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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.

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Each comment is followed by a response beginning and ending with **.

Referee 1:

It is well known from previous studies that a presence of BrO in the free troposphere would potentially be of global importance since it may affect the climate system by destruction of ozone and other more subtle effects. Advection of bromine from the boundary layer of Polar Regions to the free troposphere might be one important pathway. Therefore the general topic of the manuscript is of importance for the scientific



community. However, as detailed below, the data analysis and interpretation appears to be erroneous, which renders the manuscript unsuitable for publication at its present stage. Apart from this, the manuscript contains very little on new or improved measurement or analysis techniques, but instead focuses on the scientific question of a possible transport of BrO into the free troposphere. Therefore the general topic of the manuscript is rather unsuitable for Atmospheric Measurement Techniques and would better fit into the scope of a journal such as Atmospheric Chemistry and Physics.

** The manuscript does not discuss any chemistry or climate implications of the effect of BrO in the free troposphere, nor any meteorological interpretation of how it got there - hence it is clearly out of scope for ACP. Instead it focuses on the interpretation and vertical inversion of data from the measurements themselves, and from inter-comparison with other measurement techniques - hence it is clearly well within scope for AMT. **

General Comments:

An analysis of the MAX-DOAS measurement at Halley has been performed in two different ways: (1) using the simple assumption of a box-shaped BrO layer, and (2) by a more sophisticated retrieval algorithm based on optimal estimation. It has been deduced from approach (1) that the assumption that all BrO is present only in the boundary layer would lead to unreasonably high mixing ratios. This would imply that significant amounts of BrO were present the free troposphere. However, the analysis presented by Roscoe et al. appears to be erroneous in several ways. The airmass factors used to convert the SCDs into VCDs and mixing ratios seem to be far too small, leading to an overestimation of the derived BrO VCDs and mixing ratios. Furthermore, the BrO layer heights obtained in order to bring the MAX-DOAS measurements in agreement with in situ measurements are wrong because the decrease in sensitivity with increasing layer height has been completely ignored. From what has been published about the sensitivity of MAX-DOAS measurements (e.g., Irie et al., 2008; Clemer et al, 2010; Wagner et al., 2004; Friess et al., 2006, 2011), I strongly doubt that BrO can be detected unambiguously in the free troposphere on the basis of BrO dSCDs

only. I will discuss these points in more detail in the specific comments below.

** We respond to these issues after the first Specific Comment below. **

Furthermore, the way BrO vertical profiles were estimated from approach (2) is difficult to reproduce. A description of the basic retrieval settings (a priori, vertical grid, etc.), and a characterisation of the retrieval are completely missing. In particular, it would be crucial to see how sensitive the measurements are for BrO in the free troposphere, and how reliable BrO can be retrieved if it is present at high altitudes. It is not clear why a post-processing of the profiles (averaging over several layers, connection by smoothed lines) has been performed, instead of simply showing the retrieved BrO profiles.

** Yes. We have now listed retrieval settings, and we have stated that the mean BrO of the whole data set at 4.3 km is 2.8 pptv, almost ten times the mean random error of 0.30 pptv, so the results at 4.3 km are highly significant. The smooth lines have been replaced by straight lines joining points. As explained in many papers on inversion results (e.g. Roscoe et al., Proc. R. Soc. Lond. A. 375, 507-528, 1981), vertical layers must be averaged to the width of the averaging kernels as otherwise the solution can be unstable. Also, to show results at fine intervals produces a completely unrealistic impression of the vertical resolution. We have now said so in the text. **

Finally, I find the title somewhat inappropriate since it implies that important discrepancies were discovered in the past. Going through the literature, I cannot find a clear statement from other authors about a discrepancy between different BrO measurement techniques as large and systematic as stated by Roscoe et al. In fact, the recent studies by Friess et al. (2011) and Liao et al. (2011) show excellent agreement between active and passive DOAS as well as in situ measurements. It has been mentioned several times in the manuscript that McElroy et al. (1999) would have found such a discrepancy. However, McElroy et al. presented airborne measurements and concluded on a transport of BrO into the free troposphere over open leads. There was no comparison to any other measurement technique, and thus no discrepancy. Furthermore,



it is not motivated in the introduction why the phenomenon the authors claim to see justifies the word “important” in the title.

** As demonstrated by Referee 2 (first point in (a) below), there was significant other evidence in the literature about such a discrepancy, and we have now included it. We have also added a reference from AGU in 2009, where there was much discussion of BrO measurements. **

Respective references to literature about the importance of free tropospheric BrO (e.g. Fitzernberger et al., 2000; van Roozendael, 2002; von Glasow et al., 2004) are missing.

** The amounts we now identify in the free troposphere in Antarctica are many times the amounts at mid-latitudes in these references. The amounts at mid-latitudes have a different source and implication. **

Specific Comments

The argumentation of Roscoe et al. is mainly based on the falsification of the hypothesis that BrO is located in the boundary layer, but it has not been shown that the measured BrO dSCDs can be brought into agreement with the hypothesis that BrO is located in the free troposphere. In the following, I will show that (1) the measurements of Roscoe et al. cannot be brought into agreement with the hypothesis that BrO is in fact located at high altitudes (> 2 km) due to a general lack of sensitivity, and that (2) the measurements can be easily brought into agreement with the co-located in situ data assuming a BrO layer height of a few hundred meters. Figure 1 below shows differential (2° - 90°) airmass factors simulated for a box-shaped as a function of layer height (left panel). Also shown are the resulting VCDs V = dS/dA (middle panel) and the box-averaged BrO VMR calculated according to ro = V/h (right panel), given a BrO dSCD of 2 âĂć 1014 molec/cm2 (which is in agreement with the values shown in fig. 1 of Roscoe et al.). The calculations have been performed using the McArtim Monte Carlo RTM (Deutschmann et al., 2011) for an aerosol free atmosphere (black line) and an aerosol layer between 0 and 2 km with an extinction of 0.2 $km^{-1}$ (red

line) which represents a rather high aerosol load for Antarctic conditions. Thus the two calculations, which are in agreement with the values reported by Wagner et al. (2007), represent upper and lower limits for the BrO AMF. First of all, it is obvious that the BrO AMF rapidly decreases with layer height due to the limited sensitivity of MAX-DOAS for high altitudes. Given a measured dSCD dS and a differential AMF dA, the surface concentration amounts to ro(h) = V/h = dS/ (dA(h) âĂć h) if BrO is equally distributed over a layer of height h. Since an increase in h is partly compensated by the decrease in dA with altitude, the statement that the estimated surface concentration is “inversely proportional to layer thickness, so a layer thickness of 2000 m would be needed to obtain good agreement” (P 5430, L 6) is wrong. Instead, the estimated BrO VMR converges towards a constant value for layer heights above 1 km. An increase in the assumed layer height from 200 m to 2000 m would therefore lead to a reduction in BrO VMR by only a factor of about two (see right panel of Figure 1 below), and not by a factor of ten as claimed by Roscoe et al. More important is the absolute value of the dAMF, which, depending on the aerosol load, ranges between 17.5 (high aerosol load) and 25 (Rayleigh atmosphere) for a layer height of 200 m. There is little information in the manuscript about the way the AMFs have been calculated, but from the dSCDs shown in Figure 6 and the VCDs shown in Figure 2, one can infer a value of about 12, which is far too small. Thus the BrO VCD and VMR reported by Roscoe et al. appear to be much too high. With the exception of one datapoint, the dSCDs shown in Figure 6 are in the order of 2 âĂć 1014 molec/cm2 (when subtracting the zenith sky dSCD). For a layer thickness of 200 m, this would yield a BrO VMR between 15 and 30 ppt (right panel of Figure 1 below) and not 100 ppt as stated by Roscoe et al. For the highest BrO dSCD observed (6 âĂć 1014 molec/cm2), the mixing ratio would be about 45 ppt, which is still in agreement with BrO values measured at other places in Polar Regions (Poehler et al., 2010). Using an optimal estimation algorithm, Friess et al. reported a surface mixing ratio of 10 ppt (Figure 10 of Friess et al.) for a very similar BrO dSCD of $(2 - 3)$ âĂć 1014 molec/cm2 (Figure 4 of Friess et al). Assuming a low aerosol load, an agreement between CIMS (showing BrO mixing ratios between 5 and 10 ppt)



and MAX-DOAS can be achieved if BrO resides in the lowermost 400 to 800 m. In summary, the measurements presented by Roscoe et al. (1) do not seem to contradict the hypothesis that all BrO is located in the boundary layer, (2) can be brought into agreement with the in situ data if BrO is present in a layer extending from the surface up to about 400 m, and (3) are hardly sensitive for altitudes above 1.5 km (see, e.g., the averaging kernels shown in Fig. 5 of Friess et al, 2011).

Fig. 1. BrO dAMFs (left), estimated VCDs (middle) and BrO VMR (right) as a function of layer height for a Rayleigh atmosphere (black) and an aerosol extinction of 0.2 kmËĘ-1 (red).

** The Referee seems to have confused Figure 2’s showing of a mean of VCD at elevations 2°, 4° and 15° with the VCD at 2°. We apologise if our statements in the manuscript had not made this completely clear, and we have now moved them earlier in the sentence and figure caption. At 2° elevation in a Rayleigh atmosphere, our calculated AMF was 23.1, and at 90° it was 3.7, giving dAMF of 19.4. This is comparable to but a little lower than the 24 calculated by the Referee at 0.2 km in his/her Fig. 1, possibly due to a different wavelength selection (we used 347 nm) or a different albedo (we used 0.75), or a different SZA (the value we quote here was for 50° SZA). Our AMFs were calculated by a much-used software suite, which has been employed in many MAX-DOAS inter-comparisons. But the Referee is correct that we did not fully describe the AMF suite, and we have now included references which gives full details. **

** The Referee is also correct that the VMR converges as the layer thickness is increased, and we have changed some badly worded statements about this. However, this strengthens our case that the discrepancy is large and important. **

** More details are now given about the averaging kernels, which are more than adequate to give response at 1.5 km and 4.3 km, though with the poor resolution well known in MAX-DOAS inversions. **

The application of the optimal estimation method to the MAX-DOAS data presented in section 5 could have offered the opportunity to quantitatively investigate a possible presence of BrO at high altitudes. However, a discussion of the results is completely missing, and an interpretation of the profiles is very difficult because some kind of postprocessing of the data, i.e. vertical averaging, and connection of the data points with smoothed (how and why???) lines has been performed, instead of simply showing the retrieved BrO vertical profiles as they are.

** Yes. We have now replaced the smoothed lines by straight lines joining points. As explained in the text and above, vertical averaging over the width of the vertical resolution of the inversion technique is essential to avoid over-interpretation of the results. **

A discussion of the retrieved BrO profiles should include: (1) the choice of the a priori and a priori covariance;

** Yes. We have now added a description of the a priori. But briefly, as this is not a paper about the inversion technique. **

(2) the choice of the vertical grid; (3) a discussion of the vertical resolution and, more importantly, the sensitivity of the measurements for high altitudes, based on the averaging kernels;

** As stated in the manuscript, the vertical grid in our Figure is defined by the vertical resolution which is defined by the averaging kernels. We have now quoted the values. **

(4) an error discussion, including the uncertainties in the retrieved BrO amounts at high altitudes;

** The errors were discussed in the manuscript, but we have now given more details in the text, and a description of their size in the caption of Figure 7. They are too small to be plotted on Figure 7. **



(5) a comparison of measured and modelled BrO and O4 dSCDs in order to provide an overall picture of the retrieval quality.

** This is not a paper about the inversion technique. The quality of the inversion technique has been assessed in the reference cited in the manuscript, and it is clear from Figure 8 that the inversion is of sufficient quality for our purposes. **

I find it quite odd to see BrO vertical column densities which strongly differ for different viewing directions in Figure 5. The VCD is defined as the vertically integrated concentration and does not depend on viewing direction. Dividing slant column densities by wrong airmass factors does not yield VCDs, but physically meaningless values. Why have no attempts been made to alter the profile shape in order to achieve agreement between the different viewing directions, rather than sticking to a 200 m box profile?

** The Referee clearly has a different point of view to us. Figure 5 shows the nature of the discrepancy, which we illustrate by producing values that cannot be correct. If we wish to be literal, there is no such thing for scattered-light measurements as an exact AMF, they are all approximations to some degree. By analogy to the Referee's comment, we could claim that all AMFs are wrong, but this is not very helpful and does not progress our argument. **

Some aspects of the data are not discussed appropriately. For example, it is stated that 'GOME-2 values are of similar magnitude to our MAX-DOAS values, although there are differences of detail' (P5429, L3), although Figure 2 clearly shows that data from MAXDOAS is systematically lower than from satellite. In fact, any GOME-2 BrO VCD is significantly higher than the according MAX-DOAS value.

** Yes. We have now deleted "very" from "very similar", and have pointed out that the GOME-2 values are larger and that using them would make the discrepancy worse. **

P 5420, L22: Reactive bromine compounds (Br and BrO) are usually labelled as Brx. Bry includes all inorganic bromine species, of which some have rather low reactivity

compared to Brx (e.g., BrONO2, HBr).

** We meant Bry, which indeed has a 5-day lifetime. We did not imply that Bry was Br+BrO. **

P5423, L25: It is not true that stratospheric BrO cancels out if a zenith sky measurement at noon is used as reference spectrum. The stratospheric airmass factor, and thus the stratospheric SCD, varies with solar zenith angle. The stratospheric contribution only cancels out if a zenith sky measurement recorded closely before or after the off-axis measurement (at about the same SZA) is used as reference.

** Yes. This was carelessly worded, and we have replaced it with a more accurate statement. **

P5424: As already mentioned above, information on the parameters for the radiative transfer calculations (most importantly, the aerosol load) is completely missing.

** Yes. We have now included a reference to the widely-used AMF suite "UVspec/DISORT" that contains full details of the radiative transfer calculations we used, and a reference to an inter-comparison in which it was used. Our calculations assumed no aerosol, and we have now said so. **

P5427, L4: Why should the calculation of AMF be much more difficult with high aerosol loading or significant clouds? Perhaps you mean that it is subject to higher uncertainties.

** Yes. We meant it is subject to larger uncertainties and have now said so. **

P5427, L16: Here it is stated that, using a fixed noon reference, the stratospheric amount changes with solar zenith angle, whereas the opposite has been stated on P5423.

** Yes. This is now rectified by our response to the comment on P5423, L25 above. **

P5428, L1: Why is there less O4 if there is more cloud? The concentration of O4 is



proportional to the square of the O2 concentration and thus mainly determined by air pressure.

** As explained in the text (4th sentence of Section 3), with dense cloud above snow all elevations see the same multiply scattered scene, so that the difference in O4 between the zenith reference spectrum and the measured low-elevation spectrum becomes zero. Hence with more cloud, the slant O4 deduced at non-zenith elevations becomes less. **

P5428, L8: Again, why should the stratospheric ozone SCD increase with solar zenith angle, but not the BrO SCD, if both are analysed using a fixed noon reference?

** Yes. This is now rectified by our response above to the comment about P5423, L25. **

P5428, L25: How can the 'continuing quality of the data' be deduced from Figure 2, if not even error bars are shown?

** Yes. We have now added error bars to the MAX-DOAS data in Figure 2. **

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