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Atmospheric Chemistry and Physics Discussions

Interactive comment on "An assessment of atmospheric mercury in the Community Multiscale Air Quality (CMAQ) model" *by* T. Holloway et al.

Anonymous Referee #1

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This is a paper that uses a well-known model, CMAQ, and attempts to evaluate its performance for mercury. This is something that ought to be done, and is important given CMAQ's role in regulatory analysis. Unfortunately, the paper is not an adequate evaluation of the model, offers little if any new scientific insight, and contains numerous errors. It also fails to grasp the importance of this analysis in the context of recent literature on mercury.

The comparison of model results to only two sites, in my opinion, is a fatal flaw in this paper. The authors have not taken into account the extensive database available from AMNet, the mercury monitoring network with fourteen sites across the U.S., all of which are well within their 36x36 km domain. In addition, several research groups have collected spectated data at US sites, which would be potential comparison data sets.

The focus on the Great Lakes Region is noted, but the paper is presented as a general model evaluation, which it is not.

In sum, despite the importance of CMAQ and its use as a model for regulation, I see little to recommend this paper for publication. The model-measurement comparison is poor and not well-explained, the literature review is incomplete and somewhat sloppy, the paper is poorly organized, and there are few new scientific insights presented. An assessment of the CMAQ mercury model should be conducted, but the authors need to go back to the drawing board and take more care in their comparisons and analyses. It is not publishable in its present form, and I recommend it be rejected.

Detailed comments follow.

p 2312 line 24-25: "Reactive mercury species" – this sentence is a bit odd. There is some controversy over whether PHg is all reactive, or some fraction is nonreactive, and this is treated differently in different models. It is worth discussing, and not as a throwaway line in the introduction.

p 2133 line 3-5: "atmospheric models differ" in attribution of the dominant chemical pathway – this is a sloppy way of referring to the very real scientific uncertainty, and the fact that our understanding has changed over time. Citations to the relevant theoretical and analytical chemistry literature (e.g. Calvert and LIndberg, 2005; Hynes et al., 2009) need to be included here. Bromine is not even mentioned until the discussion section, and it should be an important focus of any paper addressing mercury chemistry.

p 2133 line 17-18: "Most studies that evaluate model estimates of ambient mercury compare with TGM and Hg(0)". This may have been true historically, but it is no longer the case. In fact, many of the studies cited by the authors do include comparisons with RGM and HgP, though the database at the time was limited. More recent studies (Amos et al., 2012, ACP) compare to a larger suite of RGM and HgP measurements. This evolution in the community should be noted. [Admittedly, the Amos et al. publication is quite recent, but was in ACPD in October, two months before this paper was submitted, so the authors should at least have been aware of it.]

p 2133 line 20-21: "These measurements have supported model development, but they do not allow for a detailed evaluation of model chemical processes." There is clearly a need for more detailed evaluation of Hg chemistry – but to say that previous analyses have not allowed for detailed evaluation is too simplistic.

p 2133 lines 23+: This literature review, as alluded to above, is out of date and misleading. The CTM-Hg model citation is eight years old, and the GEOS-Chem citation is five years old. There has also been a model intercomparison effort which compared mercury models to RGM data (Ryaboshapko et al, Science of the Total Environment, 2007);

p 2134, line 7: it is a bit of a stretch, given the limited studies reviewed, to talk about a consistent overproduction of RGHg. In addition, the authors do not take into account potential uncertainties in measurements which might compensate for this (see Lyman et al., ACP, 2010)

p 2135 and Table A1: Default boundary conditions. Previous research has shown that CMAQ results have a strong dependence on boundary conditions (see Bullock et al., 2008). Although the authors do test this later, they do not describe this test in the methods. The boundary conditions given in Table A1 do not vary with latitude, as far as I can tell. The state-of-the-art in CMAQ modeling is to use global model fields as boundary conditions; this is what the EPA does. To use default conditions, and then expect the results to be relevant to policy-making where the usual model setup is very different (considering the strong dependence) is misleading at best. It is also not stated what boundary conditions were used for non-Hg chemistry.

p 2135 line 10-30: The authors need to explain the chemistry in more detail here. There are many different versions of CMAQ – the Bullock and Brehme 2002 and Lin et al. 2007 papers have chemical differences for Hg as well – and the authors need to be clear exactly which reactions they are using. In addition, I believe the mechanism

the authors are using involves oxidation by OH, which in my opinion is obsolete. This is not a deal-breaker in and of itself, but needs to be discussed, and its importance analyzed. There is no relevant explanation of this or related chemistry issues in the model description.

p 2136 lines 1-14: This description is not particularly useful. A more quantitative description would be welcome (what physical properties are used? How is stomatal resistance calculated)?

p 2136 line 20: There is too little discussion here of the speciation of emissions, which is an area of much uncertainty, and which could strongly influence the results.

p 2137 line 16-25: The data screening procedure used here is very different from those used in other studies to address missing data. I think 50% is too low a cutoff value. This probably influenced the results.

p 2138 line 1-10: Again, as mentioned before, there are additional spectated mercury measurements that could have been used for comparison. Second, the uncertainties with the Tekran instrument should at least be mentioned. They are mentioned at the end, but this is better stated up front.

Section 3.1: These values should be compared quantitatively with typical regulatory modeling values for NMB and NME. They seem high for ozone, but this seems to be a function of the choice of metric (mean rather than max ozone). Why not compare 8-hour max?

p 2140 line 27: "O3, given the important role of this oxidant in the CMAQ-Hg chemical mechanism." – again, this is why discussion of the chemical mechanism above is critical. Again, there are substantial uncertainties about this reaction that are not acknowledged or discussed.

Section 3.2 wet deposition: These values should be compared in a quantitative way to Bullock et al., (2009), who already has done this sort of analysis. It is repeated here, with different results – and CMAQ's performance has degraded. This is noted by the authors, but I'm not convinced by their explanations of confounding errors. Again, the authors compare to outdated literature (Seigneur et al., 2003 was published nine years ago, and major aspects of our understanding of mercury have changed since then). More recent studies have improved r2 values. Lack of both quantitative and qualitative discussion of Bullock et al., (2009) is a major omission.

Section 3.3: The correlations and comparisons here are so poor that they are not worth showing. We can and should do better at modeling mercury, and other groups have done so (eg Durnford et al., 2010; Strode et al., 2008).

Section 3.3.2: If the model doesn't get Hg(0), it's not going to get RGHg, unless the authors are looking at the footprint of a local source. This comparison is thus superfluous. The attempt to discern insights of a chemical signal from these comparisons is extremely inappropriate.

Section 3.4: This test is critical, but the authors seem to disregard the findings of this in the comparisons presented in Section 3.3. Addressing the outer and inner boundaries separately would have been a better approach, in my opinion.

p 2147 lines 27-28: A quantitative comparison of dry deposition rates with the (albeit limited) information available would be warranted here.

Section 4: I agree with the author's interpretation that the model contains significant errors. However, the authors have given no evidence that their suggested "fixes" would actually improve model performance.

p 2148 lines 14-19: The authors do not discuss the potential role for atmospheric reduction, and emission speciation, which is really what is controlling these small numbers. Does in-plume reduction happen, and if so, how much? The authors do not address this issue at all.

p 2149, line 11-12: the discrepancies can't be explained by measurement efficiency

differences. Why not? Can this be shown quantitatively rather than just stated?

Conclusions: I would have liked to see a more helpful, scientific conclusion here, and a targeted intervention to improve the model.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2131, 2012.