

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

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This article describes recent changes to the chemical mechanism used in the GEOS-Chem 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 HO_2 and NO_2 , 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.

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I just have a few of comments/suggestions to make.

In the discussion of the unlikelihood of O_3 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). 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. 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 NO_2 and organic aerosol compare or references to where such comparisons may be found would be useful. I see the difficulty in comparing modelled HO_2 . However some comparison is important as the oxidation of Hg in the model is dominated by the reaction of HgBr^* by NO_2 and HO_2 .

In Section 4.1 the authors state that the vertical structure of the Hg^0 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.

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. On the same subject, in the Conclusions (line 18) oxidation and evasion are described as

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having similar seasonal phases, but anticorrelated?

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?

The article is well written and merits publication in ACP.

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