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 7.4x10-19 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.

R1.1) Reaction rate considerations:

Hg + Br: We are currently using a reaction rate (~3.6e-13 cm^3 $molec^{-1}$ 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 Hg^0 by Br.

Hg + O_3: 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 Hg^0 and O_3) 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 Hg^0 *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 O_3 and NO_2 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 O_3 and NO_2 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 Hg^0 between using the GEOS-Chem and WACCM O_3 and NO_2 profiles is <5%.*

C1.6) Pg. 28332, lines 22-25 and Figure 6. Does the WACCM apriori 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; Faïn 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 Hg0 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 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 3.0×105 and 3.4×105 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.

Referee #2

C2.1) Since only one case study day (9 April 2010) is presented and discussed, the data/results are for me over-interpreted in terms of both bromine content/vertical distribution for southeastern US and their impacts on Hg oxidation pathways. As Referee # 1, I wonder why the entire data set covering the May 2009-February 2011 has not been exploited in this work. Do we expect similar tropospheric BrO profiles (i.e. with only a significant content in the FT) throughout the year at this location? Is it possible to have at some period(s) of the year a more significant contribution from the marine boundary layer? If yes, what would be the impact on the bromine and Hg oxidation chemistry modelling? The authors should make clear in the text but also in the title that it is a one-day case study.

R2.1) We agree, and refer to our response to reviewer #1 (see R1.1). In general, the profile derived in this work shows some similarities to other reported profiles measured from aircraft (Volkamer et al., 2015; Wang et al., 2015; LeBreton et al., 2016), which cover large spatial gradients and probe different atmospheric conditions. While it is possible that there could exist periods where the MBL contributes more significantly to the total BrO column, several studies exist that point to a low upper limit of <0.5 pptv BrO in the MBL (Volkamer et al., 2015; Wang et al., 2015; Gomez Martin, 2013) which makes it seem unlikely that this would be the dominant scenario. If this were the case, the much warmer temperatures found in the MBL would increase the influence of the thermal decomposition of the HgBr adduct and the increased availability of additional molecules to stabilize the HgBr adduct would create a much more complex situation for mercury cycling.

We are explicit in the abstract and throughout the manuscript that this study represents a single day and further mention in the title would not add further to this already high level of transparency. The language in the conclusions has been modified to reflect the results of this study are from a certain set of atmospheric conditions.

C2.2) The error budget on the retrieved BrO vertical profiles and corresponding column densities is mainly derived through sensitivity tests using different a priori profiles in the Optimal Estimation retrieval. Nothing is said about the uncertainty related to the choice of the settings for the DOAS spectral analysis, although these settings can affect significantly the BrO slant column densities, and therefore the amount of BrO retrieved in both the FT and boundary layer. This is for me a crucial point and the authors should discuss it into more details in the revised manuscript. The main results of the sensitivity tests performed for the selection of the DOAS settings could for instance appear as supplementary material.

R2.2) Indeed, we have performed extensive sensitivity studies prior to the submission of this work. And the revised manuscript makes these now transparent. It was found that the choice of DOAS parameters (fitting window, intensity offset, and reference spectrum) impacted the resulting BrO dSCDs, but the final settings used estimate the BrO dSCDs conservatively. A section has been added to the supplemental material to provide greater detail regarding tests on the fitting window and intensity offset. The description of sensitivities towards reference selection is found in Sect. 2.4.2. Overall, this study estimates the BrO concentration profile (and VCD) conservatively.

C2.3) Specific comment related to major concern 1: Only a day with very low aerosol content has been selected for this study. Does it mean that even for moderate aerosol contents, the methods/concepts developed in this study are not valid anymore? The presence of a moderate aerosol content could indicate a different regime where the marine boundary layer contributes more significantly to the total BrO column. If so, a different impact on the Hg oxidation pathways should be expected.

R2.3) Even moderate aerosol loads in the marine boundary layer would impact the capability of this method to retrieve profiles of trace gases located in the free troposphere. Some information could be retained, i.e. total column, but derivation of vertical profiles would most likely be significantly impacted. This has now been mentioned in the revised manuscript.

Aerosols in the MBL could indeed indicate a different air mass regime where the MBL contributes more significantly to the total column of BrO; however, there is no experimental evidence for this. The available evidence finds low BrO upper limits (<0.5 pptv) also under conditions of acidic aerosols in the tropical MBL (Gomez-Martin, 2013; Volkamer et al., 2015; Wang et al., 2015). Only if there was BrO at *instrument altitude would this complicate the decoupling of the FT profile. Thus, we do not expect that moderate aerosol would fundamentally change the ability to apply this method to characterize free tropospheric BrO partial columns. At high aerosol load the view of the FT could be shielded because of the dominance of scattering at lower altitudes. We have added mentioning that this method is useful for future deployments from mountain tops, where aerosol variability and shielding of the FT can be overcome.*

The ability to remotely sense the BrO partial column in the FT is an analytical question, and does not imply an impact on the conclusions drawn from this study regarding the oxidation of atmospheric mercury in the free troposphere.

C2.4) Page 28333, lines 11-21: the average tropospheric column retrieved in this study (2.3E13 molec/cm2) is in the 1-3E13 molec/cm2 range reported so far in the literature. However, it is clearly above the values published for tropical regions and which are ranging from 0.4 to 1.2E13 molec/cm2. Where does this difference come from? Why not considering in your study BrO total/tropospheric columns derived from OMI and/or GOME2A over Gulf Breeze around 10 April 2010?

R2.4) The average value found in this study is above the range currently reported for the tropics, but still within the range (albeit the upper end) reported for the mid-latitudes. The values reported by the referee seem rather low for measured profiles, which are in the range 1-1.7e13 (average 1.5e13) molec cm^{-2} *for aircraft studies (Volkamer et al., 2015; Wang et al., 2015); Theys et al., (2011) reported a monthly averaged tropospheric VCD from GOME-2 of ~1.7e13 molec* cm^{-2} *with error bars extending above 2e13 molec* cm^{-2} *for the latitude range 0-30° N in using the years 2007 and 2008. While comparisons with other satellite measurements would be desirable there are few studies that report satellite derived values of tropospheric BrO at the mid-latitudes. The manuscript is already quite complex. We consider a comparison with satellite data beyond the general comparison of VCDs to be beyond the scope of this manuscript.*

C2.5) Supplementary material, aerosol extinction profile retrievals: Why a extinction value of 0.01 km-1 and a scaling height of 0.6 km are used for the a priori profile? A justification is needed. Also, what would be the impact of changing this a priori profile (e.g. by using a larger scaling height value) on the retrieved aerosol extinction profiles but also on the retrieved BrO profiles? Why aerosol extinction profiles are not directly retrieved from O4 dSCDs fitted in the UV range? In other words, why retrieving aerosol extinction profiles in the visible range (483 nm) and then scaling them to 350 nm, while observations in the UV range are available? A reference/explanation should be given for Eq. S1.

R2.5) This a-priori profile for aerosol extinction was chosen as a first guess of a profile shape and magnitude that might correspond with the measured O_4 dSCDs. Changing the a-priori profile should have little-to-no impact on the derived a-posteriori profiles, as that the technique should arrive at a similar conclusion independent of a-priori. Using a larger scaling height or total AOD would only increase the computational time needed to reach the very low values found for aerosol extinction in this case study. Additionally, because such low values are found, small changes in the derived aerosol extinction at the various grid layers of the inversion would likely have little impact on the sensitivity towards trace gas retrievals.

Aerosol profiles are derived using the visible absorption features of O_4 due to the increased absorption and better signal to noise in this wavelength range. This leads to a more robust derivation of the aerosol extinction (Volkamer et al., 2015). In general, during initial sensitivity studies the aerosol extinction values derived using the O_4 dSCDs from the UV analysis show larger error bars, and have less certainty in comparing measured and forward calculated O_4 dSCDs. However, our measurements are consistent within error also at UV wavelengths. Text has been added to this section to make these decisions more transparent.

C2.6) Technical corrections: Difficult to read texts in Figs S2 and S4 (font too small).

R2.6) Text for these figures has been changed to be more legible.

Mercury oxidation from bromine chemistry in the free troposphere over the Southeastern US

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Abstract

The elevated deposition of atmospheric mercury over the Southeastern United States is currently not well understood. Here we measure partial columns and vertical profiles of bromine monoxide (BrO) radicals, a key component of mercury oxidation chemistry, to better understand the processes and altitudes at which mercury is being oxidized in the atmosphere. We use the data from a ground-based MAX-DOAS instrument located at a coastal site ~1 km from the Gulf of Mexico in Gulf Breeze, FL, where we had previously detected tropospheric BrO (Coburn et al., 2011). Our profile retrieval assimilates information about stratospheric BrO from the WACCM chemical transport model, and uses only measurements at moderately low solar zenith angles (SZA) to estimate the BrO slant column density contained in the reference spectrum (SCD_{Ref}). The approach has 2.6 degrees of freedom, and avoids spectroscopic complications that arise at high SZA; knowledge about SCD_{Ref} helps to maximize sensitivity in the free troposphere (FT). A cloud-free case study day with low aerosol load (9 April 2010) provided optimal conditions for distinguishing marine boundary layer (MBL: 0-1 km) and free tropospheric (FT: 1-15 km) BrO from the ground. The average daytime tropospheric BrO vertical column density (VCD) of ~2.3×10^{13} molec cm^{-2} (SZA<70°) is consistent with our earlier reports on other days. The vertical profile locates essentially all tropospheric BrO above 4 km, and shows no evidence for BrO inside the MBL (detection limit < 0.5 pptv). BrO increases to ~3.5 pptv at 10-15 km altitude, consistent with recent aircraft observations. Our case study day is further consistent with recent aircraft studies, in that the oxidation of gaseous elemental mercury (GEM) by bromine radicals to form gaseous oxidized mercury (GOM) is the dominant pathway for GEM oxidation throughout the troposphere above Gulf Breeze. The column integral oxidation rates range from 3.5-3.7×10^5 molec cm^{-2} s^{-1} for bromine, while the contribution from ozone (O_3) is 0.8×10^5 molec cm^{-2} s^{-1}. Chlorine induced oxidation is estimated to add <5% to these mercury oxidation rates. The GOM formation rate is sensitive to recently proposed atmospheric scavenging reactions of the HgBr adduct by nitrogen dioxide (NO_2), and to a lesser extent also HO_2 radicals. Using a 3-D chemical transport model, we find that surface GOM variations are typical also of other days, and are mainly derived from the free troposphere. Bromine chemistry is active in the FT over Gulf Breeze, where it forms water-

soluble GOM that is subsequently available for wet scavenging by thunderstorms or transport to the boundary layer.

1 Introduction

Measurements of tropospheric halogen species are an area of increasing research interest due to the ability of halogens to destroy tropospheric ozone (O_3) (Read et al., 2008; Saiz-Lopez et al., 2012), oxidize atmospheric mercury (Holmes et al., 2009; Hynes et al., 2009), and modify oxidative capacity (Parella et al., 2012). Most assessments of the impacts of halogen chemistry are based on measurements of halogen oxides (bromine monoxide (BrO) and iodine monoxide (IO)), since these radicals are typically found at higher concentrations throughout the troposphere than the corresponding halogen atom radicals. Many of these studies take place in the planetary boundary layer (PBL) given that this region of the atmosphere is easily accessible from measurements located at the surface, and is also the most directly impacted by anthropogenic activities. However, halogen chemistry in the free troposphere (FT), albeit more challenging to measure, has the potential to affect an even larger air volume and mass. In particular, the colder temperatures of the free troposphere accelerate the bromine oxidation of gaseous elemental mercury (GEM) (Donohoue et al., 2006). Satellite-borne measurements represent a powerful resource for assessing global distributions and tropospheric vertical column densities (VCD) of BrO (GOME – van Roozendael et al., 2002; GOME-2 - Theys et al., 2011; Sihler et al., 2012). However, satellite retrievals rely on assumptions made about the vertical distribution of BrO, and uncertainties in these assumptions can lead to over/under predictions in the derived tropospheric VCD. The most direct method for measuring trace gas vertical distributions is through the use of aircraft (Prados Ramon et al., 2011; Volkamer et al., 2015), or balloons (Fitzenberger et al., 2000; Pundt et al., 2002; Dorf et al., 2006). However, this type of measurement is costly and potentially impractical if the goal is to establish long term trends in the FT. Ground-based measurements are typically more straightforward to deploy and maintain for extended periods of time, but optimizing ground-based capabilities to observe the FT remains an area of active research (Schofield et al., 2006; Theys et al., 2007; Hendrick et al. 2007; Coburn et al., 2011). Specifically, ground-based Multi-Axis Differential Optical Absorption

Spectroscopy (MAX-DOAS) measurements are uniquely suited for this type of study since this technique also assesses vertical distributions, and derived VCDs can be directly compared with models and satellites. Additionally, the DOAS retrieval allows for the detection of not only BrO, but also other trace gases that have significant impacts on the chemical cycling of bromine species in the atmosphere, such as NO_2 and some volatile organic compounds (VOCs). However, measurements of FT BrO from ground-based MAX-DOAS are not straightforward for several reasons: 1) stratospheric BrO represents a large portion of the measured signal and creates a background that has to be accounted for when attempting to assess the FT; 2) ozone absorption structures are strongly present in the same wavelength region as BrO and can create interferences due to stratospheric ozone absorption, in particular at high solar zenith angles (SZA) (Aliwell et al., 2002; van Roozendael et al., 2002); and 3) the sensitivity of this technique peaks at the instrument altitude and decreases with increasing altitude. Recent advances with testing stratospheric BrO profiles in atmospheric models (Liang et al., 2014) provide opportunities to properly account for #1 by assimilating information from atmospheric models. Further, retrievals that avoid SZA larger 70^{o} do not suffer from #2, and certain measurement geometries retain information about the FT. Figure S1 (Supplement) depicts the box Air Mass Factors (bAMFs), which represent the sensitivity of the slant column density (SCD) measurement geometry to BrO concentrations at different altitudes, for two pointing directions (or elevation angles, EA = 25° and 90° upwards) at several SZA; at SZA<70° the sensitivity of these EAs peaks between 2-15km. A more comprehensive view of the bAMFs for different EAs over a wider SZA range is shown in Figure S2 (Supplement).

Van Roozendael et al. (2002) compared ground-based and balloon-borne measurements to VCDs of BrO from the space-borne Global Ozone Monitoring Experiment (GOME) and found all platforms were consistent with a rather widespread tropospheric BrO VCD of 1-3×10^{13} molec cm^{-2} once appropriate radiative transfer effects were taken into consideration. Salawitch et al. (2005) and Theys et al. (2011) also report satellite derived tropospheric BrO VCDs (GOME and GOME-2, respectively) for the mid-latitudes of 2×10^{13} molec cm^{-2} and 1-3×10^{13} molec cm^{-2}, respectively. Ground based measurements (Theys et al. 2007; Coburn et al., 2011) in the mid-latitudes have reported BrO VCDs of 1-2×10^{13} molec cm^{-2} that are comparable to the findings from satellites. Volkamer et al. (2015) recently reported $1.6x10^{13}$ molec cm^{-2} BrO VCD in the tropics measured by limb-observations from aircraft. All of these studies point to the widespread presence of BrO in the FT, corresponding to a VCD of $1\text{-}3x10^{13}$ molec cm^{-2}. Based on these reports, tropospheric BrO could account for 20-30% of a total BrO VCD $\sim 5\text{-}6x10^{13}$ molec cm^{-2} as seen from satellite (van Roozendael et al., 2002; Theys et al., 2011), and significantly impact the lifetime of tropospheric O_3 and atmospheric GEM (Wang et al., 2015).

1.1 Atmospheric Hg in the South Eastern US

Mercury in the atmosphere exists in three forms: gaseous elemental mercury (Hg^0, GEM), gaseous oxidized mercury in the form of either Hg^{2+} or Hg^{1+} (GOM), and particle-bound mercury (PBM). Understanding the processes that cycle mercury between its various forms (GEM ↔ GOM ↔ PBM) is of great importance because this speciation controls the deposition of mercury to the environment, i.e, GOM and PBM are more readily removed from the atmosphere via wet and dry deposition than GEM (Lindberg and Stratton 1998; Bullock 2000). Once deposited, biological processes can methylate Hg^{2+} to form the neurotoxin methyl mercury, which bio-accumulates in fish. Enhancement factors for methyl mercury of up to 10^6 relative to water have been measured in predatory fish tissues (Schroeder and Munthe 1998; Selin et al., 2010).

A better understanding of the processes controlling atmospheric mercury oxidation, and therewith removal, is particularly relevant for regions that experience high levels of mercury deposition, such as the Southeastern United States. (SE U.S.). Figure 1 shows a map of the Total Mercury Wet Deposition in the US from 2013 (http://nadp.sws.uiuc.edu/maplib/pdf/mdn/hg_dep_2013.pdf). The high deposition levels experienced in the SE U.S. cannot be explained by regional anthropogenic sources of mercury alone, which are mainly located within the Ohio River Valley where the prevailing winds carry emissions northeast. Additionally, several modeling studies (Zhang et al., 2012; Nair et al., 2013) have shown that meteorological patterns above the SE U.S. greatly influence the wet deposition of mercury and that these processes are linked with deep convective activity. This indicates that a regional emission-deposition pattern is most likely not the major source-receptor relationship for mercury entering the environment over Florida, in the SE U.S., meaning that other possibilities, such as enhanced atmospheric oxidation followed by deposition, need to be explored.

2 Experimental

2.1 Atmospheric Conditions

The case study during 9 April 2010 provided optimal conditions for assessing the ability of a ground-based MAX-DOAS instrument to measure FT trace gases (see Sect. S1 Supplement for a brief overview of instrumentation and measurement site). Figure 2 shows a time series of trace gas differential slant column densities (dSCD) of BrO, IO, NO_2, and O_4 for the week surrounding the case study day; with 9 April highlighted by the blue box. The IO measurements are assimilated and used in the modeling portion of this study (Sect. 3.4), while the NO_2 measurements give an indication on the amount of influence from anthropogenic activities in the lowest layers of the BL. This day provides an excellent case study for two reasons: 1) consistent shape of the O_4 dSCDs across elevation angles as well as the clear splitting between the values is a good indicator for a cloud-free day, and 2) the relatively high O_4 dSCDs values (compared with other days) indicates a low aerosol load, enabling the instrument to realize longer light paths (increased sensitivity due to fewer extinction events), and an unobstructed view of the FT. An inspection of webcam pictures for the instrument site proved the day to be free of visual clouds, and precursory look at the aerosol load confirmed the low values. Figure 2 also contains in-situ O_3 measurements (from both the US EPA site and a nearby Mercury Deposition Network (MDN) site), oxidized mercury measurements (see below), as well as wind direction measurements from a WeatherFlow, Inc. monitoring station located in Gulf Breeze, FL near the US EPA site.

Oxidized mercury measurements (Hg^{II} = GOM+PBM) at the Pensacola MDN site during study period (see Edgerton et al., 2006 for a detailed description of the site and instrumentation) are also shown in the bottom panel of Fig. 2 (also Fig. 9, Sect. 3.4). On 9 April, Hg^{II} concentrations at the MDN site were rising from near zero on 8 April (due to rain) to peak values of 15-40 pg m^{-3} on the following days, which is above average for the season. In prior years, average daily peak concentrations at this site in spring were 15 pg m^{-3}, which is higher than during any other season (Weiss-Penzias et al., 2011; Nair et al., 2012). Observed GEM concentrations are persistently around 1.4 ng m^{-3} throughout early April, as expected for this season, and therefore not shown. It should be noted, that recent studies have found that measurements of Hg^{II} using KCl denuders can be influenced by atmospheric conditions and other trace gases (McClure et al., 2014) and these external factors can lead to an underestimation of Hg^{II}.

2.2 External Model Overview

The Whole Atmosphere Community Climate Model version 4 (WACCM4) (Garcia et al., 2007; Marsh et al., 2013) has been extensively evaluated for its representation of the stratosphere, including stratospheric BrO (SPARC CCMVal, 2010). The model does not represent tropospheric bromine sources from very short lived species (VSLS, bromocarbons); and using this model in this study is an active choice to assure a-priori information about tropospheric BrO represents a lower limit (see Sect. 2.4.1). However, $CHBr_3$ and CH_2Br_2 concentrations are fixed at the cold point and add about 5-6 pptv stratospheric Br_y (stratospheric Br_y loading is 21-22pptv). In this work, WACCM is run with specified (external) meteorological fields. This is achieved by relaxing the horizontal winds and temperatures to reanalysis fields. The reanalysis fields used are taken from the NASA Global Modeling and Assimilation Office (GMAO) Modern-Era Retrospective Analysis for Research and Applications (MERRA) (Rienecker, et al., 2011). The horizontal resolution is 1.9° x 2.5° (latitude x longitude), with 88 vertical levels from the surface to the lower thermosphere (-140 km). Other WACCM model outputs used are: HCHO, temperature, and pressure vertical profiles. Time synchronized BrO vertical profiles from WACCM are used as a-priori inputs to the inversion (tropospheric VCDs ~$1x10^{13}$ molec cm^{-2}), while HCHO profiles are used as input for the box model utilized in this study (see Sect. S4 Supplement). Temperature and pressure profiles were used to construct a molecular density profile in order to convert from concentration (output units of the inversion) to volume mixing ratios (VMR). Model data was generated specifically for this case study in order to best represent that atmospheric composition at the time of the measurements.

The GEOS-Chem global chemical transport model is used to provide a regional and seasonal context for the DOAS observations and their relevance to mercury chemistry. GEOS-Chem (v9-02, www.geos-chem.org) is driven by assimilated meteorology from the NASA Goddard Earth Observing System (GEOS-5). Simulations here have 2° × 2.5° horizontal resolution at 47 vertical layers for bromine and all species except mercury, which have 4° × 5° horizontal resolution. The bromine chemical mechanism, described by Parrella et al. (2012), includes marine bromocarbon emissions from Liang et al. (2010) and debromination of sea salt aerosols (Sander et al., 2003; Yang et al., 2005). Tropospheric bromine concentrations from GEOS-Chem are merged with stratospheric bromine from GEOS-CCM (Liang et al., 2010) to produce a complete atmospheric column (tropospheric VCD of 1.5×10^{13} molec cm^{-2}). The GEOS-Chem BrO vertical profile is also used as input to the box model in order to assess sensitivity to differences between measured and modeled BrO vertical distributions on mercury oxidation; GEOS-Chem O_3 and NO_2 profiles are also used as input to the box model. Additionally, the GEOS-CCM profile is utilized as an a-priori during the inversion of the MAX-DOAS measurements due to its representation of the stratosphere while excluding most bromine chemistry in the troposphere (lower limit of bromine in the FT, tropospheric VCD of 3.5×10^{12} molec cm^{-2}). The mercury simulation is configured as described by Zhang et al. (2012), which includes GEM and two Hg^{II} species: GOM and PBM. Anthropogenic mercury emissions are from the US EPA National Emission Inventory (NEI) 2005 and National Pollutant Release Inventory (NPRI) 2005 inventories over North America (Zhang et al., 2012), which are adjusted to account for Hg^{II} reduction in power plant plumes (Landis et al., 2014), and elsewhere from the Global Emission Inventory Activity (GEIA) (Streets et al. 2009; Corbitt et al., 2011). Emissions and cycling from oceans and the biosphere are also included (Selin et al., 2008; Soerensen et al., 2010). Atmospheric GEM is oxidized by bromine (Holmes et al., 2010) using updated kinetic rate coefficients from Goodsite et al. (2012) and bromine concentrations from GEOS-Chem. Hg^{II} partitions between GOM and PBM (Rutter et al., 2007; Amos et al., 2012) which are both quickly scavenged by precipitation or dry deposited, but also susceptible to reduction in cloud water. The bromine and mercury simulations are both spun up for at least one year. The model is then sampled hourly during April 2010 over Pensacola.

2.3 DOAS BrO Retrieval

Following is a brief description of the parameters and settings used for the DOAS analysis of BrO for this study. A series of sensitivity studies on the BrO retrieval determined the optimal wavelength window for the analysis in this study to be 338-359 nm and include a 5th order polynomial. Sensitivity studies which varied the fit window, polynomial order, and intensity offset indicate that the chosen fit settings estimate BrO dSCDs conservatively, as is discussed in more detail in the Supplement (Sect. S2). The reference cross sections used in the DOAS retrieval (WinDOAS software, Fayt and van Roozendael, 2001) were: O_3 (at 223 and 243 K, Bogumil et al., 2003), NO_2 (at 220 and 297 K, Vandaele et al., 1998), O_4 (at 293 K, Thalman and Volkamer 2013), HCHO (Meller and Moortgat 2000), BrO (Wilmouth et al., 1999), and a Ring spectrum (Chance and Spurr 1997) calculated using the software DOASIS (Kraus 2006) at 250 K for the reference used in the analysis. Additionally, a constant intensity offset was included in the fit, but limited to a range ($\pm 3 \times 10^{-3}$) determined by an estimation of the upper limit for the correction of spectrometer stray light. Details of the retrieval for other traces gases can be found in Table 1 along with an overview of the BrO retrieval settings listed here. A single zenith reference from a low SZA of the case study day was used to analyze all spectra (referred to as a fixed reference analysis); this spectrum was taken at ~18:01 UTC on 9 April 2010 (~23° SZA).

2.4 Inversion Method

The retrieval of the BrO VCDs and vertical profiles for this study is a three-step process: 1) aerosol profiles are determined based on DOAS measurements of O_4 (see Sect. S3 Supplement); 2) derived aerosol profiles are used in a Radiative Transfer Model (RTM) to calculate weighting functions for BrO; and 3) weighing functions are used in an optimal estimation inversion of the DOAS dSCDs to derive VCDs and vertical profiles (Sect. 2.4.1). Additionally, a method is presented here for determining the residual amount of BrO contained in the reference spectrum (SCD_{Ref}, Sect. 2.4.2). The relationship between SCD_{Ref} and the measured dSCDs is shown as Eq. (1).

$$SCD = dSCD + SCD_{Ref} \quad (1)$$

Both dSCDs and SCDs were used as input to the inversion, and sensitivity tests are presented to assess the impact of the SCD_{Ref} value on the derived vertical profiles and VCDs.

2.4.1 Trace Gas Inversion

Weighting functions calculated at 350 nm (for BrO) are used in an optimal estimation (OE) inversion (Rodgers 2000) to determine the trace gas vertical profiles from the MAX-DOAS dSCD measurements, as given by Eq. (2).

$$x_r = x_a + A(x_t - x_a) \qquad (2)$$

Here x_r represents the retrieved profile, x_a is the a-priori profile assumption, A is the averaging kernel matrix (AVK), and x_t is the true atmospheric state (represented by the MAX-DOAS dSCD or SCD measurements here). The AVK gives an indication of where the information in x_r is coming from, i.e. information from x_t (measurements) vs x_a (a-priori assumption). The trace of this matrix gives the degrees of freedom (DoF) of the retrieval and indicates how many independent pieces of information are contained in the retrieval (see Sect. 3.1).

One important aspect in this study is the choice of the altitude grid used for both the radiative transfer calculations and the inversion. We used a grid of varying layer thickness: 0.5 km from 0-2 km; a single 3 km layer from 2-5km, and 5 km layer thickness from 5-50 km. This grid is chosen to effectively combine the information from multiple altitudes into a single grid point to assure reasonable peaks in the averaging kernels at increasing altitude, where the MAX-DOAS measurements have limited vertical resolution.

For the BrO inversion, four different a-priori profiles are used in order to assess the robustness of the inversion (see Fig. 5 Sect. 3.2, which shows three of the a-priori profiles along with their corresponding a-posteriori results). Two of the a-priori profiles are based on WACCM model output, the third used data from the CU Airborne-MAX-DOAS (AMAX-DOAS) instrument collected during the Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO) 2012 field campaign (Volkamer et al., 2015), and the fourth is a mean profile from GEOS-CCM. The a-priori profiles from WACCM are: 1) direct model output for the time of each MAX-DOAS scan throughout the day (i.e., different a-priori profile for each MAX-DOAS scan); and 2) the profiles from 1) increased by 40% (in VMR space). The a-priori profile for the TORERO case is derived from data collected during research flight 12 (RF12, Volkamer et al., 2015), which closely represents also the tropical average BrO profile (see Fig. 2 in Wang et al., 2015). The GEOS-CCM profile is a daytime zonal mean at 30° N. The TORERO and GEOS-CCM profiles are used to invert each MAX-DOAS scan, i.e., the same profile is used for each scan inversion. This is in contrast to the WACCM a-priori profiles, which change throughout the day, due to the availability of time resolved output. For reference, diurnal variations in the WACCM model output for BrO vertical distributions are shown in Fig. S3 (Supplement) panel (a), while panel (b) shows the corresponding tropospheric and total VCDs from these profiles. The a-priori profile error used as input to the OE is constructed based on upper limit values (in units of VMR) expected throughout the troposphere; this is set at 1 pptv for altitudes 0-2 km, 3 pptv for 2-5 km, and 4 pptv for 5-20km (except for the GEOS-CCM case where this altitude range is set to 6 pptv to account for the extremely low values found in the lower FT of the a-priori). The a-priori error is constrained to 40% for the stratospheric portion of the profile (20-50 km), based on the assumption that the WACCM and GEOS-CCM profiles in this region of the atmosphere accurately represent the true atmospheric state, but allowing for sufficient room to reflect contributions of very short-lived organo halogen species (VSLS) to stratospheric BrO (Liang et al., 2014).

A similar method is also used to derive IO profiles (used as input to the modeling in Sect. 3.4). The IO inversion uses two a-priori profiles: 1) a moderate IO VMR in the BL (0.2 - 0.5 pptv) and decreasing to very low levels (<0.1 pptv) throughout the rest of the troposphere; and 2) profiles from recently reported AMAX-DOAS measurements (Dix et al., 2013; Volkamer et al., 2015). A summary of the a-priori profiles, example a-posteriori profiles, the average (for the case study) profile, and the diurnal variation in the VCD for IO is found is Fig. S4 (Supplement).

2.4.2 Determination of SCD_{Ref}

The BrO profile at the recording time of the fixed reference spectrum is included in the analysis by estimating the reference SCD (SCD_{Ref}) for BrO, which is then added to the dSCDs at off-axis EAs according to Eq. (1). Initial sensitivity studies revealed that some MAX-DOAS scans from the case study day are better suited for producing consistent values for SCD_{Ref} than others. The final choice of the reference spectrum is informed from comparing the SCD_{Ref} determined using the iterative method presented here to the SCD_{Ref} predicted by the WACCM a-priori profile 2) (see

Sect. 2.4.1), which assumes a median BrO abundance. The ratio of SCD_{Ref} divided by the BrO VCD corresponds to the AMF of the reference spectrum, which in the case of our case study was ~1.2. The following criteria are applied to select a reference spectrum: (1) the SCD_{Ref} needs to be consistent with the AMF for the a-posteriori BrO profile, as well as (2) be within ±1x10^{13} molec cm^{-2} of the WACCM profile increased by 40% (see Sect. 2.4.1). Figure S5 (Supplement) shows the results from this approach for multiple zenith spectra (potential references) on the case study day, and thus illustrates the need for active measures, such as the above, to build internal consistency between the BrO SCD_{Ref}, BrO VCD, AMF, and forward RTM calculations of the a-priori and a-posteriori BrO profiles. The results presented in this paper are produced from a single reference spectrum (see Sect. 2.3); however, other references that pass the above quality assurance criteria would not alter our conclusions. Selecting another reference spectrum that meets the aforementioned criteria only increases the variability in the derived VCD by less than 9x10^{12} molec cm^{-2} (for any given single scan), and changing the a-priori assumption has also only a small effect on the VCDs (±1.5x10^{12} molec cm^{-2} from average value).

Iterative Approach: The value of SCD_{Ref} is determined here by iteratively running the optimal estimation inversion on the MAX-DOAS scan containing the reference spectrum; this process is shown as flow chart in Fig. 3 panel (a). The initial value for SCD_{Ref} is determined from the a-priori profile, and subsequent SCD_{Ref} values are determined from the a-posteriori profile of the inversion returned from the previous iteration. For each iteration only SCD_{Ref} changes; the a-priori profile remains constant. After multiple iterations this method converges on a SCD_{Ref} that minimizes the differences between the measured and forward calculated scan SCD inputs. This value is then used as input for the inversion of the rest of the MAX-DOAS scans throughout the day. Figure 3 panel (b) depicts the iterative refinement of the SCD_{Ref} and corresponding VCD for the reference chosen as most ideal for this case study.

3 Results and Discussion

3.1 Characterizing the BrO profile retrieval

Figure 4 compares the AVK resulting from the OE inversion of BrO SCDs constructed by accounting for SCD_{Ref} (addition of this value to the measured dSCD output from the DOAS analysis prior to inversion) vs not accounting for SCD_{Ref} (where SCD = dSCD and with appropriate modification of the weighting functions to reflect this treatment). The largest differences are seen at low SZA in the FT. Panel (a) shows the AVK matrix, which gives an indication as to how much information can be derived from the measurements at specific altitudes, as a function of altitude for the inversion (at SZA = 25°) accounting for SCD_{Ref} (different colored thin lines) along with the diagonal of this matrix (thick black line) and the diagonal for the inversion not accounting for SCD_{Ref} (thick red line). Panel (b) of Fig. 4 shows the difference between the two diagonals as a function of altitude. Also listed in Fig. 4 are DoFs for the different retrieval methods, which, when SCD_{Ref} is properly accounted for, demonstrate an increase of 0.5 (mostly coming from the FT). For these reasons, we chose to include SCD_{Ref} in the inversion of the measured BrO dSCDs in order to further maximize the sensitivity of these measurements towards the FT. Additional information on the DoFs and inversion RMS for these retrievals throughout the case study day are found in Fig. S6 (Supplement). It should be noted that the presence of even moderate aerosol loads would significantly impact the ability to derive vertical profiles extending into the FT, but column integrated information would remain intact.

Recently, Volkamer et al. (2015) reported significant sensitivity of ship MAX-DOAS profiles to the magnitude of SCD_{Ref} over oceans. For several case studies independent aircraft measurements above the ship show that a significant trace gas partial column resides above the BL (IO and glyoxal). They find that while the BL VMR is insensitive to the value of SCD_{Ref}, the partial tropospheric VCD can be impacted by up to a factor of 2-3. During this study the impact of using BrO dSCDs, rather than SCDs, in the inversion lead to an average percent difference in the BrO VCD derived for each MAX-DOAS scan of ~30%. The average VCDs were 2.1×10^{13} and 2.3×10^{13} molec cm^{-2} (integrated from 0-15 km) when using dSCDs or SCDs (only ~10% difference). This reflects that the inversion based on dSCDs (not accounting for SCD_{Ref}) produced highly variable FT VCDs throughout the case study day, and that this variability is reduced for the SCD based inversion.

The reduced variability in the BrO VCD compared to the other gases investigated by Volkamer et al. (2015) is probably due to the fact that no BrO was detected in the BL in either case study.

For glyoxal and IO about 50% of the VCD resides near the instrument altitude (Volkamer et al., 2015). This BL contribution adds offsets to the SCDs also for the higher EAs that ‘partially obstruct’ the view of the FT, and makes FT partial columns subject to larger error bars. The lack of BrO in the BL seems to simplify measurements of FT partial columns from the ground. The Volkamer et al. case studies in combination with our results thus suggest that MAX-DOAS instruments that are to measure FT partial columns of gases other than BrO should actively avoid complications from absorbers near instrument altitude, for example by placing the instrument on mountaintops. The lack of aerosols from high mountaintops has the additional benefit of increased sensitivity to measure profiles for BrO and other gases.

3.2 BrO VCDs and Vertical Profiles

Figure 5 shows the results from the inversions using the three different a-priori profiles. Panel (a) shows the a-priori profiles, and the a-posteriori vertical profiles corresponding to one scan at ~23° SZA (around solar noon), as well as the median profile from all profiles. A total of 45 profiles, corresponding to SZA<70° for each a-priori case, were combined to create the median BrO vertical profile for the case study day (Fig. 5). The median profile was used for the modeling results and discussion in Sect. 3.4. Panel (b) shows the AVK (see Sect. 2.4.1) from the inversion using the un-modified WACCM BrO output as the a-priori profile. In an ideal scenario, the AVK for each layer peaks near unity within that layer. The derived vertical profiles show only slight dependence on the a-priori profile with a maximum average difference between a-posteriori profiles of ~0.6 ppt at altitudes <15km for the entire day. These profile differences have only a small effect on the free tropospheric VCDs, i.e. <20% difference for SZA<70°. The AVK peaks twice – once in the lowest layer (from the lowest looking elevation angles) and again between 5km and 20km, which reflects the combination of the optimization of the radiative transfer grid and the measurement sensitivity. This is interpreted as an indication that the DoFs remaining after accounting for the peak at instrument altitude correspond to the FT. Figure S7 (Supplement) contains a comparison of the a-posteriori profile derived BrO dSCDs and the measured dSCDs (panels a and b) and the corresponding RMS difference between measured and calculated dSCDs in panel (c).

This inversion procedure allows for the determination of the diurnal variation in the BL (0-1km), FT (1-15km), and total VCDs for BrO. These results, corresponding to the inversion utilizing WACCM output as the a-priori profile, are found in Fig. 6 panel (b) along with the corresponding DoFs panel (a). The errors bars on the tropospheric and stratospheric VCDs reflect the range of derived values resulting from the use of different a-priori assumptions. The retrieved diurnal variation in the free tropospheric (1-15 km) BrO VCD follows that of the total VCD with an average of 53% contribution to the total and varying between 47-57% throughout the day; this corresponds to a daytime average VCD of ~2.3±0.16x10^{13} molec cm^{-2}, where the error reflects the average error on the VCD as seen in Fig. 6 panel (b). The overall error on the average VCD is ~0.7x10^{13} molec cm^{-2} and takes into account change in the VCD when assuming the maximum profile error given by the OE inversion. This treatment is expressed in Eq. (3).

$$\textit{Total Error} = \frac{(VCD_{Prf} - VCD_{Prf+OE\ err})}{2} \tag{3}$$

where VCD_{Prf} is the VCD calculated directly from the OE inversion a-posteriori, $VCD_{Prf+OE\ err}$ is the VCD calculated from the OE inversion a-posteriori profile plus the OE error of that profile, and the factor of 2 reflects that the OE inversion error at each altitude covers oscillations both higher and lower than the retrieved profile at that point.

The tropospheric VCD of ~2.3±0.7x10^{13} molec cm^{-2} BrO derived from this study falls in the range of other currently reported measurements, which span from ~1-3x10^{13} molec cm^{-2} (van Roozendael et al., 2002; Salawitch et al., 2005; Theys et al., 2007; Theys et al., 2011; Coburn et al., 2011; Volkamer et al., 2015; Wang et al., 2015). The observed tropospheric BrO VCD is consistent with the VCD of 2.0x10^{13} molec cm^{-2} measured by the same instrument during a previous study in the same location (Coburn et al., 2011). This value is higher than other ground based measurements in the Southern Hemisphere tropics (Theys et al., 2007), which reported tropospheric VCDs of 1.1-1.2x10^{13} molec cm^{-2}. Aircraft profiles over the Pacific ocean have reported variable BrO VCDs ranging from 1.0 to 1.7 x10^{13} molec cm^{-2} BrO, and a campaign average of 1.3±0.2x10^{13} molec cm^{-2} BrO (Volkamer et al., 2015; Wang et al., 2015). While it appears that the BrO VCD is highly variable, depending on the location and time of measurement, the average BrO VCD measured by the GOME-2 (Global Ozone Monitoring

Experiment-2) satellite for Jan/Feb in the tropics (30N – 30S; longitudinal average) is 1.6 x10^{13} molec cm^{-2}, in reasonably close agreement with ground- and aircraft studies. Much of the current knowledge of bromine chemistry in the upper troposphere–lower stratosphere (UTLS) is currently based on balloon-borne direct-sun BrO measurements (Pundt et al., 2002; Dorf et al., 2008), which have found an order of magnitude lower BrO. This lower BrO is – at least in part – due to atmospheric variability (see e.g., Wang et al., 2015; Schmidt et al., 2016). Ground-, aircraft- and satellite measurements consistently support elevated BrO in the FT. A re-assessment of halogen chemistry in the UTLS (bromine and iodine) seems warranted (Volkamer et al., 2015; Wang et al., 2015; Saiz-Lopez et al., 2015).

3.3 Comparison with models

Global model results for BrO VCDs generally predict much lower columns than observed in this study. Yang et al. (2005), using the p-TOMCAT model, found mid-latitudes values of ~0.4x10^{13} molec cm^{-2} for spring/summer months; and Parrella et al. (2012), using GEOS-Chem, reported values of <1x10^{13} molec cm^{-2} for the entire year for the Northern Hemisphere mid-latitudes. The value from Parella et al. (2012) is slightly more comparable to that predicted by WACCM for the case study day (~1x10^{13} molec cm^{-2}, see Fig. S3, Supplement). Wang et al. (2015) reported sensitivity in the predicted BrO to updated heterogeneous chemistry of bromine (Ammann et al., 2013). Recently, Schmidt et al., (2016, in press) has incorporated the Enhanced Heterogeneous Chemistry (EHC) scheme into GEOS-Chem. The EHC bromine chemistry mechanism produces higher average tropospheric BrO columns, which are more consistent with our observations. They site that average tropospheric BrO concentrations are ~50% more than predicted from the Parrella et al., (2012) bromine mechanism; this is similar to the findings from this study where the tropospheric VCD predicted by GEOS-Chem (which uses the Parrella et al., (2012) bromine chemistry) is ~30% lower than the measured VCD. Notably, different representations of halogen chemistry can result in very different BrO vertical profile shapes (Sander et al., 2003; Fernandez et al., 2014; Long et al., 2014; Liang et al., 2014) despite an apparently good agreement (~1x10^{13} molec cm^{-2}) in the BrO VCD at tropical latitudes. The ability to predict BrO vertical profiles is particularly relevant to predict distributions of oxidized mercury in the lower troposphere (see Sect. 3.4.2).

3.4 Mercury Modeling

A detailed description of the box model utilized in this study to assess the oxidation pathways of mercury is found in the Supplement (Sect. S4). Table 2 gives an overview of the reactions controlling the cycling of atmospheric mercury included in the box model and Fig. S8 (Supplement) contains the vertical profiles of modeled and measured parameters used as input to the box model. 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).

3.4.1 Mercury oxidation rates

The primary finding from a comparison of the Hg^0 oxidation rates for the two radical species tested in this study (Br and O_3) is that the reaction with Br dominates the overall rate throughout the troposphere for the conditions tested by this case study, independent of initial BrO vertical profile used. The column integral rate is 7.8x10^4 molec cm^{-2} s^{-1} for O_3; while the Br rates are 3.5x10^5 and 3.7x10^5 molec cm^{-2} s^{-1} for the BrO vertical profiles from the MAX-DOAS measurements and GEOS-Chem respectively. Preliminary tests included chlorine (Cl) radicals as an additional oxidant using a vertical distribution estimated for the tropical troposphere (Wang et al., 2015). However, this reaction was deemed unimportant, and is thus not included here, due to the column integral oxidation rates being factors of 18 and 5 lower than column rates for Br and O_3, respectively. The reaction rates from Br are at least a factor of 3 greater than the contribution from O_3.

The vertically resolved rates are shown in Fig. 7 (panel a) for both reactions: Br (solid blue and dotted pink traces representing the BrO profiles from the MAX-DOAS measurements and GEOS-Chem, respectively, used to derive the Br radical concentrations) and O_3 (red trace); reflecting the contributions of these reactions at different altitudes. Also included in Fig. 7 (panel b) are the corresponding lifetimes of GEM (as a function of altitude) against oxidation by the two molecules. Only in the lowest layers of the atmosphere do the rates of oxidation through reaction with O_3 become comparable or greater than those of the reaction with Br. However, it should be noted that for altitudes <4 km where the rate of reaction with O_3 dominates, the BrO VMR is <0.03 pptv while the O_3 VMR is ~50 ppbv, and in cases where reaction with Br dominates (still at altitudes <4 km) the BrO VMR is still <0.3 pptv. The BrO vertical profile from the MAX-DOAS instrument below 4 km contains the highest amount of uncertainty because BrO is essentially zero within the variability of the measurements. The column integral rates of oxidation based on the MAX-DOAS measurements and the BrO profile from GEOS-Chem are actually quite similar (only ~5% difference), which is most likely due to the additional bromine chemistry included in this model (see Sect. 2.2) as compared to other models (e.g. GEOS-CCM); however, the discrepancies in the vertical distribution of BrO lead to a mismatch in the altitudes at which the oxidation can occur. For both BrO profiles, the reaction with Br dominates above 4 km (indicated by the black dashed line in Fig. 7). Altitudes above 4km are responsible for ~72% of the column integral rate of GEM oxidation (through reaction with Br) based on the MAX-DOAS measurements; while that value decreases to ~56% for the bromine profile from GEOS-Chem.

Additional differences between column oxidation rates for the MAX-DOAS and GEOS-Chem BrO profiles exists at altitudes <4km, where the MAX-DOAS measurements find no BrO and GEOS-Chem predicts up to 0.75 pptv. Similar to the findings of this study, other publications have put upper limits on marine boundary layer (MBL) BrO ~0.5 pptv, (Gomez-Martin et al., 2013; Wang et al., 2015; Volkamer et al., 2015).

3.4.2 Mercury oxidation pathways

Figure 8 shows the results of the “traditional” (panel a) and “revised” (panel b) HgBr scavenging schemes (see Sect. S4 Supplement for descriptions) on the rate of GEM oxidation as a function of altitude. In each panel, contributions of individual molecules (colored lines) are shown along with the total removal rate (black lines). Panel (c) shows the vertical profile of the ratio of the “revised” total rate to “traditional” total rate, which demonstrates the enhanced oxidation of HgBr when considering the additional scavenging reactions. In the “traditional” model the percent contributions to the column integrated rate of oxidation of HgBr are 57.5% and 42.5% for OH and Br, respectively; and in the “revised” model the percent contributions are as follows: 71.3% (NO_2); 21.3% (HO_2); 4.3% (BrO); 1.4% (OH); 1.1% (Br); 0.5% (IO); and <0.1% (I).

Note that mercury oxidation is initiated by reaction between Br radicals and GEM in both reaction schemes, and the additional scavenging reactions in the "revised" scheme primarily increase the overall rate of oxidation at altitudes where HgBr decomposition is fast. The greatest enhancement is seen below 8 km, where the overall rate of oxidation is ~100 times faster, primarily because of the reaction of HgBr with NO_2 and HO_2.

Figure 8 also illustrates the increased number of species produced from the additional oxidation mechanisms, some of which may have physical and chemical properties that differ from the two products of the "traditional" mode, which are also products in the "revised" scenario but are present at much lower concentrations. In the "traditional" scenario at 1 km, the scavenging products HgBrOH and $HgBr_2$ account for 96% and 4% of the total HgBrX, respectively, and these values drop to 0.5% and <<0.1% in the "revised" scenario where $HgBrNO_2$ accounts for 73% of HgBrX. In the "revised" scenario, $HgBrNO_2$ remains the major product throughout the atmosphere, but at free tropospheric altitudes $HgBrHO_2$ also contributes significantly at 37%, compared to $HgBrNO_2$ at 52%. There are currently no observations of the molecular composition of GOM with which to evaluate these simulated product distributions.

3.4.3 Mercury lifetime with respect to oxidation

The above oxidation rates correspond to a minimum lifetime of GEM with respect to oxidation by bromine radicals of ~20 days in the FT (based on the MAX-DOAS measurements). The average total (Hg^0 + Br and Hg^0 + O_3) tropospheric column lifetimes are 38 and 54 days (altitudes >4 km) for the scenarios including BrO profiles from the MAX-DOAS measurements and GEOS-Chem, respectively; where in both cases the contribution from the reactions with O_3 are the same and the differences are owing to the differing amounts of Br radicals. This is much shorter than the currently expected atmospheric lifetime on the order of several months. However, the box model only accounts for partitioning of the GOM species between the gas phase and aerosols; once they are in the aqueous phase they can be photo-reduced to GEM that can then subsequently return to the gas phase (Costa and Liss, 1999), thus extending the effective lifetime significantly beyond that calculated above. The kinetic coefficients for reactions involving HgBr come mainly from quantum chemical calculations, which have significant uncertainties, so the simulated GEM lifetime could be extended by reducing the rate coefficients within their uncertainties. Another possible mechanism is the photo-dissociation of HgBrX products containing species that have significant absorption cross-sections in the ultra-violet/visible (UV/Vis) region of the electromagnetic radiation spectrum, e.g. $HgBrNO_2$, $HgBrHO_2$, which could reproduce HgBr. This HgBr could then thermally decompose to re-form GEM, or be oxidized again. Our observations are consistent with previous findings (Wang et al., 2015), that establish GEM as a chemically highly dynamic component of the FT. It is expected that GOM species will go through additional processes also in the aqueous phase, which could significantly impact the ultimate fate of the mercury.

3.5 Atmospheric Implications

The rapid oxidation of mercury in the lower FT is of potential relevance in the SE U.S., where there have been several studies linking deep convective activity to the elevated levels of mercury found in rainwater (Guentzel et al., 2001; Landing et al., 2010; Nair et al., 2013). The bio-accumulation of methyl mercury in fish tissues is particularly relevant in this region, where it has been deemed unsafe to eat fish harvested from many lakes in the region (Engle et al., 2008; Liu et al., 2008). Wet deposition measurements of mercury exceed what can be explained through regional sources in the southeast. In fact, Guentzel et al., (2001) estimated that <46% of the mercury deposited in Florida was a result of local emissions, the other >50% was attributed to long-range transport of mercury in the atmosphere; the transported fraction may have increased since those data were collected in the 1990s because regional US mercury emissions have declined while global emissions have risen. This attribution, coupled with mountaintop and aircraft studies locating elevated levels of GOM in the FT (Swartzendruber et al., 2006; Faïn et al., 2009; Swartzendruber et al., 2009; Lyman and Jaffe 2012; Brooks et al., 2014; Weiss-Penzias et al., 2015, Shah et al., 2016), strongly suggests the presence of a global "pool" of mercury in the upper atmosphere that contributes to widespread mercury deposition on a local to regional scale.

On the case study day, Hg^{II} (=GOM+PBM) concentrations at the nearly Pensacola MDN site reached 25 pg m^{-3} around midday and nearly 40 pg m^{-3} on 10 April (Fig. 9). High Hg^{II} events in

Pensacola are frequently consistent with emissions from a nearby coal-fired power plant, however about 25% of such events have significant contributions from the FT (Weiss-Penzias et al., 2011). The high $Hg^{II}:SO_2$ ratios (10-20 pg m^{-3} ppb^{-1}) and high $NO_y:SO_2$ ratios (3.5-5.2 ppb ppb^{-1}) recorded on 9-10 April make the power plant an unlikely source of the Hg^{II} on these days (Fig. S9, Supplement); for comparison, Weiss-Penzias et al. (2011) reported $Hg^{II}:SO_2$ and $NO_y:SO_2$ ratios of 3.5 and 1.0, respectively, in power plant plumes. Like Hg^{II} concentrations, ozone concentrations and Hg^{II} dry deposition in Florida also peak in spring, all of which are consistent with a significant source of surface Hg^{II} being from the upper troposphere (Lyman et al., 2009; Gustin et al., 2012). We use the GEOS-Chem model to further probe the sources of this Hg^{II}. Figure 9 shows that the model generally reproduces the day-to-day variability of Hg^{II} observations during April 2010 (but not extremes), such as the low concentrations during 7-8 April and relative maxima on 5 and 10 April. In both the model and observations, Hg^{II} concentrations rise abruptly in the morning, consistent with entrainment of Hg^{II} aloft, and unlike the other combustion tracers (e.g. NO_y, SO_2) that reach high concentrations at night (Fig. S9, Supplement). The model does not reproduce the abrupt drop in Hg^{II} around 18:00 CST, however, which may be partly due to local sea breeze circulations that are evident in wind observations but not simulated at the 4°x5° model resolution. In addition, mixing depth errors in the driving meteorology are known to affect other species, particularly at night (Lin et al., 2010; McGrath-Spangler and Molod, 2014). To assess the contribution of the FT to surface Hg^{II} during April 2010, we conduct an additional model simulation with zero anthropogenic emissions in North America and no mercury redox chemistry in the lower troposphere (> 700 hPa). The simulation is initialized from the base run on 1 April. Due to its fast deposition, all boundary-layer Hg^{II} in the sensitivity simulation after about 1 day originates from oxidation of GEM in the free troposphere or, less likely, from intercontinental transport of anthropogenic Hg^{II}. Figure 9 shows there is little difference between the base and sensitivity simulations, meaning that the FT is the main source of boundary-layer Hg^{II} in the model and that variability in the FT component explains most of the day-to-day Hg^{II} variability. Thus, the 3-D model shows that conditions on 9 April are favorable for Hg^{II} transport to the boundary layer, exactly when the DOAS observations find substantial amounts of BrO are present in the FT.

The GEM oxidation mechanism in the 3-D model corresponds to the "traditional" scheme in the box model and bromine concentrations in GEOS-Chem are lower than recent aircraft observations (Volkamer et al., 2015), so the GEM oxidation may be faster than simulated. Greater Hg^{II} production in the FT might help correct the model's 20% low bias in mercury wet deposition over the Southeast US (Zhang et al., 2012), but this would depend on the rate of any compensating reduction reaction, as discussed above. The findings of this study indicate that the amount of bromine located in the FT can be sufficient to quickly oxidize GEM.

4 Conclusions

We show the benefits of determining SCD_{Ref} to maximize the sensitivity of ground based MAX-DOAS measurements to detect BrO in the FT, and improve the overall consistency of time-resolved BrO tropospheric VCDs. The retrieval can also be applied to other trace gases. Knowledge of SCD_{Ref} allows the derivation of one vertical profile for each MAX-DOAS scan throughout the day (SZA<70°) and the assessment of the diurnal variation of the partial BrO vertical columns. Our retrieval is complementary to previous studies that have characterized the stratosphere using zenith-sky measurements under twilight conditions (Theys et al., 2007; Hendrick et al. 2007), and minimizes the influence of O_3 absorption, and the contribution of stratospheric BrO to the overall BrO signal by using CTM output to constrain stratospheric BrO in combination with BrO dSCDs measured at low SZA instead. The FT VCDs reported here are in good agreement with the previously cited values for BrO, with the average BrO FT VCD (~2.3×10^{13} molec cm^{-2}) falling within the range reported by other studies ($1\text{-}3 \times 10^{13}$ molec cm^{-2}) (see Wang et al., 2015, and references therein). These measurements all point to the presence of background amounts of BrO in the FT that is larger than current models predict. The method employed here would also benefit from deployments at mountaintop sites where aerosol shielding of the FT can be overcome and tropospheric vertical distributions could be assessed more frequently.

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 and modeling studies have reported significant variability in BrO and Br_y (Wang et al., 2015; Schmidt et al., 2016). The drivers for such variability deserve further investigation. Our results confirm that mercury is rapidly oxidized by bromine, and a chemically highly dynamic species in the atmosphere. The chemical lifetime of GEM is ~45 days in the tropical FT based on calculations and vertical profiles presented in this study; longer GEM global lifetimes should thus be regarded to indicate "effective lifetimes", i.e., are the result of rapid chemical cycling of GOM back to GEM (e.g., photoreduction (Pehkonen and Lin, 1998; Gustin et al., 2002; Tong et al., 2013)). Mercury measurements during our study period show high surface Hg^{II} concentrations that likely originate in the FT, meaning that we have observed substantial BrO columns under conditions favorable for Hg^{II} transport to the boundary layer. 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; Faïn 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. Our results highlight the need to understand BrO vertical profiles in the FT, and represent them in atmospheric models to understand the location where mercury is oxidized in the atmosphere, and is available for wet and dry deposition. More studies are needed to test and represent the bromine sources in atmospheric models, test atmospheric GOM abundances by field data, and clarify the chemical identity, the global distribution, and dry and wet removal processes of GOM.

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Supplement

S1 Instrument and Measurement Site

The instrument and measurement site are identical to that described in Coburn et al. (2011). Only a brief overview will be given here. For the duration of the measurements discussed in this study, a research-grade MAX-DOAS instrument was located at a United States Environmental Protection Agency (US EPA) facility in Gulf Breeze, FL (30.3N 87.2W) and measured for time periods between May 2009 and February 2011. This site is ~10 km southeast of Pensacola, FL (population appr. 50,000) and ~1 km from the coast of the Gulf of Mexico, which enables the measurement of urban and marine air masses. The spectrometer and controlling electronics were set-up in the warehouse of the EPA facility, while the telescope was mounted on a support structure on the roof of the warehouse (~10-12 m above sea level) connected via an optical fiber. The telescope was oriented ~40° west of true north in order to realize a clear view in the lowest elevation angles to the coast. During operation the full 180° elevation angle range of the telescope was utilized to enable the characterization of air-masses over the seawater lagoon to the North, and over the coastal region of the Gulf of Mexico to the South. For the purposes of this study, the north viewing direction will be considered to minimize changes in the radiative transfer calculations due to azimuth effects throughout the day.

The instrument used for this study consists of a Princeton Instruments Acton SP2300i Czerny-Turner grating (500 groove/mm with a 300nm blaze angle) spectrometer with a PIXIS 400B back-illuminated CCD detector (Coburn et al., 2011). This setup was optimized to cover the wavelength range ~321-488 nm with an optical resolution of ~0.68 nm full-width at half the maximum (FWHM). The spectrometer is coupled to a weather-resistant telescope (capable of rotating the elevation angle by 180°, 50 mm f/4 optics) via a 10 m long 1.7 mm diameter quartz fiber. During normal field operation this instrument was routinely able to realize values of the root mean square (RMS) of the residual remaining after the DOAS fitting procedure on the order 0.9-3x10^{-4}. This system was very stable, with little need for maintenance, and was operated remotely for periods between May 2009 and February 2011 to measure multiple trace gases, including: BrO, IO, nitrogen dioxide (NO_2), formaldehyde (HCHO), glyoxal (CHOCHO), and the oxygen molecule collision induced absorption signal (referred to as O_4).

S2 DOAS retrieval sensitivity studies

S2.1 Retrieval window: Several sensitivity studies were performed to determine the most suitable analysis settings for the BrO retrieval. This was accomplished through a comparison of both O_3 and HCHO dSCD values from the BrO fitting window with dSCDs predicted using WACCM vertical profiles. Also, the effect of using different O_4 reference cross-sections was tested with respect to the O_4 dSCD in the BrO fitting window.

WACCM model output profiles for O_3 and HCHO were used to forward calculate dSCDs for comparison to measured dSCDs of O_3 and HCHO retrieved using the BrO fitting window. Five different BrO analysis setting windows were tested: 1) fitting window 345-359nm with a 2nd order polynomial (encompasses two BrO absorption peaks – 2-band analysis); 2) fitting window 346-359nm with a 2nd order polynomial (2-band analysis); 3) fitting window 340-359nm with a 3rd order polynomial (3-band analysis); 4) fitting window 340-359nm with a 5th order polynomial (3-band analysis); and 5) fitting window 338-359nm with a 5th order polynomial (4-band analysis). It was determined that analysis setting 5) (4-band analysis with 5th order polynomial) including a constrained intensity offset (Sect. S2.2) best represented both O_3 and HCHO. These are the analysis settings that were then used to assess the effects of different O_4 cross sections in the BrO fitting window: 1) Hermans (2002); 2) Greenblatt et al. (1990); and 3) Thalman and Volkamer (2013). The O_4 dSCDs retrieved from the BrO fitting window were compared with the O_4 dSCDs retrieved from an O_4 optimized fitting window in the UV (353-387 nm); and while none of the cross sections are able to fully reproduce the O_4 dSCDs from the O_4 optimized window, the Thalman and Volkamer (2013) cross-section was deemed to be an improvement over Hermans and Greenblatt/Burkholder in representing O_4 in the BrO fitting window.

S2.2 Intensity offset: An additional parameter that can be utilized in the DOAS retrieval is an intensity offset, which would be used to help account for any instrument stray light. The instrument employed for this study was designed to actively minimize spectrometer stray light through the use of cut-off filters (BG3 and BG38), as well as the method of background correction. The background correction is similar to that described in Wagner et al. (2004) and utilizes dark regions on the CCD detector to correct for dark current and offset noise as well as stray light. It was determined that stray light in the instrument was only a few percent (before correction) in the wavelength range 330-360 nm. Fitting an intensity offset should only account for uncorrected stray light and is expected to be on the order of magnitude of the error in the background correction. The fitting of this parameter typically helps reduce the RMS of the fitting routine, thus improving instrument sensitivity. However, preliminary studies found a significant effect on the retrieved BrO dSCDs depending on whether or not this parameter was included in the fitting routine, and that this effect was most pronounced in the narrower fitting windows. In the most extreme case (analysis window 346-359 nm), retrieved BrO dSCDs changed from ~$1x10^{14}$ molec cm^{-2} without fitting the intensity offset to values less than zero when an unconstrained intensity offset was included. In all fitting windows tested, utilizing an unconstrained intensity offset resulted in the highest fit factor for the offset and lowest values for the BrO dSCDs, and in some cases lead to significantly negative (non-physical) values. In these cases, it was found that periods of time existed when the fit factor for the intensity offset was much greater than what was determined to be a reasonable value for this instrument. For this reason, the intensity offset was kept in the retrieval (to help with RMS), but limited to a range determined by the upper limit of this estimated correction (±$3x10^{-3}$).

Based on the findings of the offset sensitivity tests and the dSCD comparison tests presented in this section, the dSCDs used for the BrO inversion are from the 338-359 nm fitting window utilizing a 5th order polynomial, the constrained intensity offset, and the Thalman and Volkamer (2013) O_4 cross-section.

S3 Aerosol Retrieval

Aerosol profiles are determined through an iterative comparison of measured O_4 dSCDs (analyzed in the wavelength window 437-486 nm) with O_4 dSCDs calculated from the RTM McArtim3 (Deutschmann et al., 2011) outputs based on specific aerosol extinction profiles. This process is performed on each set of MAX-DOAS viewing angles (for this point forward referred to as a scan) of the case study day (total of 56 scans) in order to determine individual aerosol profiles. The initial aerosol profile used for each scan decreased exponentially with altitude from a value of 0.01 km^{-1} at 483 nm (scale height of 0.6 km). This wavelength is chosen for its proximity to the O_4 peak absorption structure at 477 nm while avoiding the feature itself, as well as avoiding absorption structures from other trace gases (i.e. NO_2). This O_4 fitting window was chosen due to the better general agreement achieved between measured and forward calculated O_4 dSCDs (calculated after aerosol extinction profiles were determined) as compared with the O_4 retrieval in the UV range. This is similar to findings from Volkamer et al., (2015), where it is determined that using the 477 nm O_4 band for deriving aerosol profiles is much more robust than using the UV bands due to the increased Rayleigh scattering at shorter wavelengths, which can mask aerosol extinction.

The O_4 vertical profiles used for all calculations and as input to the RTM are based on temperature and pressure profiles available from NOAA's ESRL Radiosonde Database for locations close to the measurement site, which are in good agreement with the corresponding profiles from WACCM. In each step of the iteration the measured O_4 dSCDs are compared to the forward calculated dSCDs at each elevation angle of the scan being analyzed, and the differences between these values are used as input for optimizing the modification of the aerosol profile for the subsequent iteration. For this study, the convergence limit is set at a percent difference of 5% between the lowest two elevation angle dSCDs, or if the process reaches 5 iterations without finding convergence the last aerosol profile is used. The limit of 5 iterations is chosen as a compromise between achieving optimal agreement between the O_4 dSCDs and data computation time. For this case study, the 5% criterion is reached for every sequence. The resulting time series of aerosol extinction profiles are shown in Fig. S10 (Supplement).

The aerosol extinction profiles at 483 nm were scaled to derive extinction at 350 nm using the relationship found in Eq. (S1).

$$\varepsilon_{350} = \varepsilon_{483} \cdot \left(\frac{350}{483}\right)^{-1.25} \qquad \text{(S1)}$$

where ε_{350} and ε_{483} represent aerosol extinction coefficients at 350 and 483 nm, respectively. An Angstrom exponent of -1.25 was chosen as a moderate value that would be representative of an average atmosphere (Dubovik et al., 2002). The retrieved aerosol profiles at 350 nm provided input to the RTM in order to calculate the appropriate weighting functions for BrO.

S4 Box Model Description

The modeling portion of this study is designed to assess the concentration of Br radicals available to participate in the mercury oxidation reaction based on BrO vertical profiles provided from the MAX-DOAS measurements and GEOS-Chem. Other trace gas and atmospheric parameter inputs to the diurnal steady-state box model (Dix et al., 2013, Wang et al., 2015) are median daily profiles derived from the MAX-DOAS measurements, WACCM, and GEOS-Chem. A single median profile representing the entire day (daily median, for each model input) is used rather than individual profiles. From these profiles, the box model then calculates the partitioning between bromine species throughout the troposphere (including: reactions with other trace gases; photolysis; and some aqueous phase partitioning and chemistry) in order to derive vertical profiles of the Br radical, which are subsequently used for calculating mercury oxidation rates. A summary of all the reactions involving mercury compounds considered in the box model along with associated rate coefficients can be found in Table 2. The model conceptually follows the framework of Crawford et al., (1999), where model inputs are initiated and allowed to reach steady-state over several days. In the box model, the BrO and IO (to assess the impact of iodine radical species in the mercury oxidation reactions) profiles are taken from the MAX-DOAS measurements; however, the GEOS-Chem BrO profile is also used in order to assess the impact of the differences between these profiles. Other box model inputs are taken as the output profiles from the external models utilized in this study and these include: temperature, pressure, and HCHO from WACCM; and O_3 and NO_2 from GEOS-Chem. As a sensitivity test WACCM O_3 and NO_2 were also used to assess the impact on the mercury oxidation scheme towards differences in the vertical distributions of these molecules. The resulting vertical profiles of the rate of mercury oxidation using these two profiles as box model inputs is found in Fig. S11 (Supplement), which follows the same format as Fig. 7. Aerosol surface area measurements from the TORERO data set (Volkamer et al., 2015; Wang et al., 2015) are assumed representative of conditions in the marine atmosphere, and therefore used as model inputs for lack of independent measurements. The vertical distribution of Hg^0 from GEOS-Chem was used in all scenarios. Additionally, photolysis rates for a variety of species, calculated using the Tropospheric Ultraviolet and Visible (TUV) Radiation model, are included. The TUV model was initiated for a Rayleigh atmosphere (aerosol extinction = 0), with O_3 and

NO_2 columns of 380 and 0.3 Dobson Units (DU), respectively, which are derived from the average vertical profiles from WACCM. Since the median BrO profile derived by the MAX-DOAS measurements closely resembles the profiles retrieved around solar noon (see Fig. 5), the TUV calculations from this time are used. For the model runs comparing the BrO profiles from the measurements and GEOS-Chem, only the BrO profile is changed; all other inputs remain constant.

For the determination of the dominant oxidative pathways, the reaction rates for oxidation of Hg^0 against Br and O_3 are calculated as a function of altitude for the different reactant vertical profiles, which is important due to atmospheric temperature gradients. This also allows the assessment of the relative contributions of these reactions to the overall rate of oxidation as a function of altitude. Oxidation by O_3 is included in the box model due to the amount of evidence from laboratory studies indicating that this reaction might play a role in the atmosphere; although potentially not completely in the gas phase.

Following Wang et al. (2015), the box model is initiated under two different modes to investigate the sensitivity of oxidation rates, and likely product distributions to the mechanistic assumptions about mercury oxidation. The two modes differ in the scavenging reactions of the HgBr adduct. A “traditional” scenario only includes Br and OH radicals as scavengers (Holmes et al., 2009), and a “revised” mode includes species suggested by Dibble et al., 2012 (BrO, NO2, and HO2) as well as additional halogen species (I and IO). The model also tracks the concentrations of all species as a function of altitude, which gives indications for the product distributions of the various reactions.

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Table 1: Overview of DOAS settings

Cross Section, Parameter	Reference	BrO window (338-359 nm)	IO window (415-438 nm)	NO_2 window (434-460 nm)	O_4 window (437-486 nm)
Polynomial Order		5	5	3	5
O_3 T = 223 K	Bogumil et al. (2003)	X	X	X	X
O_3 T = 243 K	Bogumil et al. (2003)	X	X	X	X
NO_2 T = 220 K	Vandaele et al. (1997)	X	X	X	X
NO_2 T = 220 K	Vandaele et al. (1997)	X	X	X	X
O_4 T = 293	Thalman and Volkamer (2013)	X		X	X
BrO	Wilmouth et al. (1999)	X			
HCHO	Meller and Moortgat (2000)	X			
IO	Spietz et al. (2005)		X		
CHOCHO	Volkamer et al. (2005			X	
H_2O	Rothman et al. (2005)			X	X

Table 2: Summary of mercury reactions and rate coefficients used in box-model

Reaction	Rate or equilibrium[1] Coefficient[2]	Reference
$Hg^0 + O_3 \rightarrow HgO + O_2$	$3x10^{-20}$	Hall (1995)
$HgO_{(g)} \leftrightarrow HgO_{(aq)}$	$K_{eq}{}^1$	Rutter and Schauer (2007)
$HgO_{(aq)} \rightarrow Hg^0{}_{(g)}$	$1.12x10^{-5}$	Costa and Liss (1999)
$HgClY_{(g)} \leftrightarrow HgClY_{(aq)}$	$K_{eq}{}^1$	Rutter and Schauer (2007)
$HgClY_{(aq)} \rightarrow Hg^0{}_{(g)}$	$1.12x10^{-5}$	Costa and Liss (1999)
M HgBr	$(T298)-1.86$*[M]	Donohoue (2006)
$HgBr + M \rightarrow Hg^0 + Br + M$	$-7292T$)	Goodsite et al., (2012)
$HgBr_{(g)} \leftrightarrow HgBr_{(aq)}$	$K_{eq}{}^1$	Rutter and Schauer (2007)
$HgBr + Y^4 \rightarrow HgBrY$	$(T298)-0.57$	Goodsite et al. (2004)
$\rightarrow Hg^0 + Br_2$	$3.9x10^{-11}$	Balabanov et al., (2005)
$HgBrY_{(g)} \leftrightarrow HgBrY_{(aq)}$	$K_{eq}{}^1$	Rutter and Schauer (2007)
$HgBrY_{(aq)} \rightarrow Hg^0{}_{(g)}$	$1.12x10^{-5}$	Costa and Liss (1999)
$HgBr + Y'^5 \rightarrow HgBr\ Y'$	$1x10^{-10}$	Dibble et al. (2012)
$HgBrY'_{(g)} \leftrightarrow HgBrY'_{(aq)}$	$K_{eq}{}^1$	Rutter and Schauer (2007)
$HgBrY'_{(aq)} \rightarrow Hg^0{}_{(g)}$	$1.12x10^{-5}$	Costa and Liss (1999)

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[1] Equilibrium coefficient is parameterized according to Rutter and Schauer (2007): Keq = (SA-PM)/$10^{((-4250/T)+10)}$, where SA = the specific aerosol surface area, and PM = the particulate mass

[2] Rate coefficients are given in either cm^3 $molec^{-1}$ s^{-1} or s^{-1}

[3] Assumes that the reaction between Hg^0 and Cl is the rate limiting step to form HgCl which will then quickly react with Br to form HgClBr

[4] Y = Br, OH

[5] Y' = HO_2, NO_2, BrO, IO, I

Figure Captions

Figure 1: Total mercury wet deposition in the US for 2013. The highest levels of Hg deposition are observed in the southeastern US, where no local and regional sources are located immediately upwind. The black square indicates the measurement location.

Figure 2: Overview of the MAX-DOAS measurements for the week surrounding the case study day (9 April, highlighted with blue box). Also included are O_3 measurements from a monitor collocated with the MAX-DOAS instrument (label “CU”, black trace) and a monitor located at an Mercury Deposition Network (MDN) site ~30 km northwest of the EPA site (label “OLF”, red trace), and wind direction measurements (grey trace) from a site near the EPA facility along with Hg^{II} measurements from the MDN site (scaled by a factor of 10, orange trace).

Figure 3: Conceptual sketch of the SCD_{Ref} retrieval (panel a), and resulting SCD_{Ref} values (black trace). The sensitivity of the a-posteriori BrO VCD (red trace) to SCD_{Ref} is also shown (panel b).

Figure 4: Characterizing the retrieval averaging kernel (AVK) and Degrees of Freedom (DoF). Panel a) AVK output for an inversion of BrO SCDs (at SZA = 25°) as a function of altitude. The colored traces represent the individual altitude grids of the inversion accounting for SCD_{Ref}; the thick black trace is the diagonal of the AVK matrix; the thick red trace is the diagonal of the AVK matrix from the inversion not accounting for SCD_{Ref}. Panel b) shows the difference between the two AVK diagonals as a function of altitude.

Figure 5: BrO profiles for a single MAX-DOAS measurement scan at SZA ~23° around solar noon. Panel a) contains three of the a-priori profiles tested (dashed lines) and the respective a-posteriori profiles (solid lines); colors correspond to use of WACCM (black); GEOS-CCM (orange); and TORERO RF12 (blue) as a-priori information. Panel b) contains the AVK from the inversion using the WACCM profile as the a-priori, and gives an indication on the amount of information coming from the measurements as a function of altitude.

Figure 6: Diurnal variation in the BrO vertical profiles represented as partial VCDs for the BL (0-1 km), troposphere (0-15 km), total (0-50 km) (panel b), and the total DoFs from the inversion for each profile in panel a. The error bars on the VCDs indicate the range of values retrieved using the three different a-priori profiles.

Figure 7: Box model results of the rate of mercury oxidation as a function of altitude for two species: 1) 2) ozone (red); and 3) bromine radicals (solid blue: MAX-DOAS; dashed pink: GEOS-Chem) (panel a); the corresponding lifetimes are found in panel b. The black dashed line at 4 km shows where measurement sensitivity starts to drop because of the decreasing amount of BrO (the measured parameter) in the lower layers of the atmosphere.

Figure 8: Box model results for the scavenging of the HgBr adduct as a function altitude for two different reaction schemes: traditional (panel a) and revised (panel b). Panel c contains the ratio of the total rates (black traces in panels a) and b) to show the enhancement in the rate of the scavenging reaction when other reactants are taken into consideration.

Figure 9: Observed (black solid trace) and simulated (blue traces) concentrations of oxidized mercury (Hg^{II} = GOM + PBM) during April 2010 (9 April highlighted). Model results from GEOS-Chem (solid) include a sensitivity test, labeled FT (dashed trace), in which North American anthropogenic emissions are zero and no GEM oxidation occurs in the lower troposphere (>700 hPa); therefore all Hg^{II} in the "FT" model is derived from oxidation of in the free troposphere or long-range transport.

Figure S1: BrO box-AMFs for two elevation angles (25° and 90°, solid and dashed lines respectively) at different SZAs. For these higher pointing elevation angles, the box-AMFs peak at altitudes of 2-15km (free troposphere) for SZAs lower than 70°, while at higher SZA the box-AMFs indicate that the sensitivity towards the free troposphere is decreasing.

Figure S2: Overview of box-AMFS for SZAs less than 70° for 4 elevation angles: a) 3.8°; b) 10°; c) 25°; and d) 90°.

Figure S3: Overview of the WACCM BrO vertical profiles as a function of altitude and time of day (panel a), and then collapsed into to the corresponding partial (green trace) and total (blue trace) VCDs in panel b.

Figure S4: Example results for the inversion of IO from the MAX-DOAS measurements. Panel a) contains the three a-priori profiles used in the inversion (dashed, colored lines), the a-posteriori results from a MAX-DOAS scan at ~45° SZA (morning) corresponding to the a-priori profiles (solid lines, colors correspond with the a-priori), and the median IO profile (red trace, where the error bars reflect the 25th and 75th percentiles). Panel b) shows the averaging kernels for the inversion using a-priori “Prf1”. Panel c) shows the diurnal variation of the IO VCD for the BL (0-1 km), troposphere (0-15 km), and total (0-25 km).

Figure S5: Overview of the sensitivity of SCD_{Ref} and the derived VCDs on the choice of reference spectra/scan and a-priori profile assumption. Panel (a) contains the SCD_{Ref} determined from both forward calculations of the a-priori profiles (grey traces) and the iterative approach (blue traces) for 47 different zenith spectra. The a-priori cases corresponding to the median BrO profile based on WACCM (WACCM*1.4) are denoted with thicker and darker lines. The error bars on the forward calculated median BrO profile case (dark grey) reflect the $\pm 1\times10^{13}$ molec cm^{-2} criteria for selecting suitable references. Panel (b) contains the corresponding VCDs derived for one MAX-DOAS scan (near solar noon) for each of the references and a-priori combinations. The blue shaded vertical boxes denote references that meet the criteria for being used in the inversion; and the horizontal grey box (panel b) covers the range of $2.3\pm0.9\times10^{13}$ molec cm^{-2}, which fully captures all the references contained within the shaded blue region.

Figure S6: Time series of the DoFs and inversion RMS for three different analysis procedures: 1) changing reference analysis (reference is selected from each measurement scan throughout the day, blue trace); 2) fixed reference without accounting for any SCD_{Ref} (green trace); and 3) fixed reference analysis accounting for SCD_{Ref} (red trace). Included in the plot is SZA (black trace) for reference.

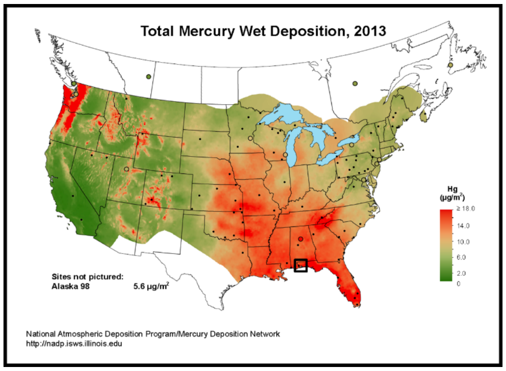
Figure S7: Shows a comparison of the measured BrO dSCDs and the dSCDs calculated from the a-posteriori profiles (inversion using the WACCM profile) for both the entire case study day (panel a) and for a small subset of scans before solar noon (panel b). Panel c contains the RMS of the difference between the measured and calculated dSCDs for each scan.

Figure S8: Overview of vertical profiles of parameters used as input to the box model utilized in this study which were: 1) from WACCM (temperature, pressure, HCHO); 2) from GEOS-Chem (BrO, O_3, NO_2, and Hg^0); 3) from the TORERO field experiment (total surface area); and 4) derived during this study (BrO and IO).

Figure S9: Observed concentrations of selected trace gases during April 2010 at the Pensacola MDN site. Note scale factors for some species given in the legend.

Figure S10: Comparison of measured O_4 dSCDs and dSCD calculated based on the derived aerosol profiles for the entire case study day (panel a) and a subset of scans (panel b). Panel c contains the diurnal variation in the derived aerosol profiles, and an example profile is found in panel d.

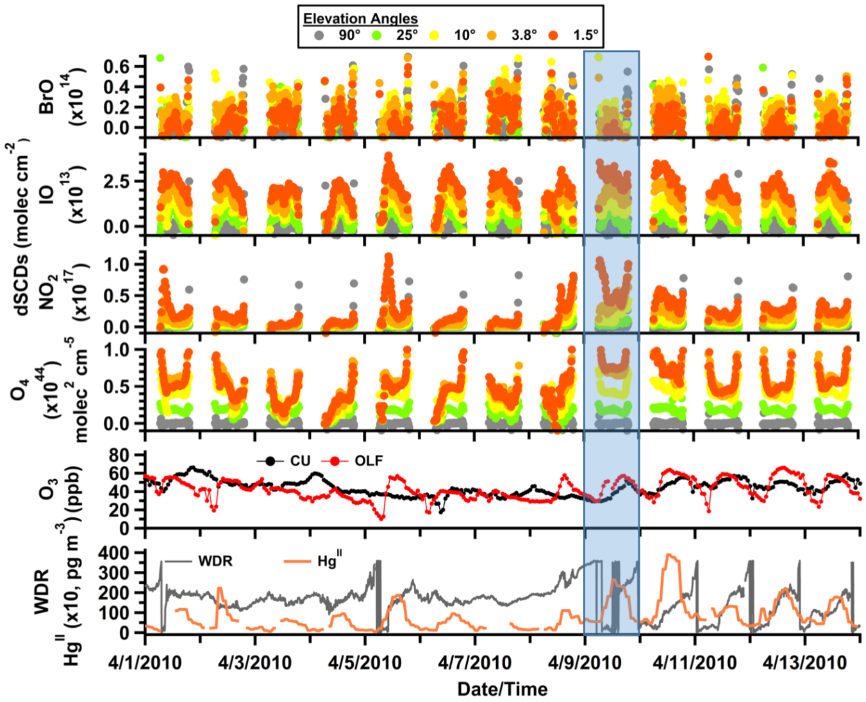
Figure S11: Box model results of the rate of mercury oxidation as a function of altitude for two species: 1) ozone (red); and 3) bromine radicals (solid blue: MAX-DOAS; dashed pink: GEOS-Chem) (panel a); the corresponding lifetimes are found in panel b. The black dashed line at 4 km shows where measurement sensitivity starts to drop because of the decreasing amount of BrO (the measured parameter) in the lower layers of the atmosphere. This figure is complementary to Fig. 7, but uses the WACCM, rather than GEOS-Chem, O_3 and NO_2 vertical profiles as input.



National Atmospheric Deposition Program/Mercury Deposition Network
http://nadp.isws.illinois.edu

Figure 1

Figure 2



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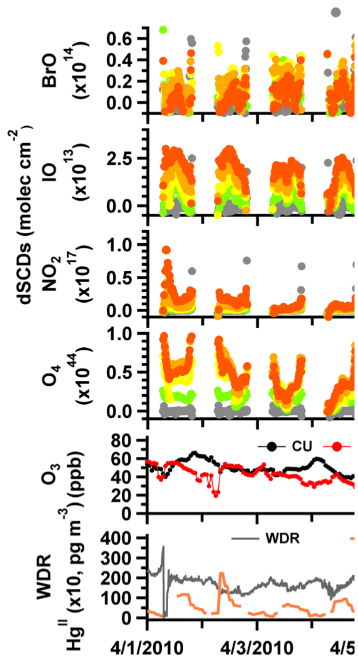

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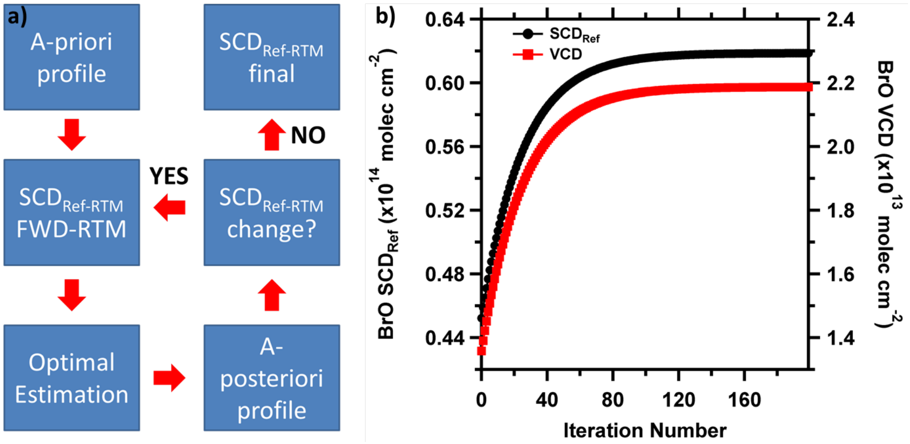
a)
A-priori profile
$SCD_{Ref\text{-}RTM}$ FWD-RTM
Optimal Estimation
A-posteriori profile
$SCD_{Ref\text{-}RTM}$ change?
YES
NO
$SCD_{Ref\text{-}RTM}$ final
b)
SCD_{Ref}
VCD
BrO SCD_{Ref} ($\times 10^{14}$ molec cm^{-2})
BrO VCD ($\times 10^{13}$ molec cm^{-2})
Iteration Number
0.44
0.48
0.52
0.56
0.60
0.64
1.4
1.6
1.8
2.0
2.2
2.4
0
40
80
120
160

Figure 3

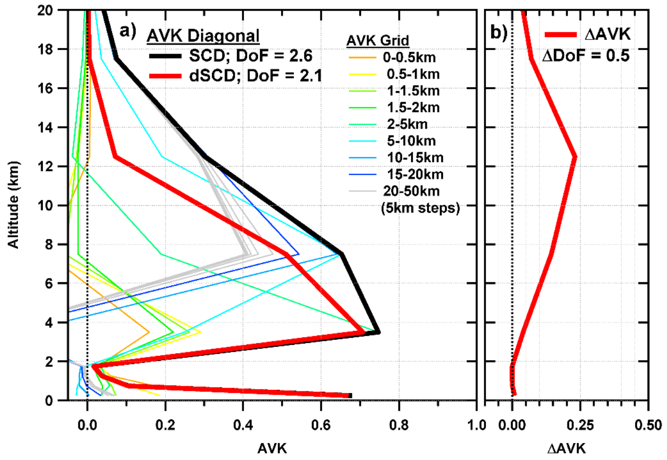
a)
AVK Diagonal
SCD; DoF = 2.6
dSCD; DoF = 2.1
AVK Grid
0-0.5km
0.5-1km
1-1.5km
1.5-2km
2-5km
5-10km
10-15km
15-20km
20-50km
(5km steps)
Altitude (km)
20
18
16
14
12
10
8
6
4
2
0
0.0
0.2
0.4
0.6
0.8
1.0
AVK
b)
ΔAVK
ΔDoF = 0.5
0.00
0.25
0.50
ΔAVK

Figure 4

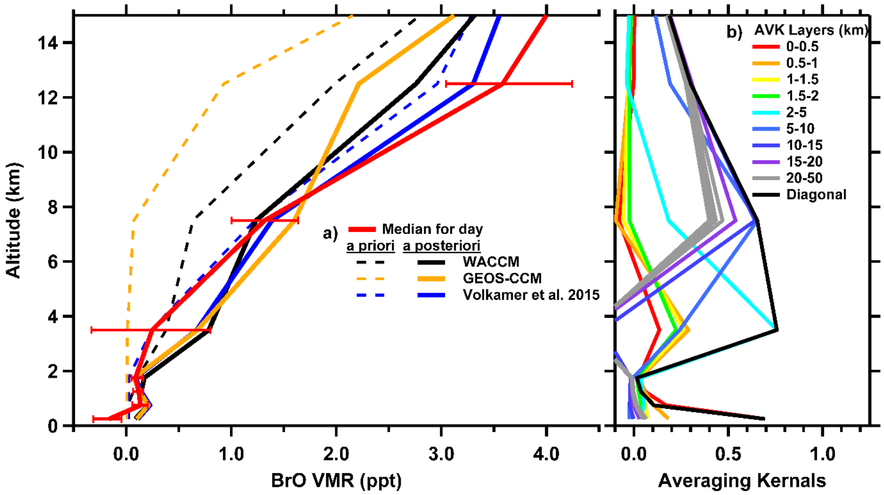
a)
Median for day
a priori
a posteriori
WACCM
GEOS-CCM
Volkamer et al. 2015
Altitude (km)
0
2
4
6
8
10
12
14
0.0
1.0
2.0
3.0
4.0
BrO VMR (ppt)
b)
AVK Layers (km)
0-0.5
0.5-1
1-1.5
1.5-2
2-5
5-10
10-15
15-20
20-50
Diagonal
0.0
0.5
1.0
Averaging Kernals

Figure 5

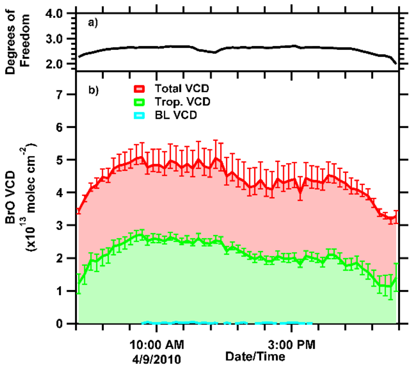
Degrees of Freedom
4.0
3.0
2.0
a)
b)
Total VCD
Trop. VCD
BL VCD
BrO VCD (x10^{13} molec cm^{-2})
7
6
5
4
3
2
1
0
10:00 AM
4/9/2010
3:00 PM
Date/Time

Figure 6

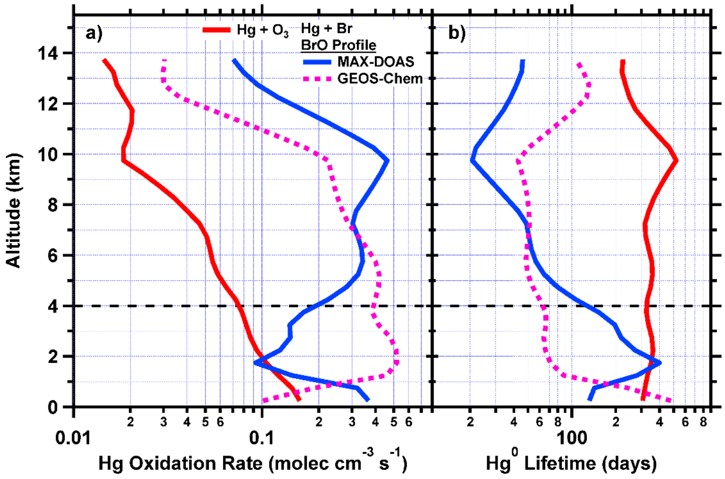

Figure 7

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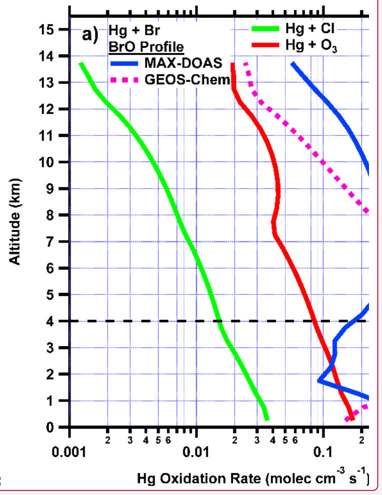

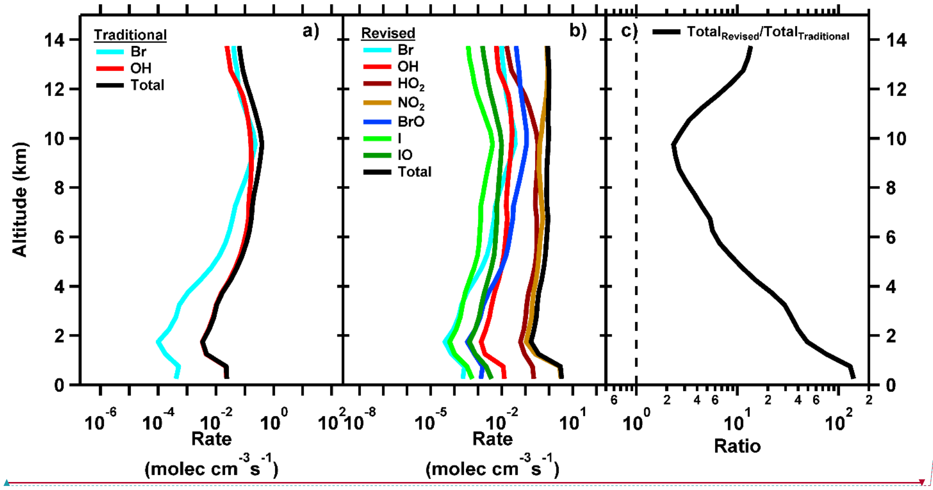

Figure 8

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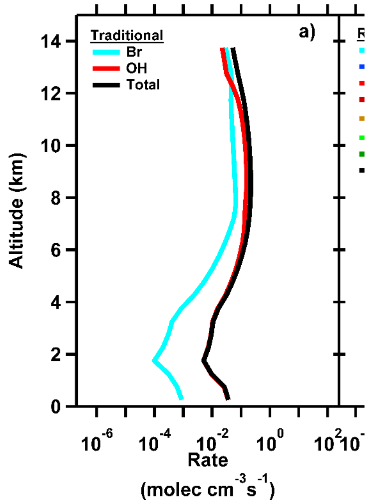

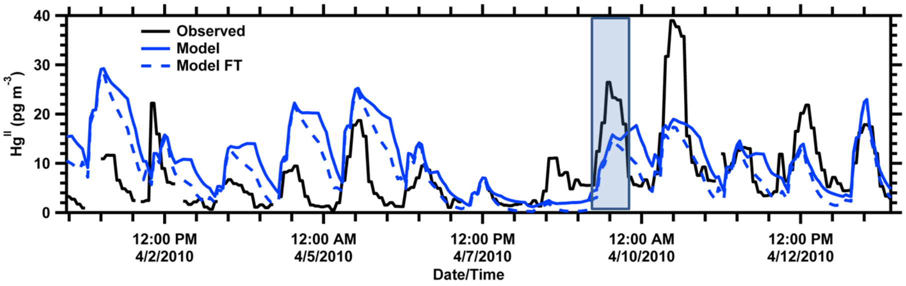

40
30
20
10
0
Hg^{II} (pg m^{-3})
Observed
Model
Model FT
12:00 PM 4/2/2010
12:00 AM 4/5/2010
12:00 PM 4/7/2010
12:00 AM 4/10/2010
12:00 PM 4/12/2010
Date/Time

Figure 9

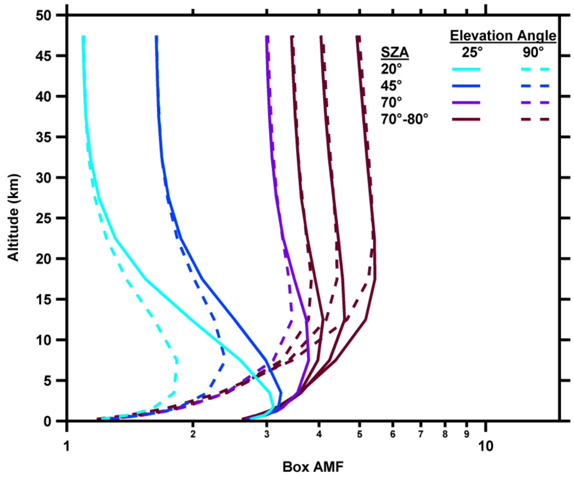
Elevation Angle
SZA
25°
90°
20°
45°
70°
70°-80°
Altitude (km)
50
45
40
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
10
Box AMF

Figure S1

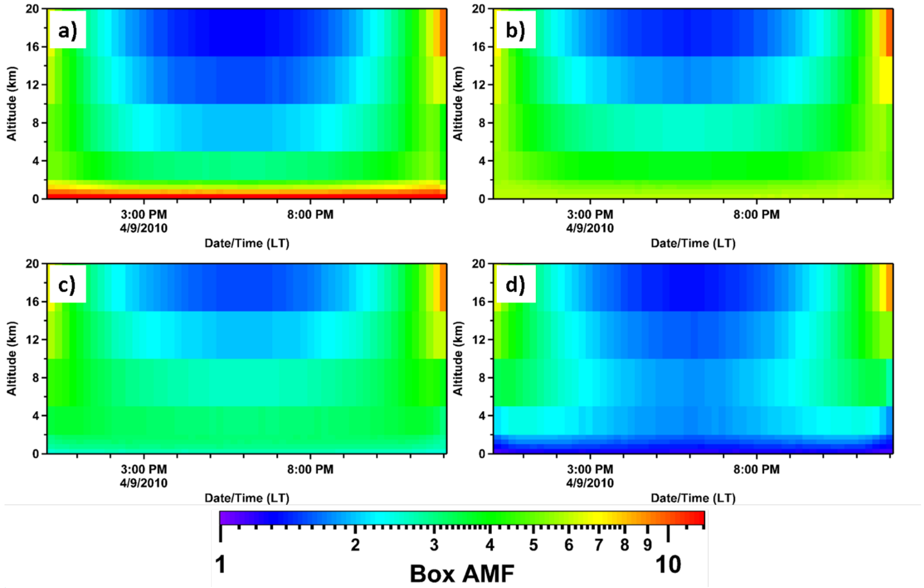

Figure S2

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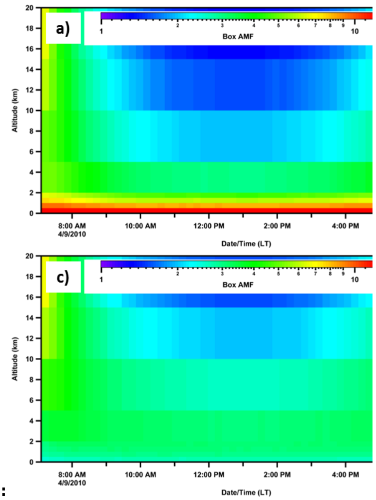

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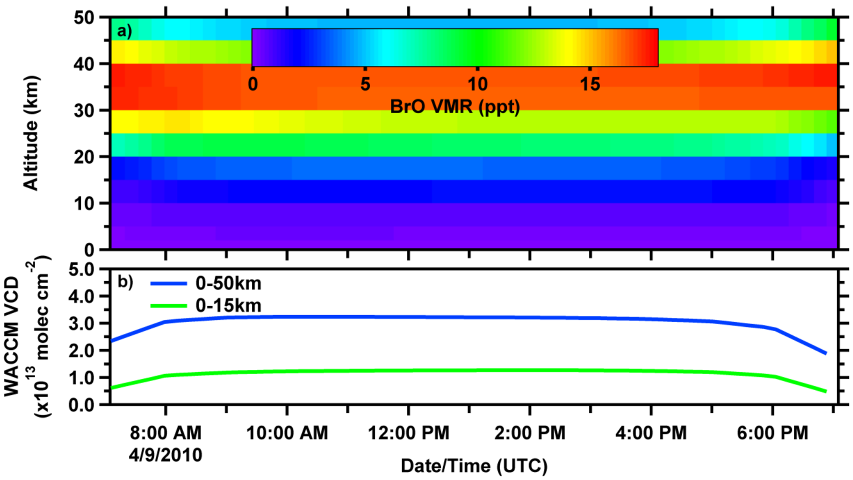
a)
b)
BrO VMR (ppt)
0
5
10
15
Altitude (km)
50
40
30
20
10
0
WACCM VCD
(x10^13 molec cm^-2)
5.0
4.0
3.0
2.0
1.0
0.0
0-50km
0-15km
8:00 AM
4/9/2010
10:00 AM
12:00 PM
2:00 PM
4:00 PM
6:00 PM
Date/Time (UTC)

Figure S3

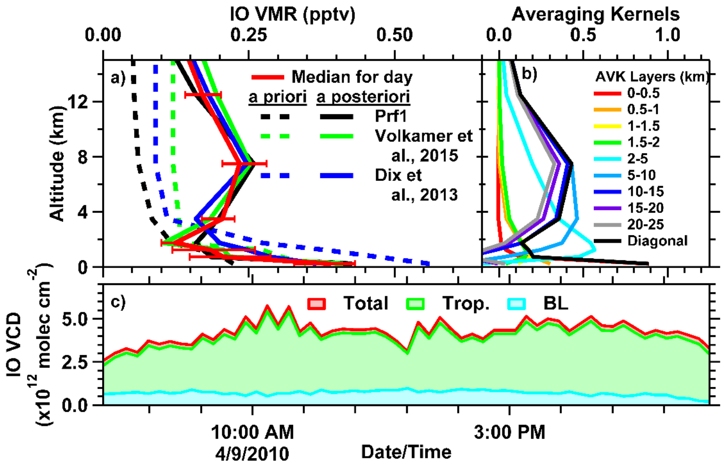

Figure S4

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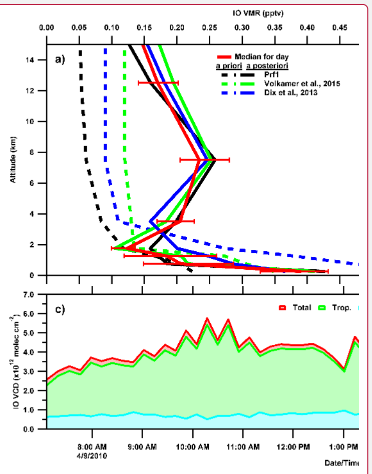

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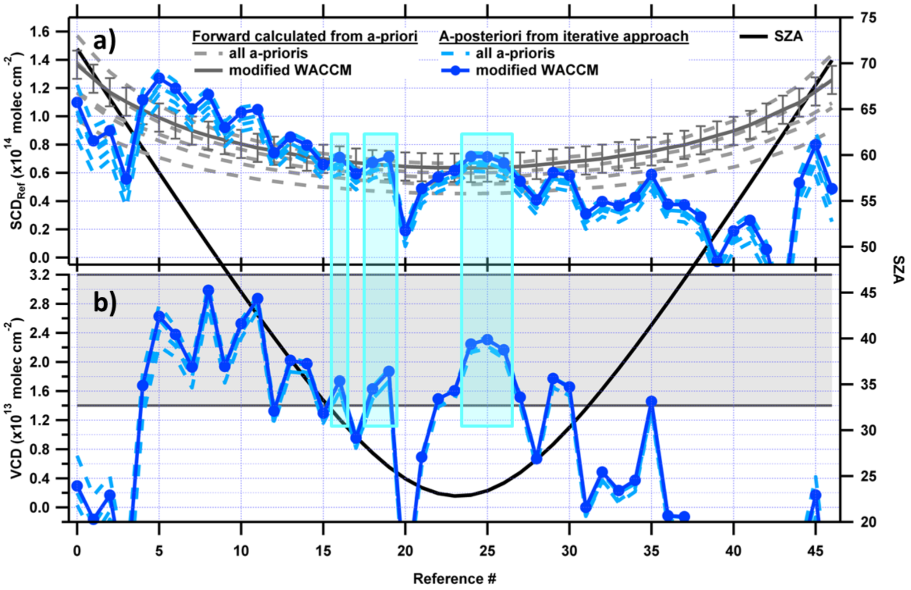
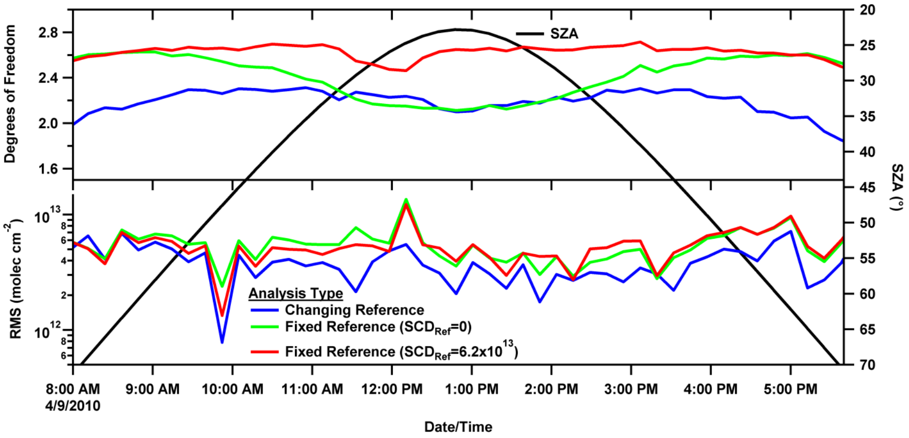

a)
Forward calculated from a-priori
all a-prioris
modified WACCM
A-posteriori from iterative approach
all a-prioris
modified WACCM
SZA
SCD$_{Ref}$ (x10^{14} molec cm^{-2})
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
b)
VCD (x10^{13} molec cm^{-2})
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
SZA
75
70
65
60
55
50
45
40
35
30
25
20
0
5
10
15
20
25
30
35
40
45
Reference #

Figure S5



SZA
Degrees of Freedom
2.8
2.4
2.0
1.6
SZA (°)
20
25
30
35
40
45
50
55
60
65
70
RMS (molec cm^{-2})
10^{13}
8
6
4
2
10^{12}
8
6
Analysis Type
Changing Reference
Fixed Reference (SCD_{Ref}=0)
Fixed Reference (SCD_{Ref}=6.2x10^{13})
8:00 AM
4/9/2010
9:00 AM
10:00 AM
11:00 AM
12:00 PM
1:00 PM
2:00 PM
3:00 PM
4:00 PM
5:00 PM
Date/Time

Figure S6

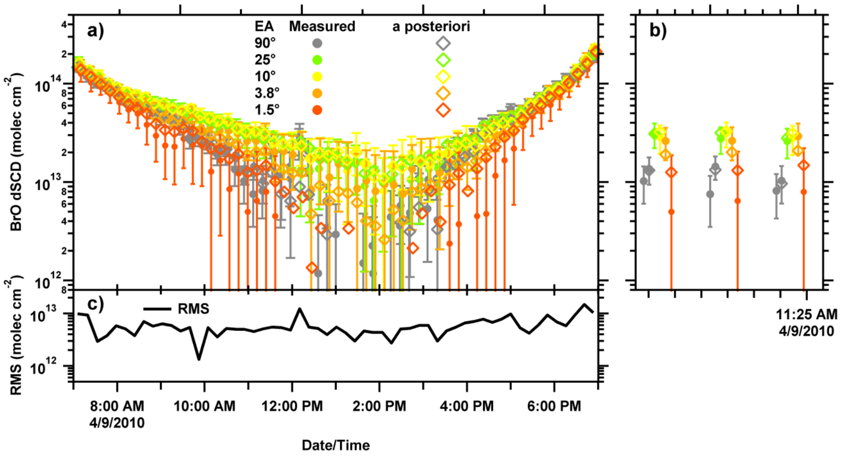

a)
EA
Measured
a posteriori
90°
25°
10°
3.8°
1.5°
BrO dSCD (molec cm^{-2})
10^{14}
10^{13}
10^{12}
b)
11:25 AM
4/9/2010
c)
RMS
RMS (molec cm^{-2})
10^{13}
10^{12}
8:00 AM
4/9/2010
10:00 AM
12:00 PM
2:00 PM
4:00 PM
6:00 PM
Date/Time

Figure S7

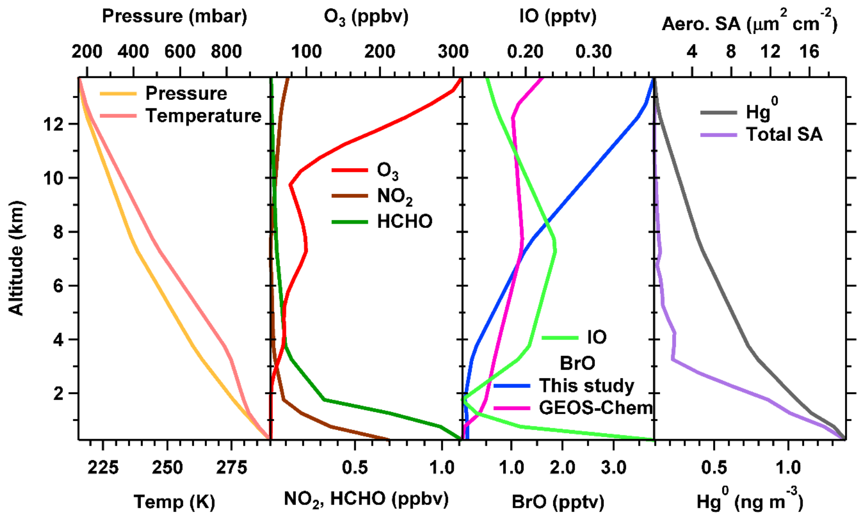
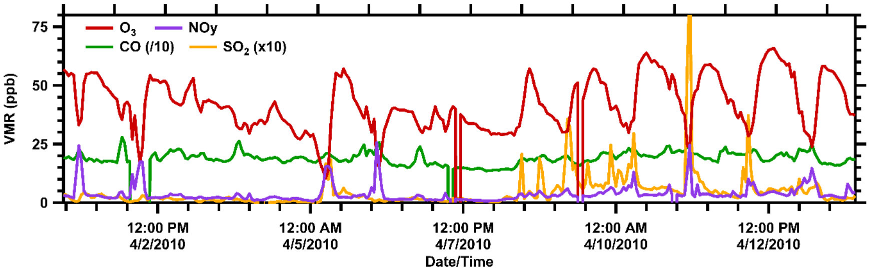

Pressure (mbar)
200 400 600 800
O_3 (ppbv)
100 200 300
IO (pptv)
0.20 0.30
Aero. SA (μm^2 cm^{-2})
4 8 12 16
Pressure
Temperature
Altitude (km)
12 10 8 6 4 2
O_3
NO_2
HCHO
IO
BrO
This study
GEOS-Chem
Hg^0
Total SA
225 250 275
Temp (K)
0.5 1.0
NO_2, HCHO (ppbv)
1.0 2.0 3.0
BrO (pptv)
0.5 1.0
Hg^0 (ng m^{-3})

Figure S8



1682

1683 Figure S9

1684

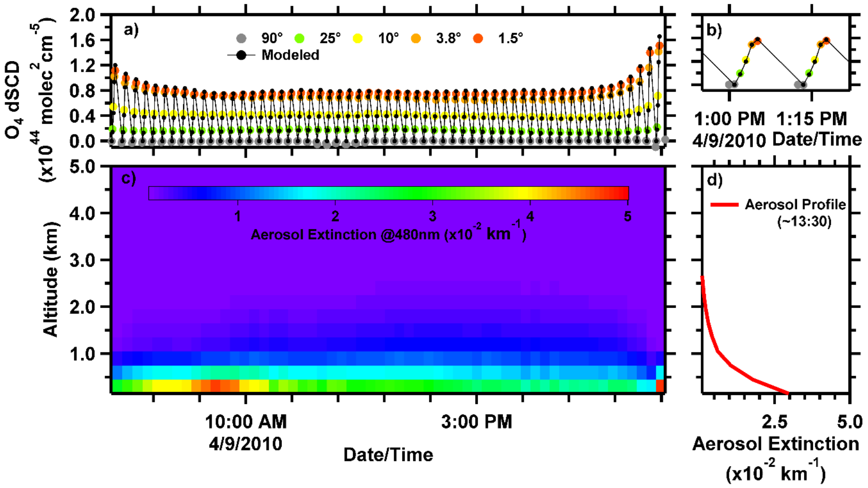

a)
90°
25°
10°
3.8°
1.5°
Modeled
O_4 dSCD ($\times10^{44}$ molec^2 cm^{-5})
2.0
1.6
1.2
0.8
0.4
0.0
b)
1:00 PM
4/9/2010
1:15 PM
Date/Time
c)
Aerosol Extinction @480nm ($\times10^{-2}$ km^{-1})
1
2
3
4
5
Altitude (km)
5.0
4.0
3.0
2.0
1.0
10:00 AM
4/9/2010
3:00 PM
Date/Time
d)
Aerosol Profile
(~13:30)
2.5
5.0
Aerosol Extinction
($\times10^{-2}$ km^{-1})

Figure S10

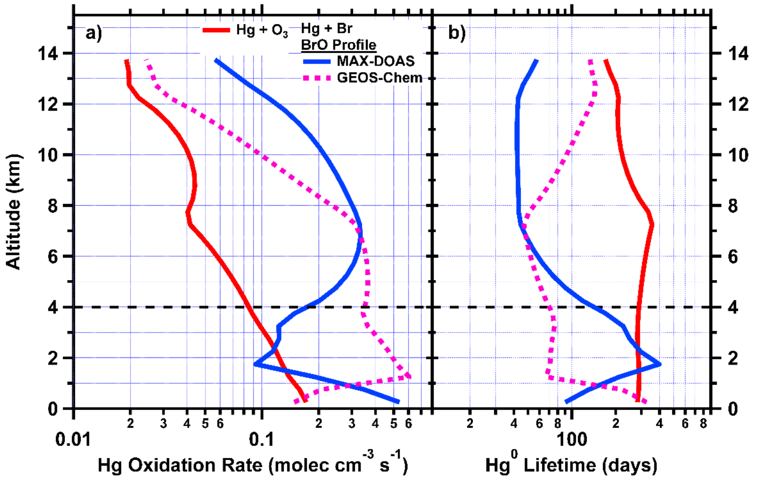


Figure S11

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