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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Investigation of processes controlling GEM oxidation at mid-latitudinal marine, coastal, and inland sites" *by* Z. Ye et al.

Anonymous Referee #2

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The authors present results of a box-model simulation of Hg chemistry at three sites in southern New Hampshire, USA. The sites are located in different environments (marine, coastal, and elevated), which allows the authors to examine the similarities and differences in Hg chemistry in these environments. The authors conclude that Br and BrO dominate Hg oxidation during the day and H2O2 at night at the marine site, while O3 and OH are dominant at the coastal and inland sites. I found the comparison in Hg chemistry between the sites interesting. Atmospheric Hg chemistry remains one of the least understood processes controlling Hg cycling in the environment. Studies like this that use models to interpret in situ Hg observations in different environments are necessary to fully characterize the oxidation of Hg in the atmosphere. However, I

have a number of major concerns that the authors should address to make their study convincing.

Major comments: 1) The authors examine the oxidation of GEM with the set of gas-phase reactions listed in Table 1. There is high uncertainty in these reaction rates, up to a factor of 10 for reactions of GEM with Br and BrO. The recent review by Ariya et al. (2015) has a compilation of all previously reported estimates for GEM oxidation reaction rates. The authors perform one sensitivity study addressing the uncertainty in the GEM+O3 rate, but seem to ignore the uncertainty in the remaining reactions. A discussion of the effect of these uncertainties are necessary before any conclusion can be reached about the dominant GEM oxidation pathways at the studies sites.

2) How were the concentrations of the species that weren't measured set? How were the concentrations of Br/Cl/I species determined at the three sites? The authors briefly mention this in Section 3.4.1. This is a key aspect of the study and should be discussed in detail in Section 2.

3) The authors performed several sensitivity studies with the box-model by varying different physical and chemical parameters. However, these sensitivity studies seem out of place. The authors do not specify why they chose to vary the parameters listed in Table 3, and not others. Secondly, the presentation of the results of the sensitivity studies is not thorough. There is no discussion of how the results of the sensitivity studies affect the overall conclusions. Section 3.3.3 addresses Br chemistry in the MBL. I do not think this fits in this study, considering that there were no BrO measurements that could be used to compare with the model results.

4) Hg2+ reduction reactions were included in the model. Is reduction an important control on GOM mixing ratios? Some discussion of the effect of the reduction pathways on GOM and PBM would be valuable. The Tekran 2537/1130/1135 typically measures GEM, RGM, and PBM. The PBM measurements are not discussed in the manuscript. Can the PBM measurements be used to constrain the reduction rates?

5) In Section 1, the authors briefly discuss previous studies of Hg chemistry by Hedgecock et al., Holmes et al., and Wang et al. The present study of Ye at al. is very similar to these previous studies. All of them examine the diurnal cycle of oxidized Hg in the mid-latitude marine boundary layer using a box-model. The authors should include a discussion of how their results compare with the findings in these previous studies.

Minor comments: Page 4, line 9: "Hg in the MBL cycles differently in coastal or inland areas." The difference needs to be expanded upon as this is directly related to the present study. How is the cycle different?

Page 5, line 23: Please add a list of reactions and their rates as a supplement, given that a few of the reactions do not seem to follow the JPL Report #17 recommendations.

Page 6, line 11: Please include a table with the reaction rates and references for the aqueous-phase reactions.

Page 7, line 1: Not all previous modeling studies have used simple approximations. The model of Hedgecock et al. (2003, 2005) uses detailed MBL chemistry.

Page 7, line 11: How are the wind speed measurements used in the box-model?

Page 7, line 19: "...were set to be constant during a simulation." Please specify the length of a simulation. Was it one day or one hour?

Page 9, line 20: It would be interesting to see how the source regions of the air masses at the three sites differed. The backtrajectories for only the AI site are discussed in the text.

Page 10, line 21: The LOD for the GOM observations was 0.1 ppqv at AI, but it appears to be much lower at PM. Figure 2 shows most GOM observations at PM below 0.05 ppqv. Please specify the LOD for GOM at PM.

Page 12, line 12: HgO is considered a GOM species here, although the authors state in the Introduction (page 3, line 22) that "a consensus has emerged that GEM+O3

reaction most likely occurs with solid-phase products..."

Page 12, line 19, I was surprised not to see HgBrNO2 as one of the more abundant GOM species. I expected HgBrNO2 to be produced faster than HgBrOOH and HgBrOBr, given the typically higher concentrations of NO2.

Page 13, line 14: Why were HgO and Hg(OH)2 more sensitive than halogenated GOM species to gas-particle partitioning?

Page 24, line 25: I do not see an order of magnitude difference between the peaks in Figure 5. I see a factor of 2-3 difference.

Page 19, lines 12 onwards: Could entrainment from the free troposphere explain this inverse relation between GOM and RH? Entrainment from the free troposphere was not treated explicitly, yet the boundary layer height at the TF site varied diurnally. Was it assumed that this entrainment does not change GOM mixing ratios in the boundary layer?

Page 21, line 29: "Clearly, the under-estimation case occurred under the strongest Bermuda High influence..." It isn't clear to me. Can the authors explain a bit more why it is the influence of the Bermuda High, and not just a transient high-pressure system?

Page 23, line 7: "It was hypothesized that..." This was not substantiated in the study, and does not belong in the conclusions.

Page 23, line 24: The authors allude to problems in GOM measurements using the Tekran instrument. If the measured GOM is indeed biased low by a factor of 2 or 3 under certain conditions, how does it affect this study's conclusions? This is important and needs to be discussed in a little more detail.

Page 23: The authors should also point out to the reader that, in the absence of speciated measurements of oxidized Hg compounds, the results of a modeling study cannot be used to conclusively identify the dominant oxidants of Hg in the atmosphere.

Table 2: Please include the standard deviation of the observed variables.

Figure 1: Please add some geographical context to the map. May be show the latitude/longitude girds, and the land/ocean boundary.

Figure 10: The backtrajectories suggest strong regional influence at the AI site. Can the authors reconcile this with their assumption for the box-model that regional transport is negligible?

Technical comments: Page 1, line 14: May be the title can specify that the study focuses on the summertime.

Page 1, line 14: The term Hg(II) is not needed here.

Page 3, line 7-8. "GOM and PBM are...subject to dry and wet deposition..." GEM is also subject to dry deposition.

Page 3, line 27: The sentence starting with "In the MBL..." needs to be rephrased for clarity.

Page 5, line 10: "...initial GEM mixing ratios...were set to be constant mimicking GEM emission flux." This sentence is unclear and should be reworded. I think removing the clause "and were set..." may help.

Page 10, line 4: FB is fractional bias.

Page 11, line 26: Reference to Section 3.2.2. Should this refer to Section 3.4?

Page 14, line 15: It seems TF_AIdry, PM_AIdry, TF_AIaero, PM_AIaero are not discussed any further. It would be better to not introduce them here.

Page 17, line 1: I think it would be more appropriate to place the model evaluation section before the sensitivity studies.

Page 19, line 27: "It was thus hypothesized that certain processes..." This sentence is vague. Please reword.

Page 23, line 15: "The updated chemical mechanism largely improved GOM simulations...". Improved with respect to what?

Figure 2: What do the "filled circles" represent? Expand the site abbreviations in the caption. The font size is too small.

Figure 3: Font size is too small. In the caption: do the bars "represent" the range of simulated GOM?

Figure 4: Please change "Other_RGM" to "Other GOM species". Please increase font size. It is hard to distinguish between the lines in Figure 3(a).

Figure 8: Caption: "("Observed", red, "Simulated", triangle)". Please correct typographical error.

Figure 9: It is difficult to distinguish between the Simulated_under-estimated, Simulated_matching, and Simulated_over-estimated lines. It would be also be helpful to maintain consistency between the figures in what is represented by the error bars.

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