

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

Anonymous Referee #1

Received and published: 14 February 2016

This paper describes a model-measurement comparison study focusing on gaseous oxidized Hg (GOM) in the atmosphere at 3 sites in New Hampshire (marine, coastal, and inland). The main motivation for this study is to use updated reaction mechanisms and physical processes that control concentrations of GOM in the atmosphere and see if the model can reasonably reproduce the observations. There are many gaps in the understanding of what controls GOM in the atmosphere and these gaps are important to close since this species is readily wet and dry deposited and contributes to the burden of Hg accumulation in aquatic and terrestrial ecosystems. The photochemical Hg box model used in this work represents the state of the art with many updated reaction mechanism and physical processes. The sensitivity testing of the model output to

C1

changing chemical and physical parameters is very good. The model reproduces the observations reasonably well, the most notable agreement is that the differing overall GOM measured concentrations between sites (AI > TF > PM) is reproduced in the model. The model also gives some indication of which chemical species comprise GOM at the different sites. This is new and valuable information if it can be corroborated by measurements. The main issue overall I have with the paper is that there is little discussion of the GOM measurements made at the 3 sites. At the end of the paper the authors acknowledge the latest papers suggesting that GOM may be systematically underestimated by the Tekran methods, but in the paper the authors do not indicate if there are any potential measurement biases in the data from the 3 sites, and if so how these might change the conclusions reached from the model-measurement comparison. This is a fundamental weakness of such a study that uses measurements with a high degree of uncertainty to validate (or compare to) a model that is also uncertain. That limitation aside, however, there is a great deal of value in such a comparison, and I find this paper to be largely acceptable as-is. Abstract: I understand word count is limited, but there should be some indication of what is new or novel about the research. Which finding contributes to our understanding the best? It should be more than a list of observations, but rather some indication of why these observations matter. Line 11, Page 3, provide reference(s) for this statement. Line 20 Page 6, “The ClO /BrO / IO radical cycles involve oxidation of Cl /Br / I radicals, photodissociation of ClNO₂ / ClONO₂ /BrNO₂ /BrONO₂, production from other halogen radicals, and sink reactions to reproduce Cl/Br/O radicals or other halides.” What is meant by “reproduce”? Do you mean to reproduce the observations? What if those observations are very uncertain? Line 15 Page 10, and Figure 2, There needs to be some discussion about the Tekran measurements. There were no mention of these in the methods section. Were the 3 instruments at the 3 locations operated in a consistent manner? Why such a large variation in GOM at AI, but very low levels at PM? The authors state the MDL for GOM is 0.1 ppqv yet most of the PM data in Figure 2 is < MDL. Hard to make interpretations about the diel cycle of these data since they are so low. Which begs the question,

C2

why are they so low at this site? Diel cycles of GOM at AI and TF are consistent with each other with an afternoon maximum, thus the statement on line 17 of Page 10 is misleading. Also, time axes in Figure 2 are not perfectly consistent for GOM and GEM. Please fix. Line 10, page 11, without some discussion of instrument intercomparison between the 3 sites, we cannot tell whether a GEM difference of 8% or 12% is simply due to the Tekran or is a real difference. Line 20, Page 11, the elevation of PM is 700 m asl, but this site is not a mountain peak and thus cannot be above the nocturnal boundary layer consistently. There may be more replenishment of GOM at this site, but again, the levels are super low and as such not much interpretation can be made of the GOM data at this site. In general, I feel the measurements from PM are of little value to the paper. The AI measurements are of greatest value since they are much higher and also are in the MBL where it appears that Br chemistry probably dominates. I would focus more on the model-measurement comparison at this site and less so on the comparison with the PM data.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2015-829, 2016.