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Interactive comment on “Inter-comparison of stratospheric O_3 and NO_2 abundances retrieved from balloon borne direct sun observations and Envisat/SCIAMACHY limb measurements” *by* A. Butz et al.

A. Butz et al.

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We are grateful to the referee’s overall positive comments and suggestions. Please find below our point-to-point reactions in italic.

1 General Comments

In the introduction the need for high precision measurements is high-lighted in order to constrain photochemical models. The analysis of the validation data can hardly establish the internal consistency of the O_3 LPMA and DOAS measurements to below the required level of around 10% in the 20 to 30 km altitude regime, which is disappointing. For the NO_2 measurements error limits are about 20% even, which renders the data almost not useful for the purpose of model validation. However, the data presented are still useful in order to identify problems and inconsistencies of the current state within the SCIAMACHY satellite retrievals.

We concur with the statement that the observed agreement of the O_3 and NO_2 abundances inferred from LPMA and DOAS measurements is not satisfying and needs further improvement. The paper (section 3.3.) lists a variety of possible sources of errors which will be addressed by future improvements of the instrumentation and retrieval techniques. In parts, the observed discrepancies might be due to errors of the spectroscopic absorption parameters which are beyond the control of the LPMA/DOAS operating team.
When assessing the suitability of LPMA/DOAS data for model validation it has to be pointed out that the accuracies of O_3 and NO_2 DOAS measurements are typically better than 5% and 10%, respectively. An example, where DOAS O_3 and NO_2 measurements are crucial for constraining a photochemical model, is given by Dorf et al. (2005) where stratospheric bromine chemistry is discussed based on simultaneous measurements of O_3, NO_2 and BrO. Further, we want to emphasize that the LPMA experiment measures a variety of stratospheric trace gases, beyond O_3 and NO_2, which exhibit accuracies better than those observed for NO_2. A modeling study on the partitioning of NO_y under high-latitude summer conditions is published by Dufour et al. (2005) who used LPMA measurements of HNO_3, NO, $ClONO_2$, NO_2 and O_3 to constrain and to validate a stratospheric chemistry model.

For the future more efforts must be made in order to isolate the causes of the

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rather large systematic differences between DOAS and LPMA measurements especially for O_3 in order to arrive at more reliable validation data sets. Unfortunately, the in-situ O_3 data which are supposed to be accurate to around the 5% level can not clearly identify as to which of the two instruments is more accurate. Regarding the obvious drawbacks in the LPMA data the priority should be given to a better characterisation of the DOAS measurements.

The error bars given in the paper represent well the actual accuracies of the LPMA and DOAS data, which is substantiated by the fact that both data sets most often agree within the combined error bars. The DOAS accuracies for O_3 and NO_2 are typically better than 5% and 10%, respectively, which in the case of O_3 is equal or even better than the stated 5% accuracy of the in-situ O_3 data. Typically, NO_2 in-situ measurements are less accurate than 10%. Moreover, Johnson (2002) observed an overestimation of the true O_3 concentration by in-situ measured O_3 concentrations by 10% to 15% at 30 km altitude when using the standard 1% KI solution in the electrochemical concentration cells (ECC). The latter observation challenges the stated accuracy of 5% of the in-situ O_3 data, in particular in the target altitude range of the presented study between 20 km and 30 km.
When comparing the in-situ and remote sensing O_3 data a caveat has to be applied since no efforts are made to correct for the spatial and temporal mismatch between the measurements. Further, the remote sensing data typically represent an horizontal average along the lines-of-sight while in-situ sondes probe the local environment close to the sonde carrier.

The availability of accurate tracer data (e.g. N_2O) might enable some new insights into the instrumental or retrieval problems by studying trace gas correlations (e.g. O_3 vs. N_2O) instead of constituent profile data.

For sure, trace gas correlations are a useful tool when comparing data sets under different dynamical, geophysical conditions. Within the scope of the LPMA/DOAS comparison we are not aware how such correlations could improve the understanding of the observed discrepancies since the compared data sets have sampled the same air masses.

2 Specific Comments

p.10750, l.8ff: Historically the Dobson technique should be mentioned when talking about UV/VIS remote sensing measurements in general.

The introduction has been changed as follows (p.10750, l.10ff):
Pioneering work on monitoring atmospheric O_3 *abundances has been conducted by Dobson (1957a,b). As far as vertical profiling of trace gases is concerned, historically first the solar occultation technique (e. g. Mauldin et al., 1985; Russell III et al., 1988; Camy-Peyret et al., 1993; Sasano et al. 1993) was applied to the UV/visible and IR spectral ranges and only more recently the satellite-borne UV/visible skylight limb technique became available (e. g. Mount et al., 1984; Rusch et al., 1984; Burrows et al., 1995; von Savigny et al., 2003; Sioris et al, 2003).*

p.10752, l.25: The Weidner et al. study, cited here, concludes an “overall good agreement" while some of the figures clearly show differences between Mini-DOAS limb measurements and occultation measurements which lie outside the error bars indicated for both techniques, especially for O_3. Therefore the statement “very good agreements" used here seems not justified.

The statement “very good agreement" is changed to “overall good agreement" *(p.10752, l.25). We are sorry for the exageration.*

p.10764, l.1: Which criteria have been used to select the aerosol loadings employed for the different validation scenarios and what is the sensitivity of the modelled NO_2? In general a table detailing the modelling input parameters for the different runs would be useful.

Aerosol loadings are represented in terms of aerosol surface densities. They are taken from balloon borne in-situ measurements at Laramie (41^{o}N), Wyoming, by Deshler et al. (2003) in 2003 and can be downloaded via ftp from ftp://trex.uwyo.edu. A plot of the aerorsol surface density measured during a similar balloon flight in 2002 can be found in Dufour et al. (2005), Fig. 9. Since current stratospheric aerosol loadings are at background levels corresponding to a volcanically quiescent period, the same aerosol surface densities are assumed for the balloon flights between March 2003 and March 2004.
The sensitivity of the modeled NO_2 profiles to aerosol abundances has been tested as part of the sensitivity studies described in section 2.4. Varying the the aerosol surface density by its stated precision of 40% (Deshler et al., 2003), results in less than 5% change of the modeled NO_2 concentration between 20 km and 30 km altitude. Below 20 km, the sensitivity to aerosols increases to at most 15% at about 15 km altitude. The inferred sensitivities are comprised within the modeling error budget and contribute accordingly to the error bars attributed to the photochemically corrected NO_2 profiles.
As described in section 2.4 SLIMCAT output (run #323) is used to initialize the 1-D chemistry model of the stratosphere. SLIMCAT output files are available for download at http://www.env.leeds.ac.uk/∼martyn/chelosba.html. All SLIMCAT data are left unchanged upon initialization of the 1-D model at 0:00 UT except for O_3, NO_2, NO and N_2O_5 which are scaled to fit the balloon borne measurements of O_3 and NO_2 (section

2.4). Since almost all model input parameters are available for download through the internet, we decided not to show a comprehensive table of input parameters in order to debalast the paper which is quite lengthy anyway.

Section 3 Internal LPMA/DOAS comparison First O_3 and NO_2 SCDs are intercompared and then the intercomparison of NO_2 profiles has a dedicated section. I miss a similar section on the intercomparison of O_3 profiles which exhibit a more significant systematic bias that should urgently be characterized.

The internal LPMA/DOAS agreement is discussed by comparing the SCDs of O_3 and NO_2 in section 3.1. Vertical profiles are directly generated from the respective SCDs and hence should reproduce the agreement observed when comparing the SCDs as long as the profile retrieval algorithm is reasonable.
By dedicating a section to the comparison of NO_2 vertical profiles we intended to give a representative example for the characteristics of the profile retrieval (altitude resolution, sensitivity to the lower stratosphere etc), which are particularly important for the validation study in section 4. A similar section on the comparison of O_3 profiles has been suppressed in the manuscript's first version in order to keep the paper short. Since the errors of the O_3 SCDs are typically smaller than those of the NO_2 SCDs, the characteristics of the O_3 profile retrieval are 'better' than those of the NO_2 profile retrieval in a sense that the altitude resolution is better and profiles can be inferred down to lower altitudes.
However, we concur with the referee's suggestion that a section explicitly discussing the retrieval of O_3 profiles from LPMA/DOAS measurements renders the paper more consistent. Hence, section 3.2 has been supplemented by a figure and a discussion part on the characteristics of the LPMA/DOAS retrieval of O_3 profiles.

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p.10767, l.23ff: It seems rather arbitrary to exclude LPMA NO_2 data points on the basis of their level of agreement with the DOAS measurements if afterwards they are used in order to intercompare these two sets of data. The resulting difference of 6.6% (ś14%) is referenced afterwards (e.g. in the discussion section) without mentioning the constraint used in the derivation. Here an independent selection criterium should be established (signal-to-noise ratio, ...), especially since the exclusion of the ”noisier” data seems to almost double the systematic difference between the DOAS and LPMA measurement. This may also give a hint to the origin of this systematic difference. This issue should be explored since also for O_3 there is a marked systematic positive bias of the DOAS with respect to the LPMA measurement.

Here, a misunderstanding is subject of discussion. We did not exclude “LPMA NO_2 data points on the basis of their level of agreement with the DOAS measurements" (see referee comment above) but we performed a further analysis “excluding all data where the corresponding SCDs show errors larger than 25%" (p.10767, l.24f). For large errors, the error bars of the SCDs are essentially a measure of the signal-to-noise ratio, since the fitting errors are the dominant error contribution. Hence, an independent selection criterion has been applied as proposed by the referee.
However, the exclusion of a subset of data indeed shows that the statistical analysis is of limited value since the mean deviation changes substantially. That is the reason why we did not draw further conclusions on possible shortcomings of external parameters, e. g. absorption cross sections. The following statements are changed in order to avoid misunderstandings:
p.10770,l.7f: LPMA O_3 and NO_2 SCDs are low biased by 6.1% and 6.6% with respect to the corresponding DOAS SCDs. → LPMA O_3 and NO_2 SCDs are low biased with respect to the corresponding DOAS SCDs.
p.10774,l.22f: We observe a bias of +6.6% of the DOAS with respect to the LPMA observations, the standard deviation of the relative differences is 14.0%. → When neglecting noisy data, we observe a bias of +6.6% of the DOAS with respect to the

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LPMA observations, the standard deviation of the relative differences is 14.0%.

3 Conclusions

Overall the detailed study validates the novel technique of SCIAMACHY limb observations which enable to retrieve vertically well resolved global trace gas profiles from UV/VIS satellite measurements. This technique may deliver new insights into various atmospheric processes, such as winter-time polar ozone loss, and therefore its validation is an important prerequisite for the further development of this technique. Therefore the paper by Butz et al. represents an important study that is suited to ACP. The study also provides valuable insights into the reliability of the underlying balloon-borne LPMA/DOAS validation measurements. I think the paper should be published with minor revisions, which are requested within the above section “Specific comments".

We thank the referee for its encouraging view of our work and the useful comments.

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