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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Model analyses of atmospheric mercury: present air quality and effects of transpacific transport on the United States" *by* H. Lei et al.

Anonymous Referee #1

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This paper documents a new version of the CAM-Chem model that contains mercury emissions chemistry and deposition. The CAM-Chem/Hg model is described and then compared to observations and an early version of the GEOS-Chem model. The comparisons quantify biases and give correlation coefficients in some cases. Independent modeling efforts, such as this one, are valuable in light of important uncertainties in mercury emissions, especially from natural processes, atmospheric chemistry and deposition.

Major comments:

Overall, the paper lacks a discussion of *why* the model performs well in some cases and poorly in others. The reader wonders what these modeling successes and failures tell us about mercury processes or fate?

Emissions should be better documented, given that this is a new model and source estimation is a key issue in mercury research, particularly for natural surfaces. I recommend including figures showing the global distribution of emissions from volcanoes, soils and vegetation, and oceans, each separately. For completeness, showing anthropogenic emissions as well would be good, although I know other papers have documented the anthropogenic inventory used in this work.

As this is a new model which includes online calculations of oxidants and reductants of Hg. The key species affecting Hg would be O3, OH, sulfite, HO2 and halogens. These reactant concentrations need to be documented, but currently only Br concentrations are, by referring to work by Parrella et al. If information for other reactants is already available in the literature, please cite it and give some summary information, such as surface O3 concentration biases compared to a measurement network, a measure of global OH, like methane lifetime, and sulfur deposition biases compared to a measurement network. If these comparisons are not already published for a closely related version of CAM-Chem, then the paper needs to include this information and probably some figures. I realize this may be significant work, but the quality of the Hg simulation hinges on the quality of the oxidant and reductant concentrations.

Lei et al. summarize the current understanding of mercury kinetics on pages 9851-9852 (hereafter, I use only the last 2 digits of the page numbers), focusing on the conflicting reports of Hg(0) reactivity with OH and O3. While this is a useful and important discussion, I disagree with some aspects of their description. Most importantly, Calvert and Lindberg (2005) and Hynes et al. (2008) argue that *neither* OH nor O3 are likely important in the atmosphere, based on the reaction enthalpies and instability of intermediate compounds. While subsequent work by Rutter et al. (2012) may suggest some role for O3, albeit via some unknown reaction mechanism, I know of no

subsequent studies that have rehabilitated an important role for OH and Lei et al. provide none. Thus, I view OH as an implausible oxidant for Hg(0), regardless of whether O3 is. The discussion should reflect this.

While the observations by Rutter et al. (2012) may indeed support some role for O3 in oxidizing Hg(0), I don't think they should be described as "more accurate" than earlier work, unless Lei et al. provide reasons why they think the earlier experiments were deficient. Furthermore, I don't think Rutter's laboratory studies "directly refute" the concerns of Calvert and Lindberg (2005) that environmental reaction rates may differ substantially from laboratory rates due to the high concentrations of radicals and surface area in all laboratory experiments.

The comparison of vertical profiles with ACE-Asia data is problematic. First, the observed values shown in Fig. 4 are very different from those in Friedli et al. (2004; Fig 4), although they should be the same. For example, Friedli et al. reported $\sim$1.3 ng/m3 at 7.5 km versus 0.6 ng/m3 in this work. Second, the ACE-Asia profile appears anomalous when compared to the extensive profiles available from NASA flights (Talbot et al., 2007; 2008), CARIBIC (Slemr et al., 2009), and Banic et al. (2003). I suggest comparing the model to these other NASA, CARIBIC and Banic profiles.

The manuscript focuses extensively on comparing CAM-Chem/Hg against an early version of the GEOS-Chem model (Selin et al. 2007). It is not clear to me why comparisons are not made to several other global and hemispheric Hg models (GRAHM, ECHMERIT, CTM-Hg, MSCE-Hg). In addition, the GEOS-Chem model has been updated several times since this early version, so comparisons to more recent versions would be more appropriate.

Although the authors' meaning is generally apparent, the paper needs careful editorial attention to use of prepositions (of vs. on) and other grammatical issues.

Minor comments:

p51/l21 - Avoid "/" as its meaning is unclear. "and" would probably suffice here.

p52/l6 - The reverse would make more sense (i.e. mercury concentrations respond to ozone) due to the far greater ozone concentrations.

p54/l10 - Please be more specific about what CAM-Chem model version this work is based on, e.g. version number. The paragraph cites Lamarque et al. (2011) who described CAM4-Chem, but the first sentence says this study is based on CCSM3, which I believe used CAM3.

p56/l10 - Sentence unclear.

p56/l19 - "uptake by the marine boundary layer" is unclear. Please specify what deposition processes are treated in the MBL.

p57/l4 - How was 20% reemission chosen? If it was tuned, please specify what observation it was designed to reproduce.

p57/l5 - "rapid reemission of mercury... does not need to be compensated for by dry deposition." Meaning unclear

p58/l2 - Something is unclear. As written, it sounds like F1 is the annual-mean emission flux from soils in GEOS-Chem (global total or for each grid box?). Since GEOS-Chem already includes temperature and solar radiation in its calculation of F1, including them also in the equation for F2 will shift the spatial distribution of emissions.

p58/l20 - Is Cw a global mean or specified separately for each ocean grid box?

Sect 2.5 This section mainly compares to past modeling results. Please also discuss budgets that are derived mainly from observations. e.g. Pirrone et al. (2010 ACP), Mason (2008 UNEP Hg report)

p59/l17 - What is the "rapid reemission" of deposited mercury over the ocean and how is it different from "emission from the mixed layer"? Sect 2.3 said that "rapid reemission" occurs only over land and snow, in lieu of a detailed model for emissions

from vegetation and snow. Since emissions from the mixed layer are already included (sect. 2.4), an additional rapid reemission appears to double count ocean emissions.

p60 - I agree with the comment by F. Slemr that the Pacyna et al. (2005) inventory likely overestimates Hg emissions from South Africa by a large amount. For further information, see Masekoameng et al. (2010), Leaner et al. (2009) and references in Slemr's comment.

p60 - A major feature of Fig 2 is the high TGM concentrations predicted by the model over upwelling regions along the west coasts of S. America and Africa. These high concentrations are not seen in the ocean or atmospheric concentrations simulated by Soerensen et al. (2010), which is the basis for the ocean emissions in this work. Please comment on the discrepancy and why emissions over upwelling regions are much larger in this work.

p61/l4 - The paper by Lamborg et al. (2002) does not discuss the inter hemispheric concentration ratio, as far as I can tell. A different paper by Lamborg and others does contain this information.

p61/l5 - The text says the inter hemispheric ratio is 1.68, but that seems incorrect based on Fig 3. I estimate the TGM concentrations in the SH to be 1.5 ng/m3 and 2.0 in the NH. That gives a ratio of 1.3, which

p61/l13 - Please explain how these comparison sites were chosen. Why are other measurement sites (e.g. other CamNet sites) not included? The text says the sites are non-urban, but several are urban, including Seoul, Tokyo, Beijing, Chongqing and Detroit.

Sect. 3.2 This would be an excellent place to remind the reader that the kinetic coefficients for Hg(0) reactions with OH, O3 and Br are uncertain. If the coefficients are much slower than assumed in this modeling work, then Br chemistry may have a larger impact on TGM and Hg cycling.

p66/l4 - This paragraph discusses the relationship between the TGM distribution and wet deposition. This is not helpful since TGM is mostly Hg(0) and Hg(0) is hardly susceptible to wet scavenging. It would be more appropriate to show and discuss the relationship between RGM and PHg concentrations and wet deposition.

p66/l9 - There are more than 4 sites with continuous records of 1999-2001 wet deposition. Why select these 4?

p66 - It would be helpful to discuss why the model correlations are much better in some regions than others. What can we learn from these correlations?

p67 - How long are the sensitivity simulations?

p67/l8 - I am unpersuaded by this paragraph. As I wrote in the pre-ACPD review, Fig. 9 incorrectly shows a surface pressure of 1000 hPa over Western N. America. The figure's vertical coordinate is probably incorrect over all regions with elevated surfaces. I believe this plotting artifact causes the apparent dip in TGM concentrations in the red box. The rising concentrations to the east of the red box are probably caused by US emissions. The panels in the right column of Fig. 10 do not show strong deposition of Asian Hg in the region of the red box. Since Fig 9 and this paragraph are not critical to the paper, I recommend cutting both.

p68/l13 - This statement seems to contradict itself. Just say that deposition to the Western US from US sources is bigger, but that Asian sources contribute significantly.

p69/l20 - This sites are definitely *not* distributed evenly. Change this.

Table 1 Why do some oxidation reactions produce PHg and RGM, while others produce only RGM? The text says that all oxidation reactions produce both.

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