Atmos. Meas. Tech. Discuss., 5, C2616–C2622, 2012
www.atmos-meas-tech-discuss.net/5/C2616/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Resolution of an important discrepancy between remote and in-situ measurements of tropospheric BrO during Antarctic enhancements" *by* H. K. Roscoe et al.

R. J. Salawitch (Referee)

rjs@atmos.umd.edu

Received and published: 23 October 2012

Review of AMT manuscript amt-2012-142, Resolution of an important discrepancy between remote and in-situ measurements of tropospheric BrO during Antarctic enhancements, by Roscoe et al.

This paper presents ground based in-situ measurements of surface BrO, ground based remote measurements of tropospheric BrO, and estimates of tropospheric BrO from the space-based GOME-2 sensor to show that an apparent discrepancy between these disparate measurement systems can be resolved if "substantial amounts of BrO were

[to be present] in the free troposphere during most enhancement episodes".

I find that this paper is generally solid and, upon revision, will likely be acceptable for publication in AMT. It is not presently acceptable in the present form because: a) it takes great liberty with prior works on this topic, which have been co-authored by this reviewer; b) some of the statements are not well supported by the analysis; c) adequate error analysis has not been performed.

Major Points:

a) The Introduction states "a similar potential discrepancy" had been suggested from Arctic measurements by McElroy et al. (1999), who speculated . . .". The Interpretation section states:

The potential for the discrepancy was strongly suggested by McElroy et al. (1999) from airborne measurements over the central Arctic Ocean in spring. They observed similarly large vertical column densities of BrO, which led them to speculate that much of the BrO must be in the free troposphere, and that lofting of boundary layer air was indeed likely via convection due to water leads. However, there were no simultaneous in-situ measurements to confirm the discrepancy, and no geometrical considerations in the measurements to confirm that BrO was present at higher altitudes.

The reader is left with the impression, nearly to the end of the paper, that this work presents the first evidence for "simultaneous in-situ measurements to confirm the discrepancy". However, paragraph 24 of Salawitch et al. (2010), a paper I led, states:

The MAX-DOAS and aircraft observations of tropospheric BrO are consistent in that they both show significant contributions to BrO^{TROP} from above the CBL (convective boundary layer). The prevalence of elevated BrO above the CBL may be due to vigorous convection over ice leads driven by warm exposed water, with BrO then dispersed horizontally by prevailing winds. This would be consistent with distribution of BrO throughout the polar boundary layer, a region in which surface emissions can be vertically mixed even if the atmosphere appears to be stable with respect to local convection [e.g., Simpson et al., 2007]. Attempts to relate satellite BrO^{VC} to ODEs and surface BrO, common in the literature, are complicated by the finding that BrO^{TROP} appears to be dominated by contributions from above the CBL.

Choi et al. (2012) states:

The satellite measurements reveal horizontal transport of activated bromine away from the source of origin, and the aircraft measurements show disbursement of BrO within the free troposphere. The strong quantitative agreement between OMI and aircraft tropospheric column BrO on 17 April 2008 supports the validity of the rapid time evolution, on synoptic scales, revealed by the OMI tropospheric BrO product. The events on 17, 18, and 19 April suggest bromine activation via high winds over snow (Yang et al., 2008; Jones et al., 2009, 2010) as well as long range transport of Bry by surface winds (Begoin et al., 2010).

Prados-Roman et al. (AMT, 2012), which is not referenced, states:

In Neuman et al. (2010) the amount of reactive bromine was found to be low (<=1 pptv and typically close to detection limit) in the free troposphere. Photochemical arguments put forward by the authors (also valid for our conditions) suggest that most (if not all) of the detected reactive bromine was actually HOBr (reservoir) rather than BrO. Since these arguments may also apply for our observations, we cannot conclude that BrO was unequivocally detected in the free troposphere during the ASTAR 2007 campaign.

There is a lot more work on the presence, or lack-thereof, of BrO above the boundary layer than the important early work of McElroy et al. (1999). Upon revision, this other work should be summarized in the Introduction and/or Interpretation sections. References to the above mentioned papers as well as Neuman et al. (2010), the source of in situ BrO discussed in Salawitch et al. and Choi et al., should be given much earlier than the very end of the paper. Also, evidence of ODEs in the free troposphere (including the Roscoe et al. 2001 paper), should be discussed much earlier. The Roscoe et al.

2001 paper is cited once in the Introduction, but not in the context of actual empirical evidence for the presence of BrO above the boundary layer (at least this is not how I read lines 4 to 6 on page 5421).

Finally, the inclusion of the third panel on Figure 10, which looks like a photoshopped rendition of Figure 4c of Salawitch et al. (2010), comes as quite a surprise. AGU owns the copyright to this figure. It is illegal to copy this figure without some alteration . . . changing the aspect ratio of the panel is not sufficient! It is also unusual to reproduce a figure from a colleague's paper, without asking permission. The authors must either obtain permission from AGU to copy this portion of Figure 4c from the Salawitch et al. paper, or contact me off-line for transmission of the data values in the file, which they can use to make a panel with their graphical software.

b) Some of the statements are not well supported by the analysis.

For instance, the Interpretation section begins "Section 3 demonstrates that two remote-sensing instruments, the first on the ground and the second in space, see very similar vertical amounts of tropospheric BrO".

The figure that supposedly supports this statement is Figure 2.

But for essentially all of the days shown in Figure 2, tropospheric BrO from GOME-2 (space based) exceeds tropospheric BrO from MAX-DOAS (ground based).

The comparison is compromised by lack of error bars (see below).

But, with or without error bars, clearly space-based tropospheric BrO exceeds ground-based tropospheric BrO.

—

Page 5430, lines 4 to 5, state "Assuming the value of 200 m, the MAX-DOAS vertical column would become 130 pptv on 6 September 2007". This is a strange statement . . . how can a column be expressed in terms of mixing ratio? I think I know what is meant, but here and in many places of this paper, it is written in "clear only if known" fashion.

Another example of loose writing is the statement on page 5422 that "Laboratory tests at BIRA with another spectrometer of the same type had shown that the shifts became significantly larger at temperatures much below 0 C". This statement has no scientific meaning. Is minus 1 C "much below 0 C"? How about minus 5 C.

I urge the authors to scour the paper and write in a manner that communicates effectively with folks with interest in this study, who are not familiar enough with the intricate details to know what is or is not meant by these types of sentences. For instance . . . "3 oktas cloud" and

c) Adequate error analysis has not been performed.

Page 5431 states "the calculation of approximate errors is problematic." I find this statement troublesome and feel, prior to publication, that a more sophisticated error analysis must be performed.

In Figure 5 of Salawitch et al. (2010), for example, we showed that the best fit between modeled and measured BrO differential SCD was found assuming a constant concentration of BrO within the lowest 1 km of the Arctic, with a column of 2.3 $\times 10^{13}$ $\mathrm{cm}\text{-}2$. A similar analysis can be performed for the Antarctic MAX-DOAS data in the submitted paper.

The discrepancy between CIMS BrO and MAX-DOAS BrO, in terms of mixing ratio, is only shown for an analysis that assumes tropospheric BrO is uniformly distributed in the lowest 200 m, and zero everywhere else. It is important to produce a similar comparison, for BrO mixing ratio inferred from MAX-DOAS, assuming uniform distribution between the surface and the altitude that gives best fit, between modeled and measured BrO differential slant column, either on a day by day basis, or for the seasonal average. Such an analysis would be an important complement to Figures 4 and 8.

The vertical profiles of BrO shown in Figure 7 should include small circles (or some

symbol) representing where the vertical pieces of info is centered (this info is in the caption) as well as error bars, representing an estimate of the uncertainty of retrieved BrO. These plots as presented, showing smooth lines (perhaps spline fit) and no error bars, are not too helpful for the expert community.

Minor points:

1. The paper should state what BrO cross sections were used in the retrieval. Also, some statement should be included regarding how absorption due to HCHO and OClO were handled. Even is these absorptions were ignored, this must be stated.

2. On page 5425, it is stated "this is achieved by subtracting from the observed total BrO a climatological value stratospheric BrO". I hope this is not what was done. The emphasis of my recent work, as well as work of Theys, is one will get erroneous estimates of tropospheric BrO if one attempts to use a stratospheric climatology. The inferred BrO is erroneous because BrO is not uniform in the stratosphere. Hopefully appearance of "climatological" is due to a poor choice of words. If not, this comment should be considered a "major point" that must be addressed upon revision, because I do not believe one can derive a valid estimate of the tropospheric BrO burden using a stratospheric climatology.

3. Page 5433, lines 8 to 15, nicely contrast the deduced presence of BrO above 1 km altitude to studies in the Arctic showing no evidence for similar enhancements. This is another place where discussion of Neuman et al. 2010, Salawitch et al. 2010, and Choi et al. 2012 could go (plus add Prados-Roman et al. to the naysayers).

The single sentence PP, lines 15 and 16 of page 5433, makes no sense as written. Are the "meteorological conditions" being contrasted for various regions of the Arctic? Or, are Arctic met conditions being contrasted to Antarctic conditions? I suspect the reason some studies report enhancement of BrO above 1 km in the Arctic, while other studies report no BrO above 1 km, has more to do with the sensitivity to BrO in the free troposphere of various measurement methods, rather than met conditions. Regardless, the meaning of this sentence is unclear.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 5419, 2012.