Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-663-RC2, 2016
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Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Sensitivity model study of regional mercury dispersion in the atmosphere" *by* Christian N. Gencarelli et al.

Anonymous Referee #2

Received and published: 8 September 2016

This paper presents the results of model sensitivity studies of anthropogenic emissions and oxidation chemistry on atmospheric concentrations and deposition of mercury over Europe. The model results of each study are evaluated against observations.

General comments:

- I recommend the paper for publication after the revisions suggested here, which are largely about adding more explanation of the sensitivity studies and results, including more connection of the results to the current state of knowledge in the field, and highlighting implications of the results.

- In general, the discussion can be hard to follow at times since only some of the results are presented in the figures but results from all sensitivity studies are discussed.

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Discussion paper

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- Every option for emissions inventories, chemistry schemes, etc. are presented as equally valid but it would be helpful to know what discussion has already been performed of these inventories/chemical mechanisms etc. to indicate the strengths and weaknesses of each and how this paper's results fit in. I think it is misleading to present Br and OH/O3 oxidation mechanisms on equal footing, for example, but then the paper shows that Br oxidation alone best represents TGM results which adds further support to what previous studies have suggested.

- I think the paper would benefit from more clearly outlining the purpose of each of the sensitivity studies. It would also be beneficial to have the explanation of most sensitivity studies be more centralized – since some of the sensitivity studies are untrue hypotheticals (e.g., NOCHEM and NOANT) while others are testing different hypothesized physical processes (e.g., BRCHEM1 vs. BRCHEM2), but both types are valuable. There is some of this scattered throughout the results section, but I think it can be more explicit; e.g., 'the ANTSPEC experiment, which assumes all anthropogenic emissions are as GEM, would represent a lower bound on deposition from local anthropogenic sources and an upper bound on long-range transport of anthropogenic emissions because GEM has a much longer lifetime against deposition than RGM/PBM' or something to that effect.

- Some background information is missing – e.g., the lifetime of GEM vs. RGM/PBM is not explained in the paper, or the sinks of GEM vs. RGM/PBM (dry deposition vs. wet deposition affinities), making the results from the ANTSPEC simulations and others less easily understood. Some aspects of atmospheric mercury are missing from the discussion (e.g., reduction of Hg(II), uncertainty in present oxidized Hg measurement capabilities that would be relevant for the 2nd to last sentence of the paper).

Specific comments:

Section 2.1: There are a lot of details given here about the models but it is not clear how the model representations of Hg are different or how their differences would affect Hg

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results. It would be helpful to rewrite this a bit and make it more explicit whether/how the differences would affect Hg (e.g., if CMAQ is offline while WRF is online meteorology, the transport of Hg will be different to some degree between the models.)

Page 4 line 2: it would be helpful to explain briefly here whether there are multiple heights in the EDGAR inventory, as it is written it is unclear what the difference is and this comes up later in the results section.

Section 2.3: It is unclear from the way the paper is written what the base model oxidation chemistry schemes include –is it OH, O3 and Br oxidation at the same time in both CMAQ and WRF-Chem Hg? This should be made clear.

Page 4 Lines 23-25: some of this would be helpful to mention in the model description section 2.1.

Table 3: add a total deposition column, just makes it easier to follow

Figure 3: It is hard to compare the results between CMAQ and WRF-Chem Hg because the same model setups do not line up. I think it is worth reordering the individual panels to lining up the ANTSPEC and ANTSPEC_C vertically, or NOCHEM with NOCHEM_C below it, etc. to make more obvious the comparisons made in Section 3 of the paper.

Figure 4: This is total dry deposition of Hg(II)+Hg(0), correct? Just making sure since wet deposition is of course just Hg(II). I think this is worth mentioning as it also helps explain the changes in dry vs. wet deposition seen in the sensitivity studies.

Figure 5a: there are two legend labels with "BASE". I assume the green square is BASE2? Also, I would explain that the order of the sites is by the magnitude of the mod/obs ratio of the BASE simulation as it is not immediately obvious.

Page 5 Lines 20-23. It is counterintuitive to me how an overestimate relative to observations for the ANTSPEC sensitivity study where all anthropogenic emissions of RGM & PBM are as GEM means long-range transport is less important than regional emissions. I think more explanation would be helpful – so when PBM and RGM are

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emitted normally as in the BASE simulation, the model is no longer overestimating the observations because the Hg(II) is deposited fast enough before it reaches the CZ03 site? I suppose part of this is defining what is local vs. "regional" vs. long-range more clearly.

Page 5 last paragraph (beginning line 29): do you have any hypotheses why TGM at ES08 is so low relative to the models?

Page 6 Lines 1-2: The discussion of OHCHEM and NOANT experiments comes as a surprise as it is not in Figures 5, 6, or 7; more connection to the rest of the section is needed.

Page 7 Lines 15-16: it is also not immediately obvious why dry deposition decreases so much more than wet deposition, since GEM is not wet deposited. Is it because even though there is higher GEM in the ANTSPEC experiment, it is dry deposited so much more slowly than the RGM/PBM species, or is it something about how RGM and PBM contribute different amounts to wet vs. dry dep of the oxidized species? Setting up the background on this in the intro or methods would be helpful.

Page 7 lines 21-23: given that a no anthropogenic emissions scenario is currently untrue, I think something more insightful can be said about the results – e.g., something about how anthro. emissions contribute to 2/3 of total deposition (not counting the fact that "natural" emissions from soil/ocean as they are tuned in models also implicitly are impacted by legacy anthropogenic sources), or how a hypothetical policy scenario of shutting off emissions could have huge local benefits?

Section 3.3 paragraph 2 (pg 7 lines 30-32): I would emphasize that this shows a significant proportion (exact percent varying on the model) of total Hg deposition to ecosystems is coming from the oxidation of GEM which can be transported from far distances as opposed to the Hg(II) locally emitted. This is an interesting result with policy implications and could be highlighted more.

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Page 8 lines 3-4: "A number of studies have shown the importance of O3, and the OH radical, and also reactive halogen compounds. . ..": I understand that there have been review papers discussing the intricacies of this and you don't want to repeat that here, but it is overly simple to group all three oxidants together and not mention that studies have found that the homogeneous gas-phase oxidation of Hg(0) by O3 and OH are thermodynamically and/or kinetically impossible (e.g., Hynes et al. (2009), Goodsite et al. (2004), Calvert and Lindberg, 2005). I think it is still interesting to compare the results from the three species, but it needs to be introduced with a bit more nuance. Moreover, as Theodore Dibble posted in his comment, there are additional HgBr+X second-step oxidation reactions that can greatly increase the total Hg(II) production and deposition through the Br-initiated pathway. Somewhere in the paper there should be a discussion of how this would affect the results presented – e.g., Hg deposition in the BRCHEM1 and 2 sensitivity simulations would be increased and TGM would be decreased.

Page 9 Lines 1-8: it is hard to understand the differences in the two Br concentration fields from the description given – would it be possible to show (perhaps in the supplemental) a difference plot of the Br concentrations over the Europe domain? (e.g., zonal mean latitude on x-axis vs. altitude on y-axis or something like that). Most GEM oxidation is not occurring in the PBL but in the free and upper troposphere (because of Br distribution and the temperature dependence of the oxidation reactions), so it is not surprising that the huge differences in Br in the PBL between the two Br fields doesn't impact on Hg(II) deposition; I am more interested in the differences at higher altitudes.

Page 9 Lines 13-16: I think it is essential to connect this to available observations of Br. The Shah et al. study tripled bromine concentrations of the GEOS-Chem Parrella et al. 2012 model which was consistent with observations of BrO during the NOMADSS field campaign (Gratz et al., 2015). Parrella et al. (2012) showed previously that BrO was underestimated in GEOS-Chem by 30% in the global mean against satellite observations. So it is not just a model exercise but shows that higher Br in GEOS-Chem (closer

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to reality but not quite there) is also closer to reality for Hg model results. But in addition – since anthropogenic Hg(II) emissions have been turned to GEM in reality there would be more deposition with just Hg+Br oxidation and anthropogenic emissions of RGM/PBM turned on. This makes me curious about the Hg(II) reduction mechanisms in CMAQ vs. WRF-Chem Hg – if this was included, was it treated the same in all sensitivity simulations? I think reduction needs to be discussed somewhere in the paper.

additional references cited here:

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