

We thank both the reviewers for their helpful comments and suggestions. In the following detailed response to all reviewer comments, the Reviewer Comment is first copied using regular text in black, followed by our response using italic font in green. A copy of the text that we have changed in the manuscript is also added to facilitate a simultaneous consideration of the reviewers' comments and our replies to those comments where appropriate.

Referee #1

C1.1) The authors simulate Hg oxidation with Br, O₃, and Cl with one set of oxidation rates presented in Table 2 (pg 28351), and conclude Br is the dominant oxidant of GEM in the free troposphere. However, the oxidation rates with Br and O₃ have high uncertainties (up to a factor of 10), which are not considered at all in this study. The uncertainties are large enough to potentially reverse their conclusions. For example, recent laboratory measurements have found the oxidation rate by O₃ to be $7.4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Rutter et al., 2012 doi:10.1016/j.atmosenv.2012.05.009), about 20 times higher than the rate considered in this study. Furthermore, BrO itself is believed to be an important oxidant of GEM. The authors do not present a reason for ignoring this oxidation pathway in their simulations. The authors should consider these two aspects before reaching a conclusion on the dominant pathway for GEM oxidation.

R1.1) Reaction rate considerations:

Hg + Br: We are currently using a reaction rate ($\sim 3.6 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) at the lower end of reported values. This should act as a conservative estimate for the relevance of this reaction. Additionally, this is the reaction rate that has been historically used by other modeling studies (Holmes et al., 2006, 2010; Seigneur and Lohman, 2008; Gratz et al., 2015) investigating the importance of oxidation of Hg⁰ by Br.

Hg + O₃: Since there are considerable discrepancies in the literature surrounding this oxidation rate, i.e. experimental and modeling/computational work, we determined that the best approach was to include this reaction in the modeling, but use a reaction rate at the lower end of experimentally reported values. Several high level thermodynamic calculation studies (Tossell, 2003; Shepler and Peterson, 2003) have found that the HgO molecule (the most likely reaction product of the oxidation reaction between Hg⁰ and O₃) would be unbound in the gas phase; making this oxidation pathway unlikely to proceed in the gas phase. Additionally, experimental measurements of this rate constant were conducted at high reactant concentrations and under conditions that would be more favorable for the stabilization/polymerization of heterogeneous reaction products than found in the atmosphere. So, for this manuscript we adopted the reaction scheme presented in several other modeling studies (Selin et al., 2007; Holmes et al., 2009, 2010) and use the lower rate constant. Text has been added to the introduction of Sect. 3.3 to make reference to this – “In general, the mercury modeling scheme employed in this study follows that as set forth in previous works (Selin et al., 2007; Holmes et al., 2009, 2010; Wang et al., 2015).”

Hg + BrO: This reaction was deemed not atmospherically relevant based on molecular quantum mechanical calculations (Balabanov and Peterson, 2003; Tossell, 2003), which found reactions between BrO and Hg⁰ to be unfavorable at atmospherically relevant conditions. The reaction of Hg-Br with BrO is already included in our model.

C1.2) The MAX-DOAS measurements were conducted for the entire month of April 2010 (as shown in Figure 2) and for additional periods between May 2009 and February 2011, yet the

retrieval of BrO tropospheric vertical column and profile are only shown for a single day. The manuscript would be much stronger if the retrievals were presented at least for the entire month. Are the BrO profiles fairly constant? How much variability is there? How confident are the authors in their conclusion if the analysis is conducted only for a single day? The authors present too strongly worded conclusions on the basis of generalizing their results for this single day of measurements: the dominant pathway of GEM oxidation, the numerical value for the oxidation rate for GEM, and the resulting lifetime of GEM against oxidation. At the very least, they should emphasize the limited nature of the measurements.

R1.2) We agree, though we liked to emphasize the consistency with previous measurements of BrO profiles in the tropics. This suggests that BrO profile variability is not a major concern. The reason for limiting this study to a single day of MAX-DOAS measurements stems from the magnitude of validation efforts that were employed to ensure the highest quality retrievals for both the raw MAX-DOAS measurements and the inversions.

That the results are based on a single day has already been highlighted in the abstract. In the revised manuscript we have expanded the comparison with recent vertical profiles of BrO measured from aircraft (Wang et al., 2015; Volkamer et al., 2015; Schmidt et al., 2016), all of which have been conducted in tropical air, though at different longitudes. The findings of this study are fairly consistent with the average profile provided by the previous studies, which provides confidence in the robustness of the derived profiles. The drivers for the observed variability in previous aircraft studies are currently not fully clear (see discussion in Wang et al., 2015). Further investigation, specifically in context of long-term measurements at a fixed site, would benefit from placing an instrument in the free troposphere, which is beyond the scope of this study. Language has also been added and changed in the Conclusions section to make the generalizations more transparent with respect to the results being the product of a single day case study.

Inserted text: "The presented box model studies indicate that for the conditions probed bromine radicals are the dominant oxidant for atmospheric GEM throughout the FT above the studied region. Given the similarities between the vertical profiles of BrO derived in this study and other profiles measured in the tropical FT (Volkamer et al., 2015; Wang et al., 2015) the results from our case study may apply more broadly, though past aircraft studies have found significant BrO variability (Wang et al., 2015; Schmidt et al., 2016), and deserve further investigation."

C1.3) Pg 28323, line 9. In addition to anthropogenic emissions and enhanced atmospheric oxidation, the authors should mention variability in precipitation as a strong controlling factor for the spatial variability of the wet deposition map shown in Figure 1. Also, numerous studies have examined Hg wet deposition and potential explanations for the pattern observed by the Mercury Deposition Network. For completeness, some of these studies should be cited.

R1.3) The discussion of mercury deposition in the Southeast US has been expanded to include mentioning of several studies (Zhang et al., 2012; and Nair et al., 2013) that support the conclusion pointed out by this comment.

C1.4) Pg. 28324. Line 7. No information is given for the HgII measurements in Pensacola. The authors should provide information as to what instrument is used and should also mention that a number of recent studies have indicated that there are significant problems with existing methods to measure HgII (see for example Jaffe et al., ES&T, 2014, 48, 7204-7206). In particular use of a

KCl denuder appears to lead to interferences from multiple compounds such as ozone and water vapor.

R1.4) Text was added to this line to make the reference to Edgerton et al., (2006) more transparent as containing the pertinent technical information for the atmospheric mercury measurements. Additionally, text was added here to acknowledge the studies that have found problems with the KCl denuder method for detecting oxidized mercury.

C1.5) pg. 28325, line 4: The O₃, NO₂, and HCHO profiles from the WACCM model are used as inputs to the box model to simulate Hg oxidation in the troposphere. It seems that the WACCM model has traditionally been used for stratospheric and mesospheric chemistry. How comprehensive is the representation of tropospheric chemistry? How do the profiles of the above species compare to profiles from GEOS-Chem, which has historically been used for simulating tropospheric chemistry. How sensitive are the authors' conclusions to this choice of vertical profiles?

R1.5) We do have GEOS-Chem profiles for O₃ and NO₂ that can be used for comparison, but unfortunately no profile for HCHO. We have updated the box model in the study to utilize the GEOS-Chem profiles for O₃ and NO₂ rather than the WACCM profiles. The figures containing the results using the WACCM profiles has been moved to the supplemental material. The difference in the column integral oxidation rate for Hg⁰ between using the GEOS-Chem and WACCM O₃ and NO₂ profiles is <5%.

C1.6) Pg. 28332, lines 22-25 and Figure 6. Does the WACCM a priori change as a function of time of day, or is it kept constant? Are the results affected by the assumption of diurnally changing a priori profiles or constant a priori profiles?

R1.6) The WACCM a-priori used for the BrO inversions in this study does change as a function of time of day; however, the a-priori assumptions have little effect on the a-posteriori profiles. This can be seen in Figure 5, where 3 different a-priori profiles are shown along with their corresponding a-posteriori results. Even though the a-priori profiles are quite different, the a-posteriori results remain similar throughout the troposphere.

C1.7) pg. 28333, line 24: How are the Cl radical concentrations estimated? Are those also from the WACCM model?

R1.7) The Cl radical profile used in this modeling study was calculated for research flights during the TORERO 2012 field campaign and deemed representative of the marine atmosphere. However, given that the discussion of this reaction does not add much merit to this manuscript and we currently do not have estimates of this vertical profile for our particular case study - we have removed the results of modeling this reaction from the final publication. Instead, we only briefly mention that the reaction was assessed and deemed unimportant (<5% on the integral oxidation rate).

C1.8) pg. 28334, line 18: The authors find that the column integral oxidation rates from the measured BrO profile and the BrO profile from the GEOS-Chem model are similar. Does this also imply that the BrO VCD simulated by the GEOS-Chem model are not too different from the measured VCD? This is at odds with the BrO vertical profiles shown in Figure 5, where the GEOS-CCM profile is at least a factor of 2 lower than the median observed profile. Or is the GEOS-CCM BrO profile different than the GEOS-Chem BrO profile? Some clarification would

be useful here. The only explanation provided by the authors is: “this is most likely due to additional bromine chemistry in this model.” Could the authors clarify what they mean, as I am unsure what the “additional bromine chemistry” is? I was under the impression that the same box model was used to calculate the rates, the only difference being the assumed BrO profile.

R1.8) The BrO VCDs for the GEOS-Chem profile and that found in this study are similar, but not to the extent as reflected in the difference in integral oxidation rates. The VCD from the GEOS-Chem profile is $1.5e13$ molec cm^{-2} , whereas the VCD from this study is $2.1e13$ molec cm^{-2} (average profile used for the modeling portion of the study) – a difference of closer to 30%. The GEOS-Chem and GEOS-CCM profiles are, in fact, different – the VCDs are $1.5e13$ and $3.5e12$ molec cm^{-2} for GEOS-Chem and GEOS-CCM, respectively. Stratospheric BrO was assimilated from the GEOS-CCM model runs for this case study so that it could be utilized as a-priori in the inversions. The use of GEOS-CCM as the a-priori is an active choice; the purpose being that the MAX-DOAS derived BrO vertical profile a-posteriori is maximally different to the a-priori assumption, thus indicating a robust retrieval.

GEOS-Chem BrO, which included the tropospheric bromine chemistry described in Sect. 2.2, was used for the modeling portion of this study. Text was added to Sect. 2.2 in order to clarify the differences between GEOS-CCM and GEOS-Chem and how they were utilized in this study.

C1.9) Figure 7. Related to the above comment, could the authors explain why the GEOS- Chem and MAX-DOAS oxidation rate vertical profiles are so different below 4 km and above 7 km?

R1.9) The oxidation rate vertical profiles shown in Fig. 7 reflect the differences in the vertical distribution of BrO between the GEOS-Chem model and the MAX-DOAS measurements. These differences are greatest at altitudes lower than 4 km (where the MAX-DOAS measurements find no BrO) and above 7 km (where GEOS-Chem predicts decreasing BrO). Currently, there are no figures that include the BrO vertical profile from GEOS-Chem, so an additional figure (new Fig. S8) was added in the supplemental information where the box model is described that contains vertical profiles of all parameters used as input to the model in this study (including GEOS-Chem BrO). Additional text has been added to this section to point out these differences.

C1.10) pg. 29339, line 16: “The chemical lifetime of GEM is ~40 days in the tropical FT..” This lifetime was calculated for one particular day under specific meteorological conditions, and cannot be generalized for the tropical FT.

R1.10) As previously mentioned, the profiles derived in this work do show consistencies with reported vertical profiles of BrO measured from aircraft (Volkamer et al., 2015; Wang et al., 2015; LeBreton et al., 2016) that do cover different atmospheric conditions and, therefore, some generalized conclusions can be drawn for regions demonstrating similar BrO vertical distributions. However, the language has been changed in this sentence (and in other portions of the manuscript) to reflect the results of this study being from a single day case study and that conclusions can only be generalized under similar atmospheric conditions.

C1.11) pg. 28339, line 25-29 “The findings of this study indicate that the amount of bromine located in the FT above the (coastal regions) of the SE US is sufficient to quickly oxidize GEM to GOM, which in turn can be wet deposited, and as such can help explain the observed elevated wet deposition pattern in this region.” This is a very strong conclusion but I do not believe that

the authors have demonstrated the link between oxidation rates and deposition. Furthermore in order to explain the spatial gradient of wet deposition, the authors would need to demonstrate that weaker oxidation rates occur in other regions.

R1.11) We do not mean to demonstrate the link between oxidation rates and deposition. This is why the sentence has been phrase in a non-affirmative language. It speaks of ‘... can be deposited’, not ‘will be deposited’. We have revised the language to clarify this further.

Revised text: “Additionally, this study suggests that the experimental observation of elevated GOM in the FT may be linked to our incomplete understanding about tropospheric bromine sources (Swartzendruber et al., 2006; Fain et al., 2009; Lyman and Jaffe 2012; Wang et al., 2015); and indicate that conditions exist where the amount of bromine located in the FT above the (coastal regions) of the SE U.S. is sufficient to quickly oxidize GEM to GOM. This can then be wet deposited and, as such, can help explain the observed elevated wet deposition pattern in this region.”

C1.12) Figure 8c. The ratio appears to be very large below 4 km altitude, where the thermal decomposition of HgBr is very fast. So the effective impact of including these additional adduct reactions might not be that large. It would be useful to include a panel, or at least discuss the overall impact of these reactions in terms of the net rate of HgO oxidation (basically how does the blue line in Figure 7a change).

R1.12) The thermal dissociation of HgBr is actually included in the box model using the rate constant determined by Goodsite et al., 2012 (see Table 2). So yes, the effect of additional scavenging reactions is actually largest below 4 km, where HgBr decomposition is fast. Fig. 8 shows the modeling results of the scavenging reactions of the HgBr adduct, so the shown rates are for reactions $\text{HgBr} + X$, where X is any of the additional molecules shown in the figure and discussed in the text. These calculations already assume that the rate limiting step is the formation of HgBr. Thus panels A and B are directly comparable and the ratio depicted in panel C is valid.

C1.13) Figure 2: What do the colors in the top four panels represent?

R1.13) These colors indicate difference elevation angle geometries of the MAX-DOAS measurements. The legend of this figure has been updated to clarify.

C1.14) Figure 7: What scheme is used for Br chemistry: the “traditional” or “additional adduct reactions” scheme? It would be helpful to add the vertical profiles of the oxidants, too.

R1.14) The “traditional” oxidation scheme was used for the runs depicted in Fig. 7 and text has been added to clarify this point. As mentioned in R1.9, Fig. S8 has been added to the supplemental information that contains the vertical profiles of parameters used as input to the box model; all other species’ profiles are calculated by the box model itself.

C1.15) Pg. 28334, line 1-2. Units are missing. “. . .while the Br rates are 3.0×10^5 and 3.4×10^5 for the BrO vertical profiles from the MAX . . .” Also, what is the height of the tropopause for this particular day?

R1.15) The units have been added to this sentence. The closest available radiosonde data available for this day is from Tallahassee, FL and shows the tropopause at ~15 km.

C1.16) Figures S2 and S4. The fonts are too small to read.

R1.16) Text for these two figures has been updated to be more legible.