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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.

Anonymous Referee #1

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Review of "Resolution of an important discrepancy between remote and in-situ measurements of tropospheric BrO during Antarctic enhancements" by Roscoe et al.

The manuscript entitled "Resolution of an important discrepancy between remote and in-situ measurements of tropospheric BrO during Antarctic enhancements" by Roscoe et al. describes MAX-DOAS measurements of bromine monoxide at Halley Bay, Antarctica. Based on these data, together with co-located in situ and satellite borne BrO measurements, the authors claim that a significant fraction of the observed BrO is located at high altitudes in the free troposphere.

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.

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

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

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. 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.

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 hypothersis that BrO is

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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 $\rho = V/h$ (right panel), given a BrO dSCD of $2 \cdot 10^{14}$ molec/cm^2 (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 $\rho(h) = V/h = dS/\left(dA(h) \cdot h\right)$ 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

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much too high. With the exception of one datapoint, the dSCDs shown in Figure 6 are in the order of $2 \cdot 10^{14}$ molec/cm^2 (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 ($6 \cdot 10^{14}$ molec/cm^2), the mixing ratio would be about 45 ppt, which is still in agreement with BrO values measured at other places in Polar Regions (P'ohler 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 $(2-3) \cdot 10^{14}$ molec/cm^2 (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 Rosoce 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).

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 post-processing 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. A discussion of the retrieved BrO profiles should include: (1) the choice of the a priori and a priori covariance; (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; (4) an error discussion, including the uncertainties in the retrieved BrO amounts at high altitudes; (5) a comparison of measured and modelled BrO and O_4 dSCDs in order to provide an overall picture of the retrieval quality.

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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?

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 MAX-DOAS is systematically lower than from satellite. In fact, any GOME-2 BrO VCD is significantly higher than the according MAX-DOAS value.

P 5420, L22: Reactive bromine compounds (Br and BrO) are usually labelled as Br_x. Br_y includes all inorganic bromine species, of which some have rather low reactivity compared to Brx (e.g., $BrONO_2$, HBr).

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.

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

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.

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

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P5423.

P5428, L1: Why is there less O_4 if there is more cloud? The concentration of O_4 is proportional to the square of the O_2 concentration and thus mainly determined by air pressure.

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?

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

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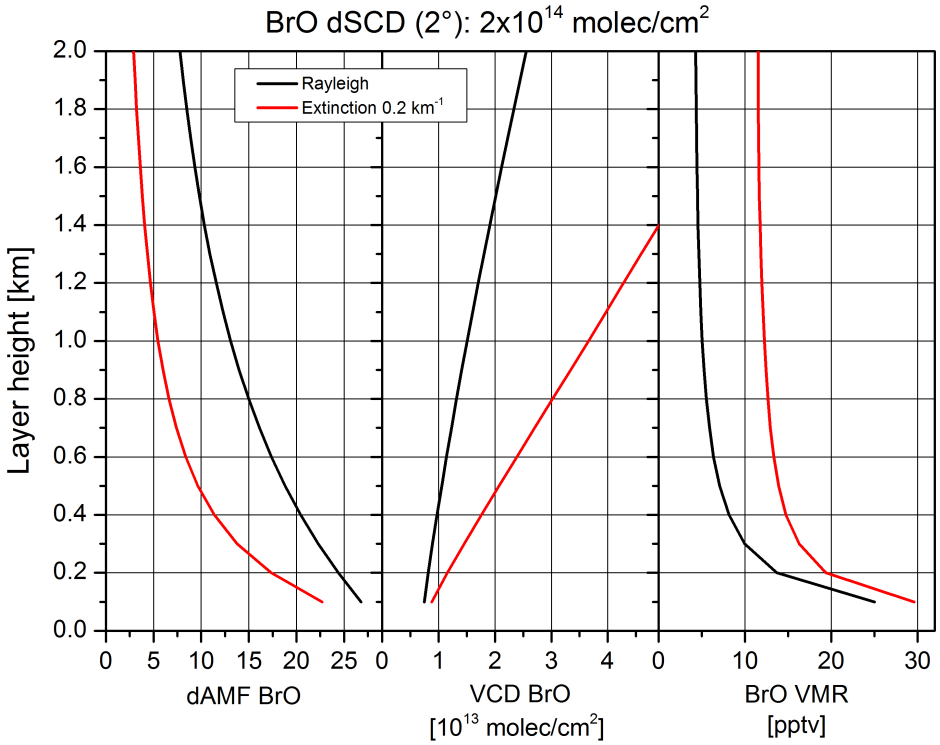

Fig. 1. BrO dAMFs (left), estimated VCDs (middle) and BrO VMR (right) as a function of layer height for a Rayleigh atmosphere (black) and an aerosol extinction of 0.2 kmˆ-1 (red).

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