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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21° S, 56° E)" *by* N. Theys et al.

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In their paper "Retrieval of stratospheric and tropospheric BrO columns from multi-axis DOAS measurements at Reunion Island (21°S, 56°E)", N. Theys et al. report on a full year of measurements of tropospheric and stratospheric BrO in a tropical location using a ground-based DOAS instrument. The manuscript describes a novel retrieval method, provides a detailed error discussion and reports several valuable results on tropospheric and stratospheric BrO and Bry. The paper is clearly structured and well written and I recommend it for publication in ACP after minor revisions.

Referee comment: Reference to Wagner & Platt - is that really appropriate here? In my recollection, this paper deals with boundary layer BrO explosions, not the free tro-

pospheric BrO.

Reply: We have removed the reference to Wagner et al. at this part of the text

Referee comment: Reference to Schofield et al, 2004a: I would read that paper as rather arguing against a significant amount of BrO in the troposphere.

Reply: We basically agree with this comment, although Schofield et al. results do not rule out the presence of BrO in the troposphere at the level of a few 1012 molec/cm2. Nevertheless, this reference has been removed from the text.

Referee comment: References to Bromine explosion - it would be worthwhile to add an earlier reference on the discussion on the role of Br in the polar ODEs or make reference to the recent overview paper by Simpson et al.

Reply: A reference to the Simpson et al. paper has been added in the text.

Referee comment: Ozone reduction on up to 40% - if that statement includes polar regions, up to 100% of ozone can be lost locally.

Reply: We agree with this referee comment.

Referee comment: Geo-location of measurement site varies through the paper, please check.

Reply: This has been verified and harmonized in the text.

Referee comment: Is flipping mirror the right word here - I assume the mirror can be rotated to arbitrary positions.

Reply:Yes, the mirror can be rotated to arbitrary positions. We have replaced “flipping mirror” by “rotating mirror” in the text.

Referee comment: Here, the slant column is introduced but later the differential slant column is discussed. In my opinion, the concept of DSCD should already be mentioned here.

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Reply: We agree with this referee comment. It has been changed in the text

Referee comment: MAXDOAS spelled differently in different parts of the paper.

Reply: It has been changed in the text. The spelling MAXDOAS has been adopted throughout the paper.

Referee comment: Equation 1: Why is the azimuth angle a function of SZA? Isn't both a function of time?

Reply: Both azimuth angle and SZA are indeed a function of the time. The text has been modified to clarify this point.

Referee comment: Equation 1: Why can the stratospheric AMF considered to be independent of viewing angle elevation? Is that an approximation or exact?

Reply: It is an approximation, which states that the optical path in the stratosphere does not depend on the viewing direction, or in other words that the scattering point is located in the troposphere, which is true most of the time. Precise calculations show that the dependency of the stratospheric AMF on the viewing elevation angle is smaller than 2%.

Referee comment: two-dimensional arrays of BrO - if altitude is one dimension, what is the second - SZA? Time?

Reply: Our formulation uses local SZA as the second dimension. This has been clarified in the text.

Referee comment: found typical => found to be typical.

Reply: Corrected.

Referee comment: Why are VCs interpolated linearly between the selected angles? A smoother interpolation (e.g. spline) appears more appropriate for the curved shape of the SZA dependence of the BrO VC at twilight.

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Reply: The VCs have been linearly interpolated for the sake of simplicity. The choice of the retrieved VCs at twilight (80°, 85°, 87.5° and 92.5° of SZA) samples reasonably well the chosen SZA grid (2.5° step), so that it is expected that a smoother interpolation will only have a small impact on the results and will not change fundamentally the findings of this work. However we will consider a switch to spline interpolation in future studies.

Referee comment: I don't understand how the errors on the SCs have been determined from the scatter of one year of measurements - do you assume that BrO is constant, and that the scatter is from measurement noise only?

Reply: To avoid effects of seasonal variation of BrO (large at twilight), the scatter for each month of measurements has been calculated and has been found relatively constant month-by-month and consistent with the scd error supplied by the DOAS procedure.

Referee comment: - Systematic uncertainties - I agree that the uncertainties in the absorption cross-sections are a large source of systematic errors, but even perfect cross-sections could have non-zero correlations and thereby interfere with the BrO columns

- I'm not convinced that the analysis of the absorption cross-section errors used is really giving the right answer. What about the changes you see when changing the fitting window by a very minor value - are such errors also covered in this analysis?

Reply: The DOAS BrO retrieval (section 3.1) indeed requires considerable attention, and therefore several tests have been performed: (1) Changes of the fitting window: the impact of fitting window modifications has been studied in the following way. First, based on synthetic spectra, test retrievals have been performed to determine the fitting interval that minimizes BrO SCD biases. As mentioned in the text (see section 3.1) optimal results were found in the 345-359 nm interval. More specifically results were found to be relatively insensitive to changes of the longer wavelengths, while the lower value of the fitting interval was found to be highly critical (see Figure 1), most likely due

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to the stronger ozone absorption at shorter wavelengths. Although the DOAS approach used in this work definitely remains an approximation for zenith-sky BrO retrieval, our results suggest that the choice of the 345-359 nm mitigate retrieval biases in the best way over the full range of relevant solar zenith angles. (2) Systematic uncertainties: our approach has been to consider that the DOAS procedure can be characterized by a cross-sections matrix (for the interval 345-359) and that it is possible to estimate the errors associated to the DOAS retrieval by using the error analysis formalism for linear inversion problems by Rodgers (2000). Since the forward model matrix (cross-sections) is composed of non-orthogonal vectors, it is clear that the covariance of the retrieval noise is non-diagonal (in other words, the DOAS results have non-zero correlations even for perfect cross-sections). The forward model parameter error calculation evaluates the error due to the errors on the used cross-sections (estimated from the literature), while the forward modeling errors have been empirically minimized based on the sensitivity test presented in Figure 1. Additional errors due to wavelength calibration and several instrumental effects have been evaluated separately using other sensitivity tests and included in final results. These were found relatively small compared to other uncertainties involved. In addition to the above error analysis, an alternative study has been performed (not mentioned in the original text) to estimate systematic errors due to the cross-sections. It consisted in running a series of test retrievals using different sources of cross-sections available from the literature and estimating the effects on the retrieved slant columns. Uncertainties empirically estimated in this way were found to be in good agreement with the values (see Table 1) deduced from the approach based on the Rodgers (2000) formalism, and therefore we decided to report on the latter. This aspect of the error analysis has been clarified in the revised version of the text.

Referee comment: Use of measured NO2 profiles in model - a good idea, but how sensitive / accurate are the ground-based profiles in the altitude range relevant for BrO chemistry?

Reply: Hendrick et al. (Atmos. Chem. Phys., 4, 2091-2106, 2004) has shown that

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the NO2 profiling technique has nominal averaging kernels from 13 to 33 km, which is relevant for BrO chemistry.

Referee comment: Diurnal variation of tropospheric BrO - I found this discussion rather optimistic - the tropospheric BrO amounts could vary a lot in response to emissions from the ocean (temperature, wind, biological activity), clouds (photolysis rates, also multiple scattering for high clouds) and e.g. NO2 from pollution (if there is any close to the measurement location).

Reply: We agree with the referee that tropospheric BrO can have large variations due to a larger number of physical and chemical processes. However, it is difficult to comprehensively account for this in the retrieval. Therefore we have adopted the approximation proposed and used in Schofield et al. 2004, namely that the tropospheric BrO concentration is likely to follow a (smooth) diurnal variation consistent with the lower stratospheric level of the photochemical model. Nonetheless, we intended to quantify the error made by doing this approximation. Since the true diurnal variation of tropospheric BrO is not known, we have made a sensitivity test by considering, in the vertical columns inversion, two extreme cases: -the baseline tropospheric BrO diurnal variation, where basically the BrO concentration drops to zero from low to high sun - the case where tropospheric BrO has no diurnal variation at all (which is very unlikely) We assumed here that in reality the tropospheric BrO diurnal variation lies somewhere in between these two scenarios. In any case the impact of this uncertainty on the retrieved tropospheric column was found to be moderate, approximately 10% of the inverted tropospheric BrO columns. Note that the effect of some of the processes mentioned by the referee are probably captured by the retrieval and may explain (at least partly) the variability of the tropospheric BrO VCDs shown in Fig.11. The retrieval of the tropospheric BrO column is performed using SZAs between 45 and 92.5°, which corresponds to ˜4 hours of observation for both sunrise and sunset conditions. The effect on tropospheric BrO due to processes with typical time scale longer than 4 hours may very well be captured by the retrieval algorithm.

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Referee comment: To my knowledge, the method described has already been used for ground-based measurements by Heckel et al., 2005.

Reply: We agree with this referee comment and we have added this reference in the text.

Referee comment: how does the altitude of the measurement site of Fietkau et al. (Nairobi is at more than 1600 m) affect the comparison?

Reply:In contrast to Reunion Island, Nairobi is a high altitude continental station most probably weakly influenced by bromine contents released from the ocean. This may possibly explain some of the differences between our results and those from the Fietkau et al. study.

Referee comment: I'm not convinced that the diurnal variation of BrO is really directly linked to NO2. In contrast NO2 which increases more or less linearly over the day, BrO first seems to increase and then decreases.

Reply: The rapid increase of BrO at sunrise is due to the fast photolysis of HOBr which is produced during the night due to heterogeneous conversion of bromine nitrate by hydrolysis on sulfate aerosols. Later on during the day, a photochemical equilibrium sets up between BrO and its reservoirs (mainly BrONO2), which leads to a progressive decrease of BrO linked to the diurnal increase of NO2 (controlling the formation of BrONO2).

Referee comment: How does the simplified treatment of additional Bry in the model affect the AMFs?

Reply: We have performed radiative transfer simulations of the AMFs using modified BrO profiles accounting for the new Bry profiles. The differences are smaller than 3% for each SZA.

Referee comment: Although I agree that the consistency between satellite and ground-based measurements is good when considering all the uncertainties involved, it would

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be interesting to speculate about the possible origins of the reproducible seasonality in the satellite data which seems to disagree with the ground-based results.

Reply: We agree that a more detailed discussion is needed regarding the seasonality of the retrieved columns. As pointed out in the paper our ground-based results do not show any marked seasonal variation, and this is somewhat in contrast with expectations based on photochemical considerations at tropical latitudes. Quantitatively speaking, model simulations of the noon or near twilight (SZA$<$80°) stratospheric BrO column at Reunion-Island show a small seasonality, with an amplitude smaller than 10%. Such an effect actually lies within the uncertainties of our retrieved stratospheric BrO columns, which moreover do not cover a complete annual cycle. Longer observational time series would certainly help characterizing better the seasonal variations. Another way to investigate seasonal effects is to focus on twilight conditions when the BrO content show a tronger dependency to NO2. Additional tests have been performed in order to check whether our measurements capture the modeled BrO seasonality between 90° and 80° SZA. Note that in this range of SZA, the sensitivity to stratospheric BrO is also maximized. Results show that for late twilight conditions modeled and measured BrO columns are consistent, both displaying a significant seasonal cycle with a minimum in summer and a maximum in winter, hence following the expected anti-correlation with NO2. Concerning SCIAMACHY results, additional tests have shown that the actual shape and amplitude of the observed seasonality can vary significantly depending on radiometric calibration settings applied to the SCIAMACHY Level 1 data as well as on the precise settings used for the BrO retrieval itself. Hence we found it difficult to draw firm conclusions on seasonal effect as determined from SCIAMACHY BrO measurements. One expect that future satellite data of better accuracy and stability will help addressing these issues.

Referee comment: I'm surprised by the excellent agreement between the Bry profiles from Pundt et al. and the present manuscript - does this imply that stratospheric Bry has not increased in between?

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Reply: The referee certainly wants to refer to recent findings on stratospheric bromine trends. According to our understanding the stratospheric bromine loading is currently thought to have reached a maximum at the end of the ninetees shortly after the Bry profile from Pundt et al. were recorded. At the time of our ground-based measurements (late 2004), one can argue from published observations of the trend in bromine sources in the troposphere (see e.g. latest WMO report on stratospheric ozone), that the total stratospheric bromine might have decreased by about 1 to 2 pptv maximum. Ground-based and balloon Bry profiles agree well considering their respective error bars, which are significantly larger than such changes. Therefore we believe it is not possible to draw meaningfull conclusions on Bry trend from Figure 9.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8261, 2007.