Atmos. Chem. Phys. Discuss., 15, C10398–C10400, 2015
www.atmos-chem-phys-discuss.net/15/C10398/2015/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 14 December 2015

This paper presents an Optimal-Estimation-Method-based BrO vertical profile and column density retrieval from MAX-DOAS measurements performed in April 2010 at the coastal site of Gulf Breeze (Gulf of Mexico, FL). This study focuses mainly on a cloud-free day with low aerosol load (9 April 2010), which allows to better distinguish the respective contribution of the marine boundary layer (0-1km asl) and free troposphere (FT) to the total BrO vertical columns. The use of a fixed reference spectrum selected around local noon helps also to maximise the sensitivity in the free troposphere. The retrieved average BrO FT vertical column (around 2.3E13 molec/cm2) is at the upper limit of the range reported so far in the literature (1-3E13 molec/cm2). These new bromine measurements are then used to constraint bromine chemistry and mercury oxidation pathways in 3D-CTM models.

This study fits well with the scope of ACP and the manuscript is well written and clearly structured. I recommend publishing it in ACP after addressing the following comments:

Major concerns:

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.

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.

Specific comments:

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.

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 ?

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.

Technical corrections:

Difficult to read texts in Figs S2 and S4 (font too small).

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28317, 2015.