

Reviewer #1:

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 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.

We thank the reviewer for their thoughtful, constructive comments and suggestions. The manuscript has been revised carefully. Below we addressed the review point by point.

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.

As the reviewer pointed out, the potential uncertainty in ambient Hg measurements especially GOM is a consensus in the community at large. Recent laboratory experiments and reviews (Lyman et al., 2010; Jaffe et al., 2014; McClure et al., 2014; Huang and Gustin, 2015; Gustin et al., 2015) reported O₃ and relative humidity (RH) interferences on mercury halides for KCl-coated denuder, which was a part of Tekran 1130 unit used for GOM field measurements commonly in the community as well as the observations of this study. Huang and Gustin (2015) suggested a linear relationship between RH and GOM loss (in %) in GOM measurements, i.e., $RH = 0.63 \text{ GOM loss \%} + 18.1$, $r^2 = 0.49$, $p < 0.01$, over a RH range of 21% - 62%. In our GOM measurements, the interferences of RH at our three sites should have largely been eliminated since we used a custom-built refrigerator assembly and a canister of drierite to cool and dry air streams before entering into the 1130 pump module (Sigler et al., 2009). As a result, the RH of air streams was kept < 25%, therefore the upper limit of GOM loss caused by RH was < 10% using Huang and Gustin (2015)'s equation.

With regard to O₃ interference, the experimental study (Lyman et al., 2010) showed 3 to 37% reduction on the collection efficiency of HgCl₂, and the proposed reaction was $\text{HgCl}_2 + 2\text{O}_3 \rightarrow \text{Hg}^0 + 2\text{O}_2 + \text{ClO}$. However, a quantitative range of the bias caused by O₃ in field GOM measurements was yet derived (Lyman et al., 2010). Huang et al. (2013) showed lower collection

efficiency of KCl denuders compared to nylon membrane and the cation exchange membrane for HgBr₂, HgCl₂, HgO, HgSO₄, and Hg(NO₃)₂ in laboratory tests. However, for field measurements (Huang et al., 2013; Gustin et al., 2013), since GOM and PBM could not be distinguished from total reactive mercury using nylon membrane and cation exchange membrane chambers, the quantitative bias extent derived for total reactive mercury could not be directly used for GOM. Moreover, Huang et al. (2013) suggested that in their marine boundary layer site and highway impacted site, ambient GOM most likely existed in forms other than the laboratory tested species. Therefore, bias low GOM collection efficiency of KCl-coated denuders in field measurements remains speculative at this point.

Quality measurement data are used as ground truth for atmospheric Hg modeling studies, notwithstanding their limitation. Better instrumentation and/or solidly quantified bias for current instruments are in urgent need and are of essential importance to atmospheric Hg modeling. Nevertheless, even if models did not perfectly reproduced observations, the information derived from model simulations and sensitivity studies could provide insight into how the mechanisms work.

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.

The abstract was revised upon the reviewer's suggestion to reflect the findings of the study that are original.

Line 11, Page 3, provide reference(s) for this statement.

Reworded and references added.

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?

Changed to "calculate". No observations of Cl, Br and I radicals.

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, why are they so low at this site?

A brief discussion about the Tekran measurements was added upon the reviewer's suggestion (lines 193 - 200 in the revised manuscript).

GOM was collected over a 2-h sampling period at a rate of 10 L min⁻¹ using a speciation unit (Tekran 1130) installed upstream of the total gaseous mercury (TGM) analyzer. The instruments for the three sites were run and calibrated in the lab first and then operated at the sites in a consistent manner. The GOM detection limit for all three instruments were derived as ~0.1 ppqv, based on three times the standard deviation of the averaged blank (Sigler et al., 2009; Mao and Talbot, 2012). We added this information in section 2.1.2.

Pack Monadnock (PM) is a heavily forested, elevated, inland site, representing continental background conditions with nearly no marine influence. PM is not the only site with frequent below LOD measurements of GOM; in fact, similar levels of GOM have been reported from other background sites over the United States (Hall et al., 2006; Engle et al., 2010; Kolker et al., 2010; Choi et al., 2013).

Several possible reasons were proposed to explain significantly lower GOM mixing ratios at PM in comparison with the higher values at AI. First, the GEM oxidation at PM is not as active as that at AI due to a lack of halogen radicals. Second, the dry deposition velocity of GOM at PM (2 cm s^{-1}) was estimated a factor of 3 greater than that at AI (0.5 cm s^{-1}) using the values from Zhang et al. (2009, 2012). Third, the gas-particle partitioning process at PM was favorable for PBM formation, which could be conducive to a high loss rate of GOM. In fact, our model sensitivity runs suggested that the strong oxidation of GEM by O_3 at PM could lead to higher GOM mixing ratios (up to 4 ppqv) during daytime if the same gas-particle partitioning and dry deposition velocity that were used for AI were applied at PM (Figure 6 and Section 3.4.2 in revised manuscript). The simulated production and loss rates of GOM were on average $3.4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ and $5.1 \text{ molecules cm}^{-3} \text{ s}^{-1}$, respectively, at 0.1 ppqv GOM. The production and loss were balanced out at 0.066 ppqv GOM. This suggests all the GOM produced from GEM oxidation at PM might have been lost rapidly via dry deposition and gas-particle partitioning. Moreover, PM would be in the residual layer at night, with air masses from the preceding daytime convective boundary layer where the GOM concentrations were typically below LOD.

Here we attached detailed information on GOM (also termed as RGM) measurements from Sigler et al. (2009):

“RGM is measured with a speciation unit (Tekran model 1130) consisting of a denuder and pump module installed upstream of the TGM analyzer. At TF and PM, the analyzer is housed in a temperature-controlled ($\sim 25^\circ\text{C}$) instrumentation shed. The denuder module is mounted on top of the shed at a height of approximately 5m. At AI, the denuder module is mounted at the top of a World War II-era observation tower ($\sim 20\text{m}$), with the TGM analyzer installed inside the top floor.

The denuder module is attached to the pump module and TGM analyzer by a heated (50°C) umbilical line. The KCl-coated denuder strips out RGM during a predetermined sampling period while the TGM analyzer continuously measures Hg^0 (see Landis et al., 2002). Over the final 30 min of the sampling period, the denuder is flushed with zero air and heated to 500°C so that the RGM is thermally absorbed and sampled (as Hg^0) by the TGM analyzer. Uncertainty of RGM measurements is high, especially at low levels, and we currently lack standard reference materials for calibration (Aspmo et al., 2005). To reduce uncertainty as much as possible, we strive for very low blanks. We measure RGM over a 2-h sampling period at a rate of 10 L min^{-1} , and with a detection limit of ~ 0.1 ppqv, based on three times the standard deviation of the averaged blank (e.g., 0.003 ± 0.03 ppqv, $n = 3626$ at TF in 2007; Sigler et al., 2009).

Clean operation of the 1130 system is verified by flushing the system with zero air. Ideally the resultant mixing ratio during zero air flushes before and after denuder heating is 0 ppqv. To ensure clean operation, the denuders, denuder module glassware, impactor frits and sample filters are replaced and cleaned on a 10-day basis at TF and PM, and typically on a 2-3 week basis at AI. At TF and especially AI, high humidity may corrode zero air canisters, saturate soda lime and lead to poor blanks or enhance cartridge passivation. To minimize the potential of

moisture damage and improve blanks during desorption, the airstream leading into the 1130 pump module is cooled and dried using a custom-built refrigerator assembly and a canister of drierite. This system ensures that even when the drierite is exhausted, the relative humidity of the air entering the pump module is ~25% or less. At AI, humidity as well as sea salts led to high blanks during the first month of deployment in 2007. Addition of the refrigerator assembly along with replacement of an aging pump diaphragm on 9 August resulted in clean blank values (0 ppqv) on more than 80% of the RGM observations at AI for the remainder of the field campaign.

In our experience, mixing ratios of 0 ppqv are achieved for > 99% of zero air flushes after desorption and for >94% of zero air flushes immediately before desorption at both TF and PM. When a level of 0 ppqv is not achieved, a blank correction is made to the resultant mixing ratio based on the average value of measurements during zero air flushes before and after desorption.”

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.

Deleted this sentence.

Also, time axes in Figure 2 are not perfectly consistent for GOM and GEM. Please fix.

Fixed.

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.

The instruments for the three sites were run and calibrated in the lab first and then operated at the sites in a consistent manner. Below information on the measurements at the three sites was added in the text (lines 193 - 197 in section 2.1.2 in the revised manuscript):

“For these three sites, the instruments were first run and calibrated in the laboratory and then operated at the sites in a consistent manner. GEM was measured at 5-min intervals and with a limit of detection (LOD) of ~5-10 ppqv (Mao et al., 2008), RGM was measured over a 2-h sampling period with a LOD of ~0.1 ppqv based on three times the standard deviation of the field blank values (Sigler et al., 2009; Mao and Talbot, 2012).”

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.

We agree that the MBL data are most interesting to understanding Hg chemistry, whereas the GOM mixing ratios at PM appear to be too low for meaningful interpretation if we used the observational data at the site alone. However, in this study, in our opinion it is important to include PM measurements because it could provide a comparison of GOM mixing ratios from three very different environments. Pack Monadnock (PM) is a heavily forested, elevated, inland site, representing continental background conditions with nearly no marine influence. PM is not the only site with frequent below LOD measurements of GOM; in fact, similar levels of GOM have

been reported from other background sites over the United States (Hall et al., 2006; Engle et al., 2010; Kolker et al., 2010; Choi et al., 2012).

We agree that interpretation of GOM mixing ratios <LOD would not be of much value. The site comparison was limited largely for the sensitivity runs to determine the processes that could potentially result in such the observed site difference in GOM mixing ratios.

REFERENCE

- Aspmo, K., Gauchard, P.-A., Steffen, A., Temme, C., Berg, T., Bahlmann, E., Banic, C., Dommergue, A., Ebinghaus, R., Ferrari, C., Pirrone, N., Sprovieri, F. and Wibetoe, G.: Measurements of atmospheric mercury species during an international study of mercury depletion events at Ny-Ålesund, Svalbard, spring 2003. How reproducible are our present methods?, *Atmospheric Environment*, 39(39 SPEC. ISS.), 7607–7619, 2005.
- Choi, H.-D., Huang, J., Mondal, S. and Holsen, T. M.: Variation in concentrations of three mercury (Hg) forms at a rural and a suburban site in New York State, *Sci. Total Environ.*, 448, 96–106, doi:10.1016/j.scitotenv.2012.08.052, 2013.
- Engle, M. A., Tate, M. T., Krabbenhoft, D. P., Schauer, J. J., Kolker, A., Shanley, J. B. and Bothner, M. H.: Comparison of atmospheric mercury speciation and deposition at nine sites across central and eastern North America, *J. Geophys. Res.*, 115(D18), D18306, doi:10.1029/2010JD014064, 2010.
- Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B. and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: a critical review, *Atmos. Chem. Phys.*, 15(10), 5697–5713, doi:10.5194/acp-15-5697-2015, 2015.
- Gustin, M. S., Huang, J., Miller, M. B., Peterson, C., Jaffe, D. A., Ambrose, J., Finley, B. D., Lyman, S. N., Call, K., Talbot, R., Feddersen, D., Mao, H. and Lindberg, S. E.: Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX, *Environmental Science and Technology*, 47(13), 7295–7306, 2013.
- Hall, B. D., Olson, M. L., Rutter, A. P., Frontiera, R. R., Krabbenhoft, D. P., Gross, D. S., Yuen, M., Rudolph, T. M. and Schauer, J. J.: Atmospheric mercury speciation in Yellowstone National Park, *Science of The Total Environment*, 367(1), 354–366, doi:10.1016/j.scitotenv.2005.12.007, 2006.
- Huang, J. and Gustin, M. S.: Uncertainties of Gaseous Oxidized Mercury Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes: Humidity Influences, *Environ. Sci. Technol.*, 49(10), 6102–6108, doi:10.1021/acs.est.5b00098, 2015.
- Huang, J., Miller, M. B., Weiss-Penzias, P. and Gustin, M. S.: Comparison of gaseous oxidized Hg measured by KCl-coated denuders, and nylon and cation exchange membranes, *Environmental Science and Technology*, 47(13), 7307–7316, 2013.
- Jaffe, D. A., Lyman, S., Amos, H. M., Gustin, M. S., Huang, J., Selin, N. E., Levin, L., ter Schure, A., Mason, R. P., Talbot, R., Rutter, A., Finley, B., Jaeglé, L., Shah, V., McClure, C., Ambrose, J., Gratz, L., Lindberg, S., Weiss-Penzias, P., Sheu, G.-R., Feddersen, D., Horvat, M., Dastoor, A., Hynes, A. J., Mao, H., Sonke, J. E., Slemr, F., Fisher, J. A., Ebinghaus, R., Zhang, Y. and Edwards,

- G.: Progress on Understanding Atmospheric Mercury Hampered by Uncertain Measurements, *Environ. Sci. Technol.*, 48(13), 7204–7206, doi:10.1021/es5026432, 2014.
- Kolker, A., Olson, M. L., Krabbenhoft, D. P., Tate, M. T. and Engle, M. A.: Patterns of mercury dispersion from local and regional emission sources, rural Central Wisconsin, USA, *Atmos. Chem. Phys.*, 10(10), 4467–4476, doi:10.5194/acp-10-4467-2010, 2010.
- Landis, M. S., Stevens, R. K., Schaedlich, F. and Prestbo, E. M.: Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air, *Environ. Sci. Technol.*, 36(13), 3000–3009, 2002.
- Lyman, S. N., Jaffe, D. A. and Gustin, M. S.: Release of mercury halides from KCl denuders in the presence of ozone, *Atmos. Chem. Phys.*, 10(17), 8197–8204, doi:10.5194/acp-10-8197-2010, 2010.
- Mao, H., Talbot, R. W., Sigler, J. M., Sive, B. C. and Hegarty, J. D.: Seasonal and diurnal variations of Hg⁰ over New England, *Atmospheric Chemistry and Physics*, 8(5), 1401–1421, 2008.
- Mao, H. and Talbot, R.: Speciated mercury at marine, coastal, and inland sites in New England-Part 1: Temporal variability, *Atmospheric Chemistry and Physics*, 12(11), 5099–5112, 2012.
- McClure, C. D., Jaffe, D. A. and Edgerton, E. S.: Evaluation of the KCl Denuder Method for Gaseous Oxidized Mercury using HgBr₂ at an In-Service AMNet Site, *Environ. Sci. Technol.*, 48(19), 11437–11444, doi:10.1021/es502545k, 2014.
- Sigler, J. M., Mao, H. and Talbot, R.: Gaseous elemental and reactive mercury in Southern New Hampshire, *Atmos. Chem. Phys.*, 9(6), 1929–1942, doi:10.5194/acp-9-1929-2009, 2009.
- Zhang, L., Wright, L. P. and Blanchard, P.: A review of current knowledge concerning dry deposition of atmospheric mercury, *Atmospheric Environment*, 43(37), 5853–5864, 2009.
- Zhang, L., Blanchard, P., Johnson, D., Dastoor, A., Ryzhkov, A., Lin, C. J., Vijayaraghavan, K., Gay, D., Holsen, T. M., Huang, J., Graydon, J. A., Louis, V. L. S., Castro, M. S., Miller, E. K., Marsik, F., Lu, J., Poissant, L., Pilote, M. and Zhang, K. M.: Assessment of modeled mercury dry deposition over the Great Lakes region, *Environmental Pollution*, 161, 272–283, 2012.