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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.

Anonymous Referee #1

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Review of 'Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60oN' Hendrick et al.

General comments This paper is well written and addresses two major scientific questions concerning atmospheric bromine - the tropospheric BrO column and stratospheric Bry budget, using with an extensive and high quality dataset. For these reasons, and the appreciable amount of work that is necessary to evaluate 7 years of ground-based data at Harestua this paper is very relevant to the readership of ACP and I recommend that this work be published.

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.

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).

Specific comments 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 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.

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 10ˆ13 smaller (or larger) than

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the truth and this translates into an under (over) estimation of the RSCD of 1x10ˆ13. (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.

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?

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 additional 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.

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.

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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?

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 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)?

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

Is the tropospause 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? 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?

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)?

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).

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 Salawitch et al. 2005 paper the range includes the Sioris SCIAMACHY retrieved BrO values that are

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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).

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?

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 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.

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.

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?).

Technical comments Pg 8669 (21) constant BrO concentration of 1x10ˆ13 molecules.cm3 (x10ˆ7?) also check consistent with page 8672 (17) Pg 8678 (26) - GOME Global Ozone Monitoring Experiment Can y scales of fig 10 be decreased to

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show the data a little more clearly?

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