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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

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 #2

At first, we would like to thank Anonymous Referee #2 for his helpful comments and suggestions.

Specific comments

Referee comment: Page 8865, Line 14: It is stated that 'The ground-based DOAS ... technique has been extensively used to study and monitor ozone depletion ... in the troposphere...'. However, scattered light DOAS instruments are usually not capable to measure tropospheric ozone.

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Reply: Study and monitor ozone depletion means not only measuring ozone but also trace gas species responsible for the ozone destruction. Scattered light DOAS instruments are capable to measure such species (BrO, NO2) also in the troposphere.

Referee comment: Section 2: One single reference spectrum for a whole year has been used for the BrO profile retrieval. As the authors mention, this significantly increases the information content of the measurements. The RSCD is determined in a two-step method using the Langley-Plot method. This method is somewhat circular: Assumptions need to be made on the BrO profile shape (which is particularly uncertain in the troposphere) to calculate AMFs which yield VCDs and the RSCD. This RSCD is in turn used as a model parameter to determine BrO profiles. Quantities which are not directly measured should actually be retrieved, and a retrieval of the RSCD by the optimal estimation algorithm would automatically ensure the calculation of 'correct' AMFs in a sense that the BrO profiles serving as input for the radiative transfer model are identical with the retrieved profiles. The authors have spent a lot of effort in determining the fraction of tropospheric BrO, although this is actually determined by the profile retrieval algorithm. It is necessary to check the consistency between the initial assumptions and the retrieval results. How does this factor f, and also the BrO profile used for the AMF calculation, compare with the results from the retrieval? How does the Langley plot look like if the profile from the retrieval is used as input for the AMF calculations?

Reply: Fitting (or retrieving) the RSCD in the retrieval algorithm 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 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

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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: A tropospheric BrO fraction of 30% is chosen, although Fig. 1 suggests that 40% is the better choice. Why? What is the average fraction obtained by the retrieval? Table 1 lists the RSCDs determined by the Langley-plot method and the corresponding standard deviations. Provide an estimate for the systematic errors of the RSCDs, e.g. due to uncertainties in the AMF calculations (uncertainties of the RTM, BrO profile shape, aerosols and other RTM parameters).

Reply: The average fraction obtained by the retrieval is 26%. 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 plots analysis, the impact of the tropospheric contribution to the total column 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 +/- 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 of constant BrO concentration in the whole troposphere as in the standard Langley-plot analyses. These errors have been calculated for each year. 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: Section 3: On which altitude levels are the BrO profiles retrieved?

Reply: Our retrieval is performed on a layer basis in the 0-90 km altitude range with a layer thickness of 2 km.

Referee comment: Page 8672, last paragraph: not the statistical measurement errors, but their square (i.e., the variance) must serve as diagonal elements of S".

Reply: corrected.

Referee comment: It is stated that the fit error is dominated by random detector noise. If this would be the case, one would expect that the magnitude of the scattering of the data is in the order of the size of the error bars. However, the diurnal variation of the BrO SCD shown in Fig. 6 seems to be much smoother than one would expect from the error bars, indicating that there are systematic errors (i.e., systematic residual structures). It would be useful for the reader to see a typical example of a BrO fit.

Reply: Our fit error is indeed dominated by random detector noise and its magnitude is in the same order of the scattering of the data. This fit error has been also use to calculate the retrieval noise. The error bars presented in Fig. 6 contain some systematic components like errors related to the uncertainties on the cross-sections (main source of systematic biases), errors related to the calibration or to other instrumental uncertainties. The caption of Fig. 6 has been modified accordingly and as suggested, we have added a plot with a typical example of a BrO fit.

Referee comment: It is stated that the a priori covariance matrix is 'generally not known'. This is not true, and if the optimal estimation method is applied strictly, the a priori covariance matrix needs to be constructed from other measurements or models, for example on the basis of a climatology (this is discussed in detail in the book of Rodgers). For the stratospheric BrO profile, one could for example construct a covariance matrix from a climatology based on the output of the RTM.

Reply: We agree and have modified this sentence. In practice, Sa acts like a tuning parameter and is empirically determined to provide a good fit of the measurements without over-fitting them.

Referee comment: Section 4.2: Here, the error budget of the retrieved BrO profiles is discussed. In this context, it is confusing to see the measurement error as an error component of the profile. Instead, the measurement error propagates into the retrieval error as the socalled retrieval noise, Sm = GyS"GTy , with Gy being the gain matrix. Do

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the values referred to as 'measurement error' in Table 2 really refer to the measurement error or to the retrieval noise?

Reply: The values refer to the retrieval noise. It has been corrected accordingly in Table 2 (Table 3 in the new version of the manuscript) and in the text.

Referee comment: As already discussed by Referee 1, a thorough discussion of the model parameter error is missing. A value of 12% is assumed, but it is not detailed where this number comes from and whether any sensitivity tests have been performed to estimate the individual error components. I think it is not sufficient to adapt a model parameter error from the Schofield paper, which deals with a different measurement technique (including direct sunlight) and uses different forward models. Apart from the uncertainties in the chemistry model and the error in RSCD, these could be uncertainties in the RTM, both since the DISORT algorithm is only an approximation and due to errors in the RTM parameters. In particular, what kind of aerosol scenario has been used, and how do the uncertainties in aerosol loading propagate into the retrieved profiles, both regarding the retrieval itself and the determination of the RSCDs?

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: Section 5, last paragraph: It is first mentioned that GB measurements underestimate the BrO total columns, and then that SCIAMACHY underestimates the other measurements. Since it is not clear which of the measurements provides the 'true' values, one should instead state that the measurements disagree.

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Reply: corrected.

Referee comment: Section 6: The tropospheric BrO column is slightly larger at am than at pm. As a priori for the diurnal variability in the troposphere, the chemistry of the lowermost stratosphere is used. Since stratospheric BrO concentrations are slightly higher in the morning (e.g., Sinnhuber et al., 2002), the question arises to what extend this effect is caused by the a priori.

Reply: This feature is systematic in spring and fall but not in late spring/summer where am and pm column values are very similar. Since p-TOMCAT model output gives a similar feature, this means that this effect is real and not caused by the a priori.

Referee comment: Section 7: The authors argue that the higher measured tropospheric BrO values in spring compared to the TOMCAT model might be caused by bromine-rich air from the Arctic. Since mid-latitude transport of polar air with high bromine content is a very interesting issue, it would be very nice to see whether this can be confirmed by trajectory models.

Reply: We agree and we will work on that in the future by combining ground-based and satellite observations, tropospheric 3D-CTM and trajectory models.

Technical corrections

Abstract, 2nd sentence: Replace with 'The sensitivity of the zenith-sky observations to tropospheric BrO is increased by using a constant reference spectrum observed during clear-sky noon summer conditions for the spectral analysis'.

P 8664, L20: replace 'feature' with 'finding'. The whole sentence is not clear and requires re-structuring.

P 8664, L23: Delete 'corresponding'.

P 8664, L25: Replace 'used' with 'used in this study'.

P 8664, L26: Replace '+ 6 extra pptv' with 'and additional 6 pptv'.

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P 8665, L14: Move ’to the stratosphere’ before ’would have a...’.

P 8667, L25: Define the acronym IASB-BIRA.

P 8668, L17: Replace ’different’ with ’fixed’ or ’single’.

P 8671, L24: Replace ’for the’ with ’of’.

P 8672, L8: Replace ’of unique solution to the’ with ’of a unique solution of the’.

P 8673, L7: Replace ’key parameter in’ with ’key parameter for’.

P 8674, L6: Replace ’limited’ with ’small’.

P 8675, L5:: Use ’T’ instead of ’t’ for the transpose, as in Eq. 4. The transpose requires no explanation in the text.

P 8677, L3: Replace ’Optimal Estimation Method’ with ’OEM’.

P 8677, L26: Replace ’kernels’ with ’kernel’.

P 8678, L9: Replace ’is observed’ with ’occurs’.

P 8679, L2, 26, 29: Replace ’equator’ with ’Equator’.

P 8679, L20: Replace ’raison’ with reason’.

P 8679, L27: Replace ’off-set’ with ’offset’.

Section 6, 1st sentence: Add ’as described in Section 4.2’ to the sentence.

Section 7: As for the TOMCAT model runs, which are labelled with ’run 1’ and ’run 2’, also the SLIMCAT model runs should be labelled with ’run 1’ (standard run), ’run 2’ (6 ppt offset) and ’run 3’ (8 ppt offset).

Figure 10: Please add error bars to the tropospheric and stratospheric VCDs retrieved from DOAS measurements.

References: Put all publication titles in lower case.

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Reply: All technical corrections done.

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

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