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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60° N" *by* F. Hendrick et al.

F. Hendrick et al.

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Reply to Anonymous Referee #1

At first, we would like to thank Anonymous Referee #1 for his helpful comments and suggestions.

General comments

Referee comment: BrO profiles are derived using exclusively zenith-sky BrO DOAS measurements. A Langley regression is used to evaluate the reference RSCD providing information on the total column and thereby constraining the tropospheric column. A relatively complicated analysis is used to derive RSCD, and as this is the first time

(to my knowledge) that such an approach has been used I believe either an independent ground-based total column (VCD verification) and/or convention profile retrieval is required to verify its robustness.

Reply: Unfortunately no external ground-based UV-vis measurements are available but the good agreement obtained for the comparison with GOME, SCIAMACHY and balloon data gives us confidence in our BrO retrievals.

Referee comment: Lacking in this study is the forward model parameter error implications of the RSCD on the derived quantities (this is not explored beyond the standard deviation derived from different SZA ranges within one Langley analysis, under systematic errors, but should be an error representative of RSCD derivation propagated through the retrieval). Similarly the forward model parameter error: the photochemical model lookup table variability needs to be quantified - ie implications for the derived (stratospheric in particular) columns (hence Bry conclusions).

Reply: We think that there is a misunderstanding concerning the RSCD: it is not a parameter of the forward model as in Hendrick et al. (2004) but this parameter is here related to the measurements. So we don't see any reasons to estimate the forward model parameter error due to the RSCD. Concerning the forward model parameter error, we have added a table with the main forward model parameters (like O3, temperature, aerosols, BrO precursors), their errors, and the corresponding forward model parameter errors. The total forward model parameter errors corresponds now to about 20% of both tropospheric and stratospheric column values, which is significantly larger than the estimates in the first version of the manuscript based on Schofield et al. (2004 and 2006).

Specific comments

Referee comment: The novelty of this work in extending previous work and at the heart of the conclusions of the tropospheric columns is the evaluation of the reference differential slant column. To explore the sensitivity of the RSCD to the Langley regression

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I ran some AMF calculations. Using the VCD 75 to define the AMF and thereby removing the impact of the photochemistry is a novel and clever thing to do. I wasn't entirely clear what the authors had done (but after calculating AMFs exactly this way it is clearer), so if this could be clarified within the text it would be useful. eg that the change in the VCD due to photochemistry is removed from the AMF, and the resulting curvature in the plot is due to a mismatch in the profile shape.

Reply: We have clarified this in Section 2.

Referee comment: I am a little concerned that when I used a 'true' profile of 30 % in the troposphere (modeled), I could get an approximately linear relationship between the DSCD(30%) and AMF(75)(calculated with only 12%), therefore in the absence of the 'truth' (i.e. measured DSCDs) I would conclude a VCD could be 0.75 x 10Ĺ13 smaller (or larger) than the truth and this translates into an under (over) estimation of the RSCD of 1x10Ĺ13. (The modeling was done without multiple scattering effects). The authors have presumably run such modeling tests (where the truth is known, and then the sensitivity to their linear criteria tested) with their model and have a feel for the VCD and RSCD variation that can be induced by changing the tropospheric fractionation or profile shape (putting more in the lower stratosphere/upper troposphere due to higher VSLS etc) on the AMF calculation and hence on the VCD and RSCD that are derived (and satisfying still the linear requirement)? Some discussion, and or model results should be included in the paper and this could provide an estimate of the error of the Langley technique.

Reply: We have improved the estimation of the error on the RSCD by investigating, in addition to the impact of the SZA range chosen for the Langley-plot analysis, the impact of the tropospheric contribution to the total BrO column (ftropo) and the shape of the BrO profile in the troposphere. In order to achieve that, Langley-plot analyses have been performed by taking a ftropo value of 20 and 40 % instead of 30% for the standard Langley-plot analysis (30 ś 10%) and for the second parameter, by using a Gaussian profile shape for BrO in the troposphere (peak at 5 km, FWHM: 4 km) instead

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of constant BrO concentration in the whole troposphere as in the standard Langley-plot analyses. These errors have been calculated for each year and are presented in Table 1. It appears that the total error on BrO RSCDs is in the 11-25% range, which is significantly larger than in the case where only the impact of the SZA range is taken into account as in the first version of the manuscript (in this case, the error on RSCD was smaller than 12%).

Referee comment: What RSCD and VCD(75) are retrieved when a full profile retrieval on the reference days- like Hendrick et al. 2004 is conducted? How does this compare to the VCD(75)s and RSCDs derived using the Langley analysis?

Reply: Applying the Hendrick et al. (2004) method is irrelevant here. In Hendrick et al. (2004), we used differential slant column column densities (DSCD) with daily reference spectra and the RSCD in the reference spectra was fitted (retrieved) by the retrieval algorithm. By doing like this (i.e. using DSCD), we removed any sensitivity of the retrieval to the troposphere and the retrieved RSCD was not the true RSCD but also included a contribution due to the tropospheric BrO column. Here, what we have done is to use a fixed summer noon reference spectrum and determining the RSCD before the retrieval with an independent method like a Langley-plot analysis in order to separate the true RSCD from the tropospheric column contribution. Therefore using the corresponding absolute slant column densities makes the retrieval sensitive to the troposphere.

Referee comment: It then follows that an estimate of the error on the RSCD that comes from different profile shape choices and the profile retrieval compared to Langley regression when added to the standard deviation given in Table 1 should be used calculate the RSCD retrieval impact. Eg: What is the forward model parameter error due to the RSCD error propagation into the final derived stratospheric and tropospheric profiles and hence columns? How is this different to the systematic error RSCD propagation (Table 2). I find it difficult to believe that the RSCD would have a similar error propagation ($<$10%) on the stratospheric columns and tropospheric columns (with ad-

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ditional information for the stratosphere coming from the diurnal variation of the SCDs, and the troposphere largely from the RSCD assumption). In section 4.2 the error budget does not explore this error implication fully and is the major difference between the method used here and that of Schofield et al. 2004 and 2006.

Reply: For the first part of the comment, see the two previous replies just above. Concerning the forward model parameter error due to the RSCD error propagation into the final derived stratospheric and tropospheric profiles, we think that there is a misunderstanding: the RSCD is not a parameter of the forward model as in Hendrick et al. (2004) but is related to the measurements. So we don't see any reason to estimate the forward model parameter error due to the RSCD.

Referee comment: Since the RSCD is used to determine the total column, I suspect the resulting error in the tropospheric columns to be large as noted in the introduction - it would be great if this could be quantified in the paper.

Reply: Yes, you are right. Since the error on the RSCD is now larger as well as the new estimate of the forward model parameter error (see below), we have now a total error on the tropospheric columns of about 40% instead of 35% in the previous version of the manuscript and 20% instead of 12% for the stratospheric columns.

Referee comment: Is there an external (also ground-based) total column measurement eg direct-sun measurements of BrO to test the total column against for a few cases? Eg are the direct-sun balloon instruments ever run for some time on the ground alongside the zenith instrument?

Reply: Unfortunately no external ground-based measurements are available but the good agreement obtained for the comparison of the retrieved total columns with GOME and SCIAMACHY gives us confidence in our retrieved column values.

Referee comment: As the photochemistry is also fixed (within a retrieval) this is also a source of forward model parameter error that is not given. How variable are the look up

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tables (ie spring time) that are derived from SLIMCAT - how does this variability translate into the error budget of the derived columns (I assume the stratospheric columns will be most impacted)?

Reply: Yes, you are right and it is not relevant to use the forward model parameter error from Schofield et al. (2004 and 2006) since in that case the BrO diurnal variation is not fixed but retrieved. So we have added a table with the main forward model parameters (like O3, temperature, aerosols, BrO precursors), their errors, and the corresponding forward model parameter errors. The total forward model parameter errors corresponds now to about 20% of both tropospheric and stratospheric column values, which is significantly larger than the previous estimate based on Schofield et al. (2004 and 2006).

Referee comment: How is the impact of tropospheric clouds / aerosols dealt with - ie are the profile retrievals only conducted for cloud-free days?

Reply: We have added a description of the aerosols settings used in the present study in Section 3. The selection of BrO retrievals is based on the residual of the retrieval fit: all the retrievals with a residual larger than a threshold value (1 x 1013 molec/cm2) are rejected. This method of selection is roughly equivalent to a selection of clear-sky days based on the diurnal variation of O4. The measured BrO SCDs corresponding to the rejected retrievals display generally a strongly unsmoothed variation during twilight due to either a changing cloud cover or strong spectral interferences (e.g., O4, NO2, and Ring interferences).

Referee comment: Is the tropopause for the tropospheric column derivation always at 10km? What is the variability of the tropopause height over the year, and is that contributing to some of the annual variability in the tropospheric columns?

Reply: The tropopause height is calculated for each day using NCEP data. At Harestua, the variability of the tropopause height over the year is about 0.6 km. So we can say that the contribution of the tropopause variability to the annual variability in

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the tropospheric columns is negligible.

Referee comment: In figure 9 the seasonality of the tropospheric columns is very similar to the stratospheric columns - why do we not see a marked tropospheric spring peak in BrO that is absent from the stratospheric columns?

Reply: We think it is not fully true: e.g., in 2003 at sunrise and sunset and in 2005 at sunrise, we can see peaks in the tropospheric BrO columns with an absence of such peaks in the stratospheric columns. We will investigate on this when the new version of p-TOMCAT including sea-ice bromine sources will be available.

Referee comment: Why is there a peak in the autumn for the tropospheric columns (eg can this be attributed to high aerosol loadings in the autumn of 2002 in the TOMCAT model run 2)?

Reply: p-TOMCAT has two types of particles: cloud particle and background aerosols where there is no rain in the gridbox. The HOBr+HBr reactivation only happens on background aerosols. So the effect from the background aerosols is likely depending on rainfall: less rain means more background aerosols. So the significant increase in BrO during 2002 autumn likely due less rainfall.

Referee comment: Pg 8675 (8) the forward model parameter error will be much larger than 12 % (I am unclear how this 12% is translated into Table 2?) due to the impact of the RSCD and photochemical lookup tables (only the residual of the RSCD is used from the Langley fit is shown in Table 2).

Reply: Yes, the new forward model parameter error corresponds to 20% of the tropospheric and stratospheric columns (see above). As already mentioned above, the RSCD is not a forward model parameter but is related to the measurements.

Referee comment: Pg 8684 (8) Pfeilsticker et al 2000, report Bry 21.5 (VSLS of 5.7+/-3 ppt) and Dorf 2006a report VSLS contribution of 4.1-4.3+/-2.5 (therefore 8 ppt is not consistent with Dorf and at the upper end of the Pfeilsticker estimate??). For the

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Salawitch et al. 2005 paper the range includes the Sioris SCIAMACHY retrieved BrO values that are being revised downwards (I believe), therefore while this is consistent with the higher 8 ppt estimates of Sioris, are these results consistent with the Salawitch values that incorporate updated BrO SCIAMACHY estimates? Also in the conclusions - it is noted as consistent with, I would argue that these results are at the upper end of the Bry estimates that exist (especially if the WMO table is recalculated for new Sioris values).

Reply: A suggested by referee #2, we have added the error bars on the ground-based columns in Figure 10. It appears that with a contribution of 6 ppt for VSLS, the modeled stratospheric columns are within the error bars associated to the ground-based columns but still underestimate them. A very good quantitative agreement is obtained when the contribution for VSLS is 8ppt. So we can say that our results are consistent with a contribution for VSLS from 6 to 8 ppt, which is consistent with previous estimates. It is also important to note that a 8 ppt contribution is not only derived from Sioris data but also for example from SAOZ balloon in the tropics (see Salawitch et al., 2005).

Referee comment: Pg 8684 - are the shortlived BrO sources (hence enhanced BrO in the LS), incorporated in the AMF calculations used to derive the RSCD? How does the Langley analysis change if calculated with the new AMFs?

Reply: We used the output from our stacked box photochemical model PSCBOX to calculate the AMF used in the RSCD determination. Since this model is initialized with SLIMCAT fields and SLIMCAT includes a contribution for VSLS of 6 pptv, the short-lived BrO sources are therefore incorporated in the AMF calculations.

Referee comment: Pg 8677 The performed comparison with the balloon data by reducing the resolution by the averaging kernel and adjusting for the photochemistry provides a very thorough comparison. I was disappointed not to see tropospheric columns also compared. Why are the SAOZ and DOAS balloons unable to provide tropospheric BrO

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profiles for this comparison (this should be possible for the sunset ascents with the solar occultation measurements)? I believe this comparison would be both interesting and useful in validating the total and tropospheric column values independently, and comparing with the total columns of the satellite measurements.

Reply: A limitation of the balloon occultation technique in measuring BrO in the lower troposphere is the presence of clouds. In case of the SAOZ, due to the absence of solar pointing system, problems related to the multiple scattering can affect the observations in the lower troposphere. Moreover observations of tropospheric BrO from a high flying stratospheric balloons is much hindered since during solar occultation the atmospheric light paths are getting extremely long (being typically 500 to 1000 km for a balloon flying at 35 km). Accordingly extinction by Rayleigh scattering of UV photons becomes extremely efficient and therefore light paths are ill defined and not particularly specific for the tropospheric observations.

Referee comment: Pg8680 (19) an underestimation of the ground-based retrievals (or an overestimation of the satellite retrievals), perhaps rephrase as: with the ground-based retrieval 20% lower than the satellite retrievals. Also in the next sentence when comparing I would avoid using 'underestimation' as this attributes fault, and here it is just a discrepancy and it is as yet unclear in origin.

Reply: corrected.

Referee comment: Pg 8681 (17) Van Roozendael state in their paper that using the Langley plot method good qualitative agreement can be obtained with GOME (yet a quantitative quote is used here?).

Reply: We say that our retrieved tropospheric BrO columns show a good consistency with previously published estimates and in particular with those from GOME.

Technical comments

Referee comment: Pg 8669 (21) constant BrO concentration of 1x10Ĺ13

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molecules.cm3 (x10Ĺ7?) also check consistent with page 8672 (17)

Reply: Corrected

Referee comment: Pg 8678 (26) - GOME Global Ozone Monitoring Experiment

Reply: Corrected

Can y scales of fig 10 be decreased to show the data a little more clearly?

Reply: we have improved this but we want to keep the same y-scale in both plots in order to allow direct comparison between tropospheric and stratospheric BrO columns.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8663, 2007.