

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.