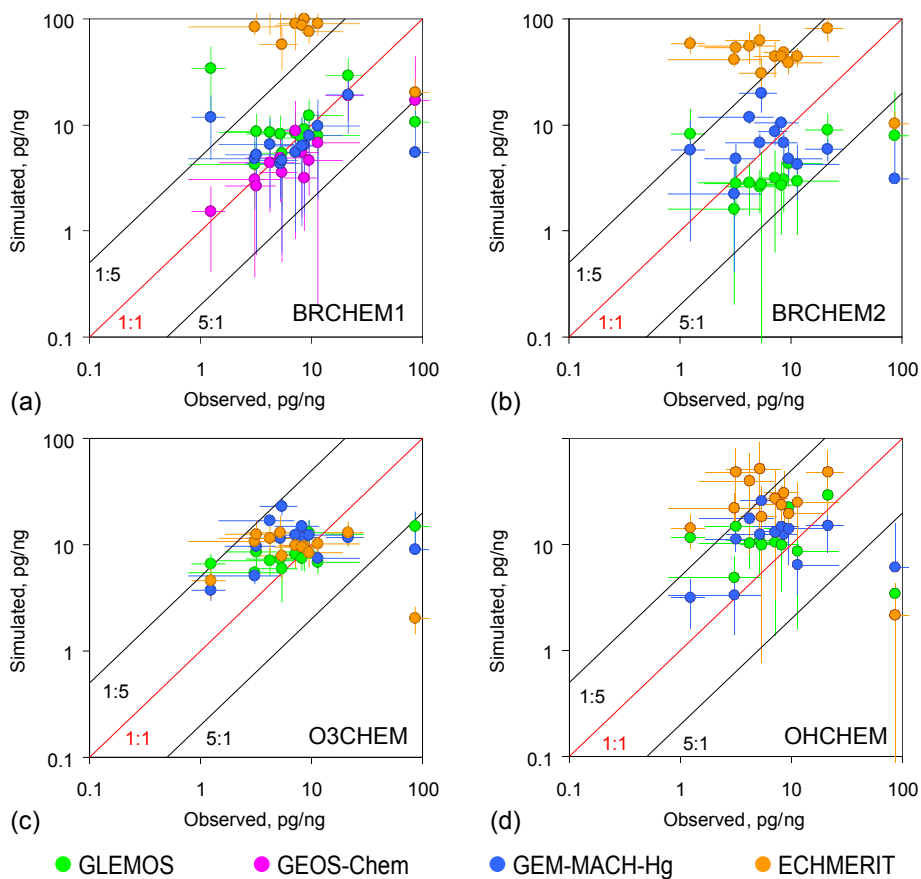


Figure 7. Scatter plots of simulated vs. observed ratios of annual mean RM concentration to GEM concentration in 2013 for different model experiments: (a) – BrCHEM1; (b) – BrCHEM2; (c) – O3CHEM; (d) – OHCHEM. Whiskers show standard deviation of monthly mean simulated and observed values. Dotted red line depicts the 1:1 ratio; dotted black lines show deviation by a factor of 5

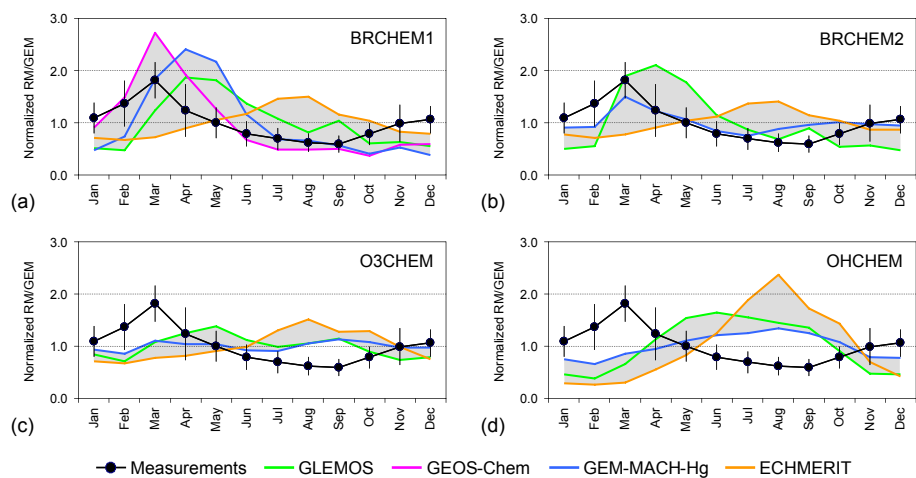


Figure 8. Normalized seasonal variation of monthly ratio of annual mean RM concentration to GEM concentration. Black line with dots shows observations averaged over selected sites (whiskers are standard deviation). Colored lines present model simulations averaged over the same [sites](#) for different model experiments: (a) – BrCHEM1; (b) – BrCHEM2; (c) – O3CHEM; (d) – OHCHEM

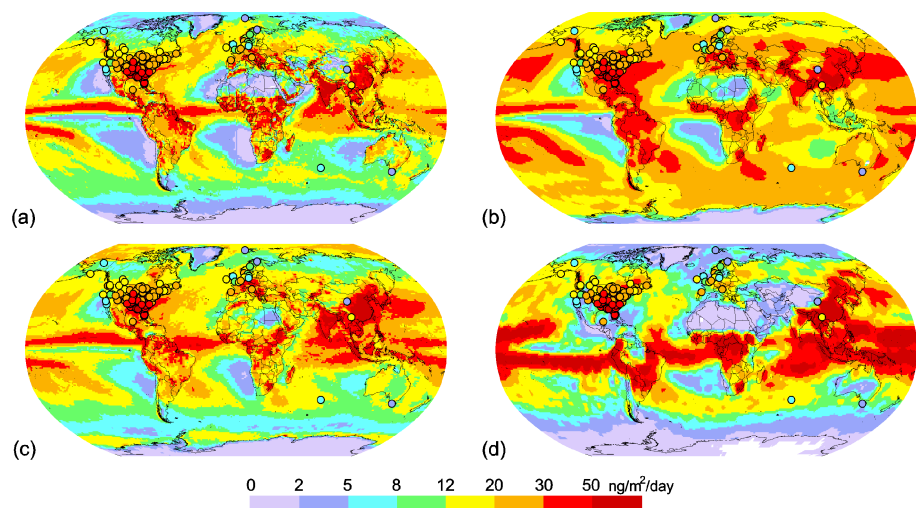


Figure 9. Spatial distribution of wet deposition flux in 2013 simulated according to the BASE case by four global models: (a) – GLEMOS; (b) – GEOS-Chem; (c) – GEM-MACH-Hg; (d) – ECHMERIT. Circles show observed values in the same colour scale.

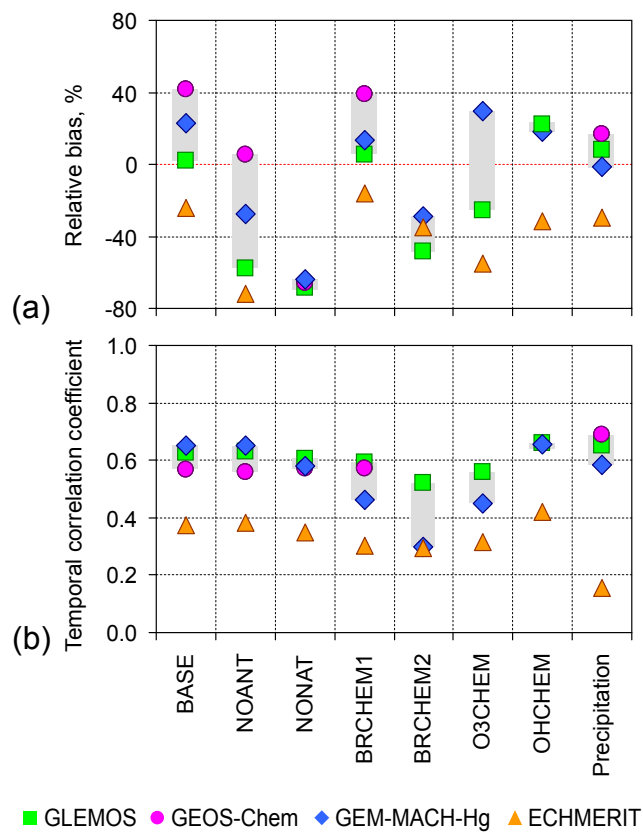


Figure 10. Relative bias (a) and spatial correlation coefficient (b) of simulated and observed annual mean wet deposition flux for different model experiments.

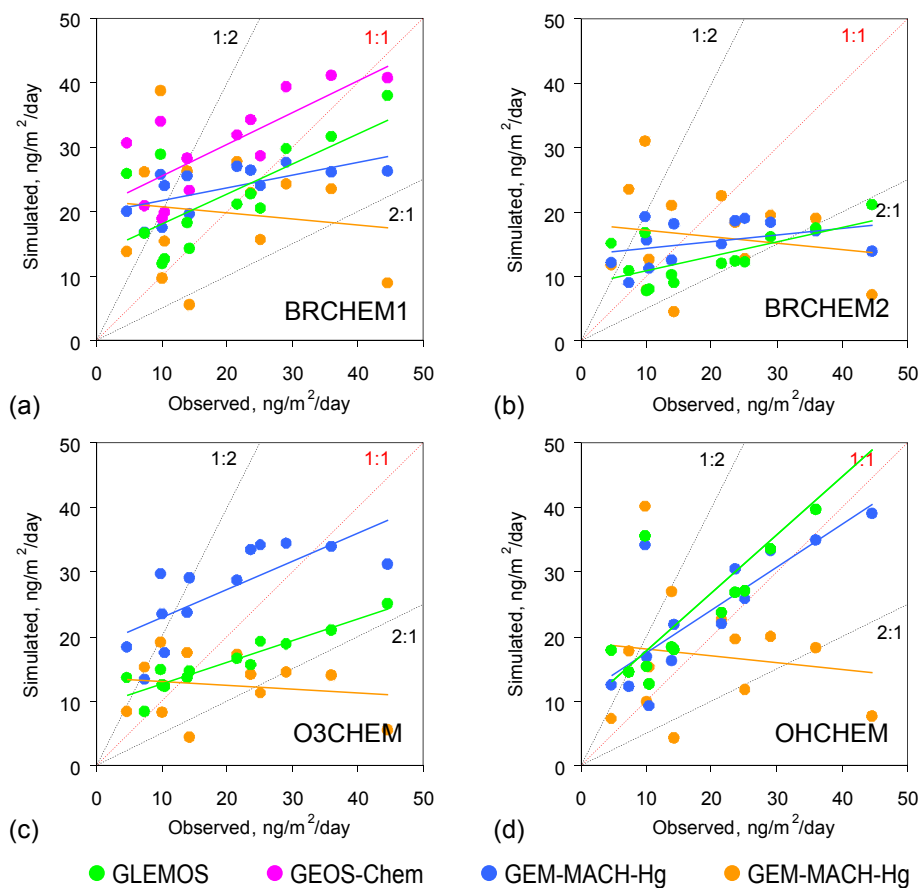


Figure 11. Scatter plots of simulated vs. observed annual mean wet deposition flux in 2013 averaged over different territorial groups of sites (see Table S3 in the Supplement) for different model experiments: (a) – BrCHEM1; (b) – BrCHEM2; (c) – O3CHEM; (d) – OHCHEM. Solid lines depict linear approximation. Dotted red line depicts the 1:1 ratio; dotted black lines show deviation by a factor of 2.

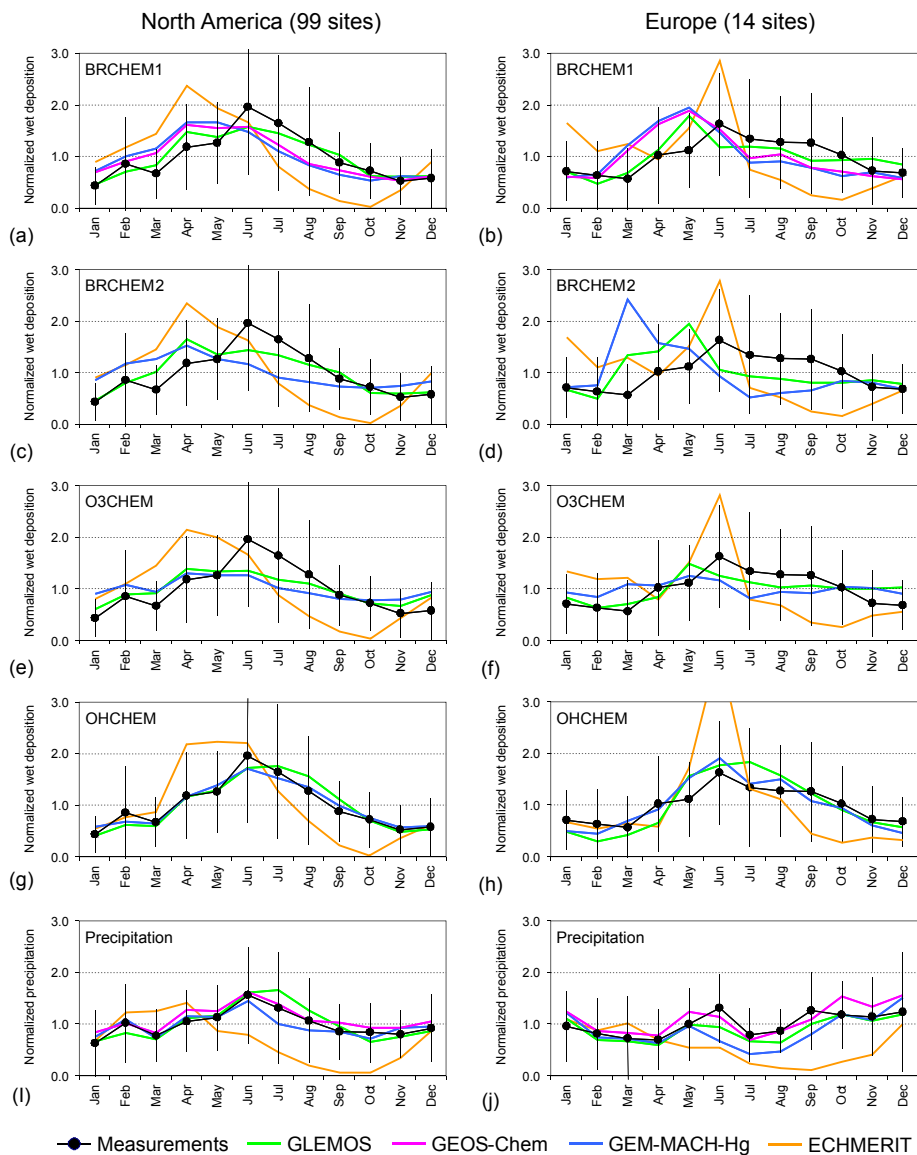


Figure 12. Normalized seasonal variation of monthly mean wet deposition flux in North America (left column) and Europe (right column). Black line with dots shows observations averaged over all sites in the regions (whiskers are standard deviation). Colored lines present model simulations averaged over the same sites for different model experiments: (a,b) – BrCHEM1; (c,d) – BrCHEM2; (e,f) – O3CHEM; (g,h) – OHCHEM. Seasonal variations of precipitation amount in North America and Europe are also shown in panels (i) and (j), respectively.

Table 1. Characteristics of the participating global chemistry transport models.

Model	GLEMOS	GEOS-Chem	GEM-MACH-Hg	ECHMERIT
Spatial resolution				
Horizontal	1° × 1°	2.5° × 2°	1° × 1°	T42 (~ 2.8° × 2.8°)
Vertical	20 levels, top 10 hPa	47 levels, top 0.01 hPa	58 levels, top 7 hPa	19 levels, top 10 hPa
Driving meteorology				
Data support type	off-line	off-line	on-line	on-line
Meteorological driver	WRF / ECMWF	GEOS-FP	GEM	ECHAM5
Anthropogenic emission				
Global emission, t/y	1875	1875	1875	1875
Average speciation (base case)				
GEM : GOM : PBM	81 : 15 : 4	81 : 19 : 0 ^(a)	96 : 3 : 1	81 : 15 : 4
Natural and re-emission				
Definition	prescribed / dynamic ^(b)	prescribed / dynamic ^(c)	prescribed / dynamic ^(d)	prescribed / dynamic ^(e)
Global emission, t/y (base case)	3995	5070	3660	8600
Gaseous chemistry (base-case reactions are in bold)				
Reaction rates ^(f) , cm ³ molec ⁻¹ s ⁻¹				
Hg ⁰ + Br → HgBr	3.7 × 10 ^{-13(g)}	3.7 × 10^{-13(g)}	3.7 × 10 ^{-13(g)}	3.7 × 10 ^{-13(g)}
HgBr → Hg ⁰ + Br	9.4 × 10 ^{-2s^{-1(h)}}	9.4 × 10^{-2s^{-1(h)}}	1.7 × 10 ^{-1s⁻¹⁽ⁱ⁾}	9.4 × 10 ^{-2s^{-1(h)}}
HgBr + Br → Hg ⁰ + Br ₂	3.9 × 10 ^{-11(j)}	3.9 × 10^{-11(j)}	—	—
HgBr + Y → HgBrY, Y = Br, OH	2.5 × 10 ^{-10(k)}	2.5 × 10^{-10(k)}	2.5 × 10 ^{-10(k)}	2.5 × 10 ^{-10(k)}
Hg ⁰ + O ₃ → Hg(II)	3.0 × 10^{-20(l)}	—	3.0 × 10 ^{-20(l)}	3.0 × 10^{-20(l)}
Hg ⁰ + OH → Hg(II)	(0.9–8.7) × 10^{-14(m)}	—	3.0 × 10⁻¹⁴⁽ⁿ⁾	8.7 × 10^{-14(o)}
Aqueous chemistry (in cloud water)				
Oxidation agents	O ₃ , HOCl/OCl ⁻	OH, —	—	O ₃ , OH
Reduction agents	SO ₃ ⁼	—	—	—

Table 1. Continued.

Model	GLEMOS	GEOS-Chem	GEM-MACH-Hg	ECHMERIT
Reference	Travnikov and Ilyin (2009); Travnikov et al. (2009)	Holmes et al. (2010); Amos et al. (2012); Song et al. (2015)	Durnford et al. (2012); Kos et al. (2013); Dator et al. (2015)	Jung et al. (2009); De Simone et al. (2014)

^(a) Dynamic gas-particle partitioning of RM in the atmosphere according to Amos et al. (2012); ^(b) Prescribed fluxes from terrestrial and aquatic surfaces as a function of temperature and solar radiation, dynamic re-emission from snow; ^(c) Prescribed fluxes from terrestrial surfaces as a function of temperature and solar radiation, dynamic fluxes from aquatic surfaces based on multi-media modelling; ^(d) Prescribed fluxes from terrestrial surfaces as a function of solar radiation and leaf area index, dynamic re-emission from snow and aquatic surfaces; ^(e) Prescribed fluxes from terrestrial surfaces as a function of temperature and solar radiation, dynamically calculated ocean emissions; ^(f) Temperature and pressure dependence applied to most reactions, the reaction rates are given at 298 K and 1 atm; ^(g) Donohoue et al. (2006); ^(h) Goodsite et al. (2012); ⁽ⁱ⁾ Dibble et al. (2012); ^(j) Balabanov et al. (2005); ^(k) Goodsite et al. (2004); ^(l) Hall (1995); ^(m) Sommar et al. (2001) scaled down by a factor 0.1 in the cloud environment and below clouds to account for reduction of photochemical activity (Seigneur et al., 2001); ⁽ⁿ⁾ Sommar et al. (2001) scaled down by a factor 0.34 to take into account possible dissociation/reduction reactions; ^(o) Sommar et al. (2001); ^(p) Parrella et al. (2012); ^(q) Yang et al. (2005, 2010); ^(r) Emmons et al. (2010).

Table 2. Specifications of model experiments.

Code	Anthropogenic emissions	Gas-phase chemistry	Comment
BASE	UNEP2010 ^(a)	Model standard configuration	Base run
NoANT	No emission	Model standard configuration	Effect of anthropogenic emissions
NoNAT ^(b)	—	—	Effect of natural/secondary emissions
BrCHEM1	UNEP2010, all emissions as GEM ^(c)	GEM oxidation by Br	Br dataset from GEOS-Chem ^(d)
BrCHEM2	UNEP2010, all emissions as GEM	GEM oxidation by Br	Br dataset from p-TOMCAT ^(e)
O3CHEM	UNEP2010, all emissions as GEM	GEM oxidation by O ₃	O ₃ dataset from MOZART ^(f)
OHCHEM	UNEP2010, all emissions as GEM	GEM oxidation by OH	OH dataset from MOZART ^(f)

^(a) AMAP/UNEP (2013b); ^(b) Virtual experiment obtained by subtraction of NoANT results from the BASE case; ^(c) All GOM and PBM emissions summed to GEM to keep constant total Hg emissions; ^(d) Parrella et al. (2012); ^(e) Yang et al. (2005, 2010); ^(f) Emmons et al. (2010).