

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

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We appreciate the detailed and helpful comments from the reviewer. Please find our responses below in bold.

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

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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 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.

We are grateful that the reviewer pointed out that our manuscript could be interpreted as dualistic or biased, since this was not our intention. The changes we have adopted to address this concern are listed below in response to the reviewer's specific comments.

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 summer time 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.

The abstract now says,

“Model comparisons to observed wet deposition fluxes of mercury in the US and

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Europe show general consistency. However the Hg+Br model does not capture the summer maximum over the southeast US because of low subtropical Br concentrations while the Hg+OH/O3 model does.”

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.

We added a sentence to the introduction to acknowledge that heterogeneous reactions are possible,

“Heterogeneous oxidation in clouds and aerosols is conceivable but hypothetical (Calvert and Lindberg, 2005; Snider et al., 2008; Ariya et al., 2009).”

We also clarified our modeling approach and assumptions in Section 2.2 (model chemistry) and again in the conclusions by adding a sentence,

“While both oxidation mechanisms, and possibly others, may operate together in the real atmosphere, these idealized simulations enable us to explore the constraints that observations place on the atmospheric chemistry of mercury.”

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., Rut-

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ter 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% per atmosphere) and be presented as an approximation rather than as an unavoidable hypothesis (“. . . not well quantified”).

We have removed the problematic phrase “not well quantified” and revised these sentences in section 2.2 (model chemistry),

“This partitioning is expected to depend on temperature, aerosol load, and aerosol composition (Lin et al., 2006; Rutter and Schauer, 2007a,b). Future work will link HgII partitioning to aerosol concentration and composition in the model, while here we assume 50/50 partitioning of HgII between the gas and aerosol phase for the purpose of calculating HgII deposition as described in the following sub-sections.”

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.

We removed the discussion of a model sensitivity test with increased BrO which

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“sounded like post-rationalization” to the reviewer. The remaining text acknowledges that the Hg+Br chemical mechanism does not provide a fully satisfactory explanation of the wet deposition observations,

“During these months OH provides a vigorous subtropical HgII source available for convective scavenging in the Hg+OH/O3 model, while there is little Br present in the Hg+Br model. Br concentrations could be larger than are specified here if ventilation of sea-salt-derived Br₂ from the MBL or heterogeneous reactivation of Br₂ are important (see Section 2.2).”

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.

The previous text said that fast reduction “apparently occurs” in power plant plumes. It now says that such reduction “may occur”. We also add a citation to Landis et al. (2009), who also concluded that reduction occurs in power plant plumes using a method that included simultaneous speciation measurements at the stack and downwind. The sentence now reads,

“Fast reduction may occur in fresh power plant plumes (Edgerton et al., 2006; Landis et al. 2009), but the global effect would be small because the anthropogenic HgII source is only 700 Mg a⁻¹.”

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

The detailed reasons for differences between the two studies are better ex-

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plained in section 3.1 than in the conclusions, so we have shortened this portion of the conclusions to,

“In particular, the Hg+Br model reproduces the interhemispheric gradient of TGM, which contradicts an earlier study (Seigneur and Lohman 2008).”

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).

We changed the text to reflect these possibilities.

“Simulated deposition in the Northeast US in winter is too high regardless of oxidant, which could reflect excessive scavenging by snow, reduction in power plant plumes, or speciation error in the emission inventory.”

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.

Although an underestimation of BrO in the model is possible, we removed this claim from the conclusions because it may be too speculative.

We modified the abstract to describe the wet deposition success of the Hg+OH/O3 model:

“Model comparisons to observed wet deposition fluxes of mercury in the US and Europe show general consistency. However the Hg+Br model does not capture the summer maximum over the southeast US because of low subtropical Br con-

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centrations while the Hg+OH/O3 model does.”

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.

This comment mainly summarizes the reviewer’s specific comments above. We have changed the abstraction, introduction, section 2.2, and the conclusions to present our work as less dualistic. Our specific changes are already described above in our responses to comments about lines 20-22, 43-45, 428-435, 591-592. In addition, we removed the statement in the final paragraph that “we suggest that Br is the major global oxidant of Hg⁰.” The paragraph now reads,

“Our results show that gas-phase bromine is viable as the main global oxidant for Hg⁰, producing a TGM lifetime and distribution consistent with nearly all available observations. Most of the oxidation occurs in the free troposphere where Br concentrations are constrained by bromocarbon measurements. We also find that atmospheric reduction of Hg^{II} may not be necessary to match observed Hg⁰ concentrations if we decrease Hg⁰ oxidation kinetics within its uncertainties.”

Editorial comments

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

Changed

Line 307: “air” concentrations.

Changed

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Line 308: wet deposition “inĆuxes”.

Changed

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 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

Changed

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