

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 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 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 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 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!