

Interactive comment on “Mercury oxidation from bromine chemistry in the free troposphere over the southeastern US” by S. Coburn et al.

Anonymous Referee #1

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The authors present vertical column density and vertical profile measurements of tropospheric BrO using a ground-based DOAS instrument at a coastal site in Florida. The measurements are reported for one case study on April 9 2010. They use a steady-state box model constrained by these measurements to calculate the contribution of Br radicals to GEM oxidation in the free troposphere over the southeastern US, and find this to be the dominant pathway for GEM oxidation. Several satellite-, ground- and aircraft-based observations of BrO suggest the presence of a background concentration of 0.5-2 pptv in the free troposphere, large enough to significantly affect ozone and mercury chemistry. This study presents further evidence for the presence of free-tropospheric BrO concentrations of about 1 pptv. These new measurements of tropospheric BrO are essential for constraining models of bromine chemistry and GEM

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oxidation.

The paper is well written and presents very interesting results. I have two major concerns that I outline below. The first concern is on the lack of discussion of uncertainties in the rate constants and the lack of discussion of BrO as an oxidant itself. The second concern is that the main conclusions of the manuscript are based on a single day of vertical BrO profile measurements, which do not justify generalized conclusions presented in the manuscript. These two major concerns are discussed below and are followed by more detailed specific comments and technical comments.

MAJOR CONCERNS

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 7.4×10^{-19} cm³ molecule⁻¹ 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.

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

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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.

SPECIFIC COMMENTS

1) 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.

2) 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.

3) 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?

4) 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?

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

6) 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.

7) 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?

8) 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.

9) 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.

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10) 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 Hg0 oxidation (basically how does the blue line in Figure 7a change).

TECHNICAL COMMENTS

Figure 2: What do the colors in the top four panels represent?

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.

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?

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

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