

Ian Hedgecock review

Thank you for your thoughtful comments. Including your suggested revisions has improved the quality of the manuscript. Our responses are indicated below in blue text.

This article describes recent changes to the chemical mechanism used in the GEOSChem model to simulate the atmospheric mercury cycle. The new mechanism includes the recent theoretical results from Dibble et al. concerning the reaction of the unstable HgBr* intermediate with HO₂ and NO₂, and also aqueous phase photoreduction of organic Hg complexes ‘tuned’ to match observed mean total gaseous mercury concentrations and variability. The results are encouraging and suggest that this mechanism may well be a major step forward in the simulation of the atmospheric mercury cycle and provides some interesting new ideas for future measurement campaigns.

I just have a few of comments/suggestions to make. In the discussion of the unlikelihood of O₃ or OH being atmospheric Hg oxidants (Introduction, line 14 onwards), it may be appropriate to point out that homogeneous reactions are being discussed and that the possibility remains that heterogeneous reactions are possible, see Ariya et al (Chem. Rev. 2015, 115, 3760–3802, DOI: 10.1021/cr500667e).

We add a sentence (Page 2, lines 19-20):

“OH and ozone could still potentially be important oxidants on aerosols (Ariya et al., 2015).”

In the General Description of the GEOS-Chem model (section 3.1) the gas-particle partitioning of Hg is described as being a local thermodynamic equilibrium dependent on aerosol mass concentration and temperature. This is an approximation as aerosol surface area and composition must also play a role in the partitioning, for instance one would expect soot particles to adsorb Hg rather effectively and be less sensitive to changes in temperature. This should be pointed out. We clarify the description of the gas-particle partitioning and add a sentence (page 4, lines 26-30):

“Gas-particle partitioning of Hg^{II} is parameterized following Amos et al. (2012) as a thermodynamic equilibrium function of local temperature and mass concentration of fine particulate matter (PM_{2.5}). This parameterization is based on observed relationships between the gas/particle Hg^{II} concentration ratio and PM_{2.5}, and does not resolve effects from particle composition or surface area.”

In section 3.2 the sources of radical, oxidant and organic aerosol concentrations are mentioned, but there is no mention of how these modelled concentrations compared to available measurement data, ground based or otherwise. The Schmidt et al. paper describes the comparison of BrO with satellite data but some mention of how NO₂ and organic aerosol compare or references to where such comparisons may be found would be useful. I see the difficulty in comparing modelled HO₂. However some comparison is important as the oxidation of Hg in the model is dominated by the reaction of HgBr* by NO₂ and HO₂.

We add the following text to this section (page 5, lines 32-36):

“GEOS-Chem concentrations of NO₂ and H₂O₂ (proxy for HO₂) have been evaluated successfully in a number of aircraft campaigns (Martin et al., 2006; Hudman et al., 2007; Singh et al., 2007; Lin and McElroy, 2010; Mao et al., 2010; Travis et al., 2016). GEOS-Chem NO₂ columns have also been evaluated against satellite observations over China (Lin et al., 2012), North America (e.g., Lamsal et al., 2014), and Africa (Marais et al., 2012).

We also add a sentence in the same paragraph regarding organic aerosol (page 6, line 3-5):
“An evaluation of modeled OA against aircraft observations globally is presented in Heald et al. (2011), which showed no systematic bias in remote environments but an underestimate of median concentrations in polluted regions.”

In Section 4.1 the authors state that the vertical structure of the Hg⁰ concentration is well established, when in reality there have actually been only a few measurements made, given that CARIBIC measures TGM, perhaps this an overstatement.

We revise this paragraph and add clarifying text as follows (page 6, lines 30 to 36) to address this and other reviewers' comments:

“Modeled Hg⁰ decreases rapidly in the stratosphere, while Hg^{II} increases with altitude and dominates total Hg in the stratosphere. This vertical structure is driven by chemistry (Selin et al., 2007; Holmes et al., 2010) and these general vertical trends in the two species are consistent with limited available observations (Murphy et al., 2006; Talbot et al., 2007; Lyman and Jaffe, 2012). The exact partitioning of total Hg in the stratosphere between Hg⁰ and Hg^{II} is uncertain and GEOS-Chem predicts a higher Hg^{II} fraction relative to other models (Bieser et al., 2016). Photodissociation of gas-phase Hg^{II} halides may be possible at ultraviolet wavelengths (Maya, 1977) but whether this is important in the mid-to-upper stratosphere requires further investigation.”

In Section 4.3 the seasonality is discussed, and states (line 27) that oxidation is faster in the summer than the winter. However the lower temperatures in the winter increase the lifetime against thermal decomposition of HgBr* , so perhaps a little more detail in the explanation would be useful. Also here one assumes that oceanic evasion is highest in the winter due to less clement weather, but it is not explicitly stated.

We clarify text in the first paragraph of Section 4.3:

“The February maximum and September minimum are driven in the model in part by Hg⁰ oxidation and in part by ocean evasion. Seasonality in radical oxidant concentrations outweighs temperature effects, leading to fastest oxidation in summer and slowest in winter. Modeled oceanic Hg⁰ evasion from the North Atlantic Ocean peaks in winter and early spring, because higher windspeeds increase mixing and entrainment of reducible Hg^{II} from subsurface waters and enhance the rate of air-sea exchange, and Hg removal via particle settling during this time is low (Sorensen et al., 2010, 2013).”

On the same subject, in the Conclusions (line 18) oxidation and evasion are described as paper having similar seasonal phases, but anticorrelated?

We reword this sentence in line 20 of page 12 to clarify:

“...with similar seasonal effects on TGM concentrations.”

In Section 5, the authors discuss the high Hg deposition over the Gulf of Mexico, the figures show that modelled deposition is higher here but it is still less than the observed values. Is this due to the model resolution and reproducing sub-grid scale convection?

We rewrite this paragraph (now page page 10, lines 34-36 to page 11, lines 1-2) to address your and other reviewers' comments:

“Previous GEOS-Chem simulations with Br-initiated oxidation of Hg⁰ failed to capture this maximum because Hg^{II} production favored higher latitudes (Holmes et al., 2010; Amos et al.,

2012). The inclusion of NO_2 and HO_2 as second-stage oxidants in our simulation shifts Hg^{II} production to lower latitudes and matches the general location of the Gulf of Mexico maximum although the magnitude is still underestimated. Increasing horizontal resolution in the model could improve the definition of the maximum (Zhang et al., 2012).”

The article is well written and merits publication in ACP.

Referee #2

Thank you for your thoughtful comments. Including your suggested revisions has improved the quality of the manuscript. Our responses are indicated below in blue text.

This is a great paper that represents great progress in the field of atmospheric chemistry. It definitely deserves publication. I have a few specific comments:

1. On page 2 lines 14-15, you talk about how oxidation by O₃ and OH is unlikely. It is important, I think, that you bring out and discuss (or debunk, if they merit it) other oxidation/reduction mechanisms that have been proposed, including heterogeneous mechanisms. No one disputes that halogen-involving reactions are important. But there are some strong voices that claim other mechanisms may also be important, and I think it would be useful to give them consideration.

We add a sentence (Page 2, lines 19-20):

“OH and ozone could still potentially be important oxidants on aerosols (Ariya et al., 2015).”

We chose to leave the more detailed discussion of other proposed mechanisms in Section 2 and Tables 1 and 2 instead of in the introduction.

2. On page 2 lines 30-32, you suggest that in-plume reduction isn't important, and give the Deeds and Landis papers as references. Both papers show evidence for in-plume reduction, and the Landis paper talks about how the process is likely widespread. Maybe I am misinterpreting your text or theirs, but I'm not sure the statement you make here is supportable by the evidence you have given.

We revised this sentence for clarity and added text (page 2 lines 33 to 37, page 3 lines 1) as follows:

“Fast in-plume reduction of Hg^{II} emitted by coal-fired power plants was first reported by Edgerton et al. (2006) and Lohman et al. (2006) but more recent field observations suggest that on average only 5% (range 0-55%) of emitted Hg^{II} is reduced in the plume (Deeds et al., 2013; Landis et al., 2014). Recent aircraft observations (Weigelt et al., 2016) and emission inventories (Zhang et al., 2016) suggest that previous reports of in-plume reduction of Hg^{II} may reflect in part an overestimate of Hg^{II} emissions.”

3. I am curious about why in Figure 1 the model shows quite high annual mean Hg^{II} at the surface near the south pole and overall shows much higher Hg^{II} in the southern troposphere than in the northern. I think this is a surprising result, and I don't think it was discussed in the manuscript. I would be glad to see some explicit discussion of the reason for the north-south difference in Hg^{II} concentrations. Unfortunately, we have very few (if any) reliable Hg^{II} measurements with which to validate this result.

We add the following discussion to Section 4.1 (page 8 lines 18-20).

“Hg^{II} reduction in the model is faster in the northern hemisphere than in the southern hemisphere because of higher OA concentrations. Hence Hg^{II} concentrations are higher in the southern than in the northern hemisphere (Figure 1).”

4. Page 7 lines 8-10: again, some discussion of how inclusion of heterogeneous oxidation chemistry might play a role could be useful here.

We add the following sentences (now page 7, lines 34-37):

“We did not consider heterogeneous Hg^0 oxidation on particle surfaces (e.g., Vidic et al., 1998; Flora et al., 1998; Lee et al., 2004) due to inadequate information to formulate atmospheric rates. Further study of heterogeneous Hg^0 oxidation is needed (Ariya et al., 2015).”

5. Page 10 lines 1-5: It is not at all clear to me that these modifications to GEOS-Chem “solve” the problem of underprediction of wet deposition in the Gulf of Mexico. Based on Figure 6, the model is still strongly underestimating Gulf of Mexico wet deposition. I don’t think the model even gets the basic spatial trends right, based on my visual inspection of Figure 6. It may be fair to say that it is doing better than before, but to say it has it all nailed down seems to be an overstatement.

We rewrite this paragraph (now page page 10, lines 34-36 to page 11, lines 1-2) to address your and other reviewers’ comments:

“Previous GEOS-Chem simulations with Br-initiated oxidation of Hg^0 failed to capture this maximum because Hg^{II} production favored higher latitudes (Holmes et al., 2010; Amos et al., 2012). The inclusion of NO_2 and HO_2 as second-stage oxidants in our simulation shifts Hg^{II} production to lower latitudes and matches the general location of the Gulf of Mexico maximum although the magnitude is still underestimated. Increasing horizontal resolution in the model could improve the definition of the maximum (Zhang et al., 2012).”

6. Page 11 lines 30-31: I don’t agree that the “wet deposition fluxes in the model are consistent with observations.” This assertion needs to be toned down.

We revised this and the following sentences as follows (page 12, lines 32-36):

“Hg wet deposition fluxes in the model are consistent with spatial patterns observed in North America and Europe. Inclusion of NO_2 and HO_2 as second-stage HgBr oxidants in the model shifts Hg^{II} production to lower latitudes compared to previous versions of GEOS-Chem and enables the model to capture the location of the observed maximum in wet deposition along the Gulf Coast of the US. However, the magnitude of this Gulf Coast maximum is still underestimated.”

We also modified the Abstract and Section 5 text, which are consistent with the above.

Referee #3

Thank you for your thoughtful comments. Including your suggested revisions has improved the quality of the manuscript. Our responses are indicated below in blue text.

In the presented paper the authors investigate the implications of two stage oxidation mechanisms for the global mercury cycle. This work is highly innovative and will have a strong impact on atmospheric mercury modelling and our understanding on mercury red-ox reactions. Thus, I strongly support publication of this manuscript after some minor revisions:

P1 L18: "Hg²⁺ controls deposition to ecosystems" I think that this is not 100% correct as it neglects the importance of Hg⁰ dry deposition. (e.g. Zhang, L., Blanchard, P., Gay, D.A., Presbo, E.M., Risch, M.R., Johnson, D., Narayan, J., Zsolway, R., Holsen, T.M., Miller, E.K., Castro, M.S., Graydon, J.A., St. Louis, V.L., Dalziel, J., (2012a). Estimation of speciated and total mercury dry deposition at monitoring locations in eastern and central North America. ACP 12, 4327-4340.)

We modify page 1 lines 17 to 18: " Oxidation to water-soluble Hg^{II} plays a major role in Hg deposition to ecosystems."

P1 L 33: "lowermost stratosphere show a strong TGM-ozone relationship" I want to add to that while this is true for many observations, that during some CARIBIC flights no such correlation was found. As Franz Slemr is a co-author I think he knows best how to phrase this correctly. In this paper we do not compare on a flight-by-flight basis but to the overall relationship across all flights.

P2 L32: For completeness, I would like to add another recent aircraft observation on the issue with similar findings: (Weigelt, A., 2016. Mercury emissions of a coal-fired power plant in Germany. Atmospheric Chemistry and Physics 16(21):13653-13668. doi: 10.5194/acp-16-13653-2016)

We edit this section, (page 2 lines 33 to 37, page 3 lines 1) as follows:

“Fast in-plume reduction of Hg^{II} emitted by coal-fired power plants was first reported by Edgerton et al. (2006) and Lohman et al. (2006) but more recent field observations suggest that on average only 5% (range 0-55%) of emitted Hg^{II} is reduced in the plume (Deeds et al., 2013; Landis et al., 2014). Recent aircraft observations (Weigelt et al., 2016) and emission inventories (Zhang et al., 2016) suggest that previous reports of in-plume reduction of Hg^{II} may reflect in part an overestimate of Hg^{II} emissions.”

P3 L35: I would appreciate if you would give a complete list of molecules considered as reaction partner Y. Such that the paragraph is consistent with Table 2 where you list (Y = HO₂, OH, Cl, BrO, ClO).

We clarify the sentence, now page 4, lines 2 to 4:

“Dibble et al. (2012) found that a broad range of radical oxidants could oxidize HgBr and HgCl including Y = NO₂ and HO₂, the most abundant atmospheric radicals, as well as Y = BrO, ClO, and Cl.”

P4 Section 3.1: You compare the recent model results from findings from Holmes et al. 2010. Here, I am missing a more detailed comparison of the Br fields used for both models as this is one major driver for the model results.

We add text to point the reader to section 3.2, page 5, lines 1-2: “In this work we update the Br concentration fields to a more recent version of GEOS-Chem (Schmidt et al., 2016), as discussed further in Section 3.2.”

P5 L 23ff: Atmospheric models are still having problems reproducing atmospheric OA concentrations mainly due to an underestimation of SOA formation. When using OA concentrations for Hg reduction processes you need to clarify the quality of the OA fields used for this purpose. Does the correction parameter alpha you use compensate for too low OA concentrations? Or does the model use increases POA emissions to compensate SOA formation? We add a sentence in this section so it now reads as follows (page 6, lines 1-5):

“Monthly mean organic aerosol (OA) concentrations are archived from a separate v9-02 GEOS-Chem simulation including primary emissions from combustion and secondary production from biogenic and anthropogenic hydrocarbons (Pye et al., 2010). An evaluation of modeled OA against aircraft observations globally is presented in Heald et al. (2011), which showed no systematic bias in remote environments but an underestimate of median concentrations in polluted regions.”

P6 L 11-15: I understand that in this paper you focus on the troposphere and thus include only a limited discussion of the stratosphere. But in my opinion (based on CARIBIC observations and a multi model study on mercury vertical distribution) the way you phrase this is not 100% correct. Hg²⁺ concentration strongly increases in the stratosphere. But most models as well as the observations do not indicate a domination (>50%) of Hg²⁺.

You might be aware of this paper also currently under review in ACPD? (Bieser, J., Slemr, F., Brenningmeijer, K., Brooks, S., Dastoor A., De Simone, F., Ebinghaus R., Gencarelli, C.N., Geyer, B., Gratz, L., Hedgecock, I.M., Jaffe, D., Kelley, P., Lin C.- C., Matthias, V., Selin, N., Shah, V., Song, S., Travnikov, O., Weigelt, A., Winston, L., Zahn, A., Pirrone, N., Multi-model study of mercury dispersion in the atmosphere: Vertical distribution of mercury species. Atmos. Chem. Phys. Disc. doi:10.5194/acp- 2016-1074 2016.)

We revise this paragraph and add clarifying text as follows (page 6, lines 30 to 36) to address this and other reviewers' comments:

“Modeled Hg⁰ decreases rapidly in the stratosphere, while Hg^{II} increases with altitude and dominates total Hg in the stratosphere. This vertical structure is driven by chemistry (Selin et al., 2007; Holmes et al., 2010) and these general vertical trends in the two species are consistent with limited available observations (Murphy et al., 2006; Talbot et al., 2007; Lyman and Jaffe, 2012). The exact partitioning of total Hg in the stratosphere between Hg⁰ and Hg^{II} is uncertain and GEOS-Chem predicts a higher Hg^{II} fraction relative to other models (Bieser et al., 2016). Photodissociation of gas-phase Hg^{II} halides may be possible at ultraviolet wavelengths (Maya, 1977) but whether this is important in the mid-to-upper stratosphere requires further investigation.”

P7 L2: I am confused by this estimated lifetime of 1.2 to 2.8 months. It is contradictory to the generally expected life time close to 6 months (which is the value you mention later on and with which I agree). I think you need to put the number from Shah et al. 2016 more into context here. e.g. During the NOMADSS campaign they found a few episodes with very high bromine concentrations. Do they dominate this estimation?

P7 L25: (Similar to last) Please clarify: 1) That the "NOMADSS simulation" is also a GEOS-Chem simulation and indicate which version, chemistry, and Br fields were used. 2) That the NOMADSS campaign was limited to certain latitudes of the US (do you compare only life times for this region?)

Here we address the previous two comments.

We add a sentence to clarify the different lifetime estimates (page 7, lines 18 to 20):

“We calculate several atmospheric lifetimes to understand the processes driving Hg deposition: the chemical lifetime of Hg^0 against oxidation, the chemical lifetime of Hg^{II} against reduction, the lifetime of Hg^{II} against deposition, and the lifetime of total gaseous mercury ($\text{TGM} \equiv \text{Hg}^0 + \text{Hg}^{\text{II}}(\text{g})$) against deposition.”

We also clarify the discussion of Shah et al. in that paragraph (page 7, lines 25 to 28):

“Our results are consistent with Shah et al. (2016), who estimated a global annual tropospheric Hg^0 lifetime against oxidation to Hg^{II} by Br atoms of 1.2 to 2.8 months, based on their simulation of measurements of Hg^{II} over the Southeast US in summer during the NOMADSS campaign (Gratz et al., 2015).

P7 L28-29: This is a very important part of your results but it seems to be circular reasoning and I would appreciate it if you could clarify this: As far as I understand you have high bromine concentrations leading to high first stage oxidation rates and a high actinic flux leading to high secondary oxidation and thus need a higher reduction rate to achieve conformity between model and observations. However, could you not also conclude that you are overestimating oxidation rates or bromine concentrations rather than underestimating reduction rates? So the question seems: Is reduction an actual sink for Hg^{2+} or could the red-ox reaction also be understood as steady state condition, and thus as a tuning parameter in the free troposphere? Or are there specific temporal or spatial signals in the observations which are only reproduced by your mechanism?

Moreover, it would be interesting if you could give more qualitative statements on the distribution of the reduction in the free troposphere. As your models need particles, organic aerosols, and liquid water I assume that the reduction is not evenly distributed in the free troposphere. I would actually expect a higher reduction potential inside the PBL due to high concentrations of particles and liquid water. Also how do you treat ice particles?

Here we respond to the above two comments:

Second-stage oxidation rates are high due to the high concentrations of second-stage oxidants. The photoreduction rate of Hg^{II} is a function of actinic flux, but is a parameterization rather than an actual mechanism; the specific Hg^{II} reduction reactions and their rates are unknown. Reduction does not occur on ice particles.

We add a sentence about the evaluation of modeled Br fields in Section 3.2 (page 5, lines 30-32): “Schmidt et al. (2016) evaluated their simulated tropospheric BrO concentrations (global daytime mean of 0.96 ppt) with observations from satellite and aircraft and found no systematic bias.”

In the section described in your above comment, we add several sentences and split the text into two paragraphs for clarity, and add text describing the latitudinal distribution of Hg^{II} reduction (page 8, lines 15-28; including sections of the paragraph which are unchanged for convenience, with additions underlined):

“Shah et al. (2016) similarly found that faster Hg⁰ oxidation as needed to match NOMADSS observations required faster Hg^{II} reduction, with a tropospheric Hg^{II} lifetime against reduction of 19 days. The lifetime of tropospheric Hg^{II} against deposition is relatively long, 26 days (see Figure 2), because most Hg^{II} production occurs in the free troposphere where precipitation is infrequent (Figure 1). Hg^{II} reduction in the model is faster in the northern hemisphere than in the southern hemisphere because of higher OA concentrations. Hence Hg^{II} concentrations are higher in the southern than in the northern hemisphere (Figure 1).

We find here that the Hg^{II} lifetime against reduction is shorter than against deposition, emphasizing the importance of reduction in controlling the atmospheric Hg budget. By contrast, Holmes et al. (2010) found an adjusted Hg^{II} tropospheric lifetime of 50 days against reduction and 36 days against deposition, which led them to conclude that no reduction was needed if Hg⁰ oxidation kinetics were decreased within their uncertainty. This is no longer possible in our simulation because of the much faster Hg⁰ oxidation. We conclude that Hg^{II} reduction must take place in the atmosphere. With Hg^{II} reduction, the overall lifetime of tropospheric TGM against deposition in our simulation is 5.2 months, similar to the estimate of 6.1 months in Holmes et al. (2010). We discuss the consistency of this estimate with observations in the next section.”

P8 L 19: Would this also be true for the inter-hemispheric gradient observed in high altitudes (CARIBIC data)?

This is a great point but beyond the scope of the current study. We modify page 9 lines 3 to 6 to clarify it is for surface data:

“However, we find the interhemispheric gradient in surface concentrations is not a sensitive diagnostic of lifetime because surface atmospheric Hg in the southern hemisphere is controlled more by atmosphere-ocean exchange than by transport from the northern hemisphere.”

P10 L10-16: I just wanted to underline how important this finding is because of the impact on long range transport of mercury from east Asia.

We add a sentence (page 11, lines 13 to 14): “Decreased wet deposition in this region has implications for the long-range transport of atmospheric Hg from East Asia (Weiss-Penzias et al., 2007).”

P10 L24-17: Can you give the net flux between atmosphere and ocean?

We add to the text (page 11, lines 24-26):

“The global ocean is a net sink for total atmospheric Hg of 1700 Mg a⁻¹ (Figure 2), with approximately half taken up by tropical oceans.”

P11 L 23-29: Is the model able to reproduce episodes where no TGM/ozone relationship was observed by CARABIC?

In this paper we do not compare on a flight-by-flight basis but to the overall relationship across all flights.

Minor remarks concerning language: P4 L8: for for (double) P1 L18: In case my sense for

punctuation is correct there is a , missing after "Here". P1 L33: southern hemispheric marine sites, not southern hemisphere marine sites.

We corrected the language errors as specified (now page 4 line 14; page 1 line 18; page 1 line 33). Thank you!

Referee #4

Thank you for your thoughtful comments. Including your suggested revisions has improved the quality of the manuscript. Our responses are indicated below in blue text.

This paper describes advancements in the modeling of global Hg cycling through up- dated redox chemistry as well as coupling to a more sophisticated ocean model. The approach is thorough and defensible and the paper well-written. I recommend publica- tion after minor revisions.

P5, l. 23-25: Can you add a summary of how accurate these OA concentrations are expected to be? If this isn't known, how does that impact your conclusions?

We respond to this and other reviewers' comments on a similar topic below.

We refer to a study evaluating modeled OA in detail, adding the following sentence (Page 6, lines 3-5): "An evaluation of modeled OA against aircraft observations globally is presented in Heald et al. (2011), which showed no systematic bias in remote environments but an underestimate of median concentrations in polluted regions."

P8, l. 1-20: This discussion of the mean and SD of TGM concentrations underplays the spatial deviations shown in Fig. 3. For example, the modeled and measured N-S gradients in Europe appear to be in opposite directions.

We reorder the discussion in this paragraph to highlight the spatial correlation coefficient (now page 8, lines 31-35).

P8, l. 28-30: I suggest you cite Soerenson et al., EST 2013, or other observation-based papers to show that this mechanism is consistent with observations.

We revise this section in response to this and others' comments (page 9, lines 22 to 24): "Modeled oceanic Hg⁰ evasion from the North Atlantic Ocean peaks in winter and early spring, because higher windspeeds increase mixing and entrainment of reducible Hg^{II} from subsurface waters and enhance the rate of air-sea exchange, and Hg removal via particle settling during this time is low (Sorensen et al., 2010, 2013)."

P9, l. 5-7: It sounds like you are suggesting that a similar analysis for the southern ocean is needed, but both the sea ice and the relatively large riverine flux relative to the Hg pool in the Arctic Ocean are not likely to have any relevance to these southern non-polar sites.

We clarify this section and include additional discussion (page 9, lines 35-37 to page 10, lines 1-3):

"Long-range transport of atmospheric Hg from Antarctica could influence observed seasonality at these sites (Angot et al., 2016). Capturing the seasonality of atmospheric Hg in the Arctic using GEOS-Chem required parameterization of unique sea-ice, oceanic, and riverine dynamics (Fisher et al., 2012; 2013; Y. Zhang et al., 2015) and a similar analysis for the Southern Ocean region, with its distinct productivity dynamics impacting Hg cycling (e.g., Cossa et al., 2011; Gionfriddo et al., 2016), has not yet been performed."

P10, l. 1-5: The figure indicates a -28% mean bias in North America, but in the Gulf of Mexico it appears to still be closer to -50%. Can you quantify the improvement in the wet deposition relative to Holmes et al. (or other models)? Consider adding a figure showing scatterplots of

model vs. observations for both TGM and wet deposition.

We rewrite this paragraph (now page page 10, lines 34-36 to page 11, lines 1-2) to address your and other reviewers' comments:

“Previous GEOS-Chem simulations with Br-initiated oxidation of Hg^0 failed to capture this maximum because Hg^{II} production favored higher latitudes (Holmes et al., 2010; Amos et al., 2012). The inclusion of NO_2 and HO_2 as second-stage oxidants in our simulation shifts Hg^{II} production to lower latitudes and matches the general location of the Gulf of Mexico maximum although the magnitude is still underestimated. Increasing horizontal resolution in the model could improve the definition of the maximum (Zhang et al., 2012).”

A new mechanism for atmospheric mercury redox chemistry: Implications for the global mercury budget

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Abstract. Mercury (Hg) is emitted to the atmosphere mainly as volatile elemental Hg⁰. Oxidation to water-soluble Hg^{II} plays a major role in Hg deposition to ecosystems. Here, we implement a new mechanism for atmospheric Hg⁰/Hg^{II} redox chemistry in the GEOS-Chem global model and examine the implications for the global atmospheric Hg budget and deposition patterns. Our simulation includes a new coupling of GEOS-Chem to an ocean general circulation model (MITgcm), enabling a global 3-D representation of atmosphere-ocean Hg⁰/Hg^{II} cycling. We find that atomic bromine (Br) of marine organobromine origin is the main atmospheric Hg⁰ oxidant, and that second-stage HgBr oxidation is mainly by the NO₂ and HO₂ radicals. The resulting chemical lifetime of tropospheric Hg⁰ against oxidation is 2.7 months, shorter than in previous models. Fast Hg^{II} atmospheric reduction must occur in order to match the ~6-month lifetime of Hg against deposition implied by the observed atmospheric variability of total gaseous mercury (TGM = Hg⁰+Hg^{II}(g)). We implement this reduction in GEOS-Chem as photolysis of aqueous-phase Hg^{II}-organic complexes in aerosols and clouds, resulting in a TGM lifetime of 5.2 months against deposition and matching both mean observed TGM and its variability. Model sensitivity analysis shows that the interhemispheric gradient of TGM, previously used to infer a longer Hg lifetime against deposition, is misleading because southern hemisphere Hg mainly originates from oceanic emissions rather than transport from the northern hemisphere. The model reproduces the observed seasonal TGM variation at northern mid-latitudes (maximum in February, minimum in September) driven by chemistry and oceanic evasion, but does not reproduce the lack of seasonality observed at southern hemispheric marine sites. Aircraft observations in the lowermost stratosphere show a strong TGM-ozone relationship indicative of fast Hg⁰ oxidation, but we show that this relationship provides only a weak test of Hg chemistry because it is also influenced by mixing. The model reproduces observed Hg wet deposition fluxes over North America, Europe, and China, with little bias (0-30%). It reproduces qualitatively the observed maximum in US deposition around the Gulf of Mexico, reflecting a combination of deep convection and availability of NO₂ and HO₂ radicals for second-stage HgBr oxidation. However, the magnitude of this maximum is underestimated. The relatively low observed Hg wet deposition over rural China is attributed to fast Hg^{II} reduction in the presence of high organic aerosol concentrations. We find that 80% of Hg^{II} deposition is to the global oceans,

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reflecting the marine origin of Br and low concentrations of [organic aerosols](#) for Hg^{II} reduction. Most of that deposition takes place to the tropical oceans due to the availability of HO₂ and NO₂ for second-stage HgBr oxidation.

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5 1. Introduction

Atmospheric mercury (Hg) cycles between two stable redox forms, elemental (Hg⁰) and divalent (Hg^{II}). Most Hg emissions are as gaseous elemental Hg⁰, which is relatively inert and sparingly soluble in water. Hg⁰ is oxidized in the atmosphere to Hg^{II} by loss of its two 6s² electrons. Hg^{II} salts are water-soluble, partition into the aerosol, and are efficiently removed from the atmosphere by wet and dry deposition, but can also be reduced back to Hg⁰. Understanding atmospheric Hg redox chemistry is critical for determining where Hg will be deposited globally. Here we propose an updated Hg⁰/Hg^{II} redox mechanism, incorporating recent kinetic data and other observational constraints, for use in atmospheric models. We implement the mechanism in the GEOS-Chem global model (Bey et al., 2001; Holmes et al., 2010) and examine the implications for the global atmospheric Hg budget and deposition patterns.

Previous work assumed gas-phase OH and ozone to be the dominant Hg⁰ oxidants (Bergan and Rodhe, 2001; Dastoor and Larocque, 2004; Selin et al., 2007; Bullock et al., 2008; Travnikov and Ilyin, 2009; De Simone et al., 2014; Gencarelli et al., 2014). It is now well established that the corresponding HgOH and HgO products are too thermally unstable to enable oxidation to Hg^{II} under atmospheric conditions (Shepler and Peterson, 2003; Goodsite et al., 2004; Calvert and Lindberg, 2005; Hynes et al., 2009; Jones et al., 2016). OH and ozone could still potentially be important oxidants on aerosols (Ariya et al., 2015). The importance of Br atoms for Hg⁰ oxidation was first recognized to explain atmospheric mercury depletion events occurring in the Arctic boundary layer in spring (Schroeder et al., 1998), where sea salt photochemistry provides a large Br source (Fan and Jacob, 1992; Steffen et al., 2008; Simpson et al., 2015). Oxidation of Hg⁰ to Hg^{II} by Br is a two-stage exothermic mechanism where the second stage conversion of HgBr to Hg^{II} can be carried out by a number of radical oxidants (Goodsite et al., 2004; Dibble et al., 2012). Holmes et al. (2006) first suggested Br atoms could be the main Hg⁰ oxidant on a global scale, with Br originating principally from photochemical decomposition of bromoform emitted by phytoplankton (Yang et al., 2005). More recent observations of background tropospheric BrO point to ubiquitous Br radical chemistry in the troposphere (Theys et al., 2011; Wang et al., 2015). Recent aircraft observations of Hg^{II} and BrO over the Southeast US are consistent with Br atoms acting as the main Hg⁰ oxidant (Gratz et al., 2015; Shah et al., 2016).

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Atmospheric Hg^{II} can be deposited or alternatively reduced back to Hg⁰. Competition between these two processes determines the global patterns of Hg deposition as well as the regional fate of Hg^{II} emitted directly by combustion. Atmospheric reduction mechanisms for Hg^{II} are poorly understood but photoreduction in aquatic systems has been widely observed (Costa and Liss, 1999; Amyot et al., 2000; Mason et al., 2001). Fast in-plume reduction of Hg^{II} emitted by coal-fired power plants was first reported by Edgerton et al. (2006) and Lohman et al. (2006) but more recent field observations suggest that on average only 5% (range 0-55%) of emitted Hg^{II} is reduced in the plume (Deeds et al., 2013; Landis et al., 2014). Recent aircraft observations (Weigelt et al., 2016) and emission inventories (Zhang et al., 2016) suggest that previous reports of in-plume reduction of Hg^{II} may reflect in

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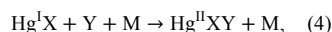
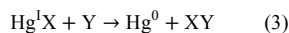
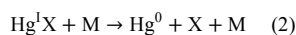
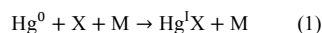
part an overestimate of Hg^{II} emissions.

The speciation of atmospheric Hg^{II} is unknown (Jaffe et al., 2014; Gustin et al., 2015; Jones et al., 2016). It is generally assumed from chemical equilibrium considerations that the main Hg^{II} species are HgCl₂ in the gas phase and Hg-chloride complexes in the aqueous phase (Hedgecock and Pirrone, 2001; Selin et al., 2007; Holmes et al., 2009). Hg-chloride complexes are relatively resistant to photoreduction (Allard and Arsenie, 1991; Pehkonen and Lin, 1998). Hg^{II} also strongly binds to organic ligands, including to reduced sulfur complexes and carboxyl groups (Pehkonen and Lin, 1998; Haitzer et al., 2002; Ravichandran, 2004; Zheng and Hintelmann, 2009). Photoreduction of Hg^{II} bound to dissolved organic carbon (DOC) and other organic matter has been widely reported in aquatic environments (Amyot et al., 1994; Xiao et al., 1995; O'Driscoll et al., 2006; Whalin and Mason, 2006) and could also possibly take place in organic aerosols. Bash et al. (2014) found that including in-cloud aqueous photoreduction via organic acids based on the mechanism proposed by Si and Ariya (2008) improved the simulation of Hg wet deposition in their regional air quality model. Observed photochemically-driven shifts in the abundance of naturally occurring Hg isotopes in the atmosphere and precipitation support the occurrence of aqueous-phase photoreduction involving Hg^{II}-organic complexes (Gratz et al., 2010; Sonke, 2011; Sonke et al., 2015).

The GEOS-Chem model is widely used for global studies of atmospheric chemistry, and has been applied in particular to simulations of atmospheric Hg and biogeochemical cycling with a focus on interpreting observations (e.g., Strode et al., 2008; Weiss-Penzias et al., 2015; Zhang et al., 2016). The Hg chemical mechanism in the current standard version of GEOS-Chem (www.geos-chem.org) is based on Holmes et al. (2010). Our updated mechanism includes more recent information and is applied here with an improved GEOS-Chem simulation of halogen chemistry (Schmidt et al., 2016). As part of this work, we also introduce a new coupling of GEOS-Chem to a global 3-D ocean model (Y. Zhang et al., 2015) to better interpret observed seasonal variations of atmospheric Hg in the context of both atmospheric chemistry and oceanic drivers of air-sea exchange (Soerensen et al., 2013).

2. Chemical mechanism

Table 1 lists the new chemical mechanism implemented in GEOS-Chem. Table 2 lists reactions proposed in the literature but subsequently estimated to be too slow to be of atmospheric relevance. Oxidation of Hg⁰ to Hg^{II} in the gas phase involves a two-stage process (1, 4) with competing reactions (2, 3):



where X is the first-stage Hg⁰ oxidant, Y is the second-stage Hg^I oxidant, and M is a molecule of air (Goodsite et al., 2004; Donohoue et al., 2006; Dibble et al., 2012). The Hg^I intermediate has a lifetime of less than a minute anywhere in the troposphere so local steady state can be assumed. Goodsite et al. (2004) found that HgBr is sufficiently stable for the Br atom to be an effective first-stage Hg⁰ oxidant, and proposed Y = OH and Br as

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effective radicals to carry out the second stage of oxidation to Hg^{II} . The Cl atom can also oxidize Hg^0 to produce HgCl (Balabanov and Peterson, 2003; Donohoue et al., 2005). Dibble et al. (2012) found that a broad range of radical oxidants could oxidize HgBr and HgCl including $\text{Y} = \text{NO}_2$ and HO_2 , the most abundant atmospheric radicals, as well as $\text{Y} = \text{BrO}$, ClO , and Cl . Other proposed first-stage gas-phase Hg^0 oxidants appear to be unimportant, including OH , O_3 , I , I_2 , Br_2 , Cl_2 , BrO , ClO , HCl , HO_2 , and NO_3 (Table 2). Hg^0 is sparingly soluble in water but it has been suggested that fast aqueous-phase oxidation could take place in cloud droplets (Munthe and McElroy, 1992; Lin and Pehkonen, 1997; Lin and Pehkonen, 1998; Whalin et al., 2007). We include these processes in our mechanism with $\text{O}_3(\text{aq})$, $\text{HOCl}(\text{aq})$, and $\text{OH}(\text{aq})$ as oxidants.

Strong complexes between Hg^{II} and organic acids may allow electrons to be transferred to Hg^{II} during photolysis (Pehkonen and Lin, 1998). Gårdfeldt and Jonsson (2003) found that direct photolysis of Hg -oxalate resulted in Hg^{II} reduction and Si and Ariya (2008) reported the same for Hg -dicarboxylates. O'Driscoll et al. (2004) reported a linear increase in the efficiency of Hg^{II} photoreduction in freshwater with increasing DOC concentrations. We assume here that Hg^{II} photoreduction is dependent on the local concentration of organic aerosol (OA) and on the NO_2 photolysis frequency (J_{NO_2}) taken as proxy for the UV actinic flux, and further assume the aerosol to be aqueous only at relative humidity greater than 35%. The scaling factor α for the reaction (Table 1) is adjusted in GEOS-Chem such that simulated total gaseous mercury ($\text{TGM} = \text{Hg}^0 + \text{Hg}^{\text{II}}(\text{g})$) concentrations match the global mean observed at land stations.

3. GEOS-Chem model

3.1 General description

We start from the standard version v9-02 of the GEOS-Chem Hg model (www.geos-chem.org; Amos et al., 2012; Song et al., 2015) and implement a new 2010 inventory for speciated anthropogenic emissions (Zhang et al., 2016) including contributions from commercial products (Horowitz et al., 2014). We then add original updates described below for atmospheric chemistry and atmosphere-ocean coupling. The standard v9-02 model includes cycling of Hg^0 and Hg^{II} between the atmosphere, land, and the surface mixed-layer of the ocean (Selin et al., 2008; Soerensen et al., 2010). The atmospheric model transports Hg^0 and Hg^{II} as separate tracers. Gas-particle partitioning of Hg^{II} is parameterized following Amos et al. (2012) as a thermodynamic equilibrium function of local temperature and mass concentration of fine particulate matter ($\text{PM}_{2.5}$). This parameterization is based on observed relationships between the gas/particle Hg^{II} concentration ratio and $\text{PM}_{2.5}$, and does not resolve effects from particle composition or surface area.

Holmes et al. (2010) presented the last detailed global atmospheric budget analysis of Hg in GEOS-Chem and we use it as a point of comparison for this study. Their model version included Hg^0 oxidation by Br atoms, with Br concentrations specified in the troposphere and stratosphere from the p-TOMCAT and NASA Global Modeling Initiative models, respectively (Yang et al., 2005; Strahan et al., 2007). The standard v9-02 model uses Br concentration fields from the GEOS-Chem tropospheric bromine simulation by Parrella et al. (2012), and features other model updates relative to Holmes et al. (2010), including gas-particle Hg^{II} equilibrium partitioning described above, a corrected washout algorithm (Amos et al., 2012), and improvements to the 2-D surface ocean model

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(Soerensen et al., 2010). [In this work we update the Br concentration fields to a more recent version of GEOS-Chem \(Schmidt et al., 2016\), as discussed further in Section 3.2.](#)

We conduct a 3-year simulation for 2009-2011 driven by GEOS-5 assimilated meteorological data from the NASA Global Modeling and Assimilation Office (GMAO) with native horizontal resolution of $1/2^\circ \times 2/3^\circ$ and 72 vertical levels extending up to the mesosphere. The GEOS-Chem simulation is conducted at $4^\circ \times 5^\circ$ horizontal resolution by regridding the GEOS-5 meteorological data. We use anthropogenic Hg emissions for the year 2010 from Zhang et al. (2016). The spatial distribution of soil Hg is determined following the method of Selin et al. (2008), with updated soil respiration emissions (910 Mg Hg a^{-1}) for consistency with the mechanistic terrestrial model developed by Smith-Downey et al. (2010). Emissions from snow and re-emission of deposited Hg follow Selin et al. (2008). The model is initialized with a 15-year simulation to equilibrate the stratosphere. We present model results as averages for the three simulation years (2009-2011).

3.2 Atmospheric chemistry

Hg⁰/Hg^{II} redox chemistry in the standard GEOS-Chem v9-02 model includes Hg⁰ oxidation by Br atoms and Hg^{II} in-cloud photoreduction as described by Holmes et al. (2010), with Br concentration fields from Parrella et al. (2012). Shah et al. (2016) updated that chemistry following Dibble et al. (2012) to include 2nd-stage oxidation of HgBr by HO₂, NO₂, and BrO, as well as new kinetics for HgBr dissociation. Here we further expand and update the chemistry using the mechanism described in Table 1. Br and Cl radical concentrations are taken from a new GEOS-Chem simulation of tropospheric oxidant-aerosol chemistry by Schmidt et al. (2016). Unlike Parrella et al. (2012), this simulation does not include a bromine radical source from sea-salt debromination as recent evidence suggests that BrO concentrations in the marine boundary layer (MBL) are generally sub-ppt (Gómez Martín et al., 2013; Wang et al., 2015). Simulated concentrations of Br in the free troposphere are on the other hand a factor of two higher than Parrella et al. (2012), reflecting more extensive heterogeneous chemistry. Schmidt et al. (2016) show that their simulation provides a better simulation of aircraft and satellite observations of tropospheric BrO. Stratospheric concentrations of Br and Cl species are from the GEOS Chemistry Climate Model (Liang et al., 2010) and Global Modeling Initiative (Considine et al., 2008; Murray et al., 2012), respectively.

We use the global 3-D monthly archive of oxidant and radical concentrations from the GEOS-Chem simulation of Schmidt et al. (2016), that included detailed gas and aerosol chemistry. We apply diurnal scaling following Holmes et al. (2010) to the monthly mean concentrations of Br, BrO, Cl, ClO, and HOCl; a cosine function of the solar zenith angle for OH and HO₂; and NO-NO₂-O₃ photochemical equilibrium for NO₂. Schmidt et al. (2016) evaluated their simulated tropospheric BrO concentrations (global daytime mean of 0.96 ppt) with observations from satellite and aircraft and found no systematic bias. GEOS-Chem concentrations of NO₂ and H₂O₂ (proxy for HO₂) have been evaluated successfully in a number of aircraft campaigns (Martin et al., 2006; Hudman et al., 2007; Singh et al., 2007; Lin and McElroy, 2010; Mao et al., 2010; Travis et al., 2016). GEOS-Chem NO₂ columns have also been evaluated against satellite observations over China (Lin et al., 2012), North America (e.g., Lamsal et al., 2014), and Africa (Marais et al., 2012). Fast Hg⁰ oxidation in the polar spring boundary layer is simulated by specifying high BrO concentrations when conditions for temperature, sea ice cover, sunlight, and

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atmospheric stability are met (Holmes et al., 2010). Monthly mean organic aerosol (OA) concentrations are archived from a separate v9-02 GEOS-Chem simulation including primary emissions from combustion and secondary production from biogenic and anthropogenic hydrocarbons (Pye et al., 2010). An evaluation of modeled OA against aircraft observations globally is presented in Heald et al. (2011), which showed no systematic bias in remote environments but an underestimate of median concentrations in polluted regions. Aqueous-phase concentrations of Hg^0 , O_3 , and HOCl are determined from the gas-phase partial pressures and Henry's law coefficients (Table 1). We estimate aqueous in-cloud OH concentrations following Jacob et al. (2005) as $[\text{OH}(\text{aq})] = \beta [\text{OH}(\text{g})]$ with $\beta = 1 \times 10^{19} \text{ M cm}^3 \text{ molecule}^{-1}$.

3.3 Atmosphere-ocean coupling

GEOS-Chem v9-02 uses a 2-D surface-slab ocean model with no lateral transport and with fixed subsurface ocean concentration boundary conditions (Soerensen et al., 2010). Oceanic circulation and mixing between the surface mixed layer and deeper ocean strongly impacts Hg^0 concentrations in the surface ocean through the supply of reducible Hg^{II} , driving changes in oceanic evasion (Soerensen et al., 2013; Soerensen et al., 2014). Here we present a new two-way coupling of the GEOS-Chem atmospheric Hg simulation to the MITgcm 3-D oceanic general circulation model with embedded ecology (Y. Zhang et al., 2015). First, the GEOS-Chem Hg model with the 2-D slab ocean is initialized over 15 years of repeated present-day emissions and meteorological data (15 years is required to equilibrate the stratosphere). Starting from these initial conditions, we conduct the GEOS-Chem simulation for the desired period (here three years, 2009-2011) and archive monthly surface air Hg^0 concentrations and total Hg^{II} deposition fluxes. We then initialize the Y. Zhang et al. (2015) ocean model for 20 years with these archived surface boundary conditions to equilibrate the upper several hundred meters of the ocean. The monthly mean surface ocean Hg^0 concentrations from the final year of the simulation are then input to GEOS-Chem, replacing the 2-D slab ocean model concentrations. The 15-year GEOS-Chem simulation is repeated with this new input. This process is iterated until convergence of results is achieved. We find that two iterations are sufficient.

4. Global budget of atmospheric mercury

4.1 Budget and lifetimes

Figure 1 (top panel) shows the simulated vertical and latitudinal distributions of annual zonal mean Hg^0 and Hg^{II} mixing ratios. The fraction of tropospheric Hg^{II} in the aerosol phase ranges from less than 10% to more than 90% (Amos et al., 2012). Modeled Hg^0 decreases rapidly in the stratosphere, while Hg^{II} increases with altitude and dominates total Hg in the stratosphere. This vertical structure is driven by chemistry (Selin et al., 2007; Holmes et al., 2010) and these general vertical trends in the two species are consistent with limited available observations (Murphy et al., 2006; Talbot et al., 2007; Lyman and Jaffe, 2012). The exact partitioning of total Hg in the stratosphere between Hg^0 and Hg^{II} is uncertain and GEOS-Chem predicts a higher Hg^{II} fraction relative to other models (Bieser et al., 2016). Photodissociation of gas-phase Hg^{II} halides may be possible at ultraviolet wavelengths (Maya, 1977) but whether this is important in the mid-to-upper stratosphere requires further investigation. The stratosphere in the model accounts for 12% of total Hg atmospheric mass and is in a very different redox regime

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from the troposphere. Here we focus on tropospheric budgets, which are most relevant to Hg deposition. The stratosphere is discussed further in Section 4.4.

Figure 2 shows the global tropospheric Hg budget from our GEOS-Chem simulation, including the rates of the major Hg⁰/Hg^{II} cycling pathways. The global tropospheric Hg reservoir is 3900 Mg, including 3500 Mg as Hg⁰ and 400 Mg as Hg^{II}, smaller than the 4500 Mg reservoir in Holmes et al. (2010). In both cases, the reservoir was adjusted through the Hg^{II} photoreduction rate coefficient to match the observed annual mean TGM at long-term monitoring sites, mainly located in northern mid-latitudes (Figure 3). Holmes et al. (2010) used observations for 2000-2008 averaging $1.87 \pm 1.00 \text{ ng m}^{-3}$ STP ($p = 1 \text{ atm}$, $T = 273 \text{ K}$; $n = 39$ sites), whereas we use observations for 2007-2013 averaging $1.46 \pm 0.25 \text{ ng m}^{-3}$ STP ($n = 37$). Observed atmospheric concentrations in North America and Europe have declined on average by 1-2% a⁻¹ since 1990, which has been attributed to the phase-out of Hg from commercial products and declines in coal Hg emissions as a co-benefit of SO₂ and NO_x emission controls (Zhang et al., 2016). Observations used in Holmes et al. (2010) also included very high concentrations at four East Asian sites (3-7 ng m⁻³ STP; Nguyen et al., 2007; Sakata and Asakura, 2007; Feng et al., 2008; Wan et al., 2009), whereas the more recent observations over East Asia used here ($n = 6$) are all less than 3 ng m⁻³ STP (Sheu et al., 2010; Fu et al., 2012a, 2012b; H. Zhang et al., 2015a). Only one site (Mt. Changbai, China) has data available during both time periods and observed TGM concentrations decreased there by a factor of two (Fu et al., 2012b). Thus, our atmospheric loadings may be more representative of recent (ca. 2010) conditions.

We calculate several atmospheric lifetimes to understand the processes driving Hg deposition: the chemical lifetime of Hg⁰ against oxidation, the chemical lifetime of Hg^{II} against reduction, the lifetime of Hg^{II} against deposition, and the lifetime of total gaseous mercury (TGM = Hg⁰+Hg^{II}(g)) against deposition. We find that the lifetime of Hg⁰ against oxidation to Hg^{II} in the troposphere is 2.7 months, with Br atom-initiated pathways contributing 97% of total oxidation. This chemical lifetime is smaller than most prior model estimates, e.g., 6 months in Holmes et al. (2010), which used lower Br concentrations. The addition of NO₂ and HO₂ as second-stage oxidants is also important in increasing the rate of HgBr conversion to Hg^{II}, more than compensating for faster thermal decomposition of HgBr relative to Holmes et al. (2010). Our results are consistent with Shah et al. (2016), who estimated a global annual tropospheric Hg⁰ lifetime against oxidation to Hg^{II} by Br atoms of 1.2 to 2.8 months, based on their simulation of measurements of Hg^{II} over the Southeast US in summer during the NOMADSS campaign (Gratz et al., 2015). The dominance of NO₂ and HO₂ as HgBr oxidants reflects their high atmospheric abundance and is consistent with results from a box modeling study over the Pacific (Wang et al., 2014). We find Cl atoms contribute less than 1% of Hg⁰ oxidation globally because the supply of Cl atoms (mean tropospheric mixing ratio of 2×10^{-4} ppt) is limited by fast conversion to the stable reservoir HCl. Aqueous-phase pathways in clouds contribute 2%. Our work suggests that the dominant Hg^{II} species produced in the gas phase are BrHgONO and BrHgOOH, though the actual speciation of Hg^{II} in the atmosphere would likely be modified through cycling in aerosols and clouds (Hedgecock and Pirrone, 2001; Lin et al., 2006). We did not consider heterogeneous Hg⁰ oxidation on particle surfaces (e.g., Vidic et al., 1998; Flora et al., 1998; Lee et al., 2004) due to inadequate information to formulate atmospheric rates. Further study of heterogeneous Hg⁰ oxidation is needed (Ariya et al., 2015).

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The vertical distribution of $\text{Hg}^0 \rightarrow \text{Hg}^{\text{II}}$ oxidation rates is shown in the bottom panel of Figure 1 in units of number density (relevant to the mass budget) and mixing ratio (relevant to transport). Only 1% of Hg^0 oxidation occurs in the stratosphere, consistent with previous work (Holmes et al., 2010). Most Hg oxidation by mass occurs in the extratropical free troposphere, consistent with the Br distribution (Schmidt et al., 2016), and is faster in the northern hemisphere because of higher NO_2 concentrations. Hg^0 oxidation in Holmes et al. (2010) was fastest in the Southern Ocean MBL due to high Br concentrations from sea-salt aerosol debromination, but debromination in that region is unlikely, since the sea salt aerosol remains alkaline (Murphy et al., 1998; Alexander et al., 2005; Schmidt et al., 2016). In general, the addition of 2nd-stage oxidants HO_2 and NO_2 shifts Hg oxidation to lower latitudes relative to Holmes et al. (2010). This has implications for Hg deposition, which we discuss in Section 5. Hg^0 oxidation in terms of mixing ratio features a secondary maximum in the tropical upper troposphere where the Br/BrO ratio is high (Parrella et al., 2012; Fernandez et al., 2014).

We find that the shorter chemical lifetime of Hg^0 in our simulation relative to Holmes et al. (2010) must be balanced by faster atmospheric reduction to reproduce observed TGM concentrations. This is implemented by adjusting the photoreduction coefficient α in Table 1. The resulting mean lifetime of Hg^{II} against reduction in the troposphere is 13 days. Shah et al. (2016) similarly found that faster Hg^0 oxidation as needed to match NOMADSS observations required faster Hg^{II} reduction, with a tropospheric Hg^{II} lifetime against reduction of 19 days. The lifetime of tropospheric Hg^{II} against deposition is relatively long, 26 days (see Figure 2), because most Hg^{II} production occurs in the free troposphere where precipitation is infrequent (Figure 1). Hg^{II} reduction in the model is faster in the northern hemisphere than in the southern hemisphere because of higher OA concentrations. Hence Hg^{II} concentrations are higher in the southern than in the northern hemisphere (Figure 1).

We find here that the Hg^{II} lifetime against reduction is shorter than against deposition, emphasizing the importance of reduction in controlling the atmospheric Hg budget. By contrast, Holmes et al. (2010) found an Hg^{II} tropospheric lifetime of 50 days against reduction and 36 days against deposition, which led them to conclude that no reduction was needed if Hg^0 oxidation kinetics were decreased within their uncertainty. This is no longer possible in our simulation because of the much faster Hg^0 oxidation. We conclude that atmospheric Hg^{II} reduction must take place although the mechanism is not established. With Hg^{II} reduction, the overall lifetime of tropospheric TGM against deposition in our simulation is 5.2 months, similar to the estimate of 6.1 months in Holmes et al. (2010). We discuss the consistency of this estimate with observations in the next section.

4.2 Global distribution

Figure 3 compares our simulation to observed 2007-2013 TGM surface concentrations. TGM includes Hg^0 and the gaseous component of Hg^{II} . Observations include annual means at 37 land sites plus ship cruises. The spatial correlation coefficient between model and observations is $r = 0.57$. The mean at land stations is $1.47 \pm 0.27 \text{ ng m}^{-3}$ STP in the observations and $1.44 \pm 0.25 \text{ ng m}^{-3}$ STP in the model, with the good agreement in the mean reflecting the adjustment of the Hg^{II} photoreduction rate coefficient as explained above.

Beyond this simulation of the mean, we successfully reproduce the observed standard deviation of TGM concentrations, which places an independent constraint on the atmospheric lifetime of Hg against deposition (Junge,

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1974; Hamrud, 1983). This constraint had previously been expressed in terms of the interhemispheric gradient of TGM from ship cruises, leading to TGM lifetime estimates ranging from 4.4 months to 2 years (Slemr et al., 1981; Fitzgerald et al., 1983; Lindqvist and Rodhe, 1985; Lamborg et al., 2002). However, we find the interhemispheric gradient in surface concentrations is not a sensitive diagnostic of lifetime because surface atmospheric Hg in the southern hemisphere is controlled more by atmosphere-ocean exchange than by transport from the northern hemisphere. For example, changing the simulation of atmosphere-ocean exchange from the slab ocean to the MITgcm (Section 3.3) increases the TGM lifetime while also increasing the interhemispheric gradient due to changed ocean emissions. We conducted a sensitivity simulation doubling the tropospheric TGM lifetime in the model (to 10.4 months) by decreasing the rate of Hg⁰ oxidation. This produced less than 20% of a decline in the interhemispheric gradient, but the relative standard deviation of TGM concentrations across land stations decreased by 40%. Thus the overall variability of TGM concentrations provides a more sensitive constraint on the TGM atmospheric lifetime, while the interhemispheric gradient can be misleading. The model's ability to reproduce the observed standard deviation across land sites supports our simulated TGM atmospheric lifetime of 5.2 months.

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4.3. Seasonality

Figure 4 compares simulated and observed seasonal cycles of TGM concentrations at land stations in the northern mid-latitudes (30° to 60° N) and southern hemisphere (see Figure 3 for site locations). Also shown are results from a sensitivity simulation with the 2-D surface-slab ocean model (Soerensen et al., 2010). The observed seasonal cycle is successfully reproduced in the northern hemisphere. The February maximum and September minimum are driven in the model in part by Hg⁰ oxidation and in part by ocean evasion. Seasonality in radical oxidant concentrations outweighs temperature effects, leading to fastest oxidation in summer and slowest in winter. Modeled oceanic Hg⁰ evasion from the North Atlantic Ocean peaks in winter and early spring, because higher windspeeds increase mixing and entrainment of reducible Hg^{II} from subsurface waters and enhance the rate of air-sea exchange, and Hg removal via particle settling during this time is low (Soerensen et al., 2010, 2013). Similar to Song et al. (2015), we find that the 2-D slab ocean overestimates the observed seasonality at northern mid-latitude sites (Figure 4). Atlantic and Pacific Ocean seawater Hg⁰ measurements indicate this overestimate results from oversimplified ocean physics and the fixed boundary condition for subsurface ocean concentrations in the slab ocean model (Soerensen et al., 2014). Previous work shows one-way coupling to the MITgcm ocean simulation improves simulated surface ocean Hg⁰ concentrations compared to observations (Soerensen et al., 2014). Here, the two-way coupling to the MITgcm also improves the seasonality in atmospheric Hg.

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In the southern hemisphere, Amsterdam Island in the Indian Ocean and Cape Point on the South African coast have similar monthly average concentrations and show no significant seasonal variation (Angot et al., 2014; Slemr et al., 2015). By contrast, the model at those sites has strong seasonality, as previously shown for the standard model version v9-02 (Song et al., 2015). We find a modest improvement in moving from the slab ocean simulation to the MITgcm but the seasonal bias is still large. Long-range transport of atmospheric Hg from Antarctica could influence observed seasonality at these sites (Angot et al., 2016). Capturing the seasonality of atmospheric Hg in the Arctic using GEOS-Chem required parameterization of unique sea-ice, oceanic, and riverine dynamics (Fisher et al.,

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2012; 2013; Y. Zhang et al., 2015) and a similar analysis for the Southern Ocean region, with its distinct productivity dynamics impacting Hg cycling (e.g., Cossa et al., 2011; Gionfriddo et al., 2016), has not yet been performed.

5 4.4. Vertical distribution and the stratosphere

Hg⁰ concentrations in the model drop rapidly above the tropopause (Figure 1), consistent with observations (Talbot et al., 2007; Slemr et al., 2009). Modeled Hg⁰ oxidation in the lower stratosphere is almost exclusively from Br atoms. There is no significant Hg^{II} reduction there because OA concentrations and relative humidity are very low. Extensive TGM observations in the lowermost stratosphere at northern extratropical latitudes are available from the CARIBIC program that collects measurements aboard commercial aircraft (Slemr et al., 2009; 2014; 2016). The early stratospheric data were biased low and we focus on corrected data available for April 2014–January 2015 (Slemr et al., 2016). TGM in the stratosphere is expected to be mainly Hg⁰ because Hg^{II} is incorporated into aerosol (Murphy et al., 2006; Lyman and Jaffe, 2012).

Figure 5 compares the stratospheric TGM concentrations measured in CARIBIC to model values sampled along the flight tracks. The CARIBIC data also include ozone (O₃) and CO concentrations (Brenninkmeijer et al., 2007). Here we use O₃ concentration as a chemical coordinate for depth into the stratosphere and exclude tropospheric data as diagnosed by [O₃]/[CO] < 1.25 mol mol⁻¹ (Hudman et al., 2007). We correlate the logarithm of TGM concentrations, as a measure of first-order loss, to the O₃ concentrations. The observations reach higher ozone than the model, indicating that they sample air with greater stratospheric influence. The model underestimates the log(TGM)-ozone slope by a factor of 2. To test whether this underestimate is due to slow Hg⁰ oxidation, we performed a sensitivity simulation doubling the stratospheric Hg⁰ oxidation rate (green line in Figure 5). The model slope increases by only 32%. This suggests that the log(TGM)-ozone relationship in the lowermost stratosphere is set in part by mixing rather than solely by chemistry (Xiao et al., 2007). The model underestimate of the log(TGM)-ozone slope could reflect excessive dynamical mixing in the lower stratosphere, a well-known problem in stratospheric transport models (Schoeberl et al., 2003; Tan et al., 2004), or errors in the timescales of air transit across the tropopause which vary on the order of months to years (Orbe et al., 2014; Ploeger and Birner, 2016).

5. Implications for global Hg deposition

Figure 6 compares simulated and observed annual Hg wet deposition at sites in North America, Europe, and China for 2007–2013. The model captures the spatial variability across sites in North America relatively well ($r = 0.57$). Some of this variability is driven by precipitation amount, which leads to higher modeled deposition along the Northwest coast and over the North Atlantic. The maximum along the coast of the Gulf of Mexico is due to deep convection scavenging upper tropospheric air enriched in Hg^{II} (Guentzel et al., 2001; Selin and Jacob, 2008; Holmes et al., 2016). Previous GEOS-Chem simulations with Br-initiated oxidation of Hg⁰ failed to capture this maximum because Hg^{II} production favored higher latitudes (Holmes et al., 2010; Amos et al., 2012). The inclusion of NO₂ and HO₂ as second-stage oxidants in our simulation shifts Hg^{II} production to lower latitudes and matches the general

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location of the Gulf of Mexico maximum, although the magnitude is still underestimated. Increasing horizontal resolution in the model could improve the definition of the maximum (Zhang et al., 2012).

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Over Europe, deposition is fairly uniform and low in the model and observations. This reflects decreased anthropogenic Hg^{II} emissions in the region from emissions controls on coal-fired power plants (Klimont et al., 2013; Muntean et al., 2014; Zhang et al., 2016). There is no area of frequent deep convection, unlike the Gulf of Mexico for the US.

Observations of Hg wet deposition over China have recently become available (Fu et al., 2015; Fu et al., 2016). Values at urban sites are high, likely reflecting local Hg^{II} emissions, and are correlated with high concentrations of particulate Hg^{II} (Fu et al., 2016). Values at rural sites are much lower and comparable to wet deposition observed in North America and Europe despite higher TGM concentrations in China (see Figure 3). We simulate these low values successfully in our model, whereas a simulation with the standard GEOS-Chem v9-02 overestimates them by a factor of 4. This reflects in part our dependence of Hg^{II} reduction on OA concentrations, which are particularly high in China (Heald et al., 2011). Decreasing wet deposition in this region in the model has implications for the long-range transport of atmospheric Hg from East Asia (Weiss-Penzias et al., 2007).

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Figure 7 shows the global distribution of wet and dry Hg^{II} deposition in the model. This deposition is the main Hg source to the open ocean (Sunderland and Mason, 2007; Soerensen et al., 2010). We find that 80% of global Hg^{II} deposition is to the oceans, compared to 71% in Holmes et al. (2010), and that 60% of this deposition is wet.

Even though surface Hg⁰ concentrations are higher over land, most Hg⁰ oxidation takes place in the free troposphere and is globally distributed (Figure 1). Concentrations of Br atoms are higher over oceans, reflecting their marine origin (Schmidt et al., 2016). The dependence of Hg^{II} reduction in our mechanism on the formation of Hg-organic complexes further shifts Hg^{II} deposition away from continents where OA concentrations are highest (Heald et al., 2011). The change in Br distribution and dominance of HO₂ and NO₂ as second-stage oxidants for HgBr shifts Hg^{II} deposition to lower latitudes relative to the simulation by Holmes et al. (2010), where most deposition occurred over high-latitude oceans. We now find 49% of global total Hg^{II} deposition is to tropical oceans (30°S - 30°N). The global ocean is a net sink for total atmospheric Hg of 1700 Mg a⁻¹ (Figure 2), with approximately half taken up by tropical oceans. A large Hg^{II} deposition flux to the tropical oceans is suggested by recent cruise observations of high oceanic Hg⁰ concentrations across the intertropical convergence zone (ITCZ), which GEOS-Chem previously underestimated (Soerensen et al., 2014).

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The change in Br distribution and dominance of HO₂ and NO₂ as second-stage oxidants for HgBr shifts Hg^{II} deposition to lower latitudes relative to the simulation by Holmes et al. (2010), where most deposition occurred over high-latitude oceans. We now find 49% of global total Hg^{II} deposition is to tropical oceans (30°S - 30°N). The global ocean is a net sink for total atmospheric Hg of 1700 Mg a⁻¹ (Figure 2), with approximately half taken up by tropical oceans. A large Hg^{II} deposition flux to the tropical oceans is suggested by recent cruise observations of high oceanic Hg⁰ concentrations across the intertropical convergence zone (ITCZ), which GEOS-Chem previously underestimated (Soerensen et al., 2014).

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6. Conclusions

The atmospheric redox chemistry of mercury (Hg⁰/Hg^{II}) determines the global patterns of Hg deposition to surface ecosystems. Here we developed an updated chemical mechanism for use in atmospheric models, and evaluated it in the GEOS-Chem global model to gain new insights into the global Hg budget and the patterns of Hg deposition. As part of this work we also developed a new coupling between GEOS-Chem and a 3-D ocean general circulation model (MITgcm), resulting in a fully resolved simulation of Hg transport and chemistry in the atmosphere-ocean system.

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The updated atmospheric Hg⁰/Hg^{II} redox mechanism includes gas-phase Br as the main Hg⁰ oxidant in the troposphere and stratosphere, and second-stage oxidation of HgBr by a number of radical oxidants including NO₂ and HO₂. Br concentrations in GEOS-Chem are from the recent simulation of Schmidt et al. (2016), and are higher than previous models and more consistent with recent aircraft and satellite observations of BrO. Atmospheric reduction of Hg^{II} is hypothesized to take place by photolysis of aqueous-phase Hg^{II}-organic complexes. This is parameterized in GEOS-Chem as a function of the local concentration of organic aerosol (OA).

The global mass of atmospheric Hg simulated by GEOS-Chem is 4400 Mg, including 3900 Mg in the troposphere. The tropospheric lifetime of Hg⁰ against oxidation is 2.7 months. Observations of the atmospheric variability of total gaseous mercury (TGM = Hg⁰ + Hg^{II}(g)) suggest an atmospheric lifetime against deposition of about 6 months. Thus, Hg^{II} must be reduced in the atmosphere, which is consistent with recent observations of atmospheric Hg isotope fractionation. Matching the observed mean surface TGM concentrations in GEOS-Chem implies a tropospheric Hg^{II} lifetime of 13 days against reduction and 26 days against deposition. This results in an overall tropospheric lifetime for TGM of 5.2 months against deposition and enables a successful simulation of the observed relative standard deviation of TGM concentrations across terrestrial sites. The interhemispheric difference in TGM concentrations had previously been interpreted to suggest a longer TGM lifetime against deposition, but we show this is misleading because TGM in the southern hemisphere is mostly controlled by oceanic emissions rather than transport from the northern hemisphere.

The observed seasonality of TGM concentrations in northern mid-latitudes (maximum in February, minimum in September) is reproduced by the model, where it is attributed to photochemical oxidation of Hg⁰ and oceanic evasion both with similar seasonal effects on TGM concentrations. Coupling GEOS-Chem to the MITgcm 3-D ocean model improves simulation of the seasonal amplitude by lowering oceanic evasion over the North Atlantic due to elimination of the static subsurface ocean boundary condition in the GEOS-Chem slab ocean, and more realistic ocean physics. Observations at southern hemisphere sites show little seasonality whereas the model features a spring maximum. More work is needed to understand this discrepancy.

Observations show a rapid depletion of TGM above the tropopause and we examined whether this could provide a test for Hg⁰ chemistry. For that purpose we used extensive lowermost-stratospheric observations from the CARIBIC program aboard commercial aircraft, and characterized TGM first-order loss as the slope of the log(TGM)-ozone relationship. We find that the model underestimates the observed log(TGM)-ozone slope by a factor of two, but that this slope is only moderately sensitive to the rate of Hg⁰ oxidation and appears to be driven in part by mixing of air parcels with different stratospheric ages. This mixing is likely too fast in GEOS-Chem, which may explain the weaker TGM-ozone slope.

Hg wet deposition fluxes in the model are consistent with spatial patterns observed in North America and Europe. Inclusion of NO₂ and HO₂ as second-stage HgBr oxidants in the model shifts Hg^{II} production to lower latitudes compared to previous versions of GEOS-Chem and enables the model to capture the location of the observed maximum in wet deposition along the Gulf Coast of the US. However, the magnitude of this Gulf Coast maximum is still underestimated. In rural areas of China, wet deposition is observed to be low despite very high

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TGM concentrations. This is reproduced by the model where it is due to fast Hg^{II} reduction, driven in part by very high OA concentrations.

We find that 80% of global Hg^{II} deposition takes place over the oceans, reflecting in part the marine origin of Br as well as the relatively low marine OA concentrations and hence slow Hg^{II} reduction. More Hg is deposited to the tropical oceans (49% of total Hg^{II} deposition) compared to previous versions of GEOS-Chem where debromination of sea salt aerosol drove fast Hg⁰ oxidation and deposition to the Southern Ocean. Observations of the latitudinal gradient of Hg^{II} wet deposition over the ocean would provide a sensitive test of Hg chemistry and improve understanding of Hg inputs to different ocean regions.

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Table 1. Chemical mechanism for atmospheric mercury.

Reaction	Rate expression ^a	Reference ^b
<i>Gas phase</i>		
$\text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M}$	$1.46 \times 10^{-32} (T/298)^{-1.86} [\text{Hg}^0][\text{Br}][\text{M}]$	(1)
$\text{HgBr} + \text{M} \rightarrow \text{Hg}^0 + \text{Br} + \text{M}$	$1.6 \times 10^{-9} (T/298)^{-1.86} \exp(-7801/T) [\text{HgBr}][\text{M}]$	(2)
$\text{HgBr} + \text{Br} \rightarrow \text{Hg}^0 + \text{Br}_2$	$3.9 \times 10^{-11} [\text{HgBr}][\text{Br}]$	(3)
$\text{HgBr} + \text{NO}_2 \rightarrow \text{Hg}^0 + \text{BrNO}_2$	$3.4 \times 10^{-12} \exp(391/T) [\text{HgBr}][\text{NO}_2]$	(4)
$\text{HgBr} + \text{Br} \xrightarrow{\text{M}} \text{HgBr}_2$	$3.0 \times 10^{-11} [\text{HgBr}][\text{Br}]$	(3) ^c
$\text{HgBr} + \text{NO}_2 \xrightarrow{\text{M}} \text{HgBrNO}_2$	$k_{\text{NO}_2}([\text{M}], T) [\text{HgBr}][\text{NO}_2]$	(4) ^d
$\text{HgBr} + \text{Y} \xrightarrow{\text{M}} \text{HgBrY}$	$k_{\text{HO}_2}([\text{M}], T) [\text{HgBr}][\text{Y}]$	(4) ^{d, e}
$\text{Hg}^0 + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$	$2.2 \times 10^{-32} \exp(680(1/T - 1/298)) [\text{Hg}^0][\text{Cl}][\text{M}]$	(5)
$\text{HgCl} + \text{Cl} \rightarrow \text{Hg}^0 + \text{Cl}_2$	$1.20 \times 10^{-11} \exp(-5942/T) [\text{HgCl}][\text{Cl}]$	(6) ^f
$\text{HgCl} + \text{Br} \xrightarrow{\text{M}} \text{HgBrCl}$	$3.0 \times 10^{-11} [\text{HgCl}][\text{Br}]$	(3) ^{c, g}
$\text{HgCl} + \text{NO}_2 \xrightarrow{\text{M}} \text{HgClNO}_2$	$k_{\text{NO}_2}([\text{M}], T) [\text{HgCl}][\text{NO}_2]$	(4) ^{d, g}
$\text{HgCl} + \text{Y} \xrightarrow{\text{M}} \text{HgClY}$	$k_{\text{HO}_2}([\text{M}], T) [\text{HgCl}][\text{Y}]$	(4) ^{d, e, g}
<i>Aqueous phase^h</i>		
$\text{Hg}^0_{(aq)} + \text{O}_{3(aq)} \rightarrow \text{Hg}^{\text{II}}_{(aq)} + \text{products}$	$4.7 \times 10^7 [\text{Hg}^0_{(aq)}][\text{O}_{3(aq)}]$	(7)
$\text{Hg}^0_{(aq)} + \text{HOCl}_{(aq)} \rightarrow \text{Hg}^{\text{II}}_{(aq)} + \text{OH}^-_{(aq)} + \text{Cl}^-_{(aq)}$	$2 \times 10^6 [\text{Hg}^0_{(aq)}][\text{HOCl}_{(aq)}]$	(8), (9) ⁱ
$\text{Hg}^0_{(aq)} + \text{OH}_{(aq)} \rightarrow \text{Hg}^{\text{II}}_{(aq)} + \text{products}$	$2.0 \times 10^9 [\text{Hg}^0_{(aq)}][\text{OH}_{(aq)}]$	(10), (11)
$\text{Hg}^{\text{II}}_{(aq)} + h\nu \rightarrow \text{Hg}^0_{(aq)}$	$\alpha_{\text{NO}_2}^j [\text{OA}][\text{Hg}^{\text{II}}_{(aq)}]$	this work ^j

^a Rate expressions for gas-phase reactions have units of molecule $\text{cm}^{-3} \text{s}^{-1}$ where [] denotes concentration in number density units of molecules cm^{-3} , [M] is the number density of air, and T is temperature in K. Rate expressions for aqueous-phase reactions have units of M s^{-1} and $[\text{aq}]$ denotes concentration in M (mol L^{-1}).

^b Henry's law coefficients (M atm^{-1}) relating gas-phase and aqueous-phase concentrations are $1.28 \times 10^{-1} \exp(2482(1/T - 1/298))$ for Hg^0 (Sanemasa, 1975), $1.1 \times 10^{-2} \exp(2400(1/T - 1/298))$ for O_3 (Jacob, 1986), $6.6 \times 10^2 \exp(5900(1/T - 1/298))$ for HOCl (Huthwelker et al., 1995), and 1.4×10^6 for Hg^{II} (HgCl_2 ; Lindqvist and Rodhe, 1985). The concentration of $\text{OH}_{(aq)}$ is estimated as given in the text. Lifetimes of Hg^{I} species are sufficiently short that steady-state can be assumed **at all times**.

^c (1) Donohoue et al., 2006; (2) Dibble et al., 2012; (3) Balabanov et al., 2005; (4) Jiao and Dibble, 2017; (5) Donohoue et al. 2005; (6) Wilcox, 2009; (7) Munthe, 1992; (8) Lin and Pehkonen, 1998; (9) Wang and Pehkonen (2004); (10) Lin and Pehkonen, 1997; (11) Buxton et al., 1988.

^d This is an effective rate constant for intermediate pressures most relevant for atmospheric oxidation and uses a higher level of theory than Goodsite et al. (2004).

^e $k([\text{M}], T) = \left(\frac{k^0(T)[\text{M}]}{1 + k^0(T)[\text{M}]/k^\infty(T)} \right) 0.6^p$, where $p = \left(1 + \left(\log_{10} \left(k^0(T)[\text{M}]/k^\infty(T) \right) \right)^2 \right)^{-1}$. Values of $k^0(T)$ and $k^\infty(T)$ are tabulated by Jiao and Dibble (2017) for different temperatures. At $T = \{220, 260, 280, 298, 320\}$ K $k_{\text{NO}_2}^0 = \{27.4, 13.5, 9.52, 7.10, 5.09\} \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$; $k_{\text{NO}_2}^\infty = \{22.0, 14.2, 12.8, 11.8, 10.9\} \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$;

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$k_{\text{HO}_2}^0 = \{8.40, 4.28, 3.01, 2.27, 1.64\} \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$; $k_{\text{HO}_2}^\infty = \{14.8, 9.10, 7.55, 6.99, 6.11\} \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^e We assume that the rate coefficient determined for $\text{HgBr} + \text{HO}_2$ holds more generally for $Y \equiv \text{HO}_2, \text{OH}, \text{Cl}, \text{BrO},$ and ClO based on [the similarity in their elementary reactions with HgBr](#) and [estimates](#) from Wang et al. (2014).

5 ^f Abstraction alone competes with oxidation to Hg^{II} for HgCl as the rate of HgCl thermal dissociation is negligibly slow (Holmes et al., 2009).

^g $\text{HgCl} + Y$ rate coefficients are assumed to be the same as $\text{HgBr} + Y$. ClHg-Y and BrHg-Y have similar bond energies (Dibble et al., 2012).

10 ^h Oxidation of $\text{Hg}_{(aq)}^0$ takes place in clouds only, with concentrations of $\text{Hg}_{(aq)}^0$ and aqueous-phase oxidants determined by Henry's law equilibrium (footnote *a*). Aerosol liquid water contents under non-cloud conditions are too low for these reactions to be significant. Photoreduction of $\text{Hg}_{(aq)}^{\text{II}}$ takes place in both aqueous aerosols and clouds, with gas-aerosol partitioning of Hg^{II} as given by Amos et al. (2012) outside of clouds and Henry's law equilibrium for HgCl_2 in cloud (footnote *a*). The aerosol is assumed aqueous if $\text{RH} > 35\%$.

15 ⁱ OCl^- has similar kinetics as HOCl but is negligible for typical cloud and aerosol pH given the $\text{HOCl/OCl}^- \text{ p}K_a = 7.53$ (Harris, 2002).

^j Parameterization for photoreduction of aqueous-phase Hg^{II} -organic complexes. Here j_{NO_2} (s^{-1}) is the local photolysis rate constant for NO_2 intended to be representative of the near-UV actinic flux, $[\text{OA}]$ ($\mu\text{g m}^{-3} \text{ STP}$) is the mass concentration of organic aerosol under standard conditions of temperature and pressure ($p = 1 \text{ atm}, T = 273 \text{ K}$), and $\alpha = 5.2 \times 10^{-2} \text{ m}^3 \text{ STP } \mu\text{g}^{-1}$ is a coefficient adjusted in GEOS-Chem to match observed TGM concentrations (see text).

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Table 2. Reactions not included in chemical mechanism.^a

Reaction	Reference ^b	Note
$\text{Hg}^0 + \text{Br}_2 \xrightarrow{\text{M}} \text{HgBr}_2$	Balabanov et al. (2005); Auzmendi-Murua et al. (2014)	c
$\text{Hg}^0 + \text{Cl}_2 \xrightarrow{\text{M}} \text{HgCl}_2$	Auzmendi-Murua et al. (2014)	c
$\text{Hg}^0 + \text{I}_2 \xrightarrow{\text{M}} \text{HgI}_2$	Auzmendi-Murua et al. (2014)	c
$\text{Hg}^0 + \text{Br}_2 \rightarrow \text{HgBr} + \text{Br}$	Auzmendi-Murua et al. (2014)	d
$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl} + \text{Cl}$	Auzmendi-Murua et al. (2014)	d
$\text{Hg}^0 + \text{I}_2 \rightarrow \text{HgI} + \text{I}$	Auzmendi-Murua et al. (2014)	d
$\text{Hg}^0 + \text{OH} \rightarrow \text{HgO} + \text{H}$	Hynes et al. (2009)	d
$\text{Hg}^0 + \text{OH} \xrightarrow{\text{M}} \text{HgOH}$	Goodsite et al. (2004); Hynes et al. (2009)	e
$\text{HgOH} + \text{O}_2 \rightarrow \text{HgO} + \text{HO}_2$	Shepler and Peterson (2003); Hynes et al. (2009)	d
$\text{Hg}^0 + \text{HO}_2 \xrightarrow{\text{M}} \text{HgOOH}$	Dibble et al. (2012)	e
$\text{Hg}^0 + \text{NO}_3 \xrightarrow{\text{M}} \text{HgONO}_2$	Dibble et al. (2012)	e, f
$\text{Hg}^0 + \text{I} \xrightarrow{\text{M}} \text{HgI}$	Greig et al. (1970); Goodsite et al. (2004); Subir et al. (2011)	e, g
$\text{Hg}^0 + \text{BrO} \xrightarrow{\text{M}} \text{HgBrO}$	Balabanov and Peterson (2003); Balabanov et al. (2005); Dibble et al. (2012, 2013)	e, h
$\text{Hg}^0 + \text{ClO} \xrightarrow{\text{M}} \text{HgClO}$	Balabanov and Peterson (2003); Dibble et al. (2012, 2013)	e, h
$\text{Hg}^0 + \text{HCl} \rightarrow \text{Hg}^{\text{II}} + \text{products}$	Hall and Bloom (1993); Subir et al. (2011)	g
$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{\text{II}} + \text{products}$	see note	i
$\text{HgBr} + \text{I} \xrightarrow{\text{M}} \text{HgBrI}$	see note	j
$\text{HgBr} + \text{IO} \xrightarrow{\text{M}} \text{HgBrOI}$	see note	j
$\text{Hg}_{(aq)}^0 + \text{HOBr}_{(aq)} \rightarrow \text{Hg}_{(aq)}^{\text{II}} + \text{OH}^-_{(aq)} + \text{Br}^-_{(aq)}$	Wang and Pehkonen (2004); Hynes et al. (2009)	k
$\text{Hg}_{(aq)}^0 + \text{OBr}_{(aq)} + \text{H}^+ \rightarrow \text{Hg}_{(aq)}^{\text{II}} + \text{OH}^- + \text{Br}_{(aq)}$	Wang and Pehkonen (2004); Hynes et al. (2009)	k
$\text{Hg}_{(aq)}^0 + \text{Br}_2_{(aq)} \rightarrow \text{Hg}_{(aq)}^{\text{II}} + 2\text{Br}^-_{(aq)}$	Wang and Pehkonen (2004); Hynes et al. (2009)	k
$\text{Hg}_{(aq)}^{\text{II}} \xrightarrow{\text{HO}_2/\text{O}_2^-} \text{Hg}_{(aq)}^{\text{I}} \xrightarrow{\text{HO}_2/\text{O}_2^-} \text{Hg}^0$	Gärdfeldt and Jonsson (2003)	d
$\text{HgSO}_{3(aq)} \rightarrow \text{Hg}_{(aq)}^0 + \text{products}$	van Loon et al. (2001)	l

5 ^a These reactions have been reported in past literature but are now thought to be too slow to be of atmospheric relevance.

^b References supporting non-inclusion in the chemical mechanism.

^c Reaction reported in laboratory studies by Ariya et al. (2002), Yan et al. (2005, 2009), Liu et al. (2007), Raofie et al. (2008), and Qu et al. (2010), but not supported by theory.

^d Endothermic reaction.

10 ^e The Hg^I compounds are weakly bound and thermally dissociate too fast to allow for 2nd step of oxidation to Hg^{II}.

^f Peleg et al. (2015) find a strong correlation between observed nighttime gaseous Hg^{II} and NO₃ radical concentrations in Jerusalem. There is theoretical evidence against NO₃ initiation of Hg⁰ oxidation (Dibble et al., 2012), and NO₃ may instead serve as the second-stage oxidant of Hg^I. This would be important only in warm urban environments where nighttime NO₃ is high.

15 ^g Found to be negligibly slow.

^h The formation of compounds with structural formulae BrHgO and ClHgO requires a prohibitively high activation energy. Note *e* applies to compounds with structural formulae HgBrO, HgOBr, HgClO, and HgOCl.

ⁱ The direct formation of HgO_(s) from this reaction is energetically unfavorable (Calvert and Lindberg, 2005; Tossell, 2006). It has been postulated that intermediate products like HgO₃ could lead to the formation of stable (HgO)_n

20 oligomers or HgO_(s) via decomposition to OHgOO_(g) (Subir et al., 2011), but these must be stabilized through heterogeneous reactions on atmospheric aerosols (Calvert and Lindberg, 2005) and the associated mechanism is unlikely to be significant in the atmosphere (Hynes et al., 2009). A gas-phase reaction has been reported in chamber studies (Hall, 1995; Pal and Ariya, 2004; Sumner et al., 2005; Snider et al., 2008; Rutter et al., 2012), but this is

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likely to have been influenced by the walls of the chamber (as seen in Pal and Ariya, 2004) and presence of secondary organic aerosols (in Rutter et al., 2012).

^j Atmospheric concentrations of I and IO (Dix et al., 2013; Prados-Roman et al., 2015; Volkamer et al., 2015) are too low for these reactions to be significant.

5 ^k Rates are too slow to be of relevance.

^l Concentrations of HgSO₃ under typical atmospheric SO₂ levels are expected to be very low.

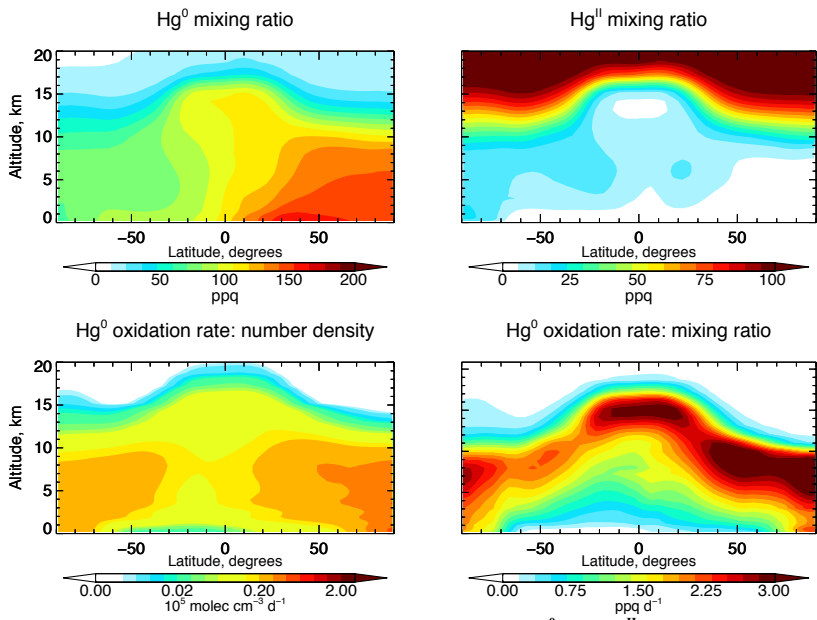


Figure 1. Annual (2009-2011) zonal mean mixing ratios of Hg⁰ and Hg^{II} in GEOS-Chem, and Hg⁰ oxidation rates in number density and mixing ratio units.

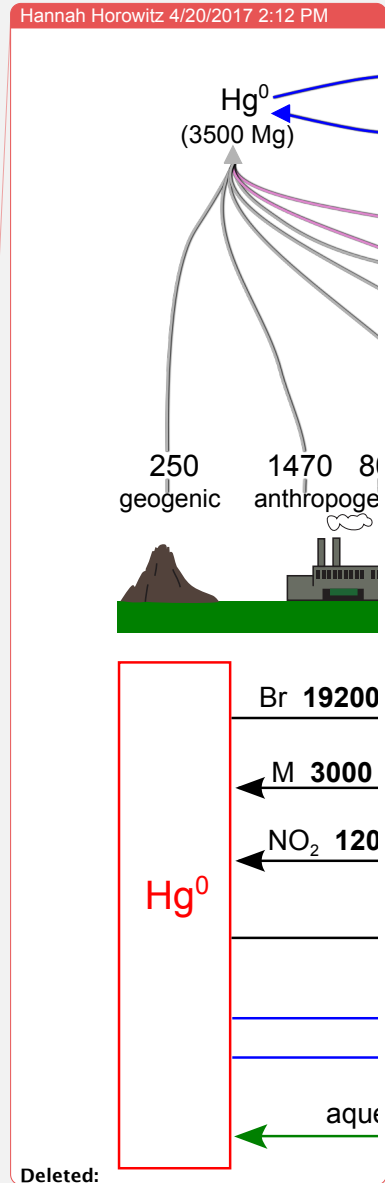
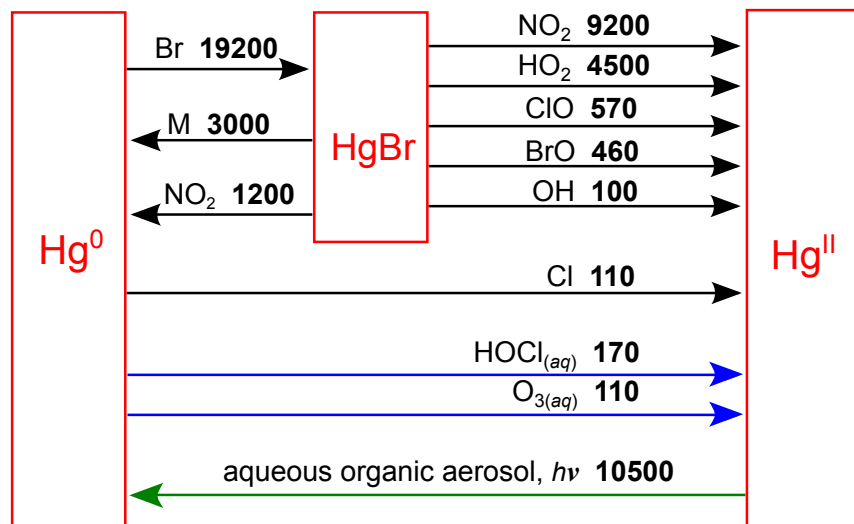
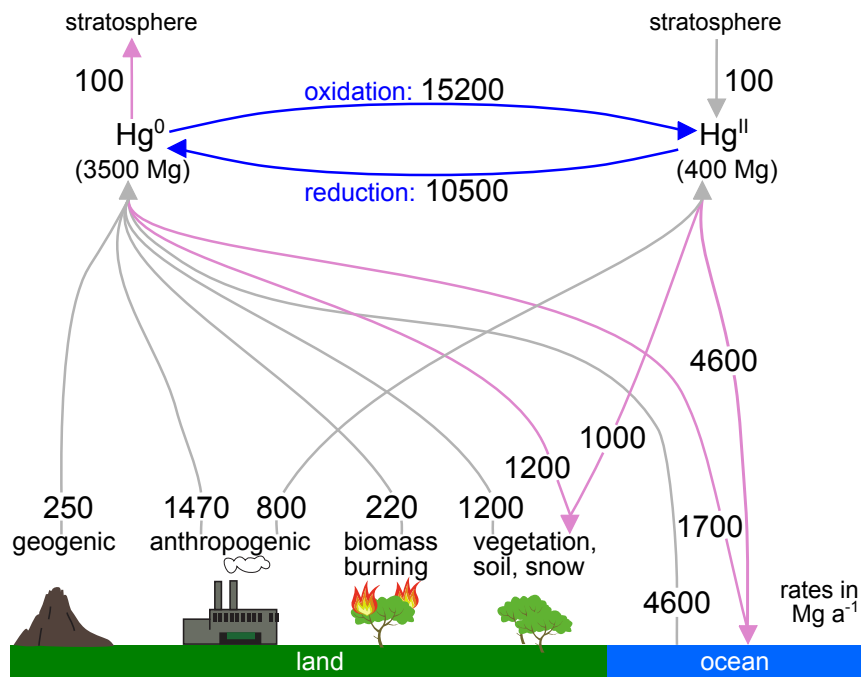
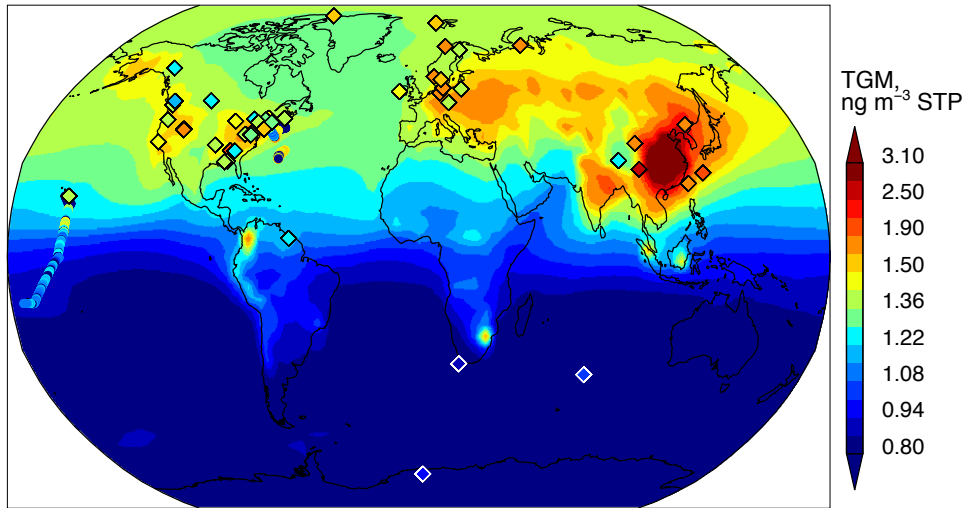


Figure 2. Global budget of tropospheric mercury in GEOS-Chem. Hg^{II} includes gaseous and particulate forms in local **thermodynamic** equilibrium (Amos et al., 2012). The bottom panel identifies the major chemical reactions from Table 1 cycling Hg^0 and Hg^{II} . Reactions with global rates lower than 100 Mg a^{-1} are not shown.

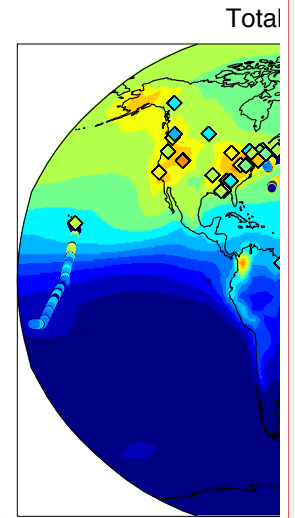
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Total gaseous Hg in surface air



5 | Figure 3. Global distribution of total gaseous mercury (TGM) concentrations in surface air, in ng m^{-3} STP ($p = 1 \text{ atm}$, $T = 273 \text{ K}$). Model values (background) are annual means for 2009-2011. Observations (symbols) are for 2007-2013. Data for land sites (diamonds) are annual means for 2007-2013 as previously compiled by Song et al. (2015) and Zhang et al. (2016). Observations from 2007-2013 ship cruises (circles) are from Soerensen et al. (2013, 2014). Note the change in the linear color scale at 1.50 ng m^{-3} .

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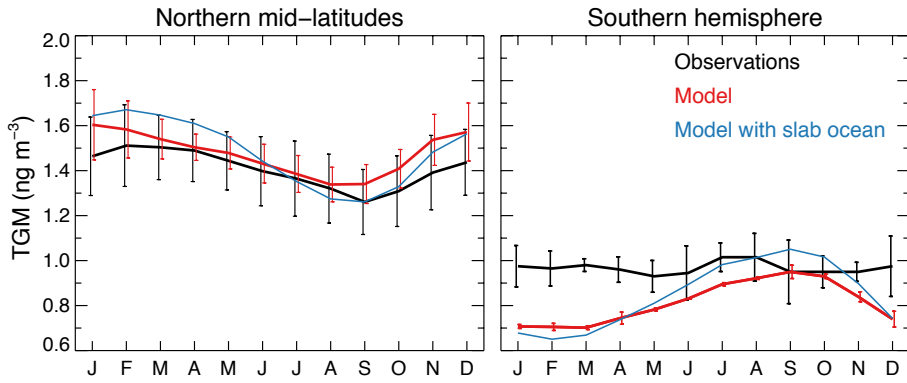
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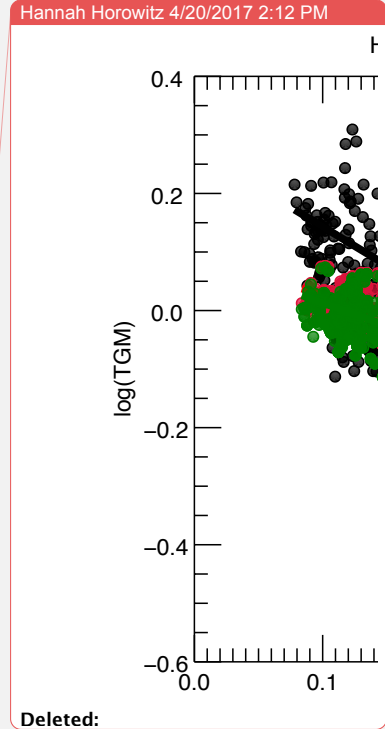
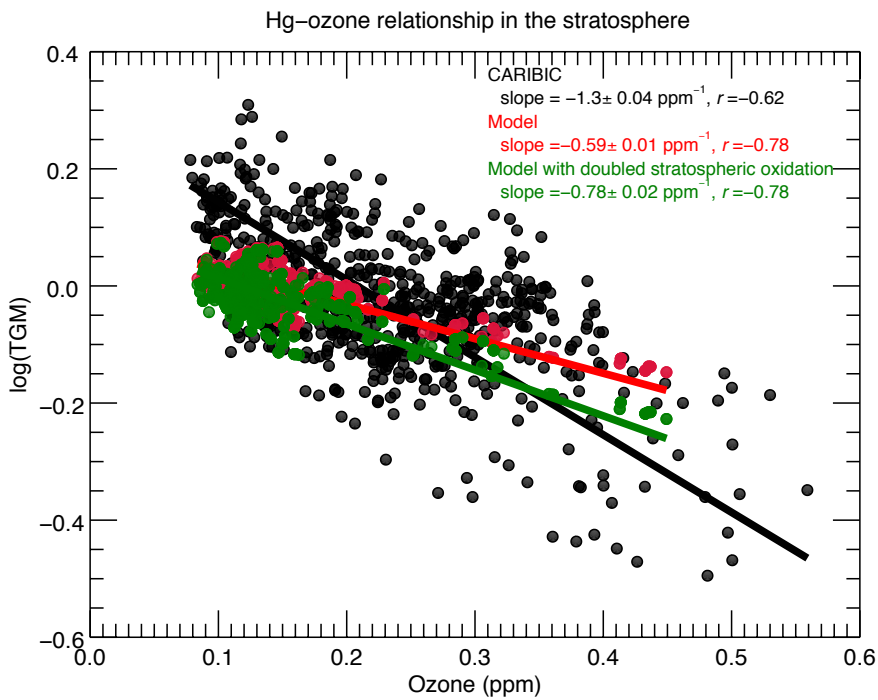
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5 | Figure 4. Mean seasonal variation and spatial standard deviation of total gaseous mercury (TGM) concentrations for northern mid-latitude sites (see Figure 3) and southern hemisphere sites (Amsterdam Island and Cape Point). Observations are compared to our standard **GEOS-Chem** simulation coupled to the MITgcm 3-D ocean model, and to a sensitivity simulation coupled to the 2-D surface-slab ocean model in GEOS-Chem.

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5 | **Figure 5.** Relationship between total gaseous mercury (TGM) and ozone concentrations in the lower
stratosphere. TGM is shown as the decimal logarithm of the concentration in ng m^{-3} STP. Observations are
from CARIBIC commercial aircraft in the extratropical northern hemisphere for April 2014-January 2015
(Slemr et al., 2015). Tropospheric data as diagnosed by $[\text{O}_3]/[\text{CO}] < 1.25 \text{ mol mol}^{-1}$ are excluded. Model points
are data for individual flights sampled along the CARIBIC flight tracks on the GEOS-Chem $4^\circ \times 5^\circ$ model
grid. Also shown are results from a model sensitivity simulation with a doubled Hg^0 oxidation rate in the
stratosphere. Reduced-major-axis (RMA) regressions for the $\log(\text{TGM})$ -ozone relationship are shown with
10 | slopes and correlation coefficients (r). Errors on the slopes are estimated by the bootstrap method.

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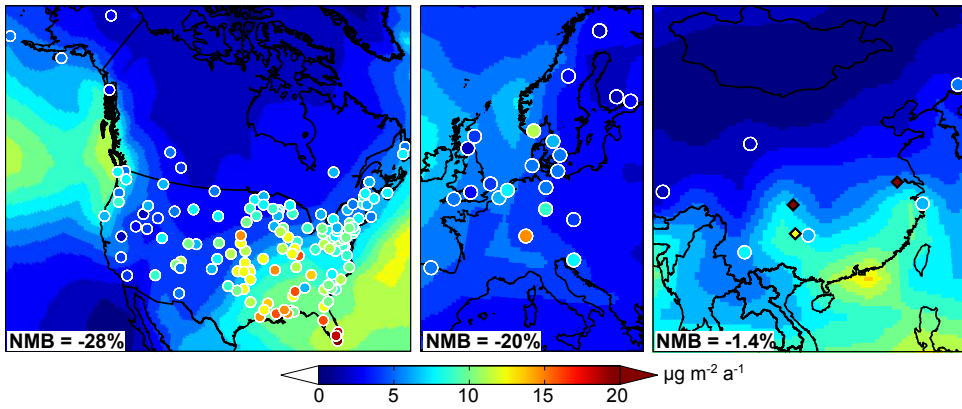


Figure 6. Annual Hg wet deposition fluxes over North America, Europe, and China. Model values for 2009-2011 (background contours) are compared to 2007-2013 observations from the Mercury Deposition Network (MDN, National Atmospheric Deposition Program, <http://nadp.sws.uiuc.edu/mdn/>) over North America (58 sites), the European Monitoring and Evaluation Program (EMEP) over Europe (20 sites), and data from Fu et al. (2015, 2016) over China (9 sites). In the China panel, circles represent rural sites and diamonds represent urban sites as identified in Fu et al. (2015, 2016). For the MDN and EMEP networks, which collect weekly or monthly integrated samples, we only include sites with at least 75% of annual data for at least one year between 2007 and 2013; for China we only include sites with at least 9 months of data over the 2007-2013 period. MDN data are formally quality-controlled, while for EMEP data we rely on a subset of sites that have been quality-controlled (Oleg Travnikov, personal communication). Legends give the normalized mean bias (NMB) for all sites, excluding urban sites in China.

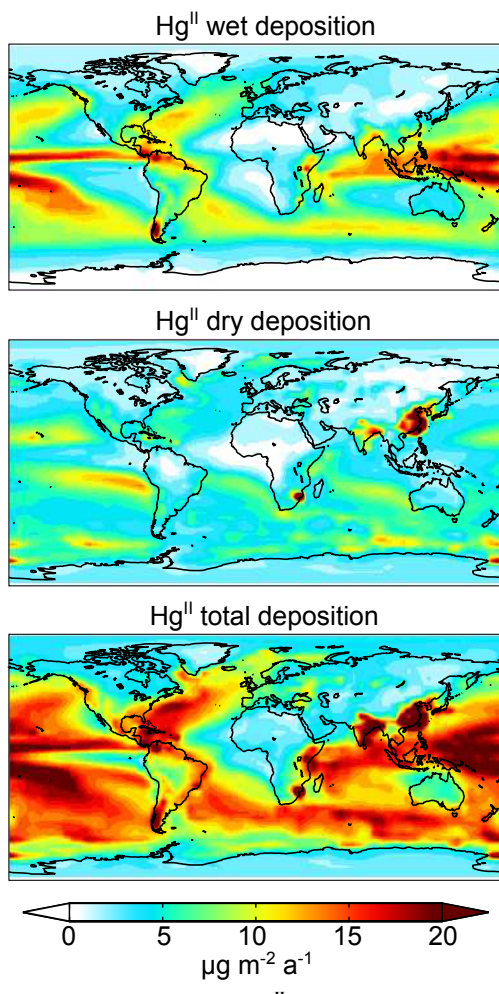


Figure 7. Annual 2009-2011 Hg^{II} deposition fluxes in GEOS-Chem.