**Atmospheric
Chemistry
and Physics
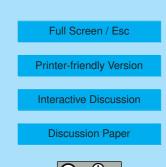Discussions**

Interactive
Comment

Interactive comment on "Global atmospheric model for mercury including oxidation by bromine atoms" *by* C. D. Holmes et al.

Anonymous Referee #1

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General comments

The authors present a comprehensive study of the global atmospheric cycle of mercury using a model coupled to land and oceans. The objective of their work is to attempt to decide whether one oxidation mechanism for elemental Hg is more likely than the other (either oxidation by bromine species or oxidation by ozone and OH radicals). They conclude that the bromine oxidation pathway leads to better agreement with the data although some significant discrepancies still remain. This work presents some new results. For example, taking into account halon chemistry leads to better agreement with measurements for the north-south interhemispheric concentration gradient. The main criticism that one may have about this work is that the conclusion is too dualistic (either oxidation by bromine or by ozone/OH) and a more scientific conclusion

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with recommendations for removing the remaining uncertainties would be more appropriate. In summary, this is a very good piece of work from a technical point of view, which deserves publication following revisions to present the results in a more objective manner.

Specific comments

Lines 15-20: The importance of bromine species for the depletion of Hg in the Arctic and Antarctic during spring is not new and has been thoroughly documented, as it is clear that the kinetics of those depletion events could not be explained by oxidation via the ozone and OH pathways (especially since the ozone concentrations are depleted as well). The reproduction of the summertime events due to subsidence is, however, an interesting point.

Lines 20-22: The ability of the Hg + ozone/OH kinetics to reproduce the seasonality of mercury deposition in the southeastern United States (which is mentioned in the text, see below) should be explicitly stated in the abstract. Otherwise, such an omission could suggest a bias of the authors in their argument that bromine chemistry by itself can explain the Hg atmospheric cycle.

Lines 43-45: The authors state that the oxidation of Hg(0) by OH and O3 is too slow to be of atmospheric relevance. They refer to the work of Calvert and Lindberg (a theoretical study) and that of Hynes et al. (an experimental study). However, there is some contradictory evidence, which at a minimum could suggest the possibility of heterogeneous reactions (e.g., Ariya et al., Chapter 15 in Mercury Fate and Transport in the Global Atmosphere, 2008). In particular, one could note that the senior author published a seminal paper on the topic of heterogeneous reactions involved in ozone formation (Jacob, Atmos. Environ., 34, 2131, 2000). Therefore, it seems odd that heterogeneous reactions are not discussed at all and a little extreme to investigate whether the oxidation of Hg0 by ozone and OH radicals is simply a "yes-or-no" matter.

Lines 221-223 and lines 287-289: The authors assumed a 50/50 partitioning between

the gas and particulate phases. This may be the weakest part of their model formulation because some relevant information exists regarding the partitioning of Hg species between the gas and particulate phases for various Hg species (e.g., Rutter and Schauer, 2007a; 2007b). Although a more detailed treatment of gas/particle partitioning is unlikely to have any major influence on the results (since it affects mostly Hg(II) species), this approximation should be better documented (for example, the temperature dependence would lead to more than 50% particulate Hg(II) in the upper atmosphere) and be presented as an approximation rather than as an unavoidable hypothesis ("... not well quantified").

Line 317: The coefficient of determination obtained in the comparison of Hg air concentrations at land sites is very good compared to most earlier studies.

Lines 428-435: This part is the weakest part of the analysis of the results. It sounds too much like post-rationalization of the modeling results given than one wants to reach the conclusion that Br species are the main path of Hg(0) oxidation. The authors should present an objective assessment of this result and accept that the Br oxidation mechanism, with the current knowledge on the Br species cycle, cannot entirely explain the Hg oxidation cycle. It could be pointed out that the senior author argued in earlier work that the oxidation by ozone and OH radicals could explain the higher deposition fluxes that are observed in the southeastern United States during summer (Selin and Jacob, 2008). Therefore, the current discussion does not seem to address all the possible explanations in an objective manner.

Lines 508-509: The authors point out the work by Edgerton et al. (2006) who found significant discrepancies between the speciation of Hg in coal-fired power plant stacks and downwind ambient air samples. It should be pointed out that two hypotheses were suggested: (1) a reaction reducing Hg(II) to Hg(0) in the plume (as mentioned by the authors here) and (2) incorrect speciation of the stack emissions (since the emission speciation was estimated rather than directly measured). The latter hypothesis should be mentioned for completeness.

Lines 580-583: It would be useful to mention that incorporating halon chemistry is the main reason for this difference between the two studies.

Lines 588-589: Another explanation that has been proposed to explain this discrepancy between observed and modeled mercury wet deposition fluxes in the northeastern United States is the possible reduction of HgII to Hg0 in power plant plumes (or the overestimation of HgII in the speciation of coal-fired power plant emissions), e.g., Vijayaraghavan et al. (J. Geophys. Res., 2008).

Lines 591-592: Is there any evidence (beside wishful thinking) of an underestimation of BrO in the model? It is a little disturbing that the ability of the Hg + ozone/OH kinetics to reproduce the seasonality of mercury deposition in the southeastern United States is mentioned in passing and is not highlighted in the abstract. Such an omission suggests a bias of the authors in their argument that bromine chemistry can explain the Hg atmospheric cycle by itself.

Conclusion and abstract: Both the conclusion and the abstract present a view, which is too much "black-and-white". One cannot rule out at this point the possibility that both Br oxidation and oxidation by ozone and/or OH radicals may occur. In particular, the importance of heterogeneous processes, which has been ignored here, may play a role in Hg0 oxidation under certain circumstances.

Editorial comments

The authors use HgP (superscript) for particulate mercury; it may be more appropriate to use Hgp (subscript) to differentiate between the oxidation states (Hg(0), Hg(II)) and the phase state (gaseous and particulate).

Line 307: "air" concentrations.

Line 308: wet deposition "fluxes".

Figure 10: This display of results is excellent, combining spatial and temporal information in a manner similar to the map of the fate of Napoleon's army during the Russian

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campaign of 1812 by Minard (E. Tufte, "The Visual Display of Quantitative Information," 1983).

Line 543: Since aerosols include the gas phase surrounding the particles, it is better to use "particles" rather than "aerosols

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19845, 2010.