

Interactive comment on “A new mechanism for atmospheric mercury redox chemistry: Implications for the global mercury budget” by Hannah M. Horowitz et al.

Anonymous Referee #3

Received and published: 17 February 2017

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

C1

eastern and central North America. ACP 12, 4327-4340.)

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.

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)

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).

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.

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?

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

C2

(>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.)

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 bromine 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?)

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 Hg²⁺ 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?

C3

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?

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

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.

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

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

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.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1165, 2017.

C4